Lenzinger Berichte

91 | **2013**

Scientific Reports on Wood, Pulp and Regenerated Cellulose

LEADING FIBER INNOVATION

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LENZINGER BERICHTE

Scientific Reports on Wood, Pulp and Regenerated Cellulose

„Bei allem, was man tut, das Ende zu bedenken, das ist Nachhaltigkeit.“

Eric Schweitzer

Anniversary Issue
“60 Years of Lenzinger Berichte”

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Foreword of Peter Untersperger/ LENZINGER BERICHTE

Lenzing has committed itself to operating in line with the motto "Leading Fiber Innovation". We are proud that our company has made significant contributions to the continuing further development of man-made cellulose fibers over many decades. Accordingly, we Lenzingers are celebrating the 75th anniversary of our company in 2013 with considerable pride. This anniversary reflects the fact that no other company has matched Lenzing's achievements in moving ahead with the optimization and the greening of the viscose fiber technology. Today Lenzing is the driving force behind the development of the specialty fibers Modal and TENCEL®.

The fact that the LENZINGER BERICHTE are celebrating their 60th anniversary in the same year is not a coincidence. It was always important for Lenzing's researchers to see their achievements and findings as contributions to the further development of the entire industry. This has helped secure the status of man-made cellulose fibers today as an indispensable niche fiber between polyester and cotton. Many new technological developments have not remained in our hands as knowledge used to dominate the industry, but have been proactively made available to a broader professional public.

The LENZINGER BERICHTE were established for precisely this purpose, i.e. as a communication but also a discussion platform for important issues facing our industry. The constantly high scientific quality and the broad range of contributions quickly transformed the LENZINGER BERICHTE into one of the most important official publications for the man-made cellulose fiber industry. The LENZINGER BERICHTE have made a contribution to the expansion of the sales market for man-made cellulosics today to an impressive five million tons annually, a volume which continues to grow dynamically. The LENZINGER BERICHTE have been able to maintain their importance even in the age of global digital communications.

I would like to sincerely congratulate all those who have made this valuable publication possible on their achievements and this landmark anniversary and wish them decades of continuing success in the future.

Peter Untersperger
Chief Executive Officer Lenzing AG Lenzing, July 2013

Geleitwort Peter Untersperger/ LENZINGER BERICHTE

Lenzing hat sich dem Leitspruch „Leading Fiber Innovation" verschrieben. Wir sind stolz darauf, dass unser Unternehmen nun schon über Jahrzehnte hinweg maßgebliche Beiträge zu stetigen Weiterentwicklung der Man-made Cellulosefasern liefert. Mit Stolz feiern wir Lenzinger daher 2013 unser 75jähriges Bestandsjubiläum. Es ist davon geprägt, dass Lenzing die Optimierung und Ökologisierung der Viscosefasertechnologie wie kein anderes Unternehmen vorangetrieben hat und heute der Entwicklungsmotor der Spezialfasern Modal und TENCEL® ist.

Dass die LENZINGER BERICHTE im selben Jahr ihr 60. Jubiläum feiern, ist kein Zufall. Denn für die Lenzinger Forscher war es immer wichtig, ihre Leistungen und Erkenntnisse auch als Beiträge für die Weiterentwicklung der gesamten Industrie zu sehen. Der heutige Status der Man-made Cellulosefasern als unverzichtbare Nischenfaser zwischen Polyester und Baumwolle konnte dadurch abgesichert werden, dass viele neue technologischen Impulse nicht nur Herrschaftswissen blieben, sondern ganz bewusst auch einem breiten Fachpublikum zur Verfügung gestellt wurden.

Dafür wurden die „LENZINGER BERICHTE" als Kommunikations- aber auch als Diskussionsplattform für wichtige Anliegen unserer Industrie gegründet. Die konstant hohe wissenschaftliche Qualität und die thematische Breite der Beiträge machten die LENZINGER BERICHTE sehr bald zu einem der wichtigsten Publikationsorgane für die Man-made Cellulosefaserindustrie. Die LENZINGER BERICHTE haben dazu einen Beitrag geleistet, dass der Absatzmarkt der Man-made Cellulosics heute bei beachtlichen fünf Millionen Tonnen jährlich liegt und weiter dynamisch wächst. Selbst im Zeitalter der globalen digitalen Kommunikation konnten die LENZINGER BERICHTE ihre Bedeutung erhalten.

Zu dieser Leistung und besonders zum runden Jubiläum gratuliere ich herzlich und wünsche all jenen, die diese wertvolle Publikation möglich machen, weitere Jahrzehnte des Erfolges.

Peter Untersperger
Vorstandsvorsitzender Lenzing AG Lenzing, im Juli 2013

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60 Years of LENZINGER BERICHTE

Editorial

LENZINGER BERICHTE is a periodical which from their first issue in 1953 have been of great importance not only to the development of „man-made cellulosic fibres“. Already within the foreword of the first issue LENZINGER BERICHTE, the editors described their motivation. Although it is 60 years old, most of the things are still up to date:

Mit der vorliegenden ersten Nummer stellt sich Lenzings neugeschaffene textiltechnische Hauszeitschrift ihren Lesern vor. Lenzing hat es bisher immer vermieden, für seine Erzeugnisse die Werbetrommel zu rühren. Dieser Verzicht auf ein allgemein übliches Werbemittel geschah und geschieht weiterhin in der Oberzeugung, daß das Gute sich in jedem Falle selbst Bahn brechen muß. Im besonderen Falle unserer Zellwolle und der künstlichen Textilfasern überhaupt geht jedoch in unseren Tagen eine weltweite Entwicklung vor sich, die ihre Wurzeln zutiefst in der technischen Grundveranlagung unseres Zeitalters hat und schlechthin nicht aufzuhalten ist. Parallel mit dieser Entwicklung der künstlichen Textilfasern ging aber noch eine zweite: Aus den ehemaligen handwerklichen Künsten des Spinnens, Webens, Färbens sind längst technische Ingenieurwissenschaften geworden. Textile Rohstoffe werden heute ebenso auf ihre Eigenschaften geprüft und die textilen Endprodukte werden nach ebenso exakten Richtlinien des Tragens und Lastens „konstruiert”, wie sie auch beim Bau etwa einer stählernen Brücke maßgebend sind. Hier auf dem Laufenden zu bleiben ist eine Notwendigkeit, der sich niemand ohne Schaden verschließen kann. In diesem Sinne will Lenzing mit seiner neugeschaffenen technischen Hauszeitschrift der Vermittlung neuer fachtechnischer Erkenntnisse, Erfahrungen und Arbeitsmethoden dienen. In den Forschungsstätten, Laboratorien und Versuchsbetrieben Lenzings ist ein Stab von Textiltechnikern, Chemikern, Wissenschaftlern und Ingenieuren tätig, um allen Problemen textiltechnischer und textilchemischer Natur nachzuspüren: von der Rohzellwolle angefangen über Spinnerei, Weberei, Wirkerei, Färberei und Ausrüstung bis zur fertigen Ware und ihren Gebrauchseigenschaften. Es sind nicht weltfremde Wissenschaftler, die daran arbeiten, sondern Männer aus der Praxis, die ihre reichen Berufserfahrungen in den Dienst der Sache stellen. Was sie erarbeiten, soll künftighin im Wege dieser Blätter unseren Freunden vermittelt werden, als Dienst am Kunden und damit als Ausdruck einer höheren Form von Werbung. Die vorliegende Hauszeitschrift wird Originalartikel und Versuchsberichte aus der Feder von Mitarbeitern Lenzings bringen, denen für ihre Arbeiten alle Möglichkeiten eines großen Unternehmens zur Verfügung gestellt worden sind. Darüber hinaus steht Lenzing mit namhaften Textilforschungsinstituten des In- und Auslandes in dauernden Wechselbeziehungen und verfolgt den Stand der Forschungsarbeit in anderen Ländern, außerdem an ihrem Niederschlag in deutsch- und fremdsprachigen Zeitschriften und in der Patentliteratur. Auch hierüber wird in Referaten, Auszügen und Übersetzungen Wichtiges und Wertvolles berichtet und unseren Kunden dadurch der Anschluß an den neuesten Stand der textiltechnologischen Entwicklung vermittelt werden. Besondere Freude aber würde es den Herausgebern dieser Zeitschrift bereiten, wenn auch aus Verarbeiterkreisen einschlägige Beiträge und Anregungen für die weitere Ausgestaltung zur Verfügung gestellt würden. Lenzing verzichtet bewußt darauf, seiner Zeitschrift ein prunkvolles Gewand und farbenprächtige Bilder auf Kunstdruckpapier mit auf den Weg zu geben. Der Wert dieser Zeitschrift soll im gediegenen Inhalt, nicht im Äußeren liegen!

Zellwolle Lenzing Aktiengesellschaft *Lenzing, im April 1953*

Today, the journal is well-known in the scientific world and represents 60 years of innovation and development. Lenzing always took care to keep the LENZINGER BERICHTE open as a platform for the whole industry, and a large number of papers even of competitors are proof for this! In the last 60 years a lot of authors used LENZINGER BERICHTE as a platform to publish news in the field of wood, cellulose and their applications. We asked a few of them to contribute to this editorial article.

Thomas Rosenau & Antje Potthast
Professors at BOKU University Vienna, Department of Chemistry, Division of Chemistry of Renewables
For 60 years the LENZINGER BERICHTE journal has shared the way with fiber and cellulose research in Austria. As for any diamond wedding, this sheer period of time is impressive – other journals with similar scope, for instance "Cellulose" and "Biomacromolecules", have been around for much shorter times only: 20 and 13 years, respectively. Having initially been established as a medium for Lenzing-internal research communication, the journal has grown since then into an integral element of dissemination in the field of cellulose and fiber science.

Already for the first Lenzing-related Christian-Doppler lab "Pulp reactivity" in Austria, which was started in 1998 at BOKU University with Paul Kosma as the lab director, LENZINGER BERICHTE was a frequent means of publication. The same was true for another Christian-Doppler lab focusing on textile aspects and Lyocell fibers (Innsbruck University, Dornbirn, head Thomas Bechtold). With the foundation of the Chair of Wood, Pulp and Fiber Chemistry at BOKU University in 2005, academic cellulose chemistry research was again institutionalized in Austria, and has since then complemented the applied research performed at Lenzing R&D in many cooperation projects and collaboration efforts. Certainly it has always been the strength of the journal to encompass both facets of research, the fundamental side as well as applied aspects, and fortunately this tradition is living on. With the Christian Doppler lab "Surface-chemical and physical fundamentals of paper strength" at Graz University of Technology" directed by Robert Schennach and the Christian Doppler lab "Advanced cellulose chemistry and analytics", founded 2008 at BOKU University with Thomas Rosenau and Antje Potthast as the lab heads, the LENZINGER BERICHTE have now gone along with four Doppler labs as a publication medium. Especially for those Doppler research constructs, which are situated at the boundary line of fundamental and applied research, the journal remains an interesting option when it comes to propagation of results.

Of course, the attractiveness of the journal as publication medium could be further increased: one might suggest regular appearance of issues, a stringent peer-review system, and an improved indexing in scientific databases, but of course the next 60 years are a long period and offer ample time for such problems to be tackled.

"Stay healthy and active" surely is a good wish for any 60-year-old jubilant, no matter whether it is a person or a scientific journal, and we certainly would like to extend this will to LENZINGER BERICHTE.

Josef Schmidtbauer

Lenzing AG, former Head of Viscose Research

For six decades LENZINGER BERICHTE has now been reporting about research and development in the fibre and textile industry with a particular focus on man-made cellulosics. In 1953 viscose – or “Zellwolle” as it was named in the German speaking countries – was perceived as a cheap substitute for cotton with less good wet properties, manufactured by a “smelly” process using carbon disulphide and associated with significant pollution problems of water and air. Would a product like this be able to overcome its deficiencies and remain competitive against cotton and the emerging synthetic fibres?

It is an exciting experience to recall the milestones and the progress, which has been achieved in the viscose fibre industry since the 1950’s and to recollect 60 years of viscose research, which is reported in the articles of LENZINGER BERICHTE. The renowned authors represent the brain trust of the viscose fibre industry and their publications reflect the complexity of research topics, the widening scope and changing fields of interest, which turned the wheel of innovation in viscose during the past 60 years.

During the 1960s a second generation of viscose was born: high wet modulus fibres - a premium product with superior wet properties, today marketed under the generic name of Modal. This product innovation also triggered new interest in fundamental studies of viscose chemistry, rheology, the regeneration process and the structural properties of the fibres by distinguished viscose researchers like Treiber, Klare, Götze and Krässig. Rogowin proposed a chemical modification process by grafting of synthetic polymers onto the cellulose chain to achieve novel fibre properties, which until then were perceived as a domain of the synthetics like flame retardency, chemical and biological resistance, ion exchange or hydrophobic properties. In the early 1970s Hüpfl published a crimped, wool-type viscose fibre especially developed for carpets while Gotschy took a new approach to obtain viscose fibres with durable flame retardancy by incorporation of a finely dispersed FR chemical into the viscose dope. Multiple papers about fibre characterization, testing and downstream processing complemented the portfolio of scientific papers.

In the mid-1970s, however, interest and innovation in viscose appeared to decline due to booming research in synthetics, increased awareness of environmental problems – at that time still an unresolved problem of viscose technology – and the search for alternative systems to dissolve cellulose but beginning of the 1980s the wheel of innovation in viscose accelerated again. Woodings presented fibres with modified cross section – hollow or inflated – and Marini introduced fibres with tailor-made absorbency by incorporation of hydrophilic polymers or inorganic filler materials into the viscose dope. The development of Modal microfibers opened a window of opportunity for spinning extremely fine yarns, perfectly suitable for high-end textile products. Increased attention was paid to pulp issues like pulp reactivity, hemicellulose management and activation by electron beam treatment. At the end of the 1980s the first papers about waste water treatment in viscose fibre plants and recovery technologies for CS_2 and H_2S appeared in LENZINGER BERICHTE indicating that these environmental issues would become a key priority for viscose fibre manufacturers.

During the 1990s Lyocell had turned out to be the most promising alternative technology to manufacture man-made cellulosic fibres. By exploring the physical and structural properties of this new material researchers also gained new and interesting insights into Viscose and Modal. While product innovation in viscose continued especially in the field of fine denier fibres and fibres with increased absorbency achieved by chemical or physical modification, a lot of work was dedicated to environmental issues in pulp and viscose manufacturing. To avoid formation of AOX totally chlorine free bleaching processes for pulp and viscose fibres were introduced and different recovery and recycling technologies for sulphide waste gases were evaluated. While it is comparably easy to measure improvements in physical fibre properties, the improvement of the eco-profile of viscose fibres from clean processes was much more difficult to assess. Tools like eco-inventories, eco-balances and LCA were emerging and first attempts were made to apply these tools to fibres.

The first decade of the new century extended the focus of viscose fibre research to an old raw material – wood – for which Harms presented the concept of a "wood refinery". Parallel to the growth of viscose in the commodity business functional and specialty fibre developments like fibres with modified cross-section, cationic fibres for single step dyeing in blends with polyester and fibres with ion exchange properties opened new fields of application. Sustainability aspects remained on top of the agenda and parallel to innovation in technology and equipment life cycle studies were published, which for the first time offered a comparable assessment of the ecological impact of natural, synthetic and man-made cellulosic fibres in uniform methodology.

Now, 120 years after the first viscose patent and 60 years after the first issue of LENZINGER BERICHTE we have seen a dramatic change in the viscose fibre industry. Technologies and equipment have matured and recovery of process chemicals and by-products as well as purification systems for waste water and flue gases have become state-of-the-art. The fibre is not a cheap substitute for cotton any more but has developed into an extremely versatile, functional raw material for the global textile and nonwovens industry. Production capacities worldwide continue to grow. Based on the renewable raw material wood supplied from sustainably managed forests and manufactured by a clean process the ecological footprint of the biodegradable fibre has become very attractive. The old dinosaur "Zellwolle" has eventually been replaced by a sustainable product of superior quality, which is still named viscose and prepared to fill the "cellulosic gap" in the global fibre market.

Thomas Bechthold

Professor for Textile Chemistry and Physiscs, University of Innsbruck, Austria

During a time of 60 years of publishing the LENZINGER BERICHTE document scientific growth and progress in the field of man-made cellulosics. Exciting fibres with a wide range of properties have led to a constant expansion into many fields of application. Lyocell, modal and viscose are on the way to replace substantial shares of cotton, however also technical applications like cellulose fibre reinforced materials have become highly interesting fields of research.

The most recent progress in the field of man-made cellulosics always has been collected and reported by the LENZINGER BERICHTE. Contributions cover all disciplines ranging from scientific reports presenting new findings, and expert options from industry and economics which highlight new concepts. This combination makes the LENZINGER BERICHTE unique and highly valuable as qualified source of expert knowledge about man made cellulosics.

The general message of the LENZINGER BERICHTE, which has been promoted through 60 years will remain valid: The future of regenerated cellulose fibres starts NOW!

Hans-Peter Fink

Professor of Biopolymer Science at the Universities of Potsdam and Kassel, Director of the Fraunhofer Institute for Applied Polymer Research, Golm, Germany

For many decades the LENZINGER BERICHTE have been a valuable and indispensable source of information in the area of industry-oriented applied cellulose research. Traditionally most contributions came from Austria and Germany and were published in German. Over the last decades, the papers in LENZINGER BERICHTE increasingly reflect trends and lines of development of European cellulose research, which is connected with the extensive transition to English-language articles. It is quite amazing – and pleasing – to recognize that the "old" research field cellulose constantly keeps producing new results and that it is now again regarded as highly innovative in the context of bioeconomy and sustainable materials management. In Europe this trend is also visible in the polysaccharide network of excellence EPNOE which has presented itself and its partners in detail in a considerable number of articles in LENZINGER BERICHTE since 2005. Only a few of the many important contributions in the LENZINGER BERICHTE of recent decades, which came from the European research community, can be appreciated here. The focus is on the research of viscose fiber spinning and alternative methods such as the carbamate and Lyocell processes. For the Lyocell process LENZINGER BERICHTE present the most comprehensive and important source of information altogether. The articles have mainly come from Austria, Germany and Great Britain with first publications in LENZINGER BERICHTE about the principles of the technology, new functional fibers, blown films, and meltblown nonwovens from cellulose. Alternative solvents for cellulose shaping, but also for the chemical conversion of cellulose in homogeneous systems, also took a broad space. Here, recently the main focus was on ionic liquids and on critical reflections on their economic use. Another highly interesting development is emerging in the context of bio-based carbon fibers for the volume market. There the main focus from an international point of view is not only on cellulose but also on lignin or lignin with mixtures of fiber-forming polymers. Finally, the European pulp research from Scandinavia to Germany and Austria for which LENZINGER BERICHTE is also a strong publication home base must be mentioned at this point. In addition to the scientific contributions, LENZINGER BERICHTE have also reflected the economic development of cellulosics fiber industry and related operational streamlining projects, thereby providing the reader over many years with up to date information of the industry in scientific and economic terms.

Andrea Borgards

Head of Innovation and Business Development, BU Pulp, Lenzing AG

This year we have been celebrating Lenzing's anniversary with "75 years of innovation". LENZINGER BERICHTE have been an important part of this innovation life for 60 years now. In the 1950s LENZINGER BERICHTE started with a high focus on "Zellwolle" properties and related further processing. Even though focus was maintained on product and application development, scope has been extended during the decades on general cellulosic research and pulp plus biorefinery related research. On numerous occasions at scientific or technological conferences I have personally experienced the high interest in our LENZINGER BERICHTE. They have proven to be a well recognized scientific medium, an effective media for high visibility of Lenzing's research and their fruitful cooperations. Therefore I like to take the opportunity to thank all the contributors and especially the editors for their passion for cellulosic and fiber research, which is reflected in the sustainable success of LENZINGER BERICHTE.

Thomas Röder

Lenzing AG, Editor

My first contact with the LENZINGER BERICHTE was in 1993 when I started my diploma thesis. A search in the literature databases concerning the topics cellulose and cellulose fibres showed that the LENZINGER BERICHTE were the journal with the most "hits".

Since then I have helped to arrange seven issues of LENZINGER BERICHTE. Last year we changed the design, but the content stayed as it was before – applied, scientific, innovative and comprehensive. We are also working on a reviewing process with internationally recognized experts in the future. Sixty years of LENZINGER BERICHTE – a great tradition which implies a great responsibility for the next sixty years. On this occasion I would like to thank all the authors and co-authors for their excellent work and their help in making the LENZINGER BERICHTE what they are today.

Research in the Fields of Man-Made Cellulosic Fibres and Cellulose in Austria*

Haio Harms

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*parts taken from Mick Stempel "75 YEARS OF INNOVATION" Lenzing AG 2013

The leading position Lenzing holds in industry can, to a large extent, be attributed to the company's continuous R&D efforts. The history of innovation in the Lenzing Group actually started in the beginning of the 1950s in the cellar of today's Management Board and Administrative building where all research work was carried out at that time. This "Research Department" mainly consisted of the trial spinning plant and a handful of experts. Among these experts was Theodor N. Kleinert who worked in Lenzing for several years and later became a world-renowned cellulose researcher, as well as Erich Treiber, who as a long time consultant made many significant contributions to the improvement of viscose quality in Lenzing.

Lenzinger Berichte

In 1953 the very first issue of the publication "Lenzinger Berichte" (Lenzing Reports) was published. Between then and today this journal has emerged as the world's foremost, regularly appearing official publication for scientific and application-oriented work in the field of dissolving pulp, cellulose, man-made cellulosic fibres and other formed cellulosic products – their production, properties, processing and use.

The "Lenzinger Berichte" have not only been of great importance in the development of manmade cellulosic fibres. Highlights of the reputed Dornbirn Man-Made Fibres Congresses have been published on a regular basis. With P. Schlack, H. F. Mark, P. Goetze, Z. A. Rogowin, T. Kleinert and O. Kratky, to name but a few, a surprising number of the „fathers“ of cellulose and polymer chemistry and of fibre producing and processing technologies have used this platform to publish papers interesting to both the academic and the concerned industrial world.

For a company brochure it is quite unique and the quality and reputation of this journal is underlined by the fact that all issues from the beginning are quoted in the "Chemical Abstracts" and are available in major University libraries. An editorial board of reputed academic and industrial scientists reviews and selects the papers. The approach is multidisciplinary: it ranges from polymer and fibre chemistry and physics, to production and processing technologies and also includes some market and marketing aspects. Lenzing AG, the editors, have naturally contributed extensively but have always taken care to keep the "Lenzinger Berichte" open as a platform for the whole industry, and the large number of papers by Lenzing's competitors are proof for this!

At the beginning of the 1960s a completely new situation arose in the textile fibre industry as a result of the onset of the triumphal advance of crude oil-based synthetic fibres. The new competition and the increasingly tough price war among the European viscose fibre producers resulted in an intensification of research efforts at Lenzing.

In order to be able to keep pace economically, the primary objective in the beginning was to enhance the productivity of the existing facilities. Lenzing succeeded, particularly on the basis of new spinneret concepts, in achieving a drastic increase in the number of holes on the same area without any corresponding reduction in spinning performance. This innovation laid the foundation for Lenzing's strategy of survival in the following decades based on the Lenzing site being able to generate economies of scale and thus steadily develop into the largest integrated and most profitable viscose fibre production site in the world.

Man-Made Fibers Congress in Dornbirn

The first Dornbirn Man-Made Fibers Congress took place in 1962 as a result of the personal initiative and political skill of Lenzing CEO Rudolf Seidl. The "Austrian Man-Made Fibers Institute" served as the organization sponsoring, driving and promoting the conference. Since the first Congress, the number of participants has grown from 130 to between 600 and 700 at the present time. For more than 50 years this annual event has served as a platform for the intensive exchange of experiences and information about state-of-the-art technologies in the field of cellulose fibres. In the early years, the conference was already broadly positioned and truly international, attracting representatives of the fibre and textile industries, their customers and suppliers, machine producers, universities and research institutes from all across Europe, and soon from the USA and China. Before 1989 it was politically significant that Dornbirn as the conference venue also enabled participants from the Eastern Bloc states to attend, in light of the fact that they were not allowed to travel to West Germany at all but could go the congress in neutral Austria.

From the very beginning, the lectures have been characterized by high scientific and technological standards and have covered the entire area of man-made fibres and related issues. In addition to Nobel Prize winners such as Hermann Mark and Manfred Eigen, the speakers regularly included almost all the big names in the field of polymer chemistry and fibre technology. From the first congress in 1962 until 2005, Professor Wilhelm Albrecht of the German company Glanzstoff/Enka served as Lenzing's partner and the heart and soul of the conference, and was responsible for program planning. Many of the lectures were milestones in the development of the industry and were published in the Lenzinger Berichte, which in the initial years also included the intensive discussions following the lectures.

Department of Research and Development

The driving force behind all these developments in Lenzing was the longstanding member of the Management Board Jürenus Harms, who was responsible for the company's fibre business. From 1944 he served as production manager, and was then appointed to the Management Board of the company in 1949. In addition to fibre production, he was also in charge of research and development.


Jürenus Harms

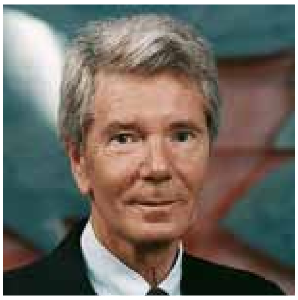
At the beginning of the 1960s, he had the research activities moved from the cellar of the Management Board building to a new, specially constructed research building which is still used for this purpose today. The new research building contained a pilot viscose and spinning facility, which was expanded at a later date to include an additional small-scale spinning plant. This enabled a large number of tests and experiments to be carried out for the purposes of viscose fibre research.

A number of young chemists were hired to work in the newly established research department. Two of them, Leopold Fermüller and Josef Zauner, who later became Management Board members at Lenzing, worked on the modernization and automation of processes, and developed Modal fibres, which ultimately became the successful second generation of man-made cellulose fibres. Modal fibres were launched on the marketplace in 1965.

In 1966 Harms named Hans Krässig, one of the most internationally renowned experts in the field of cellulose and viscose fibre research, to head the new "Central Department of Research and Development" of Lenzing AG.


Hans Krässig


Josef Zauner


Leopold Fermüller

Modal

In developing Modal fibres, Lenzing was faced with the issue of whether to strive to produce high wet modulus rayon (HWM) fibres or polynosic fibers. “We were able to successfully recreate both fibres for test purposes in our pilot plant. With respect to polynosic fibers, we even managed to create fibres which boasted a tensile strength of 130 kilometres, which was a sensation at that time. However, we knew that polynosic was more expensive and difficult to manufacture than HWM”, says Josef Zauner, looking back at the research developments. For this reason, in addition to working on polynosic fibers, Lenzing also focused on developing HWM fibres, which achieved greater wet strength than standard viscose fibres thanks to the use of zinc and a different formulation of viscose.

Lenzing’s decision to focus exclusively on Modal production was ultimately based on the realization that polynosic fibres were brittle and thus not optimally suited for textile applications. In addition, the looping and knotting strength of polynosic fibres were far inferior to those of Modal fibers. All these factors resulted in an unfavourable abrasion resistance. The concept of high wet modulus fibres (HWM) does not deliver the same high tensile strength, but the fibres are not as brittle. In short, the point of view of decision makers at Lenzing at that period of time was that Modal was more suitable as a fibre for textile applications than polynosic fibres. Modal fibres came very close to featuring the same properties as high quality cotton fibres.

History has proven that Lenzing was right. Since the beginning of the 1980s polynosic fibres have no longer been manufactured in Europe. At the end of the last century the Japanese companies also withdrew from the production of Polynosic fibres. In contrast, HWM, initially marketed by Lenzing under the name Hochmodul 333 and later changed to the brand name Lenzing Modal®, enjoyed a continuing rise in popularity in the past decades as a specialty fibre for all high quality and particularly “soft” applications. This is likely to continue in the coming decades.

Decentralized Research

After Jürgen Lenz, the successor to Professor Krässig as the Head of Research, the individual Lenzing research areas largely operated autonomously and in a decentralized manner. Basically there were four main areas of research: viscose fibre research, synthetic fibre research, physical and textile research and development, and the scientific library and patents.

Over the years the heart and soul of the scientific library and patents was Ehrentraud Faltlhansl. In addition to extensive work in the field of her core research areas, which included, for example, the comprehensive examination of patent law in the area of Lyocell, she was also highly involved in organizing the “Dornbirn Man-Made Fibers Congress”. Thanks to her efforts the “Lenzinger Berichte” continued to be published even in difficult economic times.

In the field of physical and textile research, led by Franz Puchegger, special measuring instruments were developed, including equipment designed to measure fibre titre, tensile strength and elongation. This work eventually led to the setting up of the very successful Lenzing subsidiary Lenzing Instruments, which was sold in the 1990s and still ranks today as one of the leading providers of measuring instruments for the textile industry. The field of physical and textile research also dealt with the dyeing of fibres as well as the properties and utility values of textiles made of these fibres, such as their washing and shrinking behaviour.


Ingo Marini


Heinrich Firgo


Josef Schmdtbauer

In respect of viscose fibre research, Ingo Marini and his successor Heinrich Firgo were responsible for the development of new products and for major improvements in Lenzing’s viscose process. These improvements were largely integrated into the fibre production process under the leadership of Josef Schmidtbauer.

The approach to synthetic fibre research was changed when acrylic fiber production in Lenzing ended to focus on the development of high-performance polymers. Under the guidance of Klaus Weinrotter, research not only concentrated on developing the polyimide fibre P84, but increasingly dealt with the evaluation of various new processes to manufacture cellulose fibres on the basis of alternative cellulose dissolution methods.

Following the decision in favour of the NMMO (N-methylmorpholine oxide) process in the year 1987, the "NMMO Project" led by Ingo Marini and his successor Heinrich Firgo remained a separate business unit in the company until the middle of the 1990s.

Lyocell

In the 1970s the survivability of the viscose process in Western Europe was increasingly called into question for both ecological and economic reasons as a result of increasingly strict environmental protection regulations. While most viscose producers shied away from the high investments that became necessary in environmental protection and began to implement a classical "milking strategy", Lenzing's biggest competitors began looking for alternatives to the viscose process. Enka (later renamed Akzo), the world's largest manufacturer of viscose filament yarn, was the first to succeed in manufacturing cellulose fibres in a pilot plant using an environmentally compatible production process: the "New-cell" process used the organic solvent NMMO. However, during the 1980s Akzo began to switch the focus of its strategy more to its paint and pharmaceutical businesses and was prepared to sell its fibre know-how. Lenzing and its archrival Courtaulds, which was several times bigger, both acquired a basic license from Akzo, and further development ended up as a competitive rivalry between the two fibre giants. Courtaulds exclusively focused on the new technology, while Lenzing was not convinced that there would be a quick demise of viscose technology, and decided not to terminate its focus on Viscose and Modal and the good money it could earn from those fibres.

After solving problems relating to the uncontrolled exothermic reactions of the solvent in the production process using the Filmtruder, a Lyocell pilot plant was constructed in 1990. This pilot plant helped to overcome two other crucial challenges posed by the new technology, namely the fusion of fibres in the spinning process and the closed loop recovery of the solvent. The discovery that Courtaulds was also using the Filmtruder patented by Lenzing at its new TENCEL® plant in Mobile, USA led to a bitter patent conflict, which could only be resolved at the end of the 1990s.

Following the end of the fashion-related "soft denim" and "peach skin" phases and the corresponding slackening of demand, a non-fibrillating type of Lyocell fibre was developed which was easier for the textile industry to process.

The exchange of know-how and the harmonization of two different families of technologies, which were made possible by merging the R&D functions after the acquisition of TENCEL® by Lenzing in 2004, quickly generated positive results in terms of both costs and product development. Optimization work in plant and process design drastically reduced the specific investment costs for new Lyocell facilities. Subsequent development work concentrated on the unique selling points of the new fibre and its importance for newly identified areas of application.

In the middle of the 1990s it had already become clear that NMMO-based cellulose solutions (dope), could, in a similar way to traditional viscose, also be formed to make products other than fibres. In parallel to the development of Lyocell fibres development work on films, sponges and nonwovens spun directly from the dope solution was started jointly with partners in the corresponding industries. In recent years spherical and more fibrous TENCEL® powders have been introduced to the market as additives in a series of materials and research has been carried out on a new type of TENCEL® gel for cosmetics and coatings.

The Revival of Cellulose Research in Austria

In the middle of the 1990s all innovation areas were merged once again to create a central Group research unit led by Haio Harms.

Harms began work on initiating a revival of cellulose research in Austria based on partnerships with universities. This approach was designed to expand the scope for action in dealing with issues of importance to Lenzing.

Haio Harms

Starting in the 1960s, university research on cellulose all over the world was increasingly being replaced by research into synthetic polymers on a crude oil basis.

While cellulose had in fact been the first industrially available polymer which served as a raw material for making a broad range of products it was, as a "natural" raw material, harder to manage than standard monomers under defined conditions and to achieve the same consistent quality as synthetically produced polymers. These advantages led the entire materials industry and research facilities to focus on "synthetic" raw materials based on crude oil.

Until the end of the 1960s, Austria, with its universities and researchers such as Otto Kratky, Erich Treiber, Josef Schurz, Josef Gratzl and Karl Kratzl still represented a stronghold of cellulose chemistry in Europe. However, by the middle of the 1990s, there was no longer a single public research facility in the country specializing on topics relating to cellulose chemistry. This development is even harder to understand, in light of the fact that wood, as one of the most important primary resources, and the utilization of wood comprise one of the most important sectors of Austrian industry. Moreover, close to half of Austria's land area is covered by forests.

As the world market leader in viscose fibres, Lenzing was the only company in the world which further developed new products and the related technologies throughout these years. In this regard Lenzing also co-operated fruitfully with plant and equipment manufacturers as well as textile machine producers. The top priorities, were unfolding the potential embedded in the applications of Lenzing fibres on behalf of customers, and examining the inherent properties of cellulose and the physiological compatibility of the fibres, both of which involved carrying out fundamental tests and investigations. As a consequence, partnerships with medical and pharmacological institutes were also established.

In order to support the strategic advantage of Lenzing in owning its own integrated dissolving pulp production Harms complemented the established research units in the new central Group Research function by adding a new pulp research unit led by Herbert Sixta. The working group was originally assigned the task of improving the environmental situation of the production in respect of waste water and also dealt with other biotechnological issues. But now its focus switched to continually improving the magnesium bisulfite process applied by Lenzing in producing pulp. This resulted in extensive work carried out to improve raw material yield, to develop the kraft pulping process for the new plant in Brazil, and to perfect the totally chlorine-free bleaching process, initially for the Lenzing sulphite process and later also for the sulphate process in Brazil.

Herbert Sixta

It was possible to revive interest in wood, cellulose and cellulose fibres at several Austrian universities by introducing practice-oriented issues in dialogue with university facilities and financing long-term collaborative research projects. On the basis of such research priorities, Christian Doppler laboratories and competence centres were established which today have an impact far beyond Austria's borders. In addition, several cooperative projects were initiated at the EU level. As an example, a European-wide research network of research institutions was set up, with Lenzing serving as one of the main centres devoted to the further improvement of know-how on the subjects of the renewable, natural raw material wood and its uses. Now, decades later, cellulose chemistry itself is also profiting from progress in research on synthetic polymers.

Bio-Refinery of Wood

Today cellulose is seen from a completely different perspective than it was 40 years ago, when the finite nature of raw materials based on crude oil was not considered to be a relevant issue. Growing environmental awareness and the realization that there is a limited supply to oil-based raw materials laid the theoretical foundation for the unique concept of the "biorefinery of wood" developed by Lenzing. This concept envisions the optimal exploitation of the raw material wood by the extraction of all its components and even utilizing the energy stored in the wood. From both an ecological and economic point of view, this concept is the basis for the sustainable economic success of Lenzing, which has, in the meantime, emerged as a unique production site in the world. Nowhere else is such a wide range of industrial products derived from wood as is the case in Lenzing.

In addition to developing new products and technologies, the underlying focus of decades of innovation at Lenzing has been to always enhance production volumes and efficiency at existing plants whilst maintaining the same level of product quality. Since the 1970s, Lenzing has also given priority to taking ecological parameters in to account. Innovations at Lenzing are always characterized by holistic thinking, which not only encompasses pulp production but also incorporates the issues of energy, co-products, exhaust air and waste water.

Lenzing's increased market orientation led to far-reaching organizational changes in 2005. The operating business was divided into individual business units, for example for textile applications, nonwovens and pulp, and research and application development was also fully integrated into this organizational structure. The research function is the responsibility of the individual business units, which manage and finance R&D, with the aim of closely linking research to the company's marketing efforts.

In the field of cellulose man-made fibre production and after more than 75 years of successful operation, both Kelheim Fibres, the worlds leading Specialty Viscose Fibres producer in Germany, and Lenzing, the worlds leading Manmade Cellulose Fibre producer in Austria, believe in building their positions in the industry based on the introduction of innovative products and continuous R&D efforts.

This year, the 52nd Dornbirn Man-Made Fibers Congress will again serve as a platform for the key players in industry and science to exchange intensively experiences and information about state-of-the-art technologies in the field of cellulose fibres.

The current issue 91/2013 of the „Lenzinger Berichte“ includes papers on the manufacturing and processing of several new cellulose based fibres and materials. In its 60th year the journal remains the world's foremost regularly appearing official publication for scientific and application-oriented work in the industry.

Over 60 years of focussed industrial research at Lenzing and the revival of both academic and practical research at universities and research institutions in Austria have secured a bright future for the man-made cellulosic fibres industry and cellulose as an industrial raw material.

Man-Made Cellulose Fibres – a Comparison Based on Morphology and Mechanical Properties

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Abstract

Due to the infusibility of cellulose the production of cellulose fibres for textile and nonwoven applications from wood pulp requires the dissolution of the cellulose. Dissolving cellulose means to break the strong hydrogen bonds in between the cellulose chains and to replace those by interactions with a solvent or by derivatization of the cellulosic OH-groups.

In 1892 a patent [1] written by C.F. Cross, E.C. Bevan, and C. Beadle described a derivatization process of cellulose with sodium hydroxide and CS2 to cellulose xanthogenate – the viscose process. Lenzing has been producing Viscose, the first generation of cellulose fibres, for 75 years now. The knowledge it has acquired in Viscose production is reflected in the superb quality of Lenzing Viscose®, which nowadays sets the standard for the textile industry.

In this paper the well established man-made cellulose fibres Viscose (staple fibres, tire cord, filament), Lenzing Modal® and TENCEL®, are compared with other regenerated cellulose fibres in terms of their characteristics. Properties like crystallinity, orientation and cross section dependend on the fibre processing parameters are studied systematically. The different processes presented have diverse degrees of "freedom to operate". They are shown and discussed controversially. In this paper experimental as well as commercial available cellulose fibres are compared. Especially their structure-property-relationships are presented and discussed.

Keywords: *viscose fibres, Lyocell, man-made cellulose fibres, crystallinity, acid*

Introduction

The global fibre production in 2011 counted about 79.1 Mio tons [2]. Whereat, the proportion of man-made cellulose fibres was around 6%, of cotton around 31.2%, of wool around 1.5% and of synthetic fibres around 61.3% [2].

Man-made fibres can be divided – dependent on their source of origin - into three main sub-groups: based on natural polymers, on synthetic polymers or on inorganic substances. In the sub-group natural polymers one can differentiate between cellulose based and protein based materials. The most important and used cellulose based fibres are viscose, Modal, Lyocell, Cupro and acetate fibres. These fibres can be produced as staple fibres like Lenzing Viscose®, Lenzing Modal® and TENCEL® or as filament fibres like viscose tire cord and viscose filament yarn.

In the sub-group of man-made cellulose fibres the fibre types can be additionally divided into cellulose fibres (e.g., CV, CMD, CLY, CUP) and cellulose derivative fibres (e.g., CA, CTA). This study covers non derivatized cellulose fibres only.

To form cellulose fibres it is necessary to dissolve the cellulose first. This can be done either by derivatisation (CV, CMD), complexation (CUP) or direct dissolving (CLY). Following this dissolution step the cellulose is regenerated and the fibres can be collected.

Fibre characterisation is normally done by measuring the tenacity and the elongation at break. Furthermore titre, dyeability, cross section, modulus, knot tenacity, loop tenacity, pilling behaviour and fibrillation can be determined. Nevertheless, all these data are often not enough to characterise a fibre in a way to be sure to

Table 1. *Correlation coefficient of F1 and F2 with tenacity:elongation and tenacity*elongation.*

	F1	F2
Tenacity : Elongation (cond)	0.98	-0.09
Tenacity : Elongation (wet)	0.95	-0.19
Tenacity x Elongation (cond)	0.21	0.80
Tenacity x Elongation (wet)	0.36	0.77

have the quality needed for the customer. In 1984/85 Höller [3] and Puchegger [4] developed a model which implies all the measured data and reduces it to only two factors. They used commercial viscose and modal fibres to create this model. The two factors used in this model are combinations of tenacity and elongation in conditioned and in wet state, BISFA-modulus, loop- and knot tenacity:

F1= - 1.109 + 0.03992*tenacity (cond) – 0.06502*elongation (cond) + 0.04634*tenacity (wet) - 0.04048*elongation (wet) + 0.08936*BISFA-M + 0.02748*loop tenacity + 0.02559*knot tenacity

F2= -7,070 + 0.02771*tenacity (cond) + 0.04335*elongation (cond) + 0.02541*tenacity (wet) + 0.03885*elongation (wet) – 0.01542 BISFA-M + 0.2891 loop tenacity + 0.1640 knot tenacity

Both factors were plotted in a so-called HÖLLER diagram. Viscose fibres and high wet modulus fibres claim different areas within this diagram. Based on their position one could get evidence about the fibre qualities.

Materials and Methods

Fibre Samples

For the comparison the same experimental and commercial fibres where used as described in [5]: Commercial fibres are viscose fibres (viscose, tire cord viscose), modal fibres, cupo fibres (Asahi Kasai) and Lyocell fibres (TENCEL®). Experimental fibres are Fortisan® fibres (Celanese Corp., sample kindly provided by Prof. H. Chanzy, Grenoble, France), fibre B (developed by H. Boerstoel (Akzo Nobel), sample kindly provided by Dr. S. Eichhorn, Manchester, UK) and celsol fibres (Institute of Chemical Fibres, Lodz, Poland). In addition, a standard viscose solution made in the lab was used to produce fibres with different acid content in the spin bath. The acid was increased stepwise from 60 g/L to 160 g/L (10 g/L steps). All the other parameters were kept constant. A typical spin bath consists of 7-12 wt% H2SO4, 12-24 wt% Na2SO4 and 0.5-3 wt% ZnSO4 [6, 7, 8].

Methods

All fibres mentioned above were tested regarding tenacity, elongation and modulus, both in the conditioned and in the wet state.

Solid-state ^{13}C CP-MAS NMR measurements were done on a Bruker Avance DPX300 NMR spectrometer, operating at 75.46 MHz ^{13}C resonance frequency. The spectrometer is equipped with a 7 mm 1H/BB MAS probe, and the typical sample spinning speed is 4 kHz. NMR measurements are performed at room temperature (T = 26° C) and typically involve the following acquisition parameters: acquisition time 41 ms, crosspolarization (CP) contact time 1 ms, repetition interval 3 s, 1024 accumulations, total acquisition time 53 min.[9]

SEM measurements were done on the cross sections of the fibres with a Hitachi S-4000 SEM cold field emission instrument with secondary electron detection, magnification: 2500x (10 μm) ,5000x (6 μm) and 10.000x (3 μm), accelerating voltage: 5 and 8 keV, working distance: 8-10 mm.

Results and Discussion

Viscose Type Fibres

The viscose process is very flexible. Standard viscose fibres for textile and nonwoven applications, viscose filament fibres for use as tire cord or suiting, modal fibres for high quality textiles – all these products show a great variety of properties based on the viscose process. All these fibre types can be produced by varying the following conditions: variation of pulp, CS_2 content, NaOH consumption, spin bath composition, spinning speed, different additives and more. To illustrate this great variety, Figure 1 shows the tenacity-elongation diagrams.

As to be seen, the area where viscose type fibres, having different cross sections (Figure 2 [5]), are located is quite large.

The cross section is mainly influenced by the coagulation and spinning conditions. By varying e.g. the acid concentration in the spin bath, fibres with different cross sections can be produced. The coagulation can be retarded by lower acid concentrations in the spin bath, higher alkali content in the viscose dope and

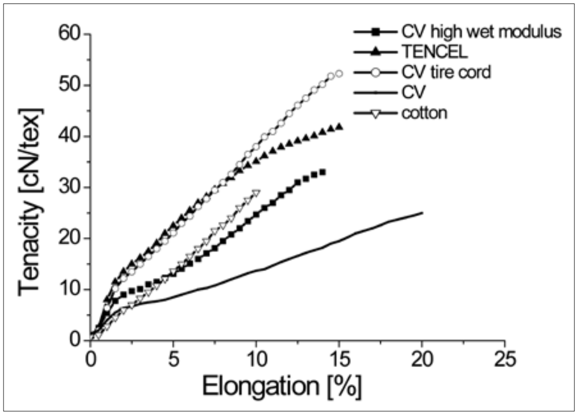

Figure 1. *Tenacity-elongation diagrams for viscose type fibres (conditioned state).*

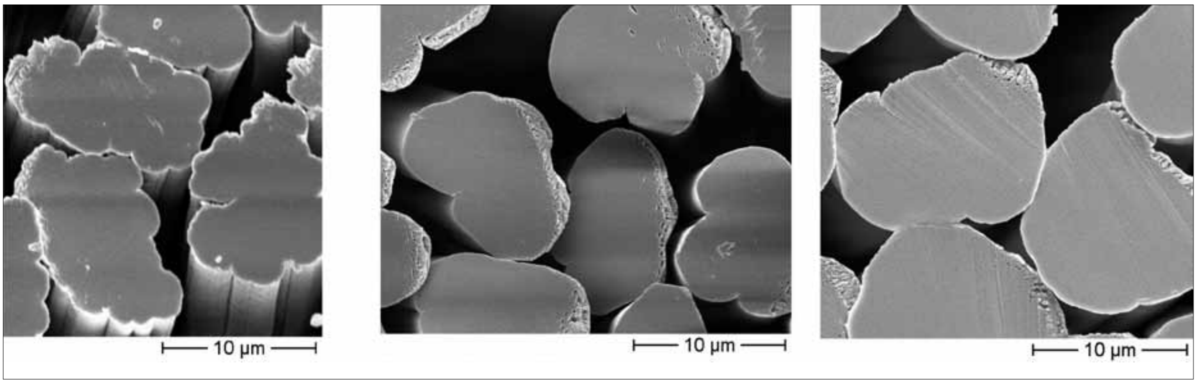

Figure 2. *SEM pictures of fibre cross sections: standard viscose (left), modal (middle) and viscose tire cord (right) [5].*

additives, like zinc ions or so-called modifiers [8]. After dissolution the semi-crystalline structure of cellulose is lost. Differences within the coagulation conditions will lead to different crystal structures in the regenerated fibre. To compare these viscose type fibres, WAXS measurements were done as described in [10]. Standard viscose fibres were in the range between 25 and 30%, viscose tire cord fibres between 24 and 27%, modal fibres between 27 and 35%, respectively.

To show the influence of the regeneration step on the structure of the fibre, a standard viscose solution from the lab was spun with different acid concentrations in the spin bath. Figure 3 shows the SEM pictures of this experiment.

Whereas the fibre data of the samples spun with 150 g/L acid or less showed no significant change, the tenacity of the samples spun with 160 g/L acid drops down significantly. Increased acid concentration in the spin bath leads to degradation of cellulose. This result indicates that acid concentrations starting from 160 g/l are not feasible within the chosen conditions and the setup. Although the viscose process is known to be nonproblematic, in this special case at this high acid concentration the process leaves its "spinning window". The differences in the regeneration steps can be visualised by ^{13}C-NMR measurements. Contrarily to the regeneration speed, the crystallinity of the fibres decreased. With 60 g/L acid 56.4% crystallinity could be reached, 100 g/L resulted in 51.4% and with 160 g/L the crystallinity dropped to 45.1%. In parallel, the degradation of the cellulose chains increased with increasing acid content. Under the chosen conditions, the process was stable up to 150 g/L. Starting from 160 g/L sulphuric acid the degradation was too strong and influenced the fibre properties negatively.

Lyocell Type Fibres

Lyocell type fibres are defined by the following process: Cellulose is directly dissolved in NMMO/water (TENCEL®) or ionic liquids, spun through an air gap and precipitated in water. All these fibres show similar properties. Slight differences can be explained by the different solvents used. But the solution structures and the regeneration seem to be comparable. Up to now the only commercial representative of this group of fibres is TENCEL®. Figure 4 [10] shows the cross sections of the fibres when using different solvents.

Tenacity and crystallinity are higher compared to viscose fibres with the exception of the tenacities for the tire cord samples. By comparing the tenacity-elongation curves (Figure 1 and Figure 5) it can be stated that Lyocell fibres are a good completion to the viscose fibres. They extend the usable area of man-made cellulose fibres at the higher (tenacity, modulus) end and open new possibilities for the textile and nonwovens industry.

The graphs for BMIM-Cl and BMIM-Ac are very similar as well as for EMIM-Cl and EMIM-Ac. In this special case the behaviour of the fibres seems to be determined by the cation only. Hence, the solution structure should be the same.

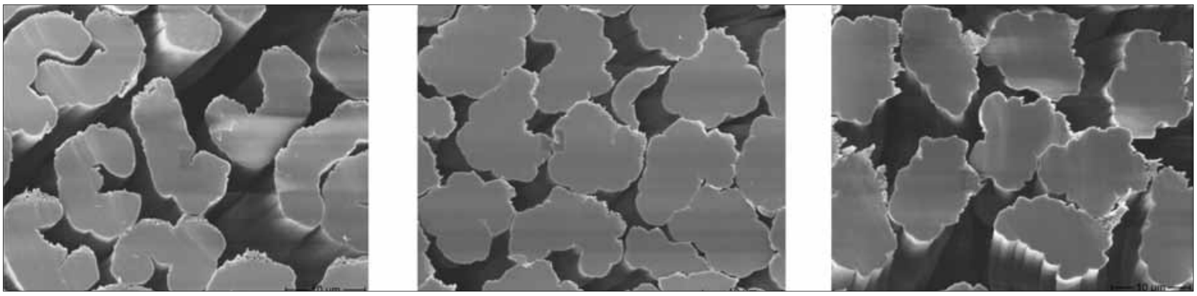

Figure 3. *Viscose fibres regenerated with 60 g/L acid (left), 100 g/L acid (middle) and 160 g/L acid (right) in the spin bath.*

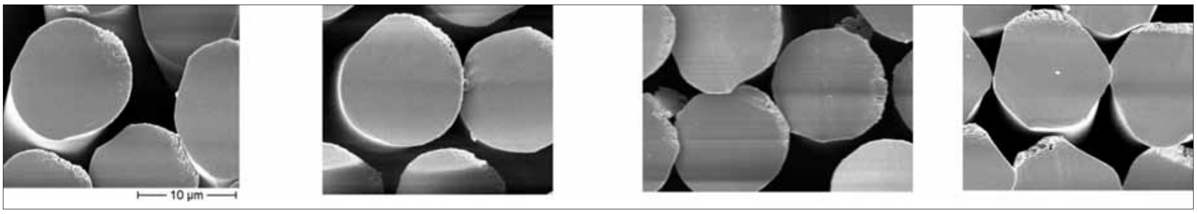

Figure 4. *Cross section of Lyocell fibres: TENCEL® (left), made from EMIM-Cl (middle, left), BMIM-Cl (middle, right) and BMIM-Ac (right).*

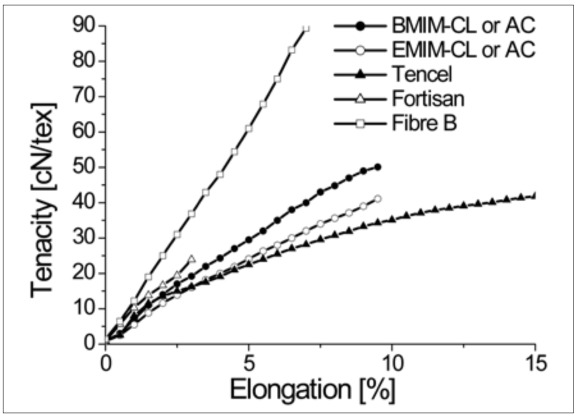

Figure 5. *Tenacity-elongation diagrams for Lyocell type fibres and fibre with high orientation/crystallinity (conditioned state).*

Highly Oriented Fibres

Two interesting experimental fibres with high orientation and crystallinity are Fortisan and "Fibre B". Fortisan fibres were made by dry spinning a solution of cellulose acetate in acetone followed by a saponification step (Celanese Corp.).

"Fibre B" (Bocell) was made from anisotropic solutions of cellulose in superphosphoric acid and spun via air-gap into acetone followed by saponification in water/soda (developed by H. Boerstoel (Akzo Nobel)).

Both fibres have a high E-modulus. The graph in the tenacity-elongation diagram in Figure 5 shows a nearly linear trend. The fibres are highly stretched, after leaving the linear-elastic region they break. They also show a low elongation. In Table 2 the fibre data are listed and compared to TENCEL®.

Crystallinity measurements showed higher values for both fibres compared to TENCEL®. WAXS crystallinities of TENCEL® fibres were around 38% or higher. The Fortisan was measured with 47%. Fibre B was measured with IR [10] having a crystallinity of 59%. The IR-method was calibrated with WAXS data. Unfortunately fibre B was outside this calibration range. Therefore the value of 59% might be not fully correct. Certainly, it is the highest value for man-made cellulose fibres we measured up to now. The high crystallinity is founded by the cellulose structure within the solution. Fibre B was spun out of a liquid crystalline solution. Such structured solutions are pre-requisite for highly ordered solid structures after precipitation. Lyocell type fibres are characterized by higher crystallinity than viscose type fibres. This leads to their tendency to fibrillate. Directly dissolved cellulose without a derivatisation reaction regenerates very fast after the air gap when it gets into contact with the precipitation bath. Solution structures of cellulose in NMMO monohydrate are described in [11, 12] as highly swollen aggregates, so-called fringed micelles. Similar fibre properties of Lyocell fibres spun from ionic liquids compared to TENCEL® suggest similar solution structures of cellulose.

Cellulose derivatives are characterized by different solution states. In consequence of the partial substitution of the cellulose OH groups the tendency to form H-bonds between the anhydroglucose units is drastically reduced. In concentrated solutions like in spinning solutions one can find an entanglement network of cellulose chains [11]. The reorder of these chains after the regeneration is inhibited by the side groups and the entanglement network itself. For viscose this results in lower values for the crystallinity of the fibres.

Fibre Data Analysis

All the fibres mentioned above were treated using the model of Höller and Puchegger [3, 4]. Figure 6 shows the HÖLLER diagram for the series of viscose fibres produced with different acid contents in the spin bath. Despite the sample with the highest acid content in the spin bath, the fibres of this viscose series are located in

Table 2. *Fibre data for high oriented fibres [5].*

	titre	Tenacity cond.	Elongation cond.	Tenacity wet	Elongation wet	BISFA modulus	modulus cond.	Commercial/ experimental fibre
	[dtex]	[cN/tex]	[%]	[cN/tex]	[%]	[cN/tex/5%]	[cN/tex/%]	
Tencel®	1.3	40.2	13.0	37.5	18.4	10.8	8.8	com.
fibre B	1.6	89.4	6.8	75.8	7.9	39.0	23.5	exp.
Fortisan®	0.7	23.9	3.2	27.7	5.1	27.0	n. a.	exp.

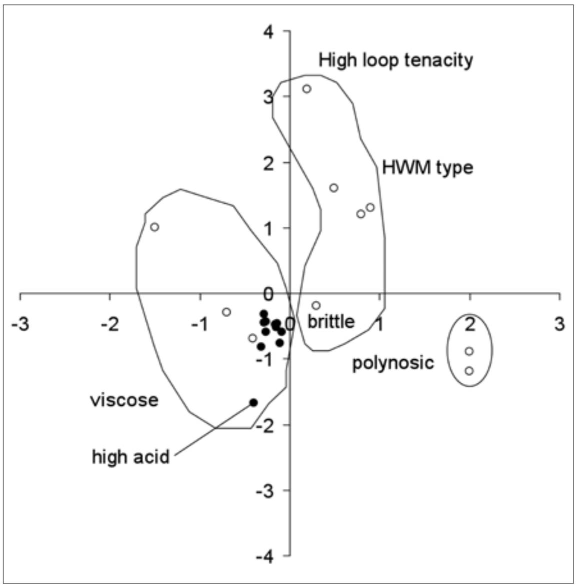

Figure 6. *HÖLLER diagram with original samples from [3, 4] and the viscose fibre series spun with different acid concentration (x-axis F1, y-axis F2).*

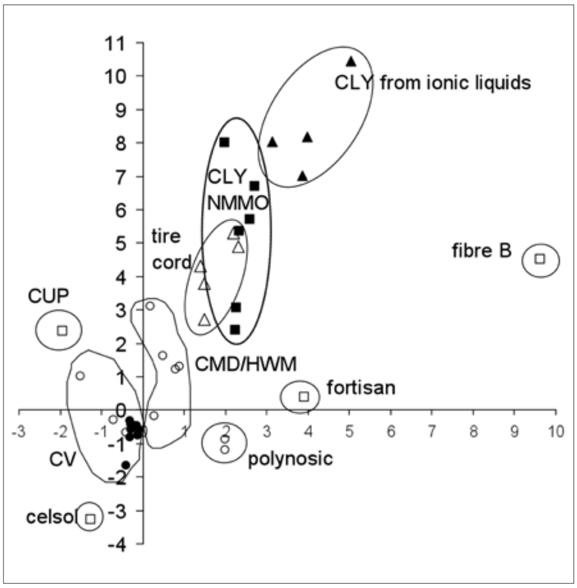

Figure 7. *HÖLLER diagram for experimental and commercial man-made cellulose fibres.*

the same area. This is an indication for the robustness of the viscose process. Only when the acid content in spin bath gets too high, changes are visible.

The HÖLLER diagram is a tool to visualize differences. A comparison of all the other fibres mentioned in this publication is shown in Figure 7.

Conclusions

The comparison of man-made cellulose fibres showed the manifold of those fibres and the great band width of properties that can be covered, by selection of the solvent/derivatisation system, the variation of spinning conditions or the variation of the after-treatment.

Evaluation of fibre properties is essential to control the fibre quality during the production process. Often standard testing cannot provide a sufficient overview on the behaviour of the fibres for the different applications. The HÖLLER diagram is one method to normalize all the data and to get a fast overview. Thus there is a large potential of man-made cellulose fibers in the future due to the great variety of properties.

While discussing a high number of degrees of freedom to operate the viscose process, one must not forget: industrial production of any kind of viscose type fibres is a combination of all effects under careful consideration of produced quality and economic feasibility. Last but not least TENCEL® fibres are an excellent completion of existing viscose type fibres and extend the usable area for man-made cellulose fibres.

Acknowledgements

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Kelheim Fibres GmbH – A Specialist Specialises

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Abstract

The viscose fibre industry has, in the past 30 years, been characterised by a geographic shift from Europe and the USA to Asia. Plants in higher cost areas, such as the USA and Europe have closed while high capacity/high throughput production units have been erected in lower cost areas.

Although Kelheim Fibres GmbH is also expanding capacity, the production volume planned for 2014 of around 100.000 t per annum remains small in the context of global viscose fibre production. So how does a relatively small producer in a high cost region survive and grow?

The success of Kelheim Fibres GmbH is based on four fundamental factors; the use of available equipment and technology to produce small lots of fibre with unique properties, building a leading and defensible position in key markets, adapting existing technologies to develop innovative fibre products, and establishing new business in new applications

Kelheim survived through the 1990s and the first years of this century by specialising and meeting the needs of the market. Continued survival will be secured by a further specialisation.

Keywords: *viscose fibre, viscose industry, strategy, speciality fibres, Kelheim*

Introduction

Over the past 30 years, the global viscose fibre industry has undergone massive changes, both in terms of installed capacities and in terms of where those capacities are located. The scale of new plants has increased in order to dilute fixed costs and the industry has increasingly focussed on the efficient production of standard products. As a relatively small producer based in a high-cost European location, Kelheim Fibres GmbH has faced some unique challenges.

In this paper we will share some of the strategies and ideas that have enabled Kelheim Fibres to survive in what has, over this period, sometimes been a very difficult environment.

To set the scene, we will look at the development of the global viscose fibre industry over the past 30 years. What we see over this time period is an industry in decline, as the world wide capacity for the production of viscose fibre dropped by some 30%, from

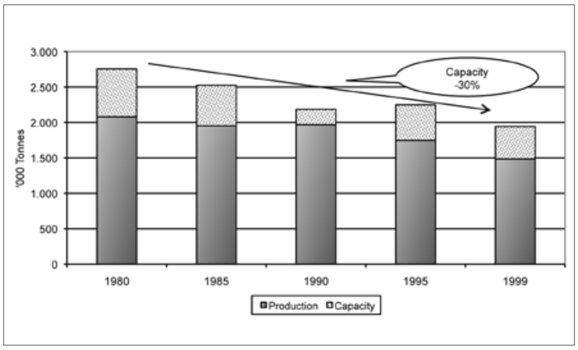

Figure 1. *Global Capacity and Production of Viscose Fibre 1980 - 1999.*

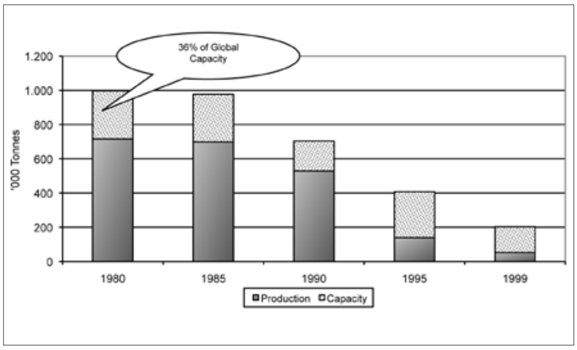

Figure 2. *Capacity and Production of Viscose Fibre 1980 - 1999 – Eastern Europe.*

close to 3 million tonnes/annum to under 2 million tonnes/annum.

While this decline is, in itself significant, some of the drivers behind it are even more extraordinary. In Eastern Europe capacity dropped from 1 million tonnes/annum – 36% of world capacity – to just 200.000 tonnes/annum over this 20 year period. In North America, capacity dropped by 52% over the same time period.

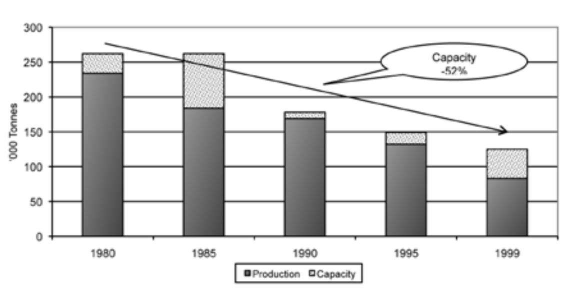

__Figure 3.__ Capacity and Production of Viscose Fibre 1980 - 1999 – North America.

There are a number of reasons for the overall decline in capacity.

Firstly, while viscose had established a position as a substitute for natural fibres, particularly cotton, as the availability of polyester grew and its cost reduced, it became a viable alternative to both natural fibres and viscose.

Secondly, the supply of natural fibres was sufficient to meet the growing world demand for textiles over this period.

Finally, and perhaps most significantly, the pace of migration of the textile industry away from West Europe and North America increased – moving to areas where there was little availability of viscose fibres but a good supply of alternatives.

At the turn of the century, the prospects for the global viscose fibre industry looked bleak.

However, what has actually happened since 2000 has been a sustained recovery, with world capacity growing by around 95% up to 2011.

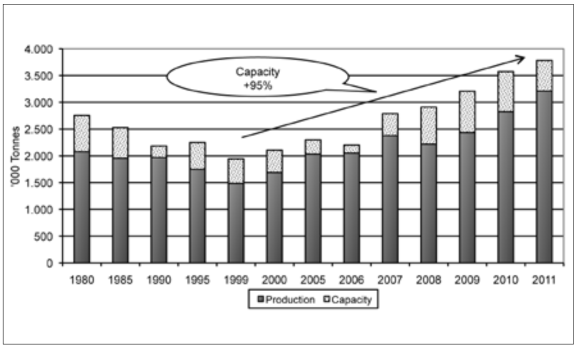

__Figure 4.__ Global Capacity and Production of Viscose Fibre 1980 - 2011.

To a great extent, this capacity increase has been driven by the growth of the viscose fibre industry in China. By 2011, Chinese capacity had grown to around 2,2 million tonnes/annum, or 59% of world capacity, from around 100.000 tonnes/annum or just 4% or world capacity in 1990.

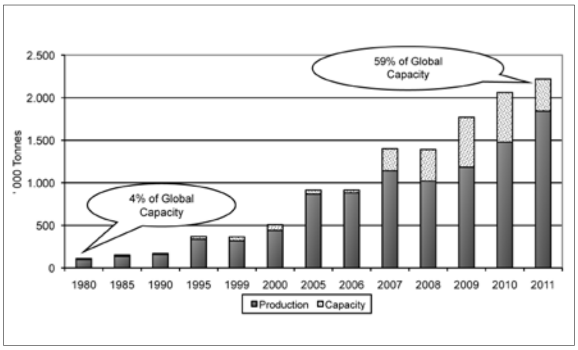

__Figure 5.__ Capacity and Production of Viscose Fibre 1980 - 2011 – China.

Capacity for the production of viscose fibre has also grown in the regions of South and Southeast Asia, including Indonesia, India and Thailand.

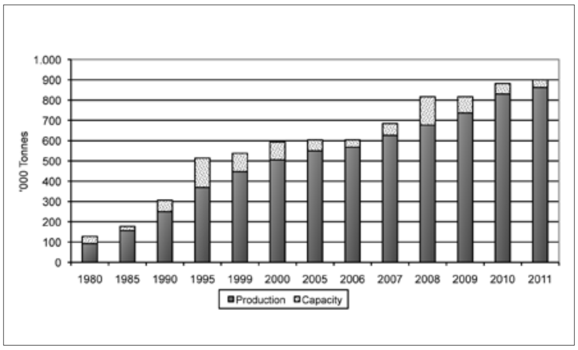

__Figure 6.__ Capacity and Production of Viscose Fibre 1980 - 2011 – S & SE Asia.

significant growth has been seen in Asia, capacity in Europe has consolidated at around 400.000 tonnes/annum following a drop in capacity between 1980 and 1985.

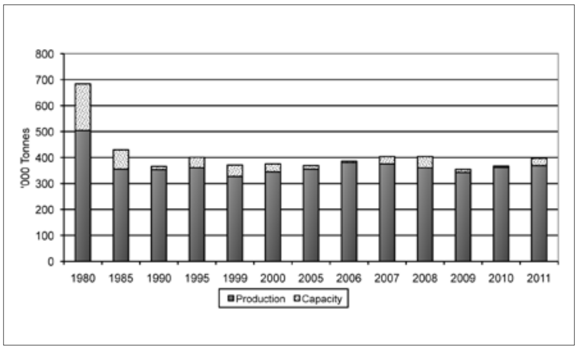

__Figure 7.__ Capacity and Production of Viscose Fibre 1980 - 2011 – Western Europe.

It should however be noted that the stability apparent in the chart masks a number of plant closures in the region. Over the period, viscose production has ceased in the United Kingdom, Sweden and France, and two plants in Spain and one in Germany have closed.

Alongside the growth in consumption of viscose in textile end uses in Asia, growth in demand from the nonwovens and hygiene industries, particularly in Europe, Israel and North America, has been significant and has been a key driver in maintaining the level of capacity in West Europe.

Globally, capacity in the industry is forecast to grow still further in the coming years, particularly in Asia. In China, a further 900.000 tonnes/annum capacity are expected to be installed by 2020, while in South and Southeast Asia 500.000 tonnes/annum capacity are planned over the same period. These numbers are impressive, and suggest an increase in global capacity of around 40% in the next 8 years or so.

The primary reason for the continued growth of capacity in the industry is the fact that, in the future, the availability of cotton will be limited driving demand for cellulosic fibre alternatives. This so called “Cellulosic Gap” [1] is a key factor driving future planning in the viscose fibre industry.

Furthermore, just as there has been growth in demand from the nonwovens industry in Europe, Israel and North America, growth is now being seen in Asia and the Far East where capacity for the production of spunlace fabrics, a key consumer of viscose fibres, continues to grow.

A further strong argument for the growth of viscose fibres is the megatrend sustainability. Viscose fibre is made from wood pulp, a renewable raw material, and as such has a strong position and a strong future in this context.

Finally, it should be considered whether there is another industry waiting to be discovered as a potential consumer of viscose or to discover viscose as a raw material – just as the nonwovens industry discovered viscose in the second half of the 20th century.

It could be concluded from these developments that the future of viscose production is very much focussed on Asia. However, it is worth taking a look at the characteristics of the industry in Asia, as this provides an important contrast to the strategy adopted by Kelheim Fibres GmbH.

The industry in Asia is characterised firstly by a focus on economies of scale; the new plants being built in the region have big lines – with a daily capacity of 200 tonnes and more – and usually a low number of lines. The production is highly efficient as a result – but lacks flexibility in terms of product types and lot sizes. This production configuration drives a concentration on standard products, mainly targeted at the textile industry, although standard products for the growing nonwovens industry in the region are now increasingly being produced locally.

Production volumes are largely driven by market demand and there is little customer loyalty, leading to high levels of cyclicality in the industry, both in terms of production utilisation and in terms of price.

This type of business model appears to be successful in Asia – to judge by the amount of capacity being installed there – but it does not offer a recipe for sustainable success for a producer operating in Europe.

Kelheim Fibres GmbH – Challenges and Opportunities

Kelheim Fibres GmbH has faced a number of challenges in recent years, but each of these has offered opportunities for the business and allowed a strong and sustainable business to be built.

As background to this there follows a brief introduction to the Kelheim business. Viscose production started on the site in 1936 and the business was integrated in to Hoechst in the late 1960s.

In the 1990s – a decade of massive change in the fibres industry – Kelheim became part of a JV with Courtaulds, passed into full ownership of the Courtaulds Group, and became part of the Acordis Group in 1999. Finally, in 2004 Kelheim passed into private ownership and has been operating successfully in its current configuration since then.

Today the capacity for the production of viscose fibres in Kelheim is around 90.000 tonnes/annum on 11 production lines, with 500 employees and a turnover of around 200 million Euros.

The plant is therefore very different to those currently being built in Asia, and has developed very differently to the way most of the industry has developed over the past 20 years.

The following are some of the key challenges that Kelheim has faced and the opportunities that have been taken from them.

Kelheim Fibres is a medium sized company in a high cost area. Medium sized is a correct term of reference in relation to the turnover and the number of employees in the business – but in terms of the industry, the business is small, and it is undeniable that Europe is a high cost area, and Germany one of the highest cost areas in Europe. However, the location of the plant provides access to a reliable, highly trained and skilled workforce and to Research and Development resources, the access to ideas, people and other resources which will allow the company to continue to innovate.

The business is located on the banks of the Danube near residential areas and this leaves it no choice but to fulfil the strictest environmental requirements, which clearly has a cost in terms of both capital and day to day running cost. This however drives a need to use raw materials and energy efficiently and to invest continuously to ensure that plant and equipment can be operated efficiently and meet all legislative requirements.

Kelheim Fibres GmbH operates 11 relatively small production lines, with daily capacities ranging from 10 to 70 tonnes and therefore has a complex plant configuration in comparison with its competitors – which also leaves it with a cost disadvantage on standard products. However, the plant configuration allows the business to offer flexibility, in terms of the products produced, how they can be modified in production, as well as the lot sizes that can be produced.

For the business in Kelheim, big is certainly not beautiful. But it is clear that Kelheim Fibres GmbH survived the decline in the global viscose fibre industry at the end of the 20th century outlined above and that the business has developed a strategy for surviving and growing in the environment of tough competition from Far Eastern producers in the first decades of this century – an environment that will become increasingly competitive.

Kelheim Fibres GmbH – A Strategy for Success

The strategy for success at Kelheim Fibres is based on the four key elements.

The first of these elements helped Kelheim through the turbulent times of the 1990s. It was focussed on the effective and efficient use of available equipment and technologies to produce small lots of fibre with unique properties. The business looked at what was available determined the best way of using it.

The management of the business also looked at the businesses they were in and decided to switch the focus of the business from standard textile fibres to the growth areas of hygiene and nonwovens. However, it was also decided to look at ways of using the equipment in Kelheim to grow speciality textile businesses – examples here are the Viloft® business and viscose microfibre. Beyond this the small lines available in Kelheim are ideal for producing small lots of spun dyed (pigmented) fibre and this advantage was used in establishing a business in the market for speciality coloured yarns.

However, not all of the business in Kelheim's portfolio which had traditionally been viewed as speciality business was earning speciality margins, and as a result these businesses were dropped from the portfolio. This also freed up capacity for the business to focus on growth areas.

The second element of the strategy was, and continues to be, the building of a leading position in key markets. Based on the experience existing in Kelheim in the production of hygiene products and the fibres developed by Courtaulds in the 1980s, Kelheim was able to build a leading position the tampon industry.

In addition to this, Kelheim successfully developed a wet tow business for flock and now supplies flock producers across the world with wet tow. Flock fibres cut from Kelheim's tow products are found in a wide range of applications – from luxury packaging to decorative flock products.

A further market that has been successfully developed by Kelheim is the speciality paper market. This is one of the key businesses that have been developed in the past five years. Tea bag papers is one of the main end uses and the company supplies 70% of the short cut viscose used world wide in speciality papers.

The company has also developed viscose fibres for carbonisation and these high-purity fibres are carbonised and used in the electronics industry and in high-temperature furnace insulation.

In each of these markets Kelheim Fibres holds the No. 1 position world wide and establishing this leading position has been a further step in securing the business for the future.

But it is also essential that the business continues to work to maintain this position. This is particularly important in the Tampon business where the focus is clearly on the continuous improvement of hygiene standards throughout the production process. A team of experts has been built, who apply the relevant requirements of ISO9001, ISO13485, CFR Part 820, ISO22000 and HACCP in production and the handling of finished goods. A high level of understanding of the relevant standards and also of customers' requirements in this area has been developed and an upgrade of FMEAs, including a full review of the production processes and an upgrade of risk analysis processes is being carried out.

The third element of strategy in Kelheim is clearly focussed on the future, and uses the technologies available to in Kelheim to produce innovative products. Kelheim Fibres GmbH also maintains strong links with research institutes and academic institutions. For example, Kelheim has been the promoter of and an active participant in discussions between the Technical University in Munich and the Bavarian State Government about the establishment of an R&D Centre for bio-based high-technology fibres in Kelheim.

The Kelheim business has also understood that the viscose process itself – although over one hundred years old – remains incredibly versatile, and has christened this versatility "The Kelheim Fibres Toolbox". The

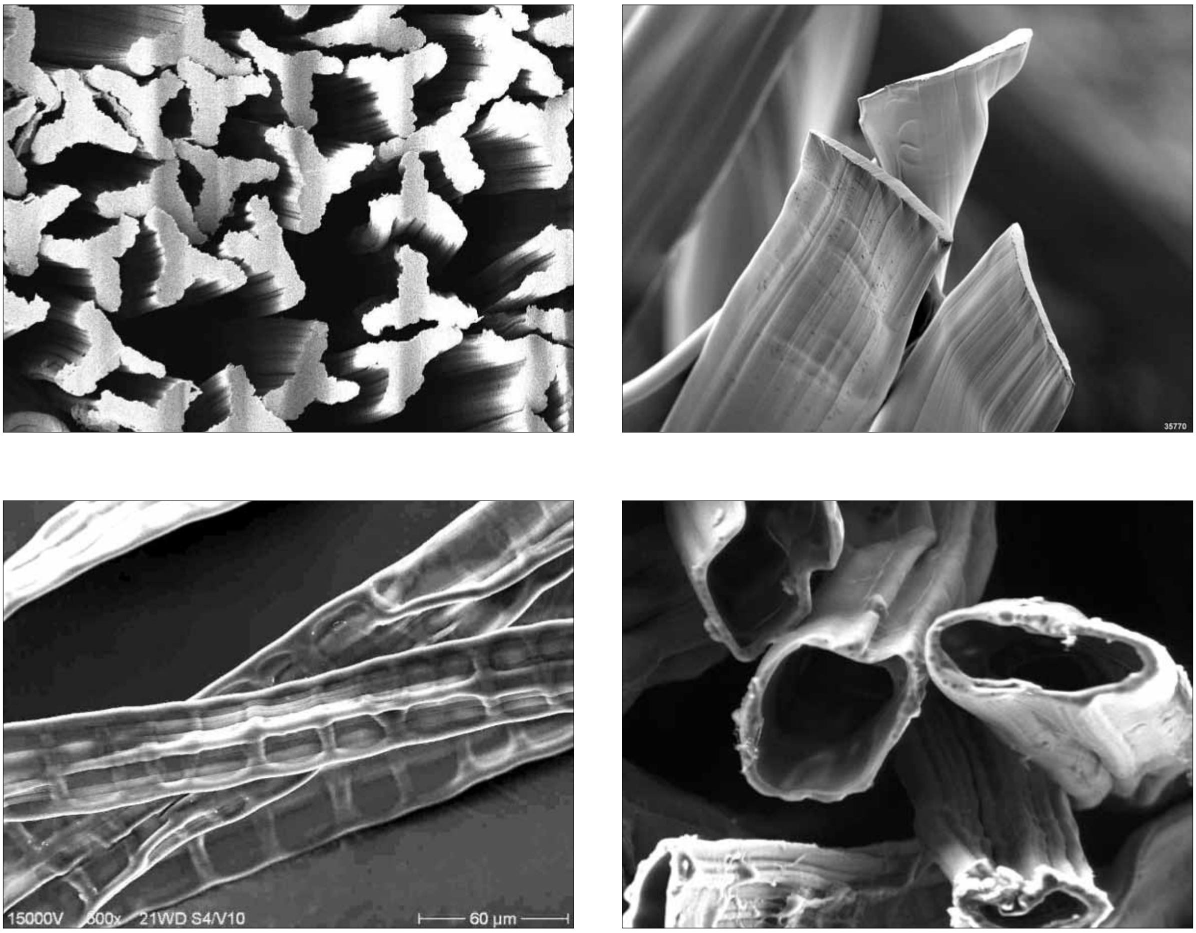

Figure 8. *Examples of Modified Viscose Fibres Produced in Kelheim – Galaxy®, Bellini, Dante, Bramante, (clockwise from top left).*

R&D function in Kelheim uses this toolbox to experiment with and develop new functionalities in the fibres produced.

Cross-section, fibre length, the incorporation of additives and chemical modifications are just some of the things that Kelheim has been able to change in the process, allowing the production of innovative fibres offering properties well beyond those of standard viscose fibres.

The fourth element of Kelheim's strategy recognises the importance of developing new applications for the products the company produces.

The R&D, Marketing and the newly established New Business Development functions in the business work in close co-operation in developing new business opportunities in new applications, not only for the new product innovations but also for existing products.

The business recognises that it produces compatible and versatile products which offer solutions in applications other than traditional textile, nonwoven and hygiene end uses. Based on the work that has been carried out in recent years, the company is convinced that there are other applications that offer a similar potential for viscose to that which has been seen in the nonwovens industry over the past thirty years.

Some examples of these new applications are in the paper industry, filtration end uses, composites and speciality textiles.

In the paper industry the compatibility of viscose with the pulps generally used is a key factor. The addition of viscose short cut can enhance the strength and porosity of papers and can help improve strength where low quality raw materials, such as recycled paper pulps have to be used.

Viscose can be used in the production of filter media to deliver enhanced performance, and viscose fibres incorporating ion exchange materials can be used to produce chemically active filters.

Viscose fibres can also be used as part of a composite system, and if a biodegradable matrix is used, the composite itself can be classed as fully biodegradable.

The business also believes that there is the potential to use the fibres we have developed in textile applications where enhanced properties, such as cooling or hydrophobic performance can be achieved.

Conclusions

It is clear that specialisation is not a new strategy in the fibre industry.

But specialisation demands commitment – both in terms of resource, in terms of hard work and in terms of thought processes.

If the chosen strategy is specialisation, it is critical to resist the temptation to service existing businesses at the expense of new business which is not yet running at full potential.

It is also important to secure the right price for the value the product delivers to the customer. It is easy to get trapped into pricing products on the basis of standard fibre price plus a premium, rather than what they are really worth.

And finally, the selection of the right development partners is also critical. Cooperation with partners who are also committed to specialisation in their businesses and markets is likely to deliver rapid and sustainable success.

Kelheim Fibres GmbH has reached the position it is in today through commitment to a specialisation strategy based on four key elements:

- The effective use of existing equipment
- The building of leading positions in key markets
- The adaption existing technologies for innovation, and
- The building of business in new applications and markets.

However the business also recognises that as soon as any competitor offers a product with the same performance and properties as its own, then these will no longer be seen as speciality products by the market.

So specialisation becomes a continuous process, and no business can rest as it strives to specialise further.

Kelheim Fibres is committed to further specialising its business using the strategies outlined here to secure the future of the business.

Acknowledgements

Kelheim Fibres GmbH would like to thank Nick Bywater (nick.bywater@btinternet.com) and CIRFS (www.cirfs.org) for the supply of historical data included here.

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Cellulose Degradation During Viscose Processing

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Abstract

Due to the infusibility of cellulose making of cellulose fibers for textile and non woven applications from Due to the infusibility of cellulose making of cellulose fibers for textile and non woven applications from wood pulp needs to dissolve the cellulose. Dissolving of cellulose means to break the strong hydrogen bonds in between the cellulose chains and to replace those by interactions with a solvent or by derivatization of the cellulose OH-groups [1]. In 1892 a patent written by C.F. Cross, E.J. Bevan, and C. Beadle described a derivatization process of cellulose with sodium hydroxide and CS_2 to cellulose xanthogenate – the viscose process. Lenzing has been producing Viscose, the first generation cellulose fiber, for more than 70 years. The knowledge it has acquired in Viscose production is reflected in the superb quality of Lenzing Viscose® quality which now sets the standard for the textile industry today.
During the whole process from pulp to viscose fiber the degree of polymerization (DP) of cellulose decreases [2]. Cellulose degradation occurs in different steps. Some of them are deliberate, like alkalization and pre-ageing [3]. Others are unintentional, like the degradation during regeneration of cellulose in the spinning bath and during the after treatment.

Keywords: *cellulose degradation, viscose, alkali*

Introduction

Viscose fibers are spun in a precipitation bath containing sulfuric acid, Glauber salt and normally zinc sulfate. To obtain staple fibers the tow must be cut, washed and treated in several ways. At least the sulfur must be removed and often the fibers have to be bleached. Sometimes there is also an acid treatment implemented. The last treatment bath before drying is the spin finishfield with soap to make the fiber spinable.
It is known that bleach [4] or acid [5, 6] will attack cellulose and even caustic [7] is known for the peeling off-reaction [8]. In this view it is to be expected to have fiber deterioration but the degree of damage is unknown.
To adjust the effect of the different after treatment sections a standard 1.3 dtex fiber was made in the lab, but instead of the usual after treatment procedure the fibers were only washed with soft water. The fibers were dried to avoid troubles in the experimental design with inhomogeneous fiber moisture.
To simulate an acid treatment sulfuric acid in a concentration of 5% at different temperatures of 70, 80 and 90° C was selected.
Instead of the desulfurization bath caustic in a concentration of 2 g/L at 50 and 70° C as well as 5 g/L at 50° C was taken.
The influence of bleach on the fiber was investigated by using 1.14 g/L as well as 5.7g/L active chlorine at 50° C.
The fibers were treated in these chemicals and temperatures at times of 10, 30, 60 and 120 minutes.
The fiber yield can be calculated either as the percentage of the received fiber or recalculate the TOC (total organic carbon) in the bath after fiber filtration as cellulose and refer it to the input of bone dry fibers. The second method seems to be the more accurate way. Nevertheless the accuracy of the results was checked by calculating the rate of retrieval adding the calculated cellulose to the mass of received fibers.
The degree of degradation was calculated using the following equation [9]:
(1/DP - 1/DP0) = fB (degree of degradation).

Materials and Methods

The used fibers where 1.3 dtex (bright) standard ZS made in the Lenzing Pilot Plant without after-treatment, but washed with water after spinning. The preparing of the viscose and spinning were done with standard lab conditions. Before using these fibers for the experiment, the fibers had to be carded.

The used chemicals were standard LAB-qualities (PA) with the exception of bleach which was of technical grade.

The TOC detection was done with the help of a “Shimadzu TOCVP”-Analyzer.

The DP calculation was done after measuring the intrinsic viscosity corresponding to “SCAN – CM 15_99”.

All extraction experiments with caustic and bleach were performed in closed 1 liter PE-bottles in a water bath.

Due to the high acid temperature of 90° C these experiments were executed in a 2 liter 2 - neck flask with thermometer and reflux condenser to avoid a loss of water. Heating was done with the help of a heating mantle and magnetic stirrer.

The experiments were all done in the same way. After the treatment bath had reached the default temperature, 30 g of air dry fiber were added, mixed to make sure that all fibers are covered with liquid and left for the given time at this temperature. Afterwards the reaction mixture was filtered through a G2 glass frit. A sample of the filtrate was taken for TOC determination. The Fibers were washed with deionized water until a neutral filtrate occurred. The washed fibers were carefully removed from the frit and spread out in a tray for drying on air at ambient temperature.

For yield calculation the fiber moisture was determined from the used and treated sample.

Results and Discussion

All the conditions were chosen in a way to see clear differences with the methods used for analysis. Therefore, the treatment time and the concentrations were increased. The fiber yield loss is increasing linear during the treatment time and higher temperatures and can be described as a zero order kinetic (Figure 1a and 1b).

The treatment with sulfuric acid shows this clearly. While at 70° C no loss of fiber material could be observed, the loss at 80° C was clearly visible. Another temperature increase up to 90° C fulfilled the Arrhenius rule of thumb by doubling the material loss during the treatment time. Bleach, also attacked the fiber furiously when a concentration of 5.7 g/L active chlorine was used. The treatment with caustic led to an almost unchanged fiber mass after 2 hours of treatment. Even with a temperature of 70° C or increased caustic concentration a surprisingly low material loss could be observed. Due to this negligible fiber loss no DP-degradation of the fibers was expected, which also could be observed (Table 1).

Contrary to caustic in case of sulfuric acid at 70° C no loss of fiber mass but a high DP degradation could be observed, which suggested that the cutting of the cellulose chain occured randomly. The DP degradation increased with the temperature drastically and could be described as a zero order kinetic, too.

The speed of the DP degradation increased with a higher bleach concentration of active chlorine. While the low concentration of 1.14 g/L the observed mass loss during the reaction time was negligible the fiber DP reduction was remarkable. The concentration of 5.7 g/L led to a notable mass and DP loss. This was caused by the oxidative force of the hypochlorite and not related to the alkaline pH because caustic gave only negligible fiber loss and no DP degradation.

The fiber properties like tenacity, elongation and the product out of these called the working capacity were extremely depending on the degree of degradation resulting in these treatments.

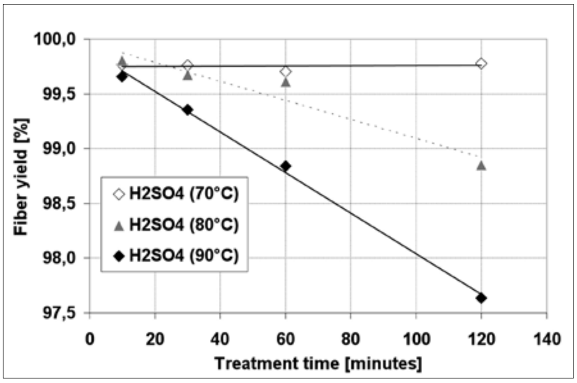

Figure 1a. Received fiber yield after acid treatment – calculated from TOC value.

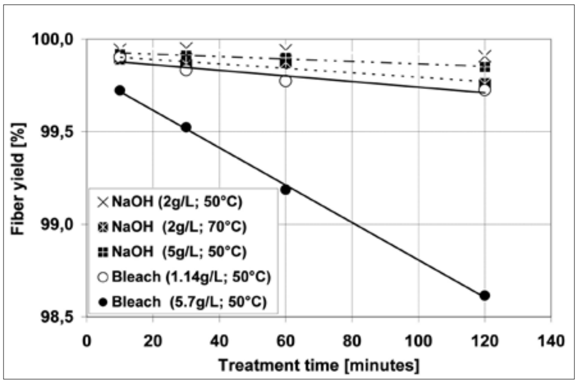

Figure 1b. Received fiber yield after alkali treatment and bleaching.

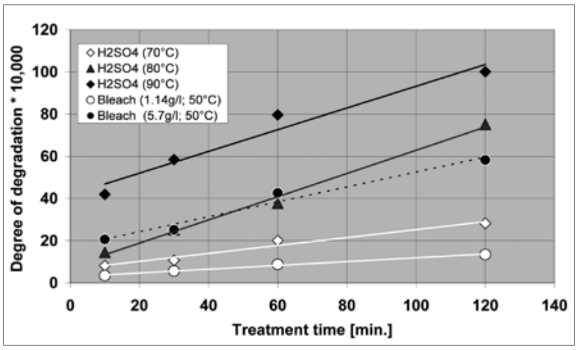

Figure 2. *Degree of degradation vs. treatment time.*

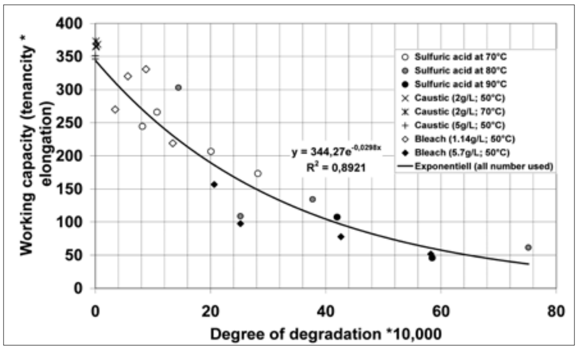

Figure 3. *Working capacity versus degree of degradation.*

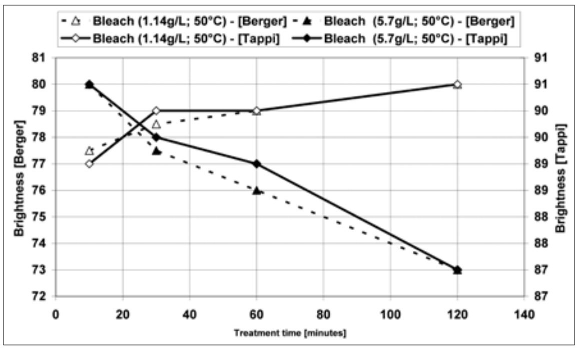

Figure 4. *Brightness evolution by treatment with bleach.*

Some work was done in the past by Krässig [10] investigating the influence of DP-degradation by hydrolysis on tenacity, but the influence on the elongation of the hydrolyzed fibers was no subject of these work.

We were not able to test some of the treated fibers for fiber properties because only fiber dust was received. This happened in an extreme way at 5% sulfuric acid for 1 and 2 hours at 90° C. The only series without any visible damaged fibers was the sulfuric acid treatment at 70° C even after two hours of treatment. Almost all of the bleach treated fibers had broken fibers in the samples especially the fibers treated with 5.7 g/L active chlorine. This started with the treatment of 10 minutes and got even worse during the treatment time. Interestingly, the treatment with caustic, which did not have any negative impact on fiber DP and fiber properties also caused short fibers after the whole procedure.

Both, tenacity and elongation decreased with increasing treatment time with the exception of the caustic treatment. The working capacity depended only on the DP – degradation no matter whether hydrolysis or oxidation caused the fiber damage.

The elevation of the brightness with bleach is dearly bought by loosing tenacity and elongation, even sodium hypochlorite is used in moderate concentrations. The bleach with the lower active hypochlorite concentration reached the maximum brightness within 30 minutes of treatment. A longer treatment time gave only a marginal influence on the brightness. But, a noticeable loss of fiber DP could be observed even within the short treatment time of 10 minutes.

Table 1. *Material loss and fB (Average values of two trial series); a) viscosity not determined.*

	Treatment time				Linear regression line			Temp. [°C]	Medium	Concentration
	10 min.	30 min.	60 min	120 min	slope	intercept	r2			
Yield from TOC [%]	99.77	99.76	99.70	99.78	0.0001	99.75	0.02	70	H_2SO_4	5%
	99.81	99.68	99.61	98.85	-0.0087	99.96	0.93	80	H_2SO_4	5%
	99.66	99.36	98.84	97.64	-0.0185	99.89	1.00	90	H_2SO_4	5%
	99.94	99.95	99.94	99.91	-0.0004	99.96	0.85	50	NaOH	2 g/L
	99.90	99.87	99.87	99.76	-0.0012	99.91	0.88	70	NaOH	2 g/L
	99.92	99.91	99.90	99.85	-0.0007	99.93	0.97	50	NaOH	5 g/L
	99.90	99.83	99.77	99.73	-0.0015	99.89	0.90	50	Bleach	1.14g/L
	99.72	99.52	99.19	98.61	-0.0101	99.82	1.00	50	Bleach	5.70g/L
degree of degradation * 10.000	8.2	10.7	20.1	28.2	0.1881	6.45	0.97	70	H_2SO_4	5%
	14.4	25.2	37.7	75.2	0.5501	7.87	0.99	80	H_2SO_4	5%
	42.0	58.5	79.7	100.1	0.5152	41.71	0.95	90	H_2SO_4	5%
	0.1	a)	a)	0.1	-0.0005	0.15		50	NaOH	2 g/L
	0.1	a)	a)	0.4	0.0027	0.07		70	NaOH	2 g/L
	0.0	0.0	0.0	0.0	0.0000	0.00		50	NaOH	5 g/L
	3.4	5.6	8.8	13.4	0.0901	2.87	0.99	50	Bleach	1.1g/L
	20.6	25.2	42.6	58.2	0.3535	17.22	0.97	50	Bleach	5.70g/L

***Table 2.** Working capacity of treated fibers (Average values of two trial series); a) only the first trial series was tested; b) not possible to receive a number due to fiber dust.*

	Working capacity of treated fibers							
Time	H_2SO_4 (70°C)	H_2SO_4 (80°C)	H_2SO_4 (90°C)	NaOH (2g/l; 50°C)	NaOH (2g/l; 70°C)	NaOH (5g/l; 50°C)	Bleach (1.14g/l; 50°C)	Bleach (5.7g/l; 50°C)
0	342							
10	244 a)	303 a)	107 a)	366	373	346	270	157
30	266 a)	109 a)	46 a)	365 a)	386 a)	339 a)	320	98
60	207 a)	134 a)	- b)	400 a)	366 a)	362 a)	331	78
120	173 a)	61 a)	- b)	364	368	351	219	52

Using the higher bleach concentration the maximum brightness was reached around 10 minutes of treatment time or earlier with a remarkable DP loss.
It is obvious that the brightness decreased steadily with longer treatment of the fibers. This can be explained by forming new chromophore groups.

Conclusions

Acid treatment of viscose fibers with sulfuric acid of 5% led to a noticeable loss of fiber material at temperatures higher than 70° C. Although no cellulose loss was observed at a treatment temperature of 70° C a slightly DP degradation and a remarkable decrease in the working capacity of the resulting fibers could be observed. Using higher treatment temperatures the cellulose loss, the DP degradation increased and the working capacity decreased dramatically. If the treatment time at 90° C extended 30 minutes the damage of the fiber was so high, that only fiber dust could be received.
The treatment with caustic in the selected conditions gave only a very small cellulose loss, no DP degradation of the fibers and no drop in the working capacity. Nonetheless, short fibers were found in the samples.
Bleach is a powerful oxidation agent which attacks the cellulose chain quickly even at moderate concentrations. Fiber DP degradation and material loss occured remarkably within 10 minutes of treatment. Also, the working capacity decreased quickly within a short treatment.
While the brightness at 1.14 g/L of bleach reached the maximum after treatment time of approximately 30 minutes and kept this value for longer treatment times it could be observed a decreasing brightness with the higher concentrated bleach (5.7 g/L) with longer treatment.
The working capacity depended only on the degree of degradation regardless whether hydrolysis or oxidation caused the fiber damage.

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Die Substantivität von Zellulose-Reaktivfarbstoffen – ihre Bedeutung, ihre Bestimmung und die Korrelation mit der chemischen Konstitution

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Abstract

Eine optimale Substantivität des Reaktivfarbstoffs zur Zellulose stellt eine entscheidende Voraussetzung für die angestrebte kovalent-chemische Fixierung in guter Ausbeute dar.
Der Farbstoff wird bei der Adsorption über sein delokalisiertes π - Elektronen-System an der Zellulose angereichert. Er wird aber auch (vorwiegend über seine Sulfo-Gruppen) molekular-löslich in die wässrige Färbeflotte gezogen. Abhängig von den vorliegenden Färbebedingungen stellt sich ein Gleichgewicht ein, welches in hohem Maße von der chemischen Konstitution eines Farbstoffs bestimmt wird. Über diese gegenläufigen Effekte musste es daher auch möglich sein, durch eine rechnerische Berücksichtigung des π -Elektronen-Systems und der hydrophilen Gruppen eine relative (vergleichende) Substantivität zu ermitteln. Die Korrelation mit der z. B. chromatographisch gefundenen Substantivität stellte sich als befriedigend heraus.

Keywords: *reactive dyestuffs, chemical constitution, substantivity to cellulose, adsorption equilibrium*

Substantivität im Verlauf eines Reaktiv-Färbeprozesses

Mit den heutigen Reaktivfarbstoffen erreicht man unter passenden färberischen Bedingungen Standard-Fixierausbeuten zwischen 65 und 95 %. Bei tiefen Färbungen, erhöhten Temperaturen, verringerten Salz-Konzentrationen und längerem Flottenverhältnis liegt die Fixierausbeute aber oft merklich niedriger. Der Rest an (nicht fixiertem) Farbstoff geht ins Abwasser.
Es bleibt die Frage: **wie und warum** hängt die Fixierausbeute so stark vom färberischen Rezept und von der chemischen Konstitution eines Reaktivfarbstoffs ab?

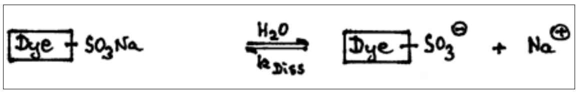
Es existiert eine ganze Reihe von Untersuchungen/Veröffentlichungen zu Teilbereichen dieses Themas [1] bis [9]. Es wurde jetzt der Versuch einer praxistauglichen, übergeordneten Betrachtung der Zusammenhänge gemacht.

Verlauf des Reaktiv-Färbeprozesses

Im Verlauf einer Reaktiv-Färbung im Auszieh-Verfahren spielen sich eine Reihe von physikalischen und chemischen Vorgängen nacheinander und z. T. nebeneinander ab:

a) Elektrolytische Dissoziation bei Sulfogruppen-haltigen Farbstoffen:

Die Na-Salze von Sulfogruppen-haltigen Reaktivfarbstoffen sind in wässriger Lösung stark dissoziiert:



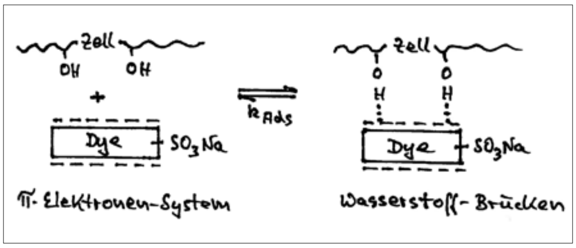
Durch den Zusatz von Na^+ (aus Kochsalz oder Glaubersalz) wird das Dissoziations-Gleichgewicht gemäß Massenwirkungsgesetz mehr oder weniger stark nach links verschoben. Diese Gleichgewichtslage ist auch von der chemischen Konstitution eines Farbstoffs, von seiner Konzentration und von der Temperatur abhängig.

b) Diffusion des Farbstoffs hin zur Zellulose und hinein in deren Poren:

Die Diffusion des Farbstoffs zu den äußeren und inneren Oberflächen der Zellulose spielt eine gewichtige Rolle, und damit bekommen die Zeit sowie die Wegstrecke/das Flottenverhältnis Bedeutung. Grundsätzlich ist die Diffusion abhängig vom Molekulargewicht des Farbstoffs, von der Badumwälzung /Warenumwälzung, von der Temperatur und von der spezifischen Oberfläche und Porenweite der Zellulose.

c) Adsorption des Farbstoffs an Zellulose vor der kovalent-chemischen Fixierung:

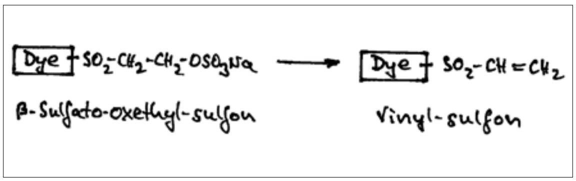
Das Farbstoff-Anion Dye-SO_3^- besitzt keine ausgeprägte Affinität zur Zellulose, da diese infolge ihres zeta-Potentials ebenfalls (leicht) anionisch ist. Der undissoziierte Farbstoff Dye-SO_3Na dagegen kann grundsätzlich an Zellulose adsorbiert werden. Die Adsorption geschieht über die Ausbildung von Wasserstoffbrücken zwischen den HO-Gruppen der Zellulose und dem delokalisierten π -Elektronen-System des Farbstoffs. Es stellt sich ein Gleichgewicht adsorbierter Farbstoff/Farbstoff in Lösung ein:



Durch die Adsorption wird eine maximale räumliche Annäherung des Farbstoffs an die Zellulose erzielt. Die Lage des Adsorptions-Gleichgewichts ist stets abhängig von der chemischen Konstitution eines Farbstoffs, von dessen Konzentration sowie von der Temperatur.

d) Chemische Vor-Reaktion (nur im Fall von Vinylsulfon-Reaktivankern):

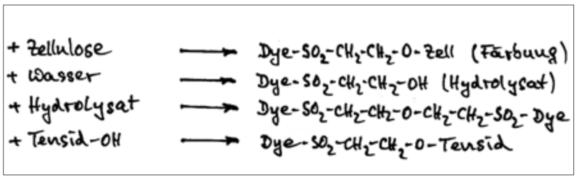
VS-Reaktivfarbstoffe tragen als Reaktivanker zunächst Gruppen des Typs β-Sulfato-oxethyl-sulfon. In wässriger Lösung trägt diese Gruppe zur guten Löslichkeit bei. Die eigentliche „reaktive Form“ stellt aber die Vinyl-sulfon-Form dar. Ihre Bildung, die Vinylisierung läuft bei neutralem pH-Wert recht langsam ab, bereits bei pH 7 – 9 aber auch bereits bei Raumtemperatur z. T. in wenigen Minuten:



Dieser Vorgang ist irreversibel. Die chemische Konstitution des Farbstoffs wird hierbei offensichtlich verändert, folglich auch das Dissoziations-Gleichgewicht, das Adsorptions-Gleichgewicht und die Diffusion (daneben natürlich auch die Wasserlöslichkeit).

e) Kovalent-chemische Reaktionen des Farbstoffs:

Prinzipiell kann bei einer Zellulose-Färbung in wässrigem Medium die chemische Reaktion des Reaktivfarbstoffs mit verschiedenen „Partnern“ erfolgen. Beispiel:



Das sukzessive entstehende Farbstoff-Hydrolysat sowie ein eventuell vorhandenes HO-Gruppen enthaltendes Tensid sind ebenfalls an der Zellulose-Oberfläche adsorbtiv angereichert und so besonders gut in der Lage, mit frischem Reaktivfarbstoff kovalent-chemisch zu nutzlosen Nebenprodukten zu reagieren.

Alle diese Vorgänge sind unter üblichen färberischen Bedingungen irreversibel.

Allgemeine Anmerkungen zu Adsorption/ Substantivität

Die Adsorption des Reaktivfarbstoffs an Zellulose steht ganz eindeutig an entscheidenden Stellen im Ablauf des Färbevorgangs. Sie ist eine absolute Voraussetzung für das Erzielen einer guten Fixierausbeute. Nicht adsorbierter Farbstoff kann eigentlich nur hydrolysieren, ist also färberisch verloren.

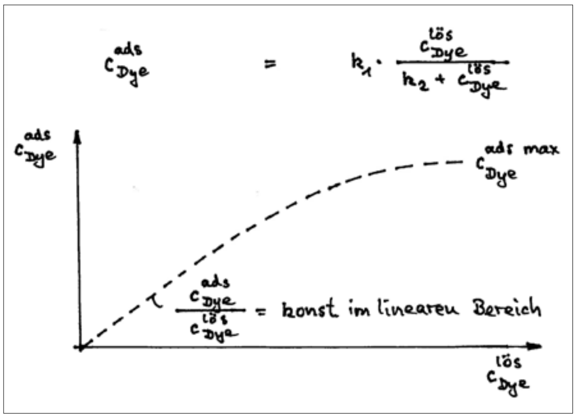
Die Substantivität von intaktem, reaktivem Farbstoff kann man bekanntlich gut steuern über die Menge an Kochsalz oder Glaubersalz sowie über die Temperatur. Die Erreichung des Adsorptions-Gleichgewichts benötigt allerdings eine gewisse Zeit.

Kleinmolekulare Farbstoffe benötigen grundsätzlich zur Erzielung einer ausreichenden Substantivität viel Salz sowie Temperaturen um 40 – 50° C, großmolekulare Farbstoffe dagegen weniger Salz und Temperaturen um 60 – 95° C. Erhöhte Temperaturen führen daneben aber auch zu einer besseren Quellung der Zellulose, wodurch die Farbstoff-Diffusion beschleunigt und eine Adsorption auch innerhalb der Zelluloseporen ermöglicht wird.

Adsorptions-Isothermen

Die Farbstoff-Adsorption an Zellulose (mit anderem Wort die Substantivität des Farbstoffs) gehorcht den bekannten physikalischen Adsorptionsgesetzen von

Freundlich, Langmuir oder BET. Nach Langmuir z. B. führt die nachfolgende Formel zu einem realitätsnahen Diagramm:



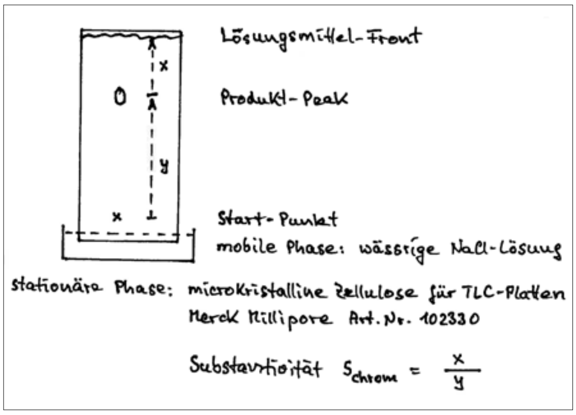
Die Steigung der Kurve (genannt Adsorptions-Isotherme) im linearen Abschnitt stellt einen spezifischen Wert für einen Reaktivfarbstoff bestimmter chemischer Konstitution dar. Sie gilt für eine definierte Salz-Konzentration sowie für eine definierte Temperatur und einen bestimmten pH-Wert sowie für ein definiertes Adsorbens (Zellulose).

Bei tiefen Färbungen, d. h. bei hoher Farbstoff-Konzentration bewegt man sich allerdings nicht mehr im linearen Abschnitt der Adsorptions-Isotherme. Die Zellulose-Oberfläche ist dann mehr oder weniger mit Farbstoff gesättigt. Folge ist, dass eine restliche Farbstoffmenge nicht mehr adsorbiert wird und als $\text{Dye}^{\text{lös}}$ tendenziell nur einer Hydrolyse unterliegen kann. Hierin liegt die Hauptursache für den zahlenmäßigen Abfall der Fixierausbeute bei tieferen Reaktiv-Färbungen.

Chromatographische Bestimmung der Substantivität

Die experimentelle Bestimmung der physikalischen Adsorption (der Substantivität) von Reaktivfarbstoffen an Zellulose erfolgt üblicherweise färberisch: man setzt eine Färbung (ohne Alkali) an und misst die Farbstoff-Konzentration nach der Endgleichgewichts-Einstellung per Transmissionsmessung gegen die anfängliche Konzentration im Bad.

Alternativ kann man die Farbstoff-Adsorption chromatographisch bestimmen, mittels Dünnschicht-Chromatographie oder nach der HPLC-Methode. Am besten verwendet man mikrokristalline Zellulose als stationäre Phase, diese kommt der Zellulose-Faser sehr nahe. Aber auch ein Arbeiten auf Chromatographie-Papier ist möglich. Eine blinde Färbeflotte, mit entsprechender Salz-Konzentration, mit bestimmtem pH-Wert und bestimmter Temperatur bildet die mobile Phase. Der resultierende RF-Wert bzw. die resultierende Retentionszeit stellen ein direktes Maß für die Substantivität dar. Man kann hieraus einen vergleichenden „relativen Substantivitäts-Koeffizienten S^{chrom}" ermitteln:



Diese relative Substantivität ist als Zahlenwert für Vergleichszwecke sehr gut geeignet. Sie kann Beträge zwischen null (nicht substantiv) und unendlich (höchst substantiv) annehmen.

Bei den chromatographischen Methoden können die Temperatur, die Salz-Konzentration und der pH-Wert fast beliebig gewählt werden, so dass man für jedes einzelne Reaktivfarbstoff-Sortiment aussagekräftige Chromatographie-Bedingungen schaffen kann.

Die S^{chrom}-Werte korrelieren gut mit der färberisch bestimmten Substantivität.

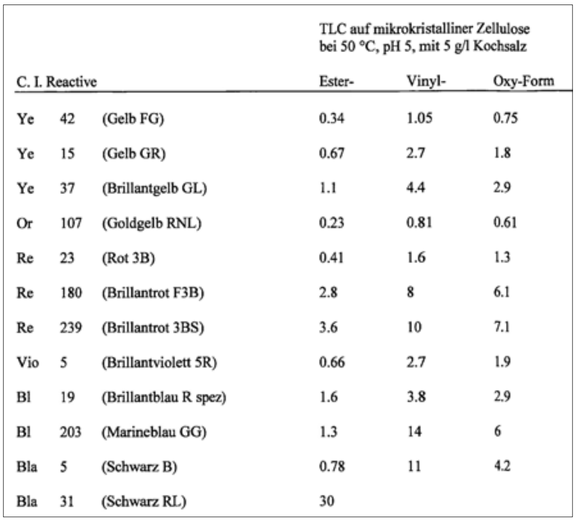
Zu beachten ist allerdings, dass hohe Farbstoff-Konzentrationen chromatographisch zu einem Tailing führen, so bald eine örtliche Sättigung der stationären Phase (Zellulose) mit Farbstoff eingetreten ist.

Was geschieht bei Farbstoff-Kombinationen/Trichromie-Färbungen? In den seltensten Fällen werden alle Kombinationspartner eines Färberezeptes die gleiche relative Substantivität zur Zellulose aufweisen. Aus der färberischen Praxis weiß man z. T. recht gut, dass bei Kombinationen aus schwach substantiven mit hoch substantiven Farbstoffen desselben Sortiments der schwach substantive Typ stark an einer Adsorption gehindert werden kann. Insbesondere bei tiefen Färbungen z. B. auf Basis von C. I. Reactive Black 31 (Schwarz RL) mit Nuanciersätzen von Yellow 42 (Gelb FG) wird der Gelb-Anteil sehr weitgehend unterdrückt. Die farbmetrische Rezeptrechnung stößt hier entsprechend auf echte Probleme.

Substantivitäts-Unterschiede innerhalb eines Reaktivfarbstoff-Sortiments

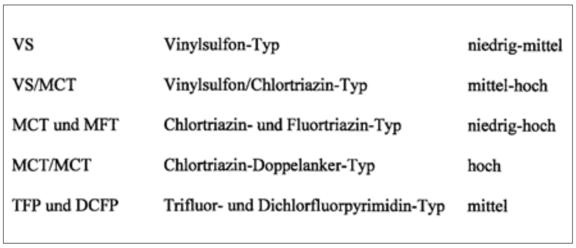
Interessant ist die Frage, ob innerhalb eines Handels-Sortiments von Reaktiv-Farbstoffen bezüglich der relativen Substantivität alle Einzelfarbstoffe gleich oder zumindest sehr ähnlich sind.

Die Substantivität einer Reihe von Einzelprodukten verschiedener Reaktiv-Sortimente wurde experimentell und rechnerisch (s. später in diesem Aufsatz) bestimmt. Es zeigte sich eine erstaunlich große Streubreite:



C. I. Reactive			TLC auf mikrokristalliner Zellulose bei 50 °C, pH 5, mit 5 g/l Kochsalz		
			Ester-	Vinyl-	Oxy-Form
Ye	42	(Gelb FG)	0.34	1.05	0.75
Ye	15	(Gelb GR)	0.67	2.7	1.8
Ye	37	(Brillantgelb GL)	1.1	4.4	2.9
Or	107	(Goldgelb RNL)	0.23	0.81	0.61
Re	23	(Rot 3B)	0.41	1.6	1.3
Re	180	(Brillantrot F3B)	2.8	8	6.1
Re	239	(Brillantrot 3BS)	3.6	10	7.1
Vio	5	(Brillantviolett 5R)	0.66	2.7	1.9
Bl	19	(Brillantblau R spez)	1.6	3.8	2.9
Bl	203	(Marineblau GG)	1.3	14	6
Bla	5	(Schwarz B)	0.78	11	4.2
Bla	31	(Schwarz RL)	30		

Bei anderen Sortimenten (mit anderem Reaktivanker oder z. B. mit Doppel-Molekülen) kommt ein ähnliches Bild zustande. Grundsätzlich gilt für die relative Substantivität bestimmter Reaktivfarbstoff-Typen folgende grobe Einordnung:



VS	Vinylsulfon-Typ	niedrig-mittel
VS/MCT	Vinylsulfon/Chlortriazin-Typ	mittel-hoch
MCT und MFT	Chlortriazin- und Fluortriazin-Typ	niedrig-hoch
MCT/MCT	Chlortriazin-Doppelanker-Typ	hoch
TFP und DCFP	Trifluor- und Dichlorfluorpyrimidin-Typ	mittel

Die praktischen Färbebedingungen werden vom Farbstoff-Anbieter grundsätzlich so gestaltet und empfohlen, dass die „richtige“ Substantivität entsteht, um eine hohe Fixierausbeute und eine gute Egalfärbung zu gewährleisten.

Rechnerische Ermittlung der relativen Substantivität von Farbstoffen

In der Farbstoffforschung ist in den letzten Jahren ein breiter Erfahrungsschatz aufgebaut worden. Man weiß recht gut, wie man die chemische Konstitution gestalten muss, um bestimmte färberische Eigenschaften von Reaktivfarbstoffen zu verändern.

Es erhebt sich aber die Frage, in wie weit sich die relative Substantivität zwanglos aus der chemischen Konstitution rechnerisch herleiten lässt. Orientierende Versuche und Berechnungen zu diesem Thema sind bereits durchgeführt worden [10], aber nur unter teilweiser Berücksichtigung von chemisch-konstitutionellen Gegebenheiten. Ganz offensichtlich stehen sich bei jedem Farbstoff 2 Kräfte gegenüber: einerseits die Anziehungskraft zwischen Zellulose und Farbstoff (Adsorption), andererseits das Streben des Farbstoffs in wässrige Lösung (Hydrophilie). Es stellen sich folgende Fragen:

a) Wie groß ist definitiv die Anziehungskraft zwischen Farbstoff und Zellulose, welche zur Adsorption führt? Kann man die Wasserstoffbrücken-Bindung zwischen dem delokalisierten π - Elektronen-System des Farbstoffs und den HO-Gruppen der Zellulose rechnerisch bestimmen oder zumindest vernünftig abschätzen?

b) Wie groß ist die Hydrophilie eines Farbstoffs? Kann man die Hydratisierung/die Lösungstendenz über die hydrophilen Gruppen des Farbstoffs rechnerisch ermitteln?

Aus dem Gleichgewicht beider Kräfte muss sich dann zwangsläufig eine Konstitutions-spezifische relative Substantivität S_{konst} ergeben. Es zeigt sich allerdings rasch, dass die einfache rechnerische Beziehung

$$S_{konst} = \frac{\text{Anzahl konjugierte } \pi\text{- Elektronen}}{\text{Anzahl Sulfo-Gruppen}}$$

nicht mit der experimentell bestimmten relativen Substantivität korreliert. Folgende Verbesserungsmaßnahmen führen aber zu einer gewissen Optimierung der Korrelation:

a) Der Zähler wird in die 2. oder 3. Potenz gesetzt

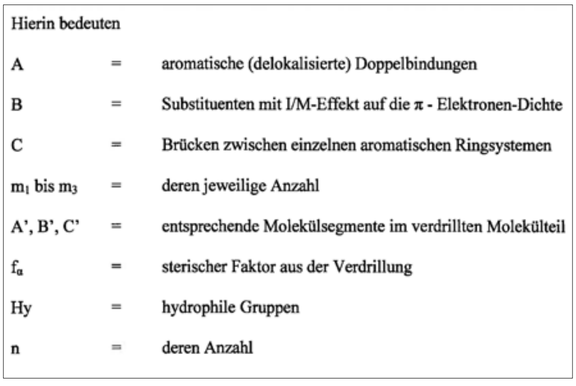
b) Substituenten, welche die π - Elektronen-Dichte beeinflussen (mit I/M-Effekt) werden berücksichtigt

c) Verdrillungen, welche die Planarität des Farbstoff-Moleküls und somit die π - Elektronen-Delokalisierung stören, werden berücksichtigt

d) Im Nenner werden alle potentiell hydrophilen Substituenten aufsummiert

Es wird also folgender Algorithmus für die Bestimmung/Abschätzung der relativen Substantivität S_{konst} entwickelt:

$$S_{konst} = \frac{\left[m_1 \cdot A + m_2 \cdot B + m_3 \cdot C + (m_1 \cdot A' + m_2 \cdot B' + m_3 \cdot C') \cdot f_\alpha\right]^3}{n \cdot Hy}$$



Hierin bedeuten

A = aromatische (delokalisierte) Doppelbindungen

B = Substituenten mit I/M-Effekt auf die π - Elektronen-Dichte

C = Brücken zwischen einzelnen aromatischen Ringsystemen

m_1 bis m_3 = deren jeweilige Anzahl

A', B', C' = entsprechende Molekülsegmente im verdrillten Molekülteil

f_α = sterischer Faktor aus der Verdrillung

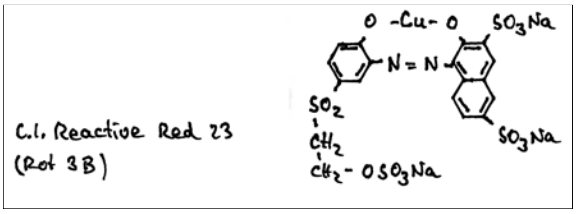
Hy = hydrophile Gruppen

n = deren Anzahl

Anmerkung: o-Oxy- und o-Amino-azo-Verbindungen sollen in der o-chinoiden Darstellung der Berechnung zugrundegelegt werden.

Über die Untersuchung und Auswertung einer Vielzahl von Farbstoffen und über deren chemische Struktur sind Zahlenwerte für die einzelnen Molekül-Segmente erarbeitet worden, welche beim Autor abgerufen werden können.

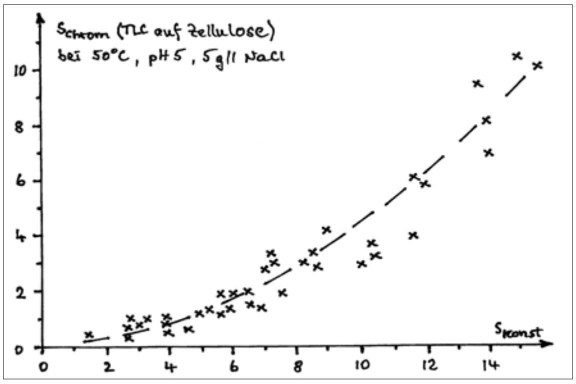
Für eine eventuelle Berücksichtigung der Substitutions-Positionen im Molekül lagen im Rahmen der vorliegenden Arbeit zu wenige Farbstoff-Präparate vor.
Rechen-Beispiel:



Mit 8 aromatischen Doppelbindungen, 1 Azo-Brücke, 1 –O-Cu-O-Brücke, 2 Sulfo-Gruppen und 1 Vinylsulfon-Gruppe im Zähler sowie mit 2 Sulfo-Gruppen, 1 Vinylsulfon-Gruppe (Ester-Form) und 1 –O-Cu-O-Gruppe im Nenner, f_a=1 (keine Verdrillung) ergibt sich

$$S_{konst} = \frac{\left[8 \cdot 0{,}3 + 1 \cdot 0{,}3 + 1 \cdot 0{,}2 - 2 \cdot 0{,}2 - 1 \cdot 0{,}2\right]^3}{2 \cdot 1 + 1 \cdot 1 + 1 \cdot 0{,}3} = 3.7$$

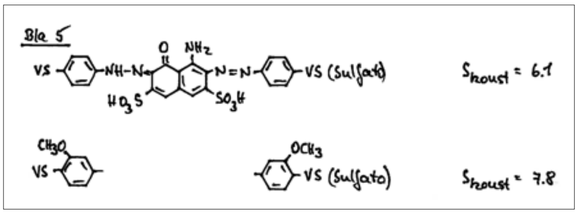
Eine graphische Auswertung zeigt, dass die mittels dieses Algorithmus' rechnerisch ermittelten Zahlenwerte für S_{konst} recht gut mit den experimentell ermittelten Zahlenwerten für S_{chrom} korrelieren:



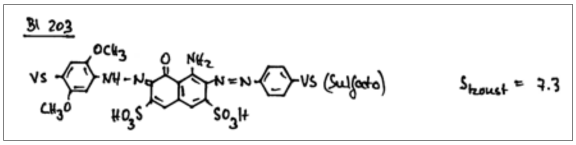
Auswirkung konstitutioneller Veränderungen

Es erhebt sich die Frage, wie wirken sich bestimmte konstitutionelle Veränderungen in einem Farbstoff-Molekül zahlenmäßig aus? Einige Beispiele sollen die Auswirkungen veranschaulichen.

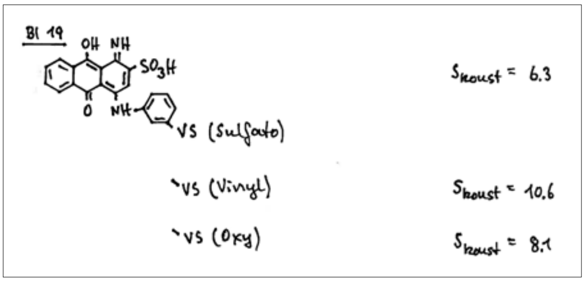
a) Erhöhung der Elektronen-Dichte durch +I – Substituenten:



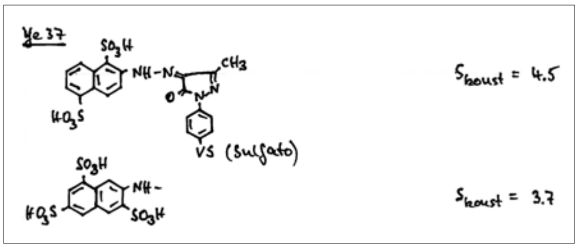
b) Änderung der Planarität (Verdrillung durch sterische Hinderung):



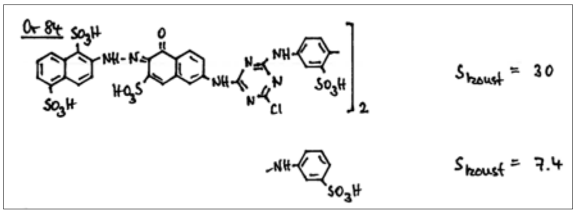
c) Veränderung der VS-Gruppe im Färbeverlauf:



d) Änderung der Anzahl an Sulfo-Gruppen:



e) „Verdopplung des Moleküls":



Bei allen diesen Beispielen korrelieren die gerechneten Werte in befriedigendem Ausmaß mit den experimentellen Werten der relativen Substantivität. Eine grundsätzliche Tauglichkeit des Berechnungs-Algorithmus scheint gegeben, Verbesserungen sind aber wünschenswert.

Berücksichtigung von Temperatur und Salz-Konzentration

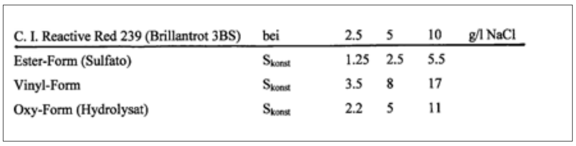
In der färberischen Praxis hat die Festlegung von Temperatur und Salz-Konzentration wie bereits erwähnt eine große Bedeutung für einen optimalen Färbeprozess. Die vom Farbstoff-Anbieter empfohlenen Färbebedingungen basieren sehr weitgehend auf diesen Einflussfaktoren auf die Substantivität.

Es stellt sich die Frage, ob man die Abhängigkeit der relativen Substantivität von Temperatur, Salz-Konzentration und pH-Wert auch rechnerisch greifen kann.

Dabei stellt sich als großer Vorteil heraus, dass alle Reaktivfarbstoffe prinzipiell das gleiche Verhaltensmuster bei derartigen Veränderungen zeigen. Daher musste es auch eine Möglichkeit geben, den Einfluss in den verwendeten Rechen-Algorithmus zu integrieren.

Versuche zum Thema Salz-Konzentration:

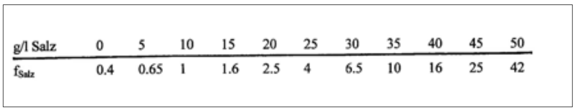
Als Basis-Methode ist die Dünnschicht-Chromatographie (TLC) auf mikrokristalliner Zellulose verwendet worden. Experimentell wurde bei 50° C und pH 5 jeweils mit einer Verdopplung der NaCl-Konzentration gearbeitet. Dabei zeigte sich, dass der experimentelle Wert Von S_{chrom} jeweils um einen Faktor von ungefähr 2 ansteigt. Dies gilt mit einer für die Praxis ausreichenden Genauigkeit für alle untersuchten Reaktivfarbstoffe. Beispiel:



C. I. Reactive Red 239 (Brillantrot 3BS)	bei	2.5	5	10	g/l NaCl
Ester-Form (Sulfato)	S_{konst}	1.25	2.5	5.5	
Vinyl-Form	S_{konst}	3.5	8	17	
Oxy-Form (Hydrolysat)	S_{konst}	2.2	5	11	

Die Ester-Form, die Vinyl-Form und das VS-Hydrolysat (Oxy-Form) verhalten sich offensichtlich weitgehend analog.

In ausgedehnten Experimenten wurde ein allgemein anwendbarer Salz-Faktor f_{Salz} ermittelt:

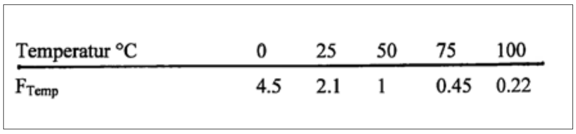


g/l Salz	0	5	10	15	20	25	30	35	40	45	50
f_{Salz}	0.4	0.65	1	1.6	2.5	4	6.5	10	16	25	42

Es wird klar, warum bei bestimmten Reaktivfarbstoffen eine Portionierung des Salzes empfohlen wird: sie dient der Vermeidung von Unegalität infolge zu hoher Substantivität.

Versuche zum Thema Temperatur

Auf analoge Weise wurde über TLC bei 5 g/l Kochsalz und pH 5 mit einer Variierung der Temperatur gearbeitet. Dabei wurde ein allgemein anwendbarer Temperatur-Faktor fTemp gefunden.

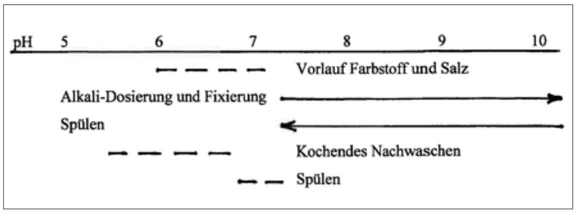


Temperatur °C	0	25	50	75	100
F_{Temp}	4.5	2.1	1	0.45	0.22

Auf dieser „Spielwiese“ kann in der Praxis mit Salz und Temperatur so „gespielt“ werden, dass man in möglichst kurzer Zeit einen gleichmäßigen Aufbau der optimalen Substantivität (und folglich einer egalen, fixierten Reaktivfärbung) erzielt und nebenher eine Minimierung an Farbstoff-Kosten, Energie und Färbezeit.

Einfluss des pH-Werts

In einem isothermen Reaktiv-Färbeprozess mit progressiver Alkali-Dosierung wird ein weiter pH-Bereich berührt:



In diesen pH-Zonen verändert sich in gewissem Ausmaß das zeta-Potential (die schwach anionische Ladung) der Zellulose. Außerdem kann ein Farbstoff pH-bedingt seine elektrostatische Ladung verändern, z. B. durch Bildung von Phenolat-Anionen bei stark alkalischem pH oder von Ammonium-Kationen bei stark saurem pH. Es liegt also nahe, dass die relative Substantivität vom pH-Wert abhängig sein kann.

Zwischen pH 4 – 5 und pH 9 – 10 wurden allerdings keinerlei Konstitutions-spezifischen pH-Abhängigkeiten gefunden.

Generell fällt der experimentelle Wert der relativen Substantivität zwischen pH 4 – 5 und 9 – 10 aber um einen gewissen pH-Faktor f_{pH} ab:

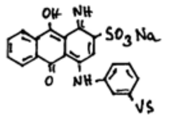
Berücksichtigung der Korrektur-Faktoren im Rechen-Algorithmus

Wenn man die relative Substantivität Schrom eines Reaktivfarbstoffs bei einer anderen Salz-Konzentration, einer anderen Temperatur und einem anderen pH-Wert rechnerisch ermitteln will, kann man also folgenden Algorithmus verwenden:

$$S_{konst} = \frac{[m_1 \cdot A + m_2 \cdot B + m_3 \cdot C + (m_1' \cdot A' + m_2' \cdot B' + m_3' \cdot C') \cdot f_{\alpha}}{n \cdot Hy} \cdot f_{Salz} \cdot f_{Temp}$$

An einem konkreten Farbstoff-Beispiel führt dieser Algorithmus zu nachfolgender Auswirkung von Salz,

Temperatur und pH-Wert auf die relative Substantivität S_{konst}:
Isotherme Zellulose_Färbung im Auszieh-Verfahren mit progressiver Alkali-Dosierung mit C. I. Reactive Blue 19 (Brillantblau R spez):



Vorlauf Farbstoff (Ester-Form) bei 50 °C ohne Salz bei pH 6	S_{konst} = 0.64
Zugabe 50 g/l NaCl	S_{konst} = 40
Beginnende Alkali-Dosierung (pH 8-9)	S_{konst} = 95
Kovalent-chemische Fixierung (pH 10-11)	
Hydrolysat (Oxy-Form) im End-Färbebad	S_{konst} = 73
Hydrolysat nach dem Vorspülen bis auf 2 g/l NaCl	S_{konst} = 1.45
Hydrolysat bei der kochenden Nachwäsche	S_{konst} = 0.32
Hydrolysat beim Nachspülen	S_{konst} ≈ 0

An diesem Beispiel zeigt sich überaus deutlich, wie sich die Substantivität von C. I. Reactive Blue 19 zur Zellulose im Verlauf eines Färbeprozesses verändert: Der niedrige Wert ganz am Anfang sorgt für eine best mögliche Anfangs-Egalität. Nach der Salz-Zugabe und während einer beginnenden Alkali-Dosierung baut sich eine beträchtliche Substantivität auf. Eine gewisse Menge an Hydrolysat am Ende des Fixier-Vorgangs und dann bei der kochenden Nachwäsche ist dann infolge der niedrigen Substantivität besonders leicht auswaschbar. Es wird auch klar, warum kleinmolekulare VS-Reaktivfarbstoffe eine Färbetemperatur nahe 40° C besonders lieben.

Hinzu kommt bei Blue 19 infolge des niedrigen Molekulargewichts eine sehr gute Diffusion, was der Egalfärbung und später der guten Auswaschbarkeit zugute kommt. Im Rahmen der vorliegenden Arbeiten ist die Diffusion allerdings nicht wirklich berücksichtigt worden.

Schlussbemerkung

Ist dies alles nur eine aufwendige Spielerei? Ja und nein! Ja, weil die Sachverhalte und Zusammenhänge zumindest bei den Farbstoff-Chemikern qualitativ ganz gut bekannt sind. Nein, weil das Ausmaß der Farbstoff- und Färbe-Parameter zahlenmäßig vielleicht manchen überraschen mag.

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No Matter of Course: Ionic Liquids as SO_2-Selective Gas Absorbers

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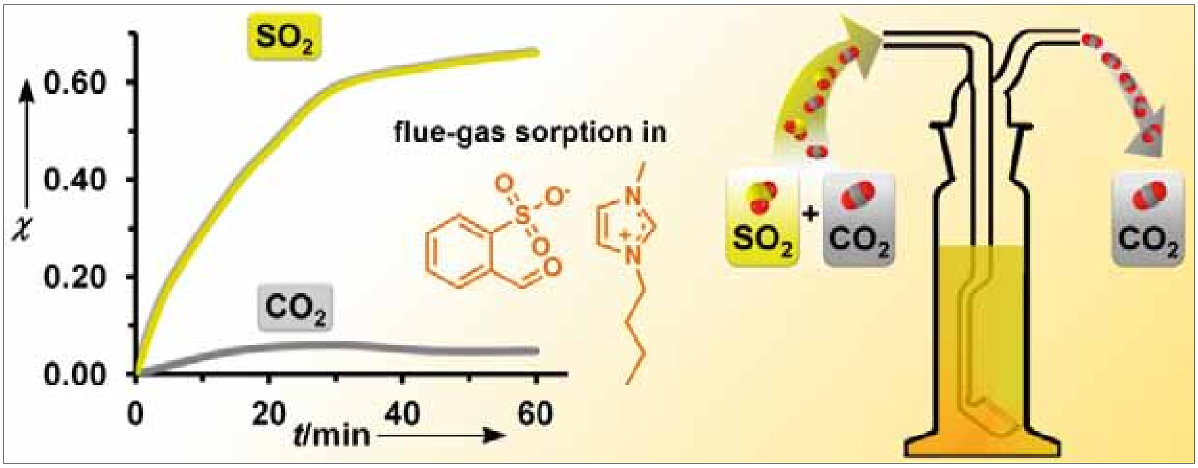
Abstract

Under the perspective of potential technical off-gas recovery and recycling, a series of ionic liquids (ILs) was compared and screened for their applicability as environmentally benign solvents for absorbing sulfur dioxide (SO_2). New molten salts based on imidazolium cations, combined with the 2-formylbenzenesulfonate anion were developed and identified as unique, regenerative scrubbing agents for SO_2. In particular, the room temperature ILs 1-butyl-3-methylimidazolium 2-formylbenzenesulfonate (BMIM OFBS) and 1-allyl-3-methylimidazolium 2-formylbenzenesulfonate (AMIM OFBS) were compared to already known SO_2-absorbing systems. In their entirety of required properties for absorb-ing and desorbing SO_2, the newly introduced systems are superior to all IL-based scrubbing media described so far: These innovative task-specific ILs exhibit low hygroscopicity, good recyclability and, most notably, a remarkable selectivity between the sour gases SO_2 and CO_2, even in the state of ambient moisture saturation. As such, the compounds are providing a high application potential for pressure or temperature swing absorption cycles. The presented primary results substantiate the advantage of the sheer number of compositional possibilities in developing ionic liquids for special purposes.

Keywords: *process gas desulfurization, waste prevention, gas absorption, selective absorption, sustainable chemistry*



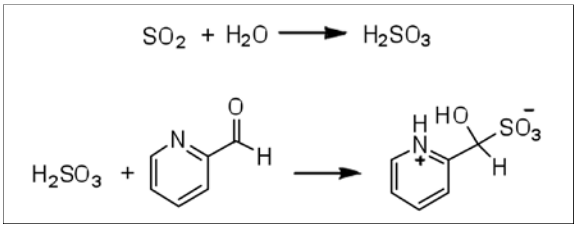
Introduction

Although sulfur dioxide (SO_2) is one of the major air pollutants, its use in industrial processes remains indispens-able. Thus, technical measures with respect to recycling and process containment are of high relevance. SO_2 is widely used as a valuable intermediate in chemical production, as a key reactant in pulping processes, as a preservative and as an antioxidant. However, when originating from flue gas emissions, SO_2 fatally contributes to environmental pollution as the main source of acid rain. Therefore, flue gas desulfurization (FGD) and emission control of SO_2 are integral parts of combustion technology. Unfortunately, conventional FGD suffers from various disadvantages, such as the generation of large amounts of caustic waste that need to be disposed of or the volatilization of solvents [1]. Current alternative approaches for SO_2 gas separation are pressure swing absorption (PSA) or temperature swing absorption (TSA) technologies, which are energy saving, avoid by-products and allow recirculation of SO_2 in continuous technical processes [2]. Due to the disadvantages of classic FGD as outlined above, ILs and especially room temperature ionic liquids (RTILs) have been proposed for such separations as cost-effective and environmentally benign alternative. RTILs are currently intensely investigated as high potential absorption fluids for PSA and TSA. They offer functional tunability, adequate thermal and chemical stability, low volatility, and adjustable affinity to flue gas compounds [3]. The absorption efficiency of an IL is primarily determined by the interaction between the gas and the specific functionalities of the IL. The strength of these interactions should be ideally balanced, in order to ensure optimal absorption/desorption behavior.

The mechanistic details of SO_2-uptake in ILs are still under discussion since gas sorption processes are in general attributable to physical intermolecular interactions with no chemical reactions or absorption processes involving two phenomena, physical and chemical interactions [1, 4]. Even for long known systems, no final conclusions regarding the dissolving and discrimination mechanism could be established so far, although various profound gas absorption studies with experimental and theoretical focus have been conducted [5].

Similar to the frequent demand for CO_2-responsive ILs [6], it is desirable to provide new, SO_2-responsive ILs and related salts. The large number of ILs generally available or easily synthesizable facilitates the choice of components with task-specific properties regarding the separation of a specific gas from a mixture of gases. The ultimate technical goal should be the selective separation of different flue gas constituents in practical consecutive steps under dynamic conditions, and their recovery or recirculation to enable a continuous chemical process. If considering the extreme low SO_2 concentration in flue gas, namely 1000 ppm SO_2 versus 15% CO_2, selective SO_2- versus CO_2- flue gas scrubbing is likely to remain an unreachable goal, since a selectivity of 50 or even above would be too low for respective practical FGD-applications. However, in gas stream management of pulping processes, having inversed concentration profiles with SO_2 as the predominant constituent, the recycling criteria for SO_2 are much easier to be met. This would be a great advantage compared to conventional alkaline (or even neutral) scrubbing agents, which mostly separate CO_2 and SO_2 simultaneously from other flue gas constituents (N_2, O_2, CO), and thus require another separation step for the subsequently expelled CO_2/SO_2 co-condensate [7]. Several studies present excellent selectivity for CO_2/N_2, CO_2/CH_4 or similar gas mixtures [8]. Nevertheless, due to the striking chemical differences between the gases compared, such proofs of principle should not be overestimated. For challenging mixtures like SO_2/CO_2, only scarce elaborate selectivity studies exist, with the exception of theoretical investigations [4c, 4d, 9]. Conceptual precedents to IL-, or other salt-related compounds with pronounced affinity towards SO_2, are exploiting the different fundamental reactivity pathways of SO_2 like, for example, aldehyde-functionalities to form bisulfite adducts by absorbing H_2O and SO_2 (Scheme 1) [10].

***Scheme 1.** Formation of zwitterionic aldehyde bisulfite adducts in aqueous sorption systems [10].*



Direct SO_2 absorption has also been described for triphenylmethane dyes like malachite green, which are evident to provide the required SO_2 affinity by their electron poor tritylium resonance centre [11]. In principle, a convenient, selective sorption mechanism should take advantage of the functional discrimination between CO_2 and SO_2. A concept relating to the amphoteric character of the latter, namely addressing the remaining lone pair of the sulfur atom, should permit the desired separation without any unwanted segregation of chemical adducts or salts [10]. Generally, for a durable absorbing system any chemisorption of gases should be avoided, because these mechanisms alter the IL, resulting in a reduced recyclability [12]. Studies on 1,3-dialkylimidazolium acetate ILs revealed chemisorption of CO_2, partially even through direct formation of in situ generated nitrogen-heterocyclic-carbene (NHC) adducts [13]. In aqueous solutions, the resulting chemisorptive equilibria are consisting mainly of betainic imidazolium-2-carboxylates, and imidazolium carbonates, respectively [14]. NHC-adducts of SO_2 have been described as well [15], but not yet identified as IL-derived sequestration products. Sour gases like SO_2 and CO_2 are not satisfactorily separable by acid-base reactions, neither via aqueous protic Bronsted-systems, nor via Lewis acid-base adduct formation. Solvents containing basic lone pairs or aprotic, highly basic heterocyclic or aromatic anions, like the numerously described aqueous liquid amines, pyrrolides, pyrazolides, tetrazolides suffer from a potential deliquescent collapse induced by the formation of hydro-

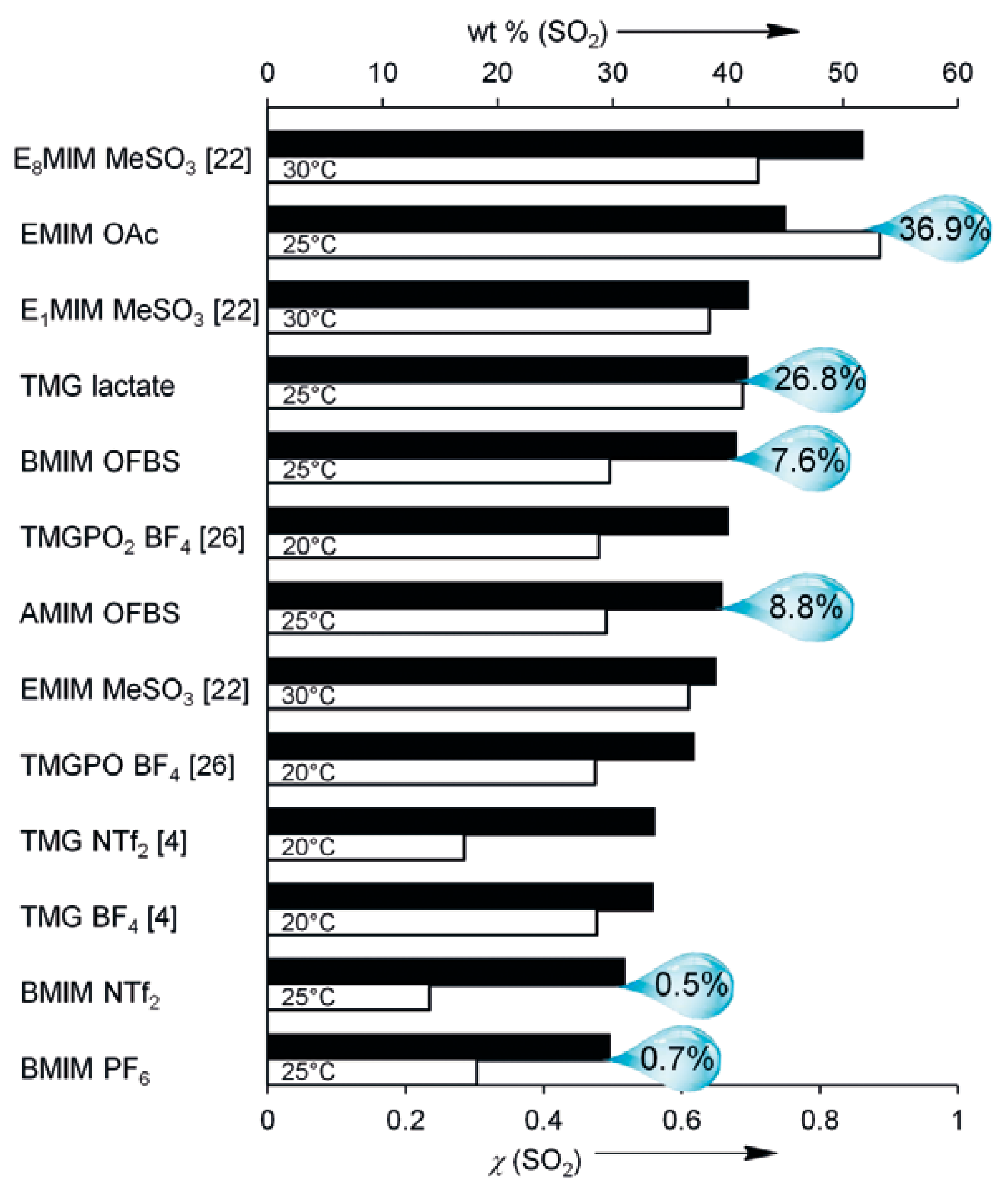
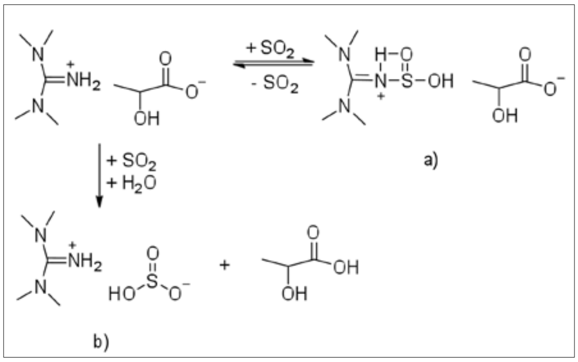


Figure 1. *SO_2 uptake capacity in weight percent (upper bar) and mole fraction (χ, lower bar) of different selected ILs and water content (in weight percent) after equilibration of the ILs at 43% rH (droplets).*

philic salts [16]. Thus, such chemisorptive absorption mechanisms promote the formation of carbonates and bisulfites upon uptake of moisture, or, with-out adventive humidity, the formation of carbamates and sulfamates, respectively [17]. Generally, the uptake of ambient moisture during FGD of process gases is a severe drawback of all hydrophilic ILs. An overview of selected ILs and their hygroscopicity (expressed in water content in wt% after equilibration at a relative humidity of 43%) is given in Figure 1.

Astonishingly, these issues are mostly ignored by the research community focusing on IL-based gas scrubbers. This is also evident for the widely recognized reference system for SO_2 scrubbing, 1,1,3,3-tetramethylguanidinium lactate (TMG lactate, Figure 1d and Scheme 2) [18].

Scheme 2. *a) Proposed reaction between TMG lactate and SO_2 by Wu,W. et al. 2004 [18]. b) Formation of the respective hydrogen sulfite [3].*



Due to both, high hygroscopicity and basicity of the carboxylate anion, moist TMG lactate shows low stability upon prolonged exposure to SO_2. This is perceptible by color change and gradual formation of a precipitate which was identified as TMG hydrogen sulfite (see also Experimental Section) [3].

Even though greenhouse gas absorption is enhanced by the basic character of a particular IL [19], basicity and hydrophilicity are barely compatible with selectivity and recyclability. The reduction of the hydrophilicity by introducing long alkyl chain substituents in the respective cation, as reported for tetraalkyl phosphonium-based ILs [16c, 16d], can result in misleadingly high mole fractions (χ) of absorbed gas molecules, but actually, the absorbtivity in terms of weight percent is lowered [20].

Furthermore, the generally higher viscosities of phosphonium-based RTILs compared to imidazolium-based RTILs are of course altering the permeability of gases, and the viscosity-diffusivity relationship of different classes of ILs can vary considerably, despite they are exhibiting comparable ranges of gas solubility [21].

Chain elongations as described for ethylene glycol functionalized imidazolium mesylates (Figure 1a, c, h) indeed enhance the overall gas absorptivity [22], but also result in increased viscosity and hygroscopicity. For example, ether-functionalized imidazolium hexafluorophosphates have been intentionally designed for improved water miscibilities [23]. Likewise, the direct comparison of polyethylene glycol tethered guanidinium or amidinium salts [24] with ILs based on common organic cations is rather lopsided, unless any gas uptake performance (given in weight percent ratios or molality numbers) is evaluated in parallel [25]. The first ILs to be known and appraised to reversibly absorb SO_2 in stoichiometric ratios were 1,3-dialkylimidazolium and 1,1,3,3-tetramethylguanidinium triflimides (TMG NTf_2, Figure 1j), tetrafluoroborates (TMG BF_4, Figure 1k). Very recently TMG phenolates have been introduced as well [1, 26]. However, they all suffered from several of the abovementioned crucial disadvantages. Hybrid organic-inorganic materials or metal organic frameworks (MOFs), a new class of porous adsorbent materials, have been recently modified for toxic gas separations (cyanogen chloride and sulfur dioxide [27] or carbon dioxide and sulfur dioxide [28]). Nevertheless, even such sophisticated systems are suffering from a detrimental uptake of water in humid environment [27, 28].

Consequently, the anionic constituents of task specific or selective scrubbing ILs should preferably

- contain only neutral, base-free moieties precluding any unselective formation of Lewis acid-base adducts with acidic greenhouse gases
- be halide-free (non-corrosive)
- exhibit low viscosity (sprayability and compatibility with Venturi scrubbers or related technical fluid processing devices) [29]
- be non-hygroscopic, stable and recyclable
- rely on low cost industrial bulk chemicals
- be liquid at room temperature or below (higher absorptivity, better capability of swing cycles)
- be physisorptive, with reversible absorption mechanisms and no chemical derivation
- be inert to phase collapsing behavior by cumulation of ambient moisture and subsequent salt forming equilibria
- exhibit significant absorption selectivity between CO_2 and SO_2 (for eventual sequential scrubbing cycles)

Exploiting the general trend of sulfonate-based ILs to differentiate significantly between CO_2 and SO_2 [9b, 30], the structural motif of 2-formyl-benzenesulfonate was envisaged. In the present study, the newly introduced ILs are characterized and the SO_2 absorption capacity and selectivity of 2-formyl-benzenesulfonate-based ionic liquids is disclosed in detail. Additionally, results regarding their stability and recyclability are included.

Experimental

Materials

SO_2 (minimum purity of 99.9%), 1,1,3,3-tetramethylguanidine, lactic acid, sodium 2-formylbenzenesulfonate, allylimidazole and 3-hydroxypropane sulfonic acid were purchased from Sigma Aldrich and used as received. 1-Ethyl-3-methylimidazolium acetate (EMIM acetate), 1-butyl-3-methylimidazolium chloride (99%) and 1-allyl-3-methylimidazolium chloride (99%) were purchased from IoLiTec and used without further purification.

The ILs were synthesized using standard procedures. 1,1,3,3-tetramethylguanidinium lactate (TMG lactate) was synthesized by direct neutralization of 1,1,3,3-tetramethylguanidine and lactic acid [18]. 1-Butyl-3-methylimidazolium hexafluorophosphate (BMIM PF_6), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (BMIM NTf_2), 1-butyl-3-methylimidazolium 2-formylbenzenesulfonate, 1-allyl-3-methylimidazolium 2-formylbenzenesulfonate, 1,3-dimethoxyimidazolium bis(trifluoromethylsulfonyl)imide, 1-butyl-3-methylimidazolium 2-hydroxyethanesulfonate, tetramethylguanidiunium 3-hydroxypropanesulfonate and 1-ethyl-3-methylimidazolium 2,5-dimethylbenzenesulfonate were synthesized according to previously described procedures [31].

Equipment

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX 300 spectrometer (magnetic flux density: 7.04925 Tesla).

IR spectra were recorded on a Perkin Elmer Spectrum GX FT-IR instrument in ATR mode.

Sorption analyses were performed on a Sorption Analyzer SPS11-10: Resolution: 10 g/100 g (dual range); Temperature Range: +10° C to +60° C; Humidity Range: 0% rH (relative humidity) to 98% rH; Gas supply: compressed air/nitrogen, dried, oil-free; Validation: DKD Calibration Certificate with "Min Weight" certification; Salt Validation test with humidity standards. In a so-called dynamic vapour sorption (DVS) measurement, a sample is subjected to an atmosphere of varying humidity and the sample response is measured gravimetrically. Thereby, the tested ILs were kept at 25° C and exposed to a certain humidity which was increased stepwise until a relative humidity (rH) of 90% was reached and then decreased correspondingly. The weight increase was recorded as a function of time at a constant humidity level for at least 120 min and no longer than 48 hours or until each sample has reached the equilibrium state, *i.e.* the weight change was less than 0.01% after 30 min. After that, the humidity in the testing chamber was changed. Verification of the 0% rH point was carried out by thermogravimetric analyses (TGA) and Karl Fischer titrations. Karl Fischer titrations were conducted using the standard procedure and by using a Stromboli sample changer equipped with a temperature-controlled oven from which an applied gas flow transfers the evaporated water into the titration cell. Thermogravimetric analyses were performed on a TGA-7 (Perkin Elmer, Norwalk, Ct., USA) containing the Pyris 2.0 software for Windows. Approximately 2 to 10 mg samples were weighed into a platinum-pan (50 μL). Dry nitrogen was used as purge gas (sample purge: 20 mL min^{-1}, balance purge: 40 mL min^{-1}). The weight calibration was performed with a 100-mg Class M calibration standard. The temperature calibration (two standard Curie Point temperature calibration) was performed with magnetic calibration standards of nickel (magnetic transition temperature: 354° C) and Alumel (magnetic transition temperature: 163° C). Heating rate: 10 K min^{-1}. Differential scanning calorimetry measurements were performed on a NETZSCH DSC 204 F1 Phoenix. Heating/cooling rate: 10 K min^{-1}.

Synthesis and Characterization of the Newly Synthesized ILs

1-Butyl-3-methylimidazolium 2-formylbenzenesulfonate (BMIM OFBS), 1

Sodium 2-formylbenzenesulfonate and an equimolar amount of 1-butyl-3-methylimidazolium chloride were placed in a round bottom flask and suspended in acetone by stirring at room temperature for three days. Upon stirring, sodium chloride started to precipitate, which was then filtered with a sintered glass frit. The solvent was evaporated by means of a rotary evaporator and the yellow liquid (97%) was finally dried via rotary vane pump vacuum while keeping the temperature at 80° C by means of an oil bath.

^1H-NMR (300 MHz, [D_6]DMSO, 25° C): δ= 0.82 (3H, t, 7.4 Hz), 1.18 (2H, m, 7.5 Hz), 1.70 (2H, m, 7.4 Hz), 3.83 (3H, s), 4.12 (2H, t, 7.2 Hz), 7.50 (1H, t,7.4 Hz), 7.61 (1H, t, 7.5 Hz), 7.69 (1H, s), 7.75 (1H, s), 7.76 (1H, s), 7.85 (1H, d, 7.6 Hz), 9.14 (1H, s), 10.93 (1H, s) ppm. ^{13}C NMR (75 MHz, [D_6]DMSO, 25° C): δ = 13.2, 18.8, 31.4, 35.7, 48.5, 122.2, 123.6, 126.5, 126.8, 129.4, 132.6, 136.5, 149.7, 193.7 ppm.

Chloride content: 4 mg Cl/g IL. IR (neat): ν_{max}/cm^{-1} = 3145, 3099, 2960, 2933, 2873, 1687, 1585, 1570, 1464, 1396, 1338, 1298, 1259, 1188, 1132, 1080, 1018, 827, 768, 731, 642, 611, 563 cm^{-1}. Viscosity: 1.65 Pa s (25° C). Differential scanning calorimetry

(DSC): sample mass: 5.965 mg; pan: Al, closed; atmosphere: N_2, 20.0 ml min^{-1}; measuring range: 5000 μV, heating/cooling rate: 10 K min^{-1}.

1-Allyl-3-methylimidazolium 2-formylbenzenesulfonate (AMIM OFBS), 2

Sodium 2-formylbenzenesulfonate and an equimolar amount of 1-allyl-3-methylimidazolium chloride were placed in a round bottom flask and suspended in acetone by stirring at room temperature for three days. Upon stirring, sodium chloride started to precipitate, which was then filtered with a sintered glass frit. The solvent was evaporated by means of a rotary evaporator and finally the yellow liquid (96%) was dried via rotary vane pump vacuum while keeping the temperature at 80° C by means of an oil bath.

^{1}H NMR (300 MHz, [D_6]DMSO, 25° C): δ = 3.84 (3H, s), 4.81 (2H, d, 6.0 Hz), 5.27 (2H, m), 5.99 (1H, m, 6.3 Hz), 7.51 (1H, t, 7.5 Hz), 7.62 (1H, t, 7.5 Hz), 7.69 (1H, d, 6.8 Hz), 7.77 (1H, d, 7.6 Hz), 7.87 (1H, d, 7.7 Hz), 9.12 (1H, s), 10.95 (1H, s) ppm. ^{13}C NMR (75 MHz, [D_6]DMSO, 25° C): δ = 35.8, 50.8, 120.3, 122.3, 123.7, 126.6, 126.8, 129.5, 131.6, 132.6, 133.3, 136.7, 149.6, 193.7 ppm. Chloride content: 1.4 mg Cl/g IL IR (neat): ν_{max}/cm^{-1} = 3147, 3104, 1688, 1647, 1586, 1572, 1449, 1424, 1399, 1189, 1134, 1082, 1019, 947, 828, 768, 616, 566 cm^{-1}.

1-Allyl-3-propargylimidazolium benzenesulfonate, 3

Allylimidazole and an equimolar amount of 1-propynyl benzenesulfonate were placed in a cooled round bottom flask and stirred for one hour. After stirring for another two hours at room temperature, the spectroscopically pure liquid product was dried via oil pump vacuum.

^{1}H-NMR (300 MHz, [D_6]DMSO, 25° C): δ= 3.82 (1H, s), 4.84 (2H, d, 6.1 Hz), 5.27 (4H, m), 5.94 (1H, m), 7.31 (3H, m), 7.69 (2H, m), 7.76 (1H, s), 7.81 (1H, s), 9.34 (1H, s). ppm. ^{13}C NMR (75 MHz, [D_6]DMSO, 25° C): δ= 39.2, 51.6, 76.6, 79.5, 121.2, 123.0, 123.5, 126.0, 128.5, 129.5, 132.0, 136.8, 148.2 ppm.

1,1,3,3-Tetramethylguanidinium hydroxypropanesulfonate, 4

3-Hydroxypropane sulfonic acid was added carefully to an equimolar amount of 1,1,3,3-tetramethylguanidine in a cooled round bottom flask. After stirring at room temperature for one hour, the highly viscous liquid was dried via oil pump vacuum.

^{1}H-NMR (300 MHz, [D_6]DMSO, 25° C): δ= 1.71 (2H, m, 6.4 Hz), 2.44 (2H, m), 2.87 (12H, s), 3.37 (2H, m, 6.7 Hz), 7.83 (2H, s) ppm. ^{13}C NMR (75 MHz, [D_6] DMSO, 25° C): δ= 25.7, 39.4, 48.5, 60.3, 161.1 ppm.

1-Ethyl-3-methylimidazolium 2,5-dimethylbenzenesulfonate, 5

p-Xylene-2-sulfonic acid hydrate was added to an equimolar amount of a 1-ethyl-3-methylimidazolium methylcarbonate solution (50% in methanol) in a round bottom flask.

After stirring the solution at room temperature for 2 hours, the solvent was evaporated by means of a rotary evaporator and finally via oil pump vacuum.

^{1}H-NMR (300 MHz, [D_6]DMSO, 25° C): δ= 1.34 (3H, t, 7.3 Hz), 2.22 (3H, s), 2.51 (3H, s), 3.82 (3H, s), 4.15 (2H, q, 7.3 Hz), 7.01 (2H, s), 7.61 (1H, s), 7.71 (1H, s), 7.80 (1H, s), 9.26 (1H, s) ppm. ^{13}C NMR (75 MHz, [D_6]DMSO, 25° C): δ= 15.1, 19.6, 20.5, 35.5, 44.0, 121.9, 123.5, 127.0, 129.2, 130.7, 132.3, 133.7, 136.5, 145.8 ppm.

1-Butyl-3-methylimidazolium 2-hydroxyethanesulfonate, 6

Sodium 2-hydroxyethanesulfonate and an equimolar amount of 1-butyl-3-methylimidazolium chloride were placed in a round bottom flask and, after ultrasonication for 30 minutes, suspended in acetonitrile by stirring at room temperature for six days. Upon stirring, sodium chloride starts to precipitate, which was then filtered with a sintered glass frit. The solvent was evaporated by means of a rotary evaporator and finally the yellow liquid was dried vial oil pump vacuum while keeping the temperature at 80° C by means of an oil bath. NMR analysis shows a content of 83.3% of hydroxyethanesulfonate in relation to the 1-butyl-3-methylimidazolium cation. It can therefore be concluded, that still a sub-stantial amount of chloride is present due to incomplete salt metathesis. Changing the solvent to acetone resulted in no improvement.

^{1}H-NMR (300 MHz, [D_6]DMSO, 25° C): δ= 0.80 (3H, t, 7.4 Hz), 1.18 (2H, m, 7.6 Hz), 1.71 (2H, m, 7.4 Hz), 2.67 (1.44 H, t, 7.1 Hz), 3.56. (0.82 H, s), 3.62 (1.45 H, d, 4.0 Hz), 3.85 (3H, s), 4.16 (2H, t, 7.1 Hz), 7.76 (1H, s), 7.84 (1H, s), 9.36 (1H, s) ppm. ^{13}C NMR (75 MHz, [D_6]DMSO, 25° C): δ=13.8, 19.3, 32.0, 36.2, 49.0, 54.5, 58.2, 122.8, 124.1, 137.3 ppm.

Absorption Procedure

After synthesis, the ILs were dried via oil pump vacuum, but not directly before use for absorption measurements (water content of the ILs ~1 wt%) to simulate humid process conditions. The maximum moisture content of the ILs in environments of different humidity can be directly derived from the respective moisture sorption analysis.

The apparatus for the gas absorption consisted of a glass vial filled with 2 to 3 g of the IL fixed in a water bath. Continuous stirring of the IL was achieved by a magnetic stirrer. The vial was closed with a septum.

Two syringe needles were punctured through the septum, one to bubble the flue gas through the IL and one to convey the excess SO_2 into a NaOH solution for binding. The gas flow rate was controlled using a flowmeter (purchased from Supelco) and was adjusted to about 30 mL min^{-1}. The vial filled with the IL was weighed at the beginning of the absorption and then after certain time intervals. The amount of absorbed gas was calculated by the weight difference of the vial before and after absorption. Equilibrium was reached after 2 to 3 hours. The absorbing apparatus was first validated by reproducing results already described in literature. After the absorption measurement, an aliquot of the sample was removed for NMR and IR testing for possible chemical alteration of the IL upon exposure to the gas. To study the recovery of SO_2 and the recyclability of the IL, gravimetric desorption experiments on ILs saturated with SO_2 were conducted at 80° C and 100° C. To this purpose, the vial with the SO_2-saturated IL was opened and heated by means of an oil bath under concomitant stirring with a magnetic stir bar. The vial was again weighed after defined periods of time and the loss of weight versus time was evaluated. For the absorption/desorption cycles, these procedures where alternately repeated five times.

TMG Lactate Collapse Upon SO_2 Scrubbing

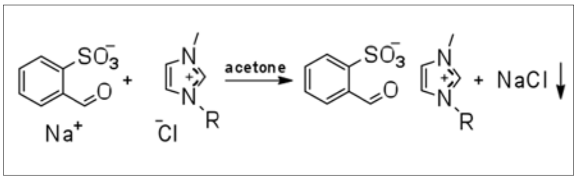
At least, concomitantly to the proposed sorption mechanism, moist 1,1,3,3-tetramethylguanidinium lactate (TMG lactate) is collapsing to an inhomogeneous system upon prolonged exposure to sulfur dioxide (SO_2) under gradual precipitate formation and colour change. An immediate colour change can be noticed. The color of the IL changed from colorless to yellow and then to brown within 30 minutes. After 60 minutes of bubbling SO_2 through the TMG lactate, a white precipitate formed, which at first increased until 90 minutes of absorbing and then disappeared after 120 minutes. A dark brown liquid was the result of 2.5 hours of SO_2 absorption. By interrupting the absorption after 60 minutes and leaving the suspension at room temperature for 20 hours, the precipitate formed TMG hydrogen sulfite crystals suitable for x-ray measurements [3].

Results and Discussion

The family of room temperature ILs (RTILs), comprising a 2-formylbenzenesulfonate anion, exhibit an outstanding performance in absorption-desorption cycles of SO_2, particularly in conjunction with moisture-sensitivity, reversibility, selectivity, and sorption capacity.

The new affinity-tailored RTILs 1-butyl-3-methylimidazolium 2-formylbenzenesulfonate (BMIM OFBS, 1) and 1-allyl-3-methylimidazolium 2-formylbenzensulfonate (AMIM OFBS, 2) are accessible by a single step salt metathesis, starting from commercial bulk chemicals (Scheme 3) [32].

Scheme 3. *Synthesis of BMIM OFBS (R=n-butyl, 1) and AMIM OFBS (R=allyl, 2).*



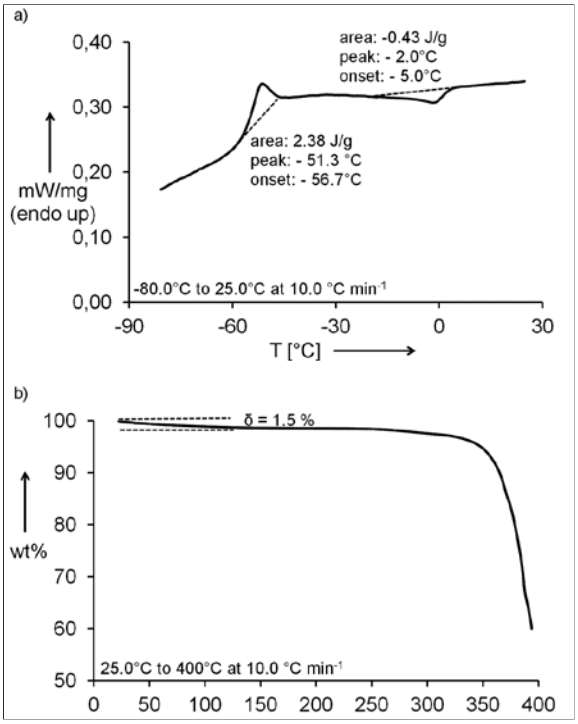


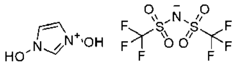
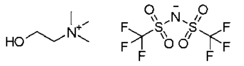
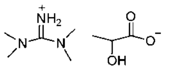
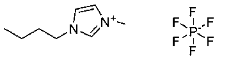
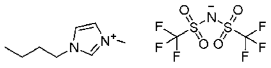
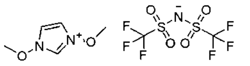
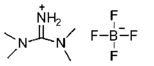
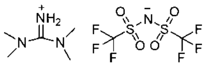
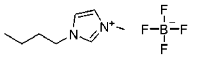
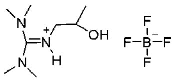
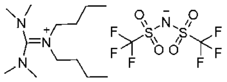
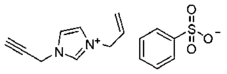
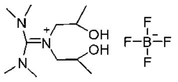
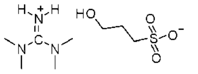
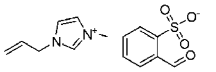
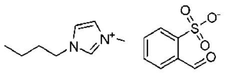
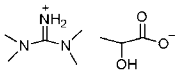
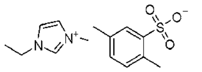
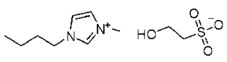
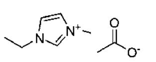
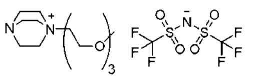
Figure 2. *a) DSC demonstrating the liquidus range of neat BMIM OFBS. b) TGA of BMIM OFBS shows thermal stability up to 350° C.*

In addition to all requirements listed above, these new ILs show no solidification above -30° C, which was proven by differential scanning calorimetry (DSC, Figure 2a) and a high thermal stability up to 350° C, demonstrated by thermogravimetric analysis (TGA, Figure 2b).

Gas Absorption

The maximum mole fractions of all SO_2 absorption measurements conducted during this study are presented in Table 1 and compared to literature data. A focal point was the investigation of water absorption from adventive moisture using a sorption analyzer. From the absorption isotherms of the respective moisture absorption analyses, the equilibrated water contents of the different ILs, at 43% rH can be derived and are also

Table 1. *SO_2 uptake at 25° C in mole fraction and wt%, uptake of adventive moisture in wt% of water of the moist sample at 43% rH.*

substance [CAS registry number]	**structure**	**formula weight**	**molar fraction**	**SO_2 wt%**	**wt% H_2O at 43% rH**
Dihydroxyimidazolium NTf$_2$ [951021-12-8]		381.2	0.380	9.3	
Cholinium NTf$_2$ [827027-25-8]		384.3	0.485	13.6	
TMG lactate [†] (40°C) [686349-06-4]		205.3	0.494	23.4	1.5
BMIM PF$_6$ [174501-64-5]		284.2	0.497	18.2	0.7
BMIM NTF$_2$ [174899-83-3]		419.4	0.518	14.1	0.5
1,3-Dimethoxyimidazolium NTf$_2$ [951021-03-7]		409.3	0.507	13.9	
TMG BF$_4$ [918540-08-6]		203.0	0.515	25.1	
TMG NTf$_2$* [912573-00-3]		396.3	0.518	14.8	
BMIM BF$_4$* [174501-65-6]		226.0	0.563	26.7	
TMGPO BF$_4$* [1020538-00-4]		261.1	0.578	25.2	
TMGB$_2$ NTf$_2$* [862564-78-1]		508.5	0.599	15.8	
1-Allyl-3-propargylimidazolium benzenesulfonate, **3**		304.4	0.644	27.6	7.7
TMGPO$_2$ BF$_4$* [1020538-02-06]		319.1	0.643	26.6	
TMG hydroxypropane-sulfonate, **4**		255.3	0.650	31.8	19.1
AMIM OFBS, **2**		308.4	0.659	28.6	8.8
BMIM OFBS, **1**		324.4	0.680	29.6	7.8
TMG lactate [686349-06-4]		205.3	0.696	41.7	26.8
EMIM 2,5-dimethylbenzenesulfonate, **5**		296.4	0.705	34.1	13.8
BMIM 2-hydroxyethanesulfonate, **6**		264.3	0.717	38.0	18.1
EMIM acetate [143314-17-4]		170.2	0.751	53.2	38.0
PEG$_{150}$MeDABCO NTf$_2$[§]		539.5	0.810	33.6	

[†] see Wu et al. [18]; * see Huang et al. [1]; [§] see Yang et al. [24].

listed in Table 1, specified as wt% of water in the "moist" IL at 43% rH.

As the most intriguing features of the new ILs, a remarkable SO_2-selectivity (factor 40 vs. CO_2, based on wt%, Figure 3) and no interference with oxidative formation of SO_3 and subsequent hydrolysis to free sulfuric acid could be observed. Regardless of their hydrophobic or hydrophilic nature, the preferential affinity towards SO_2 in favor of CO_2 seems to be a peculiar feature of ILs containing aliphatic or aromatic sulfonate moieties [9b, 22, 33].

Additionally, it was found that the absorption mechanism of SO_2 in 2-formylbenzenesulfonates is not accompanied by any detectable formation of bisulfite adducts [10] or any other relevant structural change observable by routine spectroscopy (Figure 4 and Figure 5). Instead, it is serviceable without any uptake of H_2O as confirmed unambiguously by NMR and infrared spectroscopy. Varying signal patterns in the aromatic region are typically depending on the concentration of the solvent.

In Figure 1, a comparison of the SO_2 uptake capacity of BMIM OFBS (Figure 1e) and AMIM OBFS (Figure 1g) to known systems is depicted. The graph also illustrates the ILs' affinity to water. A sorption analyzer was used to investigate the uptake of water at different relative humidities (rH), the results were verified by thermogravimetric analyses and Karl Fischer titration. It could be demonstrated that BMIM OFBS and AMIM OFBS absorb significantly less water in terms of weight percentage (7.6% and 8.8%) than TMG lactate (26.8%) or EMIM OAc (36.9%) when equilibrated at a rH of 43%, which represents approximately ambient humidity. Since the efficiency of scrubbing agents is also dependent on their absorption kinetics, the time dependent SO_2 absorption profile as absorbed mole fraction of SO_2 at 25° C is shown in Figure 3.

It can be seen that TMG lactate takes much longer to reach its maximum capacity than BMIM OFBS or AMIM OFBS. Maximum mole fractions of 0.68 for BMIM OFBS (this equates 420 g of SO_2 per kg IL) and 0.67 for AMIM OFBS could be reached. The SO_2 uptake was determined gravimetrically by frequently weighing the sample vial, where SO_2 was bubbled through the thermostatted IL. Expectedly, the SO_2 uptake capacity decreases with an increasing absorption temperature and results in a lowered saturation with a mole fraction of 0.35 for BMIM OFBS at 80° C (Figure 6). This fact provides the basis for quick and efficient thermal desorption and in this regard, reconstitution of the IL for further sorption cycles and recovery of SO_2.

By desorbing SO_2 at 80° C a mole fraction of 0.13 can be reached after 60 minutes (equates 30 g of SO_2 per kg BMIM OFBS), applying 100° C allows a reduction of the SO_2 content in BMIM OFBS to a mole fraction of 0.04 (equates 8 g of SO_2 per kg BMIM OFBS) within one hour (Figure 7).

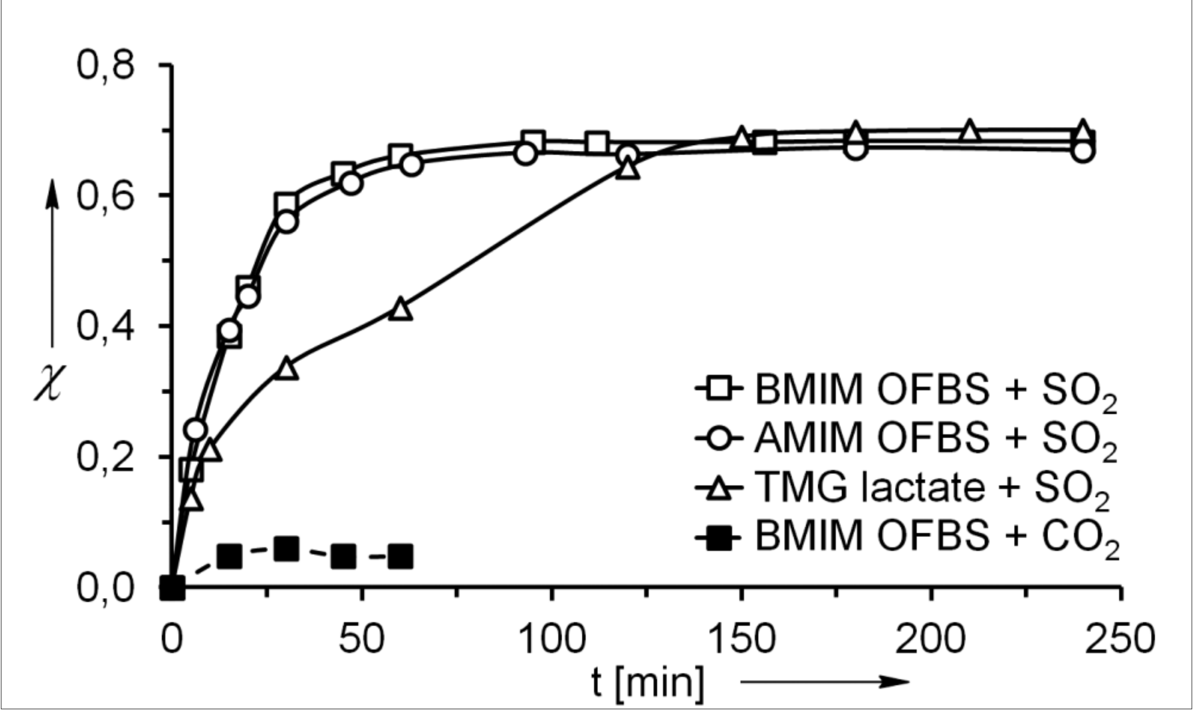


Figure 3. *Mole fraction (χ) of SO_2 in BMIM OFBS, AMIM OFBS and TMG lactate as a function of time at 25° C. In contrast, the much lower CO_2 uptake capacity of BMIM OFBS (dashed line).*

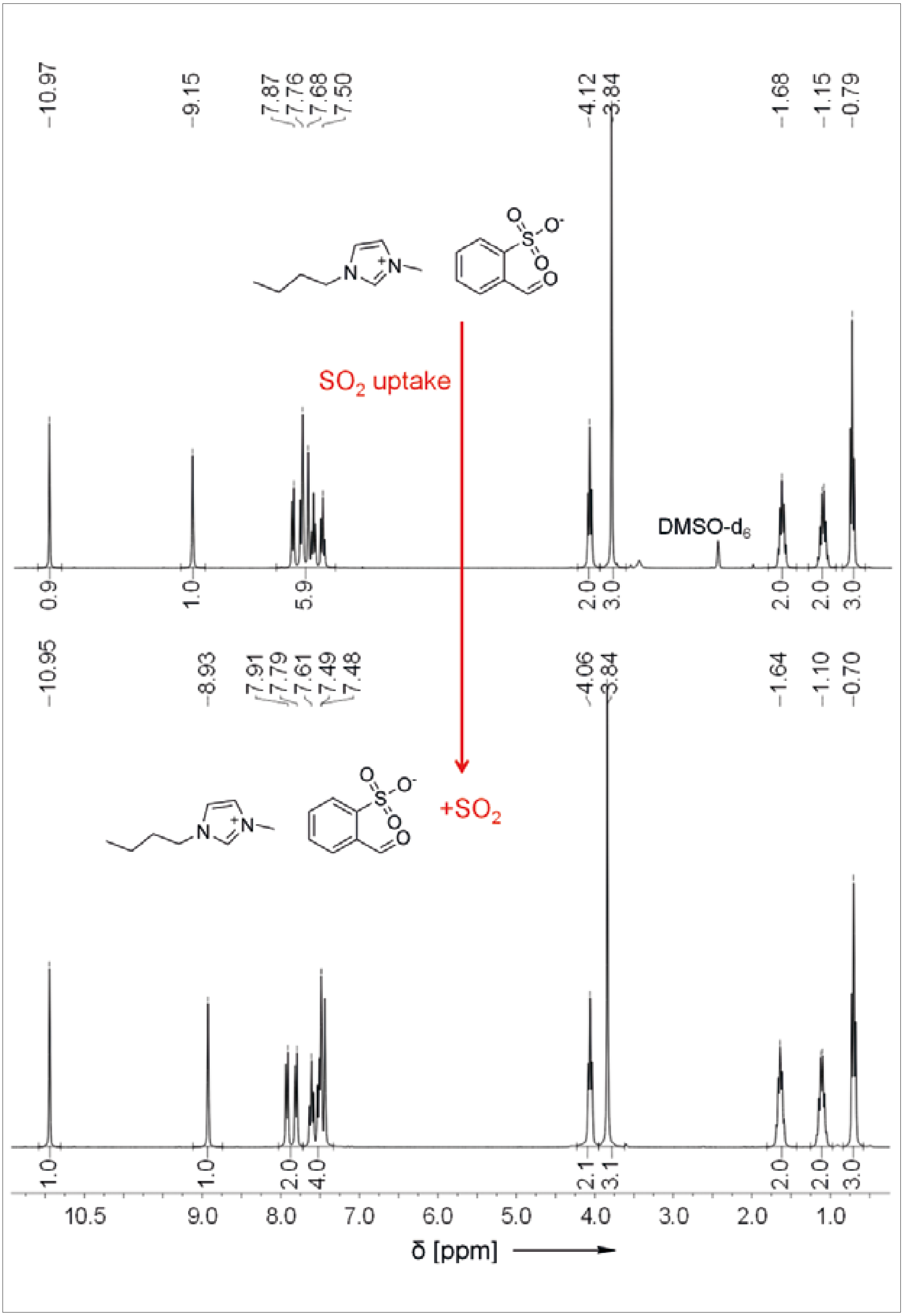


Figure 4. *^{1}H NMR spectra in DMSO-d$_6$ of BMIM OFBS before and after absorption of SO$_2$. Top: neat IL; bottom: IL charged with SO$_2$. Relevant structural changes are not observable, not even for neat BMIM OFBS+SO$_2$ (when deuterated DMSO is absent).*

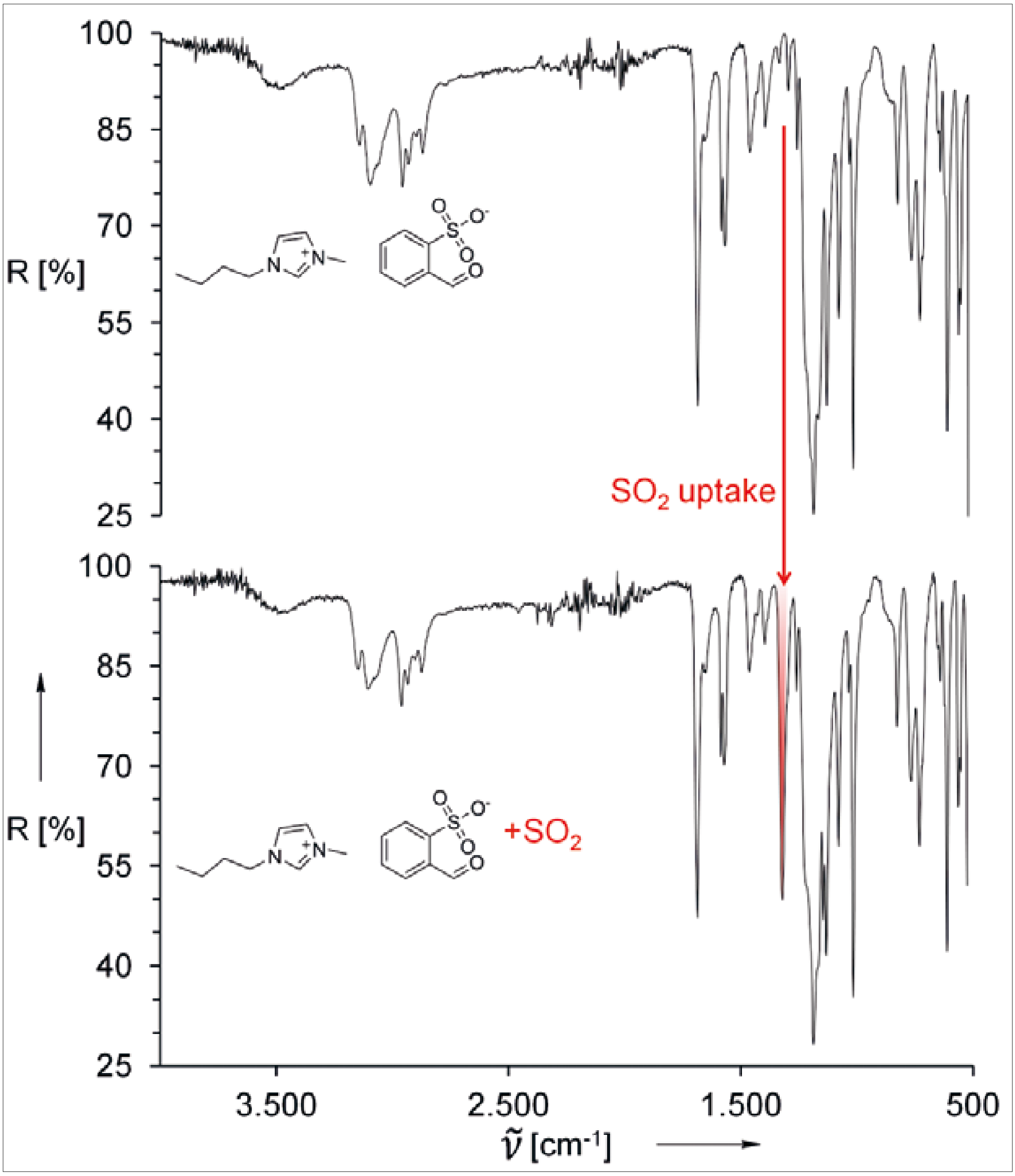


Figure 5. IR spectra (neat) of BMIM OFBS before and after absorption of SO_2, evidencing the lack of any significant structural difference. Top: neat IL; bottom: IL charged with SO_2. The IR spectrum of the SO_2 –treated BMIM OFBS clearly shows a new absorption band at 1325 cm^{-1}, which can be assigned to SO stretches.

In order to demonstrate the constancy of the SO_2 uptake capacity, multiple SO_2-absorption and desorption sequences were conducted. Absorption was conducted at 25° C; for desorption a temperature of 80° C was chosen as a compromise between efficiency and energy demand. After 5 absorption-desorption-cycles, the related systems BMIM OFBS and AMIM OFBS showed only a negligible loss of SO_2 uptake capacity and no change of their chemical integrity, as confirmed by NMR. In contrast, TMG lactate continuously lost its scrubbing capacity due to partial chemical absorption. The amount of SO_2 which could be absorbed and de-sorbed in consecutive steps decreased for TMG lactate (Figure 8, p. 41). Absorption measurements of the pure flue and greenhouse gases SO_2, CO_2 and N_2O in BMIM OFBS showed an extraordinary selectivity towards SO_2 (max. mole fraction 0.68, 42 wt%, 29 vol%); whereas CO_2 (max. mole fraction 0.07, 1.1 wt%) and N_2O (max. mole fraction

0.01, 0.1 wt%) were absorbed only marginally. This high selectivity would allow continuous off-gas sweetening by innovative simultaneous scrubbing cycles. Thus, the new RTILs are promising candidates for implementation in swing cycles, potentially accompanied by surface optimization like electrospraying [7b] or nebulization by ultrasound agitation [34], which may result in absorption acceleration.

Conclusions and Outlook

In their entirety of properties, and in particular their absorption profiles, the newly introduced RTILs recommend themselves as simple expedient candidates for technical sour gas recycling.

These affinity-tailored, affordable and non-deliquescent ILs provide fully reversible SO_2-selective scrubbing systems without any chemical alteration of the ILs.

In pulp manufacturing as well as for sequestering sulfur during the production of viscose, sulfur dioxide is a key constituent in the particular off-gas and process streams. Provided that this successful basic research can be transferred into an utilizable economic process by further technological elaboration, this would represent a milestone in recycling of SO_2. This innovative method of optimized recovery of SO_2 from process gas streams would offer two high-potential benefits

- the overall reduction of air pollution by SO_2, and thus the option of implementing higher production capacities without exceeding the allowed emission levels.
- higher efficiency of resources and, as a consequence, lowered costs of raw materials.

A recent review focusing on the state-of-the-art of CO_2 capture with ILs is providing a detailed overview of the achievements and difficulties that have been encountered in finding a suitable IL for CO_2 capture from flue-gas streams [35]. Trends highlighted therein have been recommended to solvent designers to navigate through the massive amount of theoretically possible and practically applicable ILs.

Specific surveys concerning SO_2 capture by means of ILs are obviously lagging behind, but some analogous rules of thumb are becoming apparent and may push forward this special field of industrially relevant IL-research.

Furthermore, the exploration of new structural motifs is certainly beneficial for stimulating interest in the wider research community, thus propagating their application in other fields of materials chemistry, like membrane-based separation technologies [8a, 8c, 9b].

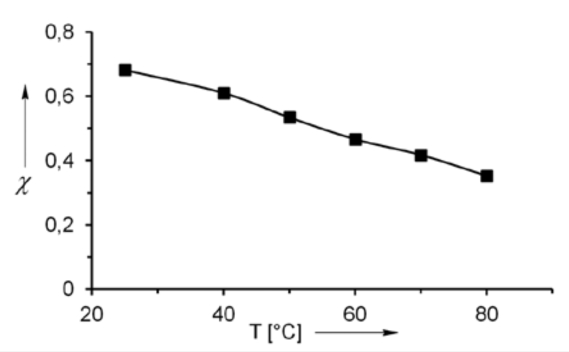


Figure 6. *Maximum of SO_2 absorption capacity shown as mole fraction (χ) of SO_2 versus temperature (°C). A decreased absorption capacity at elevated temperatures facilitates thermal desorption.*

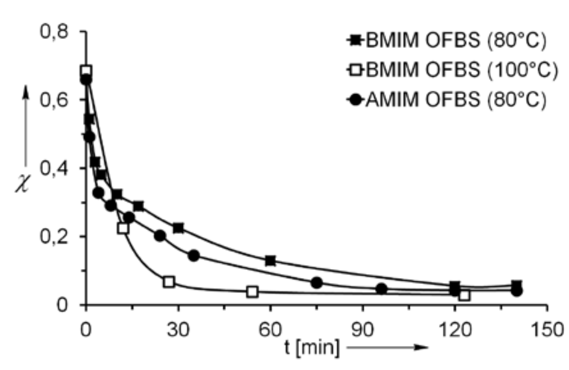


Figure 7. *SO_2 desorption from BMIM OFBS at 80° C and 100° C and from AMIM OFBS at 80° C shown as mole fraction (χ) of SO_2 versus time (min).*

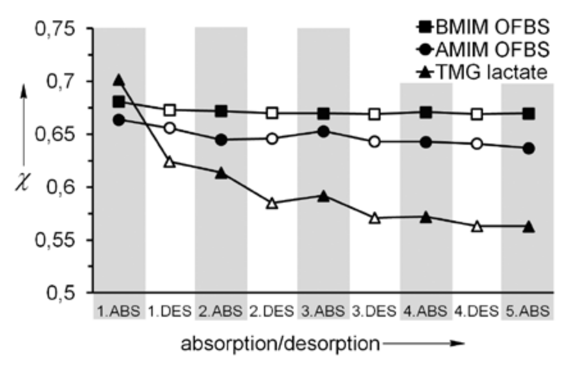


Figure 8. *Absorbed (ABS, 25° C, filled symbols) and desorbed (DES, 80° C, open symbols) mole fraction (χ) of SO_2 in each step. BMIM OFBS and AMIM OFBS show a stable SO_2 uptake and release capacity compared to TMG lactate.*

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Flyweight Replaces Sandcastle – Automatic Backwash Filter for Use in Deionised Water Treatment

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Abstract

Due to its special design, the automatic backwash filter OptiFil®, from Lenzing Technik, has the ability to form a filter-cake. This technology makes it possible to filter very finely – to 1 μm – and with a large amount of solid content and high throughput. For these reasons the OptiFil® is also suitable to replace sand-filtering in deionised water treatment.

Keywords: *filtration, automatic backwash, separation*

Some years ago Lenzing Technik developed the backwash filter OptiFil® with the distinguishing feature that it could filter not only to a very fine level but also concurrently throughput a large amount of solid content at high rates. Since its introduction to the market, the filter has opened up new possibilities for use and delivered good results in various applications. For example, since December last year, the filter has been in use for the filtration of deionised water.

Raw water is extracted from river water in a multiple step process. Previously, the corresponding technology used for the filter step between the decarbonisation through limewater precipitation and the downstream ion-exchange was a sand-filter.

For a throughput of 108 m³/h, one requires a sand-filter that can be as big as 3m wide and over 5m high. The sand-filter needs to operate with a very low filtration speed so that one can be sure that there is not more than 1 ppm (1 mg/l) of solids present in the filtered output and also to ensure that no blockage of ion-exchange-resin occurs. The sand-filter must stop operation during the backwashing. Therefore, in single machine installations, there must be at least one spare sand-filter for the continuous operation of the filtration unit. Additionally, an allowance must be made for a volume of at least 160 m³ backwash liquid. Finally, the backwashing of a filter requires a period of 20 minutes. The backwash liquid of the sand-filters is then channelled into the waste water cleaning equipment.

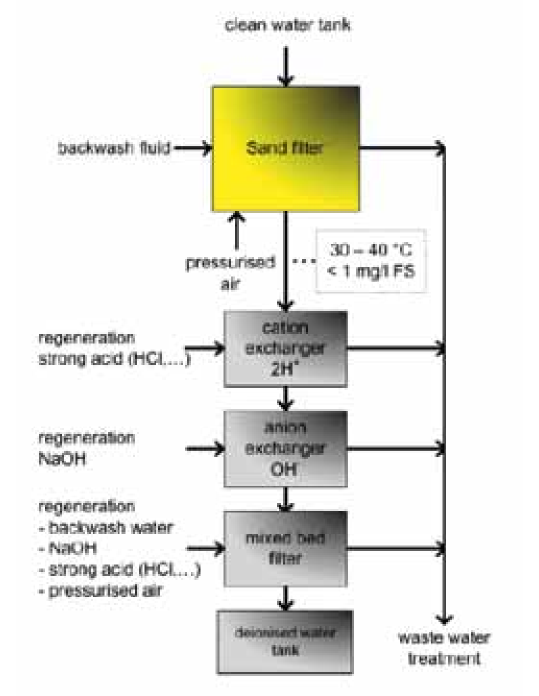

Figure 1. *The treatment from rainwater to deionised water. Until now, sand-filters have been used between the decarbonisation and the ION exchange.*

Without Interruption

The OptiFil®-filter has a partial backwash. With this, a backwash only needs to use approximately 20 to 30 litres of water. During the backwashing, the filtration of 95% of the filter surface is continued.

Thanks to the special filter geometry, a very fine filtering level can be achieved and, at the same time, a high degree of impurity separation.

The particle removal curve shows that already at 5 to 6 μm there are absolute removal rates. Even at 1 μm, as much as 35% of the particles have been removed – and this at filter throughput rates of 120 m^3/h. The impurity concentration in the filtrate of the OptiFil® filter permanently accounts for less than 0.5 mg/l at an inflow concentration of between 35 and 150 mg/l.

The filters are, depending on their application, operated with a very fine filter-cloth or even with a metal fibre fleece, here absolute removal rates of up to 3 μm are achievable.

The deposition mechanisms of the sand-filter system and the OptiFil® automatic backwash filter have significant differences. In the sand-filter, the particles sit on the surface area of the sand grains. The dirt particles that are to be deposited must have specific electrochemical properties as they are often caught through chemical dosing. The deposition succeeds only to a certain extent through a sieving effect of the pores between the sand grains, as they are by definition too big to pass through.

Figure 2. *The automatic backwash filters OptiFil leads, through its special design, to filter-caking. This technology makes very fine filtering – to 1 µm – a possibility.*

For the treatment of deionised water a 10-μm-filter-cloth is used with the OptiFil®. At the beginning of the filtration cycle surface-filtration takes place. After only a few seconds, a filter layer has already started to build up – an effect made possible by the patented design of the OptiFil®. Filtering is then performed via a thin filter-cake. It is through this cake-filtration that the especially high particle removal is made possible.

Significantly Lower Costs

Users of deionised water applications can experience up to 50% lower investment costs as a result of the use of an OptiFil® filter. In addition to this, the OptiFil® filter is significantly simpler compared to the complexity of a sand-filter. This results in lower equipment investment costs for filters, and minimum expenses for plumbing, fittings, controls and above all buildings. The surface area requirement for a single sand-filter with approx. 110 m^3/h throughput is approximately 7 m^2. In contrast the surface area requirement of an OptiFil® with a throughput of 120 m^3/h is only about 1.3 m^2.

More impressive is the difference in the weight of each system. The sand-filter described above weighs about 47 t. In comparison, the automatic OptiFil® filter proves to be a pure flyweight weighing only 350 kg. In total space requirements – converted space and weight – about 95% can be saved.

The more than 30% lower running costs are reached because of the significantly reduced backwash water. OptiFil® uses approximately 1% in comparison with

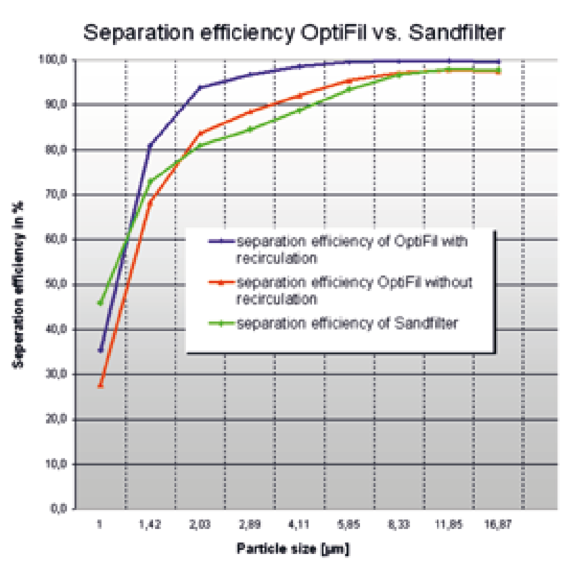

Figure 3. *Separation efficiency OptiFil versus sand filter. Through the reprocessing of the first filtrate it is possible to raise the deposit degree even higher.*

about 8% used by the sand-filter. The disadvantages of the sand-filter are the consumption of air and the very manpower-intensive and time-intensive maintenance (change of sand) in connection with the longer standstill of the filter. In comparison, the once or twice yearly filter-material change required in the OptiFil® is accomplished within one to two hours.

Crucial for the implementation of the automatic backwash filter was the achievement of the required quality parameters, such as a level of undissolved solids of < 1 mg/l. From the analysis data it is obvious that the filter quality of the water from each of the filter types is about the same. It would be possible, through reprocessing the first filtrate output immediately after the backwash, to achieve a significant improvement in the filtrate quality. This is, however, not necessary with the previously described deionised water treatment.

Summary

The application of the automatic backwash filter OptiFil® is a commercially attractive solution for investment in new installations, investment in expansion or for the replacement of a sand-filter.

The simplicity of the OptiFil® filter equipment and the greatly reduced space and building requirements are convincing reasons to purchase the equipment. The function of the filtration before the ion exchange is that the Ion exchange resin is protected from getting blocked by the accumulation of impurities. For this reason, a very effective particle removal is required. As can be seen in the overview table and is also easy to see in the particle removal diagram, OptiFil® meets this requirement. Even further optimization is possible – if necessary – through the reprocessing of the first filtrate.

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Requirements to Eliminate Gel Particles in Different Processes

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Abstract

Gel particles can cause more serious problems in the process industry. Insoluble particles can be present wherever solids are dissolved in a solvent, resulting in product quality degradation or equipment malfunction. The consistency of gel particles can vary considerably, ranging from a rubbery consistency to particles which are still in the fluid state and merely have a higher viscosity than the surrounding fluid. Gel particles can have different properties, and that places significant demands on the filtration system

Depth filtration:

Compared to screens, the material used for depth filtration is much more effective at removing soft particles. The reason is that a gel, which fits through a pore in the material, is captured in a deeper layer. In order to exploit this effect, Lenzing Technik uses a multi-layer, stainless steel, non-woven fiber fabric on its ViscoFil® and AKF series for backwash depth filtration applications.

Differential pressure:

For gel particles the differential pressure must be kept low during filtration to prevent the particles from being forced through the pores in the filter material.

Lenzing Technik uses extremely fine stainless steel fibers (as small as 2 µm) to produce a highly porous filter material. This feature, plus the absence of any pleating, makes the filtration systems suitable for very high viscosity media at very low differential pressures.

Texture of the filter materials:

Soft filter material, for example filter felt, has one major disadvantage. If the flow rate varies or particle loading increases, the differential pressure and the shape of the pores in the filter also change. A particle, particularly a gel, obviously exerts a force on the surrounding material (e.g. the felt fibers) when a pore is blocked, eventually causing the particle to slip through. On the Lenzing filters, the problem was solved by mounting a special tensioning frame which holds the filter material over a perforated support tube and the filter material retains its structure.

Gel particle residence time in the filter:

Lenzing filters have a patented backwash feature which automatically removes gel particles from the metal fiber fabric. Backwashing can take place at regular 30 second intervals if necessary. This ensures that there is not enough time for the gel particles to be pressed through the pores.

Keywords: *automatic filters, filter media for liquids; meshes, metal, porous filter media, self cleaning filters, stainless steel filters*

Introduction

What is a Gel Particle

On Wikipedia you will find the following definition for the term gel:

“Gel (from the Latin gelu ›frost, cold, ice‹ or gelatus ›frozen, rigid‹)”

This definition of the term is misleading in two ways.

First of all gel particles are not, as one might deduce from the definition, crystal-like congealed liquids which would in turn be hard and thus easy to filter. They occur more often in consistencies which are at best similar to gum sweets (Gummibärchen) and are in worst case still liquid and only have a higher viscosity than the fluid in which they occur.

Moreover, in most cases when producing man-made fibers this is not a “congealing process” from one fluid but more the insufficient dissolution process of a solid in a fluid or an insufficient melting procedure.

How Gel Particles Arise

Two mechanisms are known in the production processes of man-made fibers or films of solvents for the creation of gel particles.

Insufficient Dissolution of Solid

In most of the processes based on solvents for the production of man-made fibers or films, a polymer (cellulose acetate, polyacrylonitrile, polyimide, polyvinyl alcohol, polycarbonate, polyurethane, or pulp of wood or cotton linters) is dissolved in a solvent.

A dissolution process of this kind demands above all time and in most cases additional processing such as stirring, the introduction of heat or shearing forces, an increase in pressure, etc. In some cases, e.g. when using dissolving pulp, it is also necessary to prepare the solid in a chemical way to make it accessible for the solvent.

When dissolving a solid the gel phase is always an intermediate step in the transition of the aggregate condition from solid to homogenous liquid.

If the time, stirring energy, temperature or shearing force is not sufficient, the gel particles will stay behind in the liquid. The best way of dealing with this, however, is not filtration. Instead, it is appropriate to work on the process-technological details already mentioned or to simply give the process more time wherever this is possible.

Insufficient Solubility of Solid

In addition to the insufficient dissolution of the solid, the insufficient solubility of this can also be a reason for the creation of gels.

Thus, with cellulose acetates for example, there is always a small share of not sufficiently converted (acetylated) components. These would still be in the form of gel particles after an endlessly long dissolution time and must therefore be removed in another way.

Likewise with polymer fibers, for example of polyacrylonitrile in most cases gel particles are formed due to the inhomogenities in the raw material.

In addition when introducing the powder to the solvent, lumps can result in gels which cannot then be dissolved.

For the viscose process the formation of gel from incompletely saponified resin particles is to be mentioned in addition to the insufficient conversion (sulphidation) of the raw material (similar to the example of cellulose acetate).

Problem of Gels in the Different Processes

Optical Films

Optical films are mostly produced in the dry cast process of cellulose acetate which was dissolved in methylene chloride prior to this.

The films are traditionally used in the photography field and in the last few years to an increasing extent in the production of TFT screens in the electronic industry, from mobile phones to computer screens through to large LCD TVs.

The problem here lies in the fact that gels have a different refractive index than the rest of the film due to their composition. Thus these become visible in the final application on the lit-up display.

***Figure 1.** Example for a LCD screen.*

Man-Made Fibers

In the spinning process of man-made fibers the polymer solution is pressed through a very fine nozzle and on the nozzle outlet side either precipitated in a chemical bath by means of coagulation or the solvent evaporates as a result of introducing temperature and the polymer is dried. In both cases the polymer remains in the form of a fiber.

Problem: the gels here lead to blocking in the spinning station as well as to a reduction in the fiber tenacity through to fiber breakage particularly since the fibers are then mostly stretched via rolls following spinning which further reduces the fiber cross section.

Carbon Fibers

Carbon fibers are used to reinforce plastics and are gaining in popularity since these plastics can be made with the strength of steel but with only a fraction of the weight.

The problem with carbon fibers is that as a result of the process of „carbonization“ (similar to the production of charcoal) of a conventional man-made fiber (viscose or polyacrylonitrile) a part of the polymer is carbonized and the fiber is therefore tapered further in its cross section. This already leads to considerable quality impairments with gel particles of a size of only 5 µm (microns).

Factors Influencing the Filtration of Gels

Depth Effect

It does not come as a surprise that a filter material with a depth effect is much better suited to filtering soft particles than a sieve. This is quite simply because a gel which penetrates a pore has much more chance of possibly being retained in pores lying further back.

The Lenzing filter:

Here Lenzing Technik uses a special multi-layer high-grade steel fiber fleece with a depth effect which has been specially adapted to the backwash filtration of spinning solutions (see Figure 2).

Figure 2. *Photo of filter material used for the Lenzing filter.*

Influence of Differential Pressure

Moreover it is not hard to understand that with a particle which is completely hard and a completely hard pore of the filter material, the differential pressure impacting on the particle in the filter material during filtration can become endlessly high without this having a negative influence on the filtrate quality.

The softer the gel particle, the lower the differential pressure has to be during filtration so that this cannot be pressed through the pore in the filter material.

The Lenzing filter:

A very high porosity of the filter material can be obtained by using extremely fine (down to 2 µm) high-grade stainless steel fibers. In this way and due to the lack of any pleating the filters are operated even with the highest

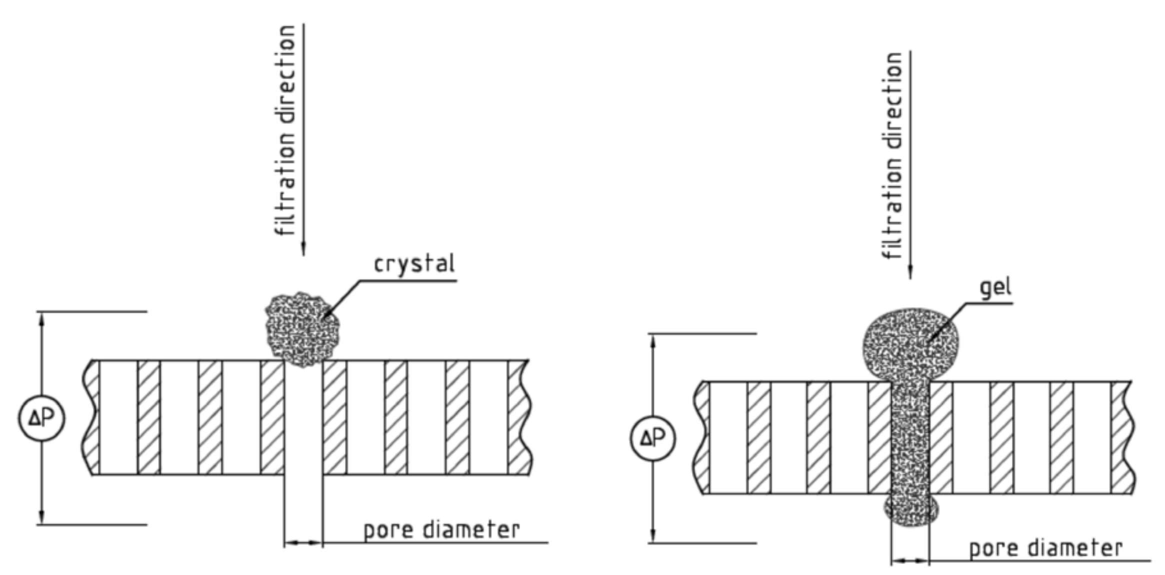

Figure 3. *Comparison – filtration of a crystal and a gel.*

possible viscosities with differential pressures of between 1 and 3 bar. Only in a few rare cases differential pressure can rise to approx. 5 bar after longer periods of operation of several months.

Influence of the Texture (Deformability) of the Filter Material

With regard to the filtration of spinning solutions for the production of man-made fibers, in the past filter felts were mainly used, made of cotton, PP, PES or nylon fiber. These filter media have a relatively soft texture and can thus be easily deformed.

The disadvantage of this kind of filter media is, that when the conditions vary (change in throughput, increase in particle load raises the differential pressure etc.) the shape of the pores changes. The filter medium is compressed to a greater or lesser extent. The pores close or open more.

As a result of these changes forces are exerted on the gel particle which can deform it and in the most unfavorable case "extrude" it through the filter medium.

In addition of course a particle and in particular a gel, when it blocks a pore, exerts a force on the surrounding material (e.g. the fiber of the felt) and tries to extend the pore which ultimately again leads to the extrusion of the particle (see Figure 4).

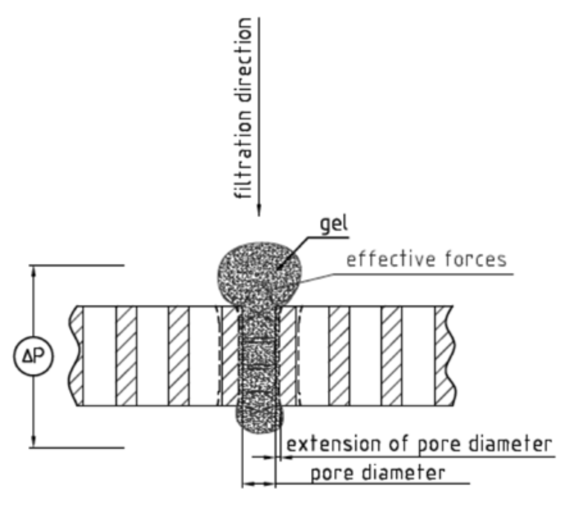

Figure 4. Forces within a gel filtration.

The Lenzing Filter

With the ViscoFil® and AKF filters, the filter material is mounted on to the perforated support tube by means of a special mounting basket (= "Fixing cage") (see Figure 5).

This mounting is performed by means of a precisely defined screw forces so that the load exerted on the filter material by the fixing cage equals a differential pressure of 6 bar. If one now looks at the other side of the filter material with due consideration to the laws of the balance of forces then it becomes clear that the perforated drum (perforated support tube) exerts the same force on the filter material in the opposite direction. Therefore the filter material is balanced in terms of the forces.

If one now starts with filtration from the inside outwards, the differential pressure via the filtermaterial rises. Let us assume that this equals 2 bar. To obtain the balance of forces, the differential pressure disburdens the perforated drum due to the direction of filtration. This means that the new balance of forces is now: from the one side 4 bar from the perforated cover plus 2 bar from the filtration differential pressure. From the opposite direction the same 6 bar of the mounting basket. Therefore, up until the value of the pre-tension pressure of the mounting basket (6 bar) the filter material does not change its structure, thickness and thus pore size, even if the differential pressures change. Together with the natural rigidity of a sintered metallic fiber fleece this results in an extremely rigid structure.

Influence of the Retention Time of Gels in the Filter

One realization which became obvious in recent reference applications is the influence of the retention time of the particle in the pore on the filtration quality of the gels.

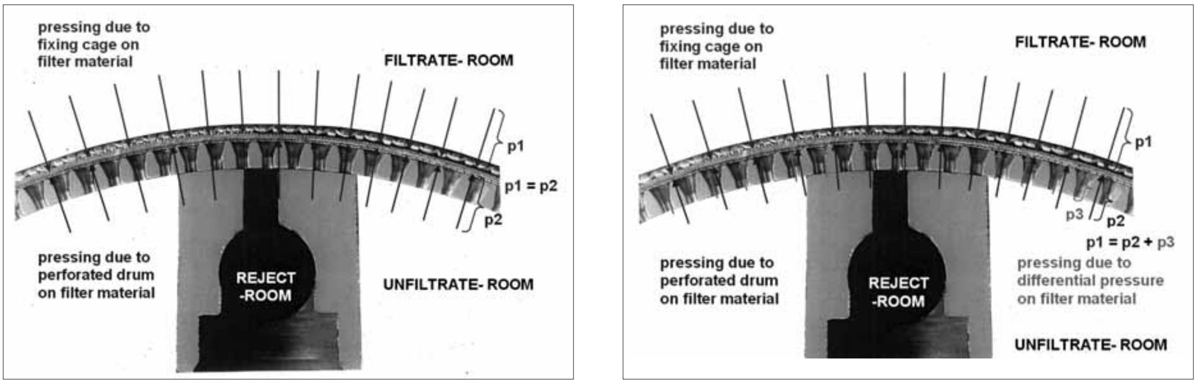

Figure 5. Scheme of Lenzing filter operation.

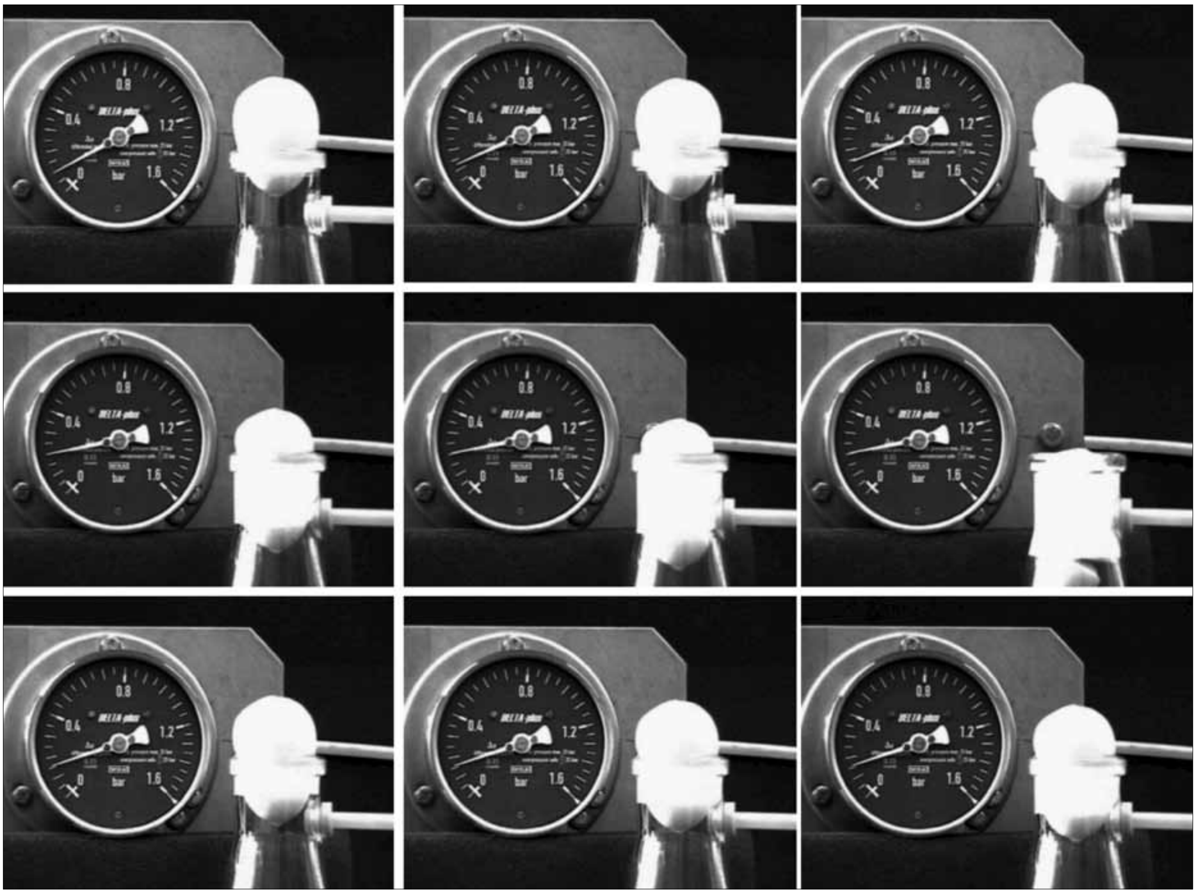

Figure 6. *Time-dependent behavior of gels under constant differential pressure.*

Figure 6 shows a typical gel particle in the form of a hard boiled and peeled egg. It should be remembered that the boiled egg represents a comparably hard gel particle. The effect depicted will be much faster with very soft gels in spinning solutions.

Test course: A hard boiled egg is placed at the opening of a bottle too narrow to allow direct passage. The bottle is then placed in a slight vacuum i.e. the differential pressure between the gel inlet side and gel outlet side is simulated. One should now observe the time. The differential pressure does not change very much. However, the egg begins to deform bit by bit, it becomes longer, tapered and then finally it emerges again in the bottle ("on the filtrate side").

Conclusions

Within t = 3 ½ minutes a gel particle with the viscosity of a peeled egg and a diameter of d = 51 mm penetrates an opening with a diameter of D = 33 mm of a pore, if one applies a constant differential pressure of Δp = 20.000 Pascal.

One can now apply this conclusion to any viscose gel, high differential pressure, small diameter of the gel particle and even smaller pore.

The fact always remains that gels can penetrate any filter material after a certain time.

The Lenzing Filter

The filters in the AKF and ViscoFil® series have a patented backwash mechanism in which the metallic fiber fleeces are freed of gel particles and naturally also of solids in a fully automatic way. This can, if necessary, be done up to every 30 seconds.

In this way the gel particle simply does not have enough time to be extruded through the pore. Filtration remains intact during the backwash which is only taking place partially. (At a small portion of the filter area at a given time)

Some more recent examples, in particular with regard to the filtration of optical film, an extremely demanding filtration task, have shown that the film quality had clearly improved only as a result of increasing the backwash frequency and this was the case although no increase in the differential pressure had indicated a filter material blockage.

Suitable processes for recycling backwash solution ("Reject") are available for a wide range of different fluids.

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TENCEL®Biosoft – a Completely New Fiber Development: Soft – Hydrophobic – Botanic

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Abstract

TENCEL®Biosoft [1, 2] is a hydrophobic and extra soft new fiber development [3]. Additionally, the fiber is oil absorbent. The fiber is totally compostable because of its plant origin.
In wipes applications, it can be used in a variety of blends which tailor the absorbency and cleaning performance to suit a number of different functions from full oil absorbency through to specific lotion management and water absorbency.
In a hygiene products top sheet, it marries the performance of a synthetic product with the botanic advantages of a renewable raw material and a biodegradable product.

Keywords: *TENCEL®, hydrophobic, biodegradability, lotion management, surface energy*

Introduction

Lenzing®Viscose and TENCEL® fibers are well known for their absorbent and sustainable behaviour because they are made from wood. This is the first time that an extra soft, hydrophobic and fully biodegradable TENCEL® fiber was developed for applications in the nonwovens industry.
In the wake of the Deepwater Horizon oil disaster, many people were looking for new materials for oil clean up. So did the innovation group of Business Unit Nonwoven Fibers in Lenzing to see if Lenzing®Viscose or TENCEL® could be used for oil absorbency while retaining its biodegradability. Typical oil absorbing products include clay or oil absorbing gels. In terms of fibers, polypropylene and polyester are commonly used because of their natural hydrophobicity and low density which allow them to float or to coagulate with the oil and be swept away. Unfortunately, most of these materials are not biodegradable and so these materials themselves need to be collected for disposal.
However, the actual benefits from the treatment went far beyond and in a different direction from the original objective. The behaviour of TENCEL®Biosoft's was extraordinary – it was softer, bulkier and smoother to touch. Experience with feminine hygiene products and wipes encouraged to work on alternative applications beyond the oil clean-up originally considered.

Materials and Methods

All developments are based on Standard TENCEL® Nonwoven 1.7/38 dull production – with the only change in after treatment – the installation of the hydrophobic treatment step.

To test the behaviour of fibers and spunlaced materials, these test fabrics had to be produced on Pilot Lines.

Oil absorbency

The test was carried out according to sinking time in the European Pharmacopoeia just using peanut oil instead of water.

Water holding capacity

These measurements were done according to European Pharmacopoeia.

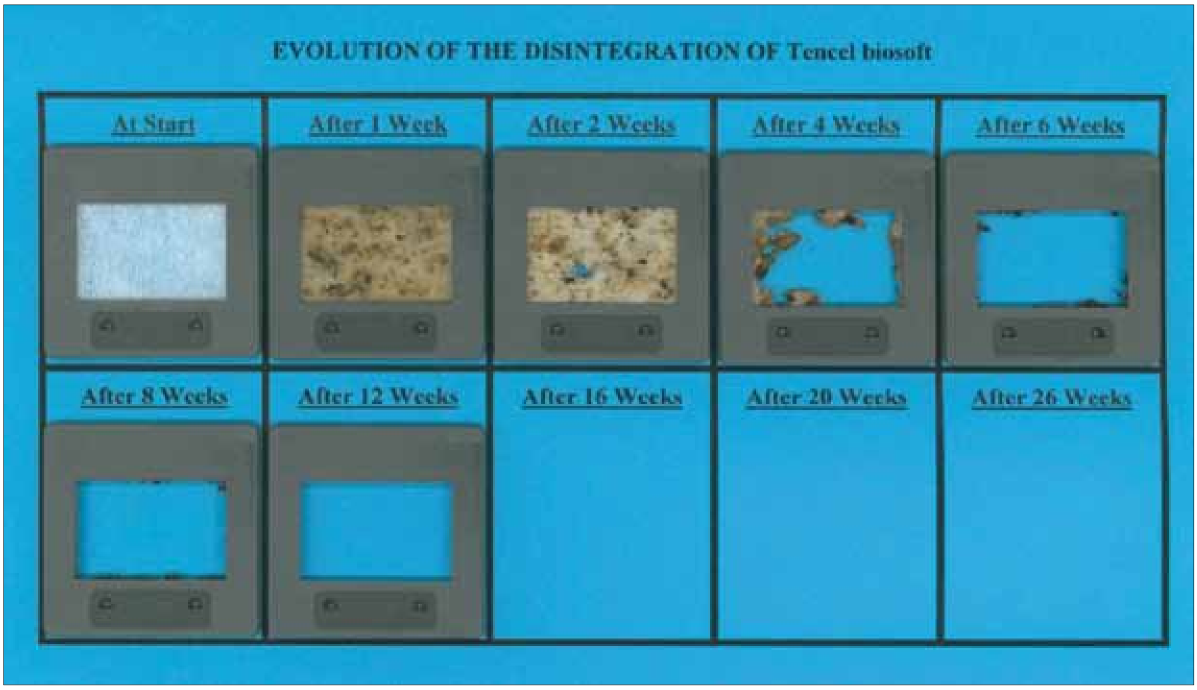

Figure 1. *TENCEL®Biosoft is totally disintegrated within 12 weeks.*

Biodegradability

Spunlaced (60gsm) TENCEL®Biosoft samples were disintegrated in the OWS laboratories (Vincotte Bio compostable logo) according to the Controlled composting test at ambient temperature FHO-2/4:

Table 1. *Liquids with different SE used in the droptest*

Nr.	Liquid tested	Surface Energy
		mn/M
1	100% Methanol	22,6
2	90% Methanol 10% HPLC Water	25,4
3	80% Methanol 20% HPLC Water	27,3
4	Ethyleneglycolmonoethylether	30
5	73,5 EGMEE 26,5 Formamide	34
6	57,5 EGMEE 42,5 Formamide	36
7	36,5 EGMEE 63,5 Formamide	40
8	Ethylenglykol	48
9	9,3 EGMEE 90.7 Formamide	50
10	6,3 EGMEE 93,7 Formamide	52
11	Formamide	58
12	80 % Formamide 20% Water	60
13	64% Formamide 36% Water	62
14	50% Formamide 50% Water	63
15	Water	73
16	Test Ink	76
17	Test Ink	84
18	Test Ink	90

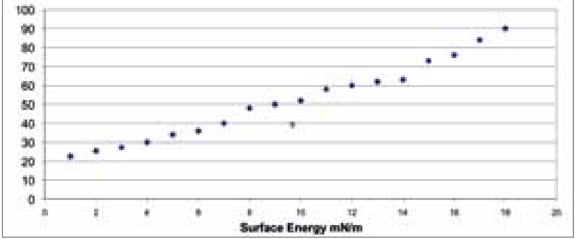

Figure 2. *Graph shows theoretical curvature of the surface energy of different liquids (Table 1) used in the droptest.*

Intensive testing on both the chemical additive and on treated fibers and fabrics had to be carried out to ensure that the result is suitable for sensitive end uses. In addition, products made from TENCEL®Biosoft meet even the enhanced compostability standards of Vincotte Home compostability.

Surface Energy Measurement: Krüss Contact Angle Equipment DSA 100HS

The test was done close to the British Standard ISO 8296:2003

Droplets of liquids with different surface energy (see Table1) were put on the nonwoven. The test works like that: If the droplet stays for more than 10 seconds, the surface energy of the substrate is lower and it repels the liquid. E.g. Water: 100% Viscose or TENCEL® are in the area of SE ~ 90. Water has a SE of ~ 73mN/m – so

Figure 3. *TENCEL®Biosoft floating on water, absorbing peanut oil.*

it gets absorbed really well and fast. TENCEL®Biosoft has a SE in the area of ~35mN/m which makes it water repellent.

Results and Discussion

Oil Absorbency

A chemical treatment was identified to produce TENCEL®Biosoft which was hydrophobic, floated on water and absorbed 3 to 4 times more oil than standard fiber.

Fiber Development

A whole range of materials were made for different applications. Different levels of treatment were checked on different fiber types and it was discovered that this treatment works very well on never dried TENCEL®. The development procedure started in the laboratory (looking at dwell times, additive concentrations, fiber types), progressed to pilot plant trials to achieve larger amounts of treated fibers and finally to the first commercial production at the Heiligenkreuz TENCEL® plant. At the same time, the fiber was converted on both needle punching and spun lacing equipment to prove that fabrics retained the same benefits seen in the fiber. As part of this work, it also became clear that the treatment withstands spunlacing conditions without losing functionality.

Another notable feature is that for the first time it is possible to make a blend of hydrophilic TENCEL® fiber with a hydrophobic TENCEL® fiber. In evaluating a range of blends from the extremes of 100% hydrophilic to 100% hydrophobic TENCEL®, it became clear that absorbent capacity was not linear as might have been expected.

Liquid Absorbency and Surface Energy

A deeper investigation was carried out using different blends of TENCEL® and TENCEL®Biosoft and using liquids of different surface tensions to measure the surface tension of different blends. An easy droplet test for surface tension was established where a few droplets of a liquid with a known surface tension were put onto the spun laced fabric. If the droplets just sink in within a defined time the surface tension of the material (blend) is equal to the surface tension of the liquid. A drop from the next liquid with higher surface tension would remain on the surface of the fabric.

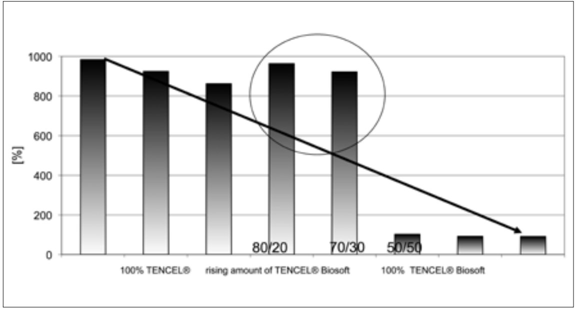

Figure 4. *Graph shows the non-linear LAC from TENCEL®Biosoft blends.*

The hypothesis was that there would be a linear correlation between the blend ratio of TENCEL® and the new TENCEL®Biosoft and the measured surface tension. Accordingly, there must be a blend which correlates to the surface tension of water. This was found in the area of 30% TENCEL®Biosoft and 70% TENCEL® which explains the non linear absorbency results mentioned earlier (best results for the range between 80% TENCEL® / 20% TENCEL®Biosoft to 70% TENCEL® / 30% TENCEL®Biosoft).

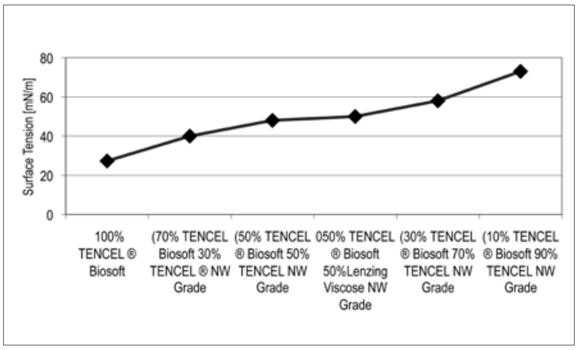

Figure 5. *Surface Tension / Theory and Practical work showed good correlation.*

Lotion Management

The outcome from this work is that 100% man-made cellulose fabrics can be tailored for the first time by changing the blend ratio to optimize their performance with different liquids, e.g. lotions, whether water or oil based.

For wet wipes applications an enhanced, more equal distribution of lotion in wet wipe packs was found. A blend comprising TENCEL®Biosoft gives much greater uniformity in lotion retention throughout the wipes pack in comparison to a Polyester/TENCEL® blend.

Application Development: Mascara Removal

In terms of touch, panel tests were backed up by results on fiber and fabrics using a sledge friction test and a Handle-O-Meter which showed that smoothness could be improved by up to 100% and that drape ability was improved by between 20 to 40%. Improvements in fabric bulk were also identified. The softness was confirmed qualitatively in wet wipes with typical lotions and improved cleaning of oil based materials (such as waterproof mascara) was quantitatively demonstrated.

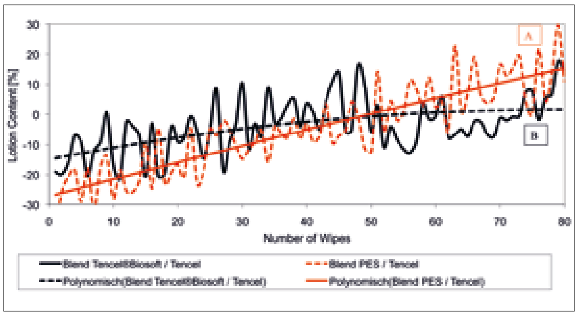

Figure 6. *Comparison of Liquid retention release in A) 70% PES 30% TENCEL® and B) 80% TENCEL® and 20% TENCEL®Biosoft.*

Hygiene Application

In the Hygiene area, work has been carried out on a number of applications with very positive results on a sustainable, biodegradable top sheet. Using the hygiene grade of TENCEL®Biosoft, fabrics exhibit excellent strike through and wet back properties which are comparable with commercially available synthetic top sheets.

Figure 7. *Apparatus to wipe Mascara from artificial skin.*

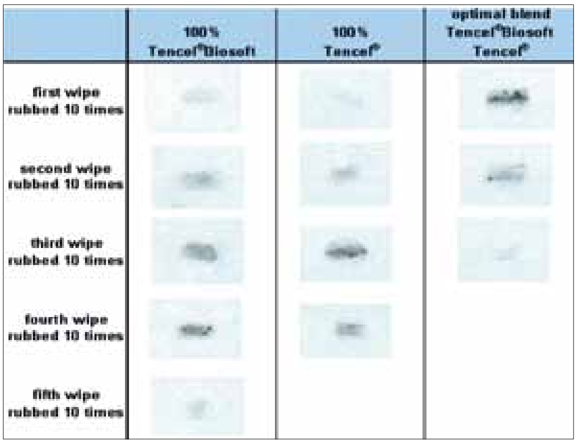

Figure 8. *Test results: Tailor made blend (right side) shows best results (fast and complete removal).*

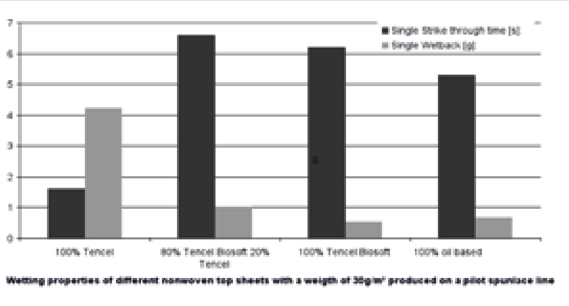

Figure 9. *Wetting properties change with TENCEL®Biosoft.*

Conclusions

TENCEL®Biosoft is the first totally biodegradeable, fully certified, hydrophobic fiber for Nonwoven, which adds extra softness. In wipes applications, it can be used in a variety of blends which tailor the absorbency and cleaning performance to suit a number of different functions from full oil absorbency through to specific lotion management.

In hygiene products like topsheets, it marries the performance of a synthetic product with the botanic advantages of a renewable raw material and a biodegradable product.

Acknowledgements

Special thanks to Shayda Rahbaran and Bettina Schrenk for sharing application data.

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Lenzing PROFILEN® PTFE Fibers in Medical Textile Applications

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Abstract

PTFE fibers are an absolute niche product in the global fiber industry. However over the years due to the outstanding and unique characteristics, PTFE fibers got well established in many technical applications. Lenzing Plastics together with its customers is continuously working to introduce PTFE fibers into new markets, where the outstanding performance can add value to textile products. One core target market is medical textiles, where Lenzing PROFILEN® PTFE fibers are successfully used in a few different product groups already. In this article the PTFE fiber and the characteristics relevant for medical applications will be introduced. Three product groups based on PTFE fibers will be described including the findings in clinical tests on the corresponding end products. Finally an outlook to future possible applications within the medical sector will be done.

Keywords: *PTFE, fibre, decubitus*

Introduction

The polymer PTFE (Polytetrafluorethylen) is an outstanding polymer regarding its performance in many ways. It shows a very broad temperature resistance from minus 200° C up to 280° C in permanent exposure. PTFE is also the polymer with the highest chemical resistance among all plastics due to the extremely strong bond between the carbon and the fluor atom. So it is considered as chemically inert. And the third key characteristic is its very low friction coefficient of around 0.1, in dry as well as in humid condition. Beside that it is totally UV resistant and completely hydrophobic.

Normally such a number of great advantages are accompanied with some disadvantages; in case of PTFE the disadvantage is the difficulty to produce fibres and filaments out of this polymer, as PTFE is not meltable. Nevertheless Lenzing Plastics GmbH was able to overcome this hurdle and is producing PTFE fibres and filaments now since more than 30 years, sold as Lenzing PROFILEN®. In the beginning the above mentioned key benefits of Lenzing PROFILEN® PTFE were mainly valued in the technical textiles industry, such as the field of filtration or compression packing. The use of PTFE fibres is absolutely necessary in applications where every other textile material is rapidly getting destroyed.

Nevertheless over the years Lenzing Plastics explored new markets, where PTFE can add value to existing or

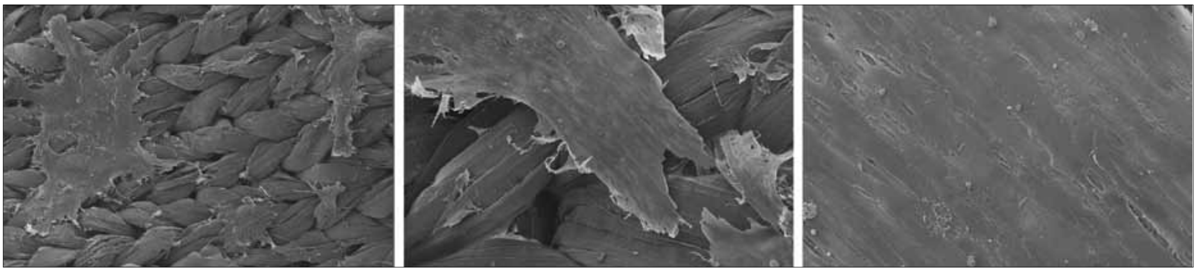

Figure 1. *Biocompatibility - human cell growth on Lenzing PROFILEN® fabric (day 0 to 8).* [1]

new products, one of those is the market of medical textiles and permanent implants. PTFE is nearly chemically inert and does not react with any substance, resulting in a very high biocompatibility of Lenzing PROFILEN® PTFE fibres (see Figure 1).

The low friction coefficient and the related low surface tension of PTFE bring two benefits in the medical surrounding: very low skin irritation when used in medical textiles outside the body and the "non-stick effect". Due to this low surface tension and the slippery surface nothing is sticking on a PTFE fabric.

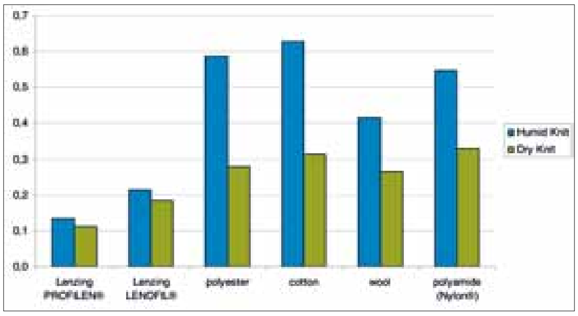

Figure 2. Coefficient of friction of different fibres. [2]

Additionally to those key advantages the strong hydrophobia of PTFE enables an efficient moisture management in a fabric and Lenzing PROFILEN® fibres are extremely durable in contact with the skin. Even many industrial washing cycles will not attack the fibre, as the high temperature window and the chemical resistance prevent the fibre from any damage.

Applications for PTFE Fibers in Medical textilesT

Over the last few years Lenzing Plastics was working to support customers in developments in many fields of medical applications and currently in the following areas Lenzing PROFILEN® PTFE fibres are used successfully:

1) Surgical sutures and yarns for permanent implants (heart valves)
   Key benefits: excellent biocompatibility, softness, "non-stick effect"
2) Garments for patients suffering Psoriasis
   Key benefits: low friction of fibre on the skin; "non stick effect"; perfect moisture management of fabric
2) Bed sheets for hospitals to prevent Decubitus / Pressure ulcer
   Key benefits: low friction, perfect moisture management, "non-stick effect"

In all three applications clinical trials were done to prove the effect of PTFE in the respective surrounding and all showed very positive results, which will be summarized in the following section.

Surgical Sutures and Yarns for Permanent Implants

Every medical device for permanent or partial implant constructed with Lenzing PROFILEN® yarns has to be certified and approved by regulatory affairs in the region it is meant to be sold in. Lenzing Plastics itself got certified with ISO 13485. So far there are no cases where Lenzing PROFILEN® yarns did not pass the evaluation and already several devices are sold regularly, starting from heart valves (class 3 implants) to relatively simple surgical sutures (sterilized yarn with a needle attached). This application is not the focus of this article, if you look for further details, please contact the author.

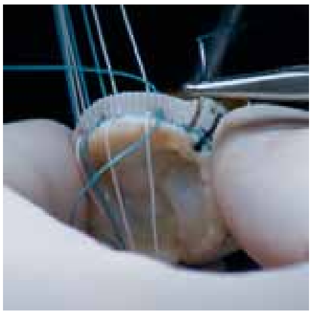

Figure 3.
Surgical sutures.

Garments For Patients Suffering from Psoriasis

Psoriasis is a non-curable disease were actually 2-3% of world population (125 Million people) is suffering from.[3] Psoriasis is not a cosmetic problem; nearly 60% of the people with psoriasis reported their disease to be a large problem in their everyday life.[4] Just in the USA total direct and indirect health care costs of psoriasis for patients are calculated at USD 11.25 billion annually, with work loss accounting for 40 percent of the cost burden.[5]

Current treatment is mainly creams to reduce the itching and prevent further damage of the skin as well as several pharmaceuticals. In order to offer a sustainable and long term solution, one of our customers developed a product line using 51 to 100% of Lenzing PROFILEN® PTFE fibres sold as TEPSO® in form of socks, underwear, shirts, sleeves and bed sheets.[6] TEPSO® garments are not a cure but an effective instrument that provides relief and an increased sense of wellbeing.

Depending on the product, PTFE fibers are blended in the knit structure with Elastan, Polyamide or cotton in the following product lines:

- Skin Bed: 67% PTFE fiber; 33% cotton
- Skin comfort: 51% PTFE fiber; 46% cotton; 3% Polyamide
- Skin Protector: 100% PTFE fiber
- Skin Active: 95% PTFE fiber, 5% Elastan

Table 1. *Fabric comparison – permeability.*

fabric type	Area weight g/m²	Thickness mm	R(ct) m²K/W	R(ct) Average	R(et) m²Pa/W	R(et) Average
Skin bed 1	160,0000	0,1400	0,0180	0,0160	5,8383	5,5875
Skin bed 2			0,0151		5,4278	
Skin bed 3			0,0150		5,4964	
Skin comfort 1	230,0000	0,5800	0,0181	0,0158	3,0847	3,2078
Skin comfort 2			0,0148		3,2075	
Skin comfort 3			0,0144		3,3313	
Skin protector 1	160,0000	0,2600	0,0037	0,0031	0,8618	0,9300
Skin protector 2			0,0032		0,7069	
Skin protector 3			0,0024		1,2212	
Skin active 1	220,0000	0,3300	0,0040	0,0037	2,2185	2,2484
Skin active 2			0,0038		2,5327	
Skin active 3			0,0034		1,9939	

To prove the effect of the TEPSO® fabric containing Lenzing PROFILEN® PTFE fibres the following clinical tests were conducted: pilot study, palmoplantar psoriasis study and pustular palmoplantar psoriasis study. In all three studies patients were randomly equipped with garments (socks) either out of the TEPSO® product line or similar products out of 100% cotton. With a quality of life judgement by the patients based on visual analogue scale (VAS) and a global assessment by a physician both products were evaluated after a period of 4 weeks of testing. In all three clinical studies with a total of 52 patients there was a clear statistical significance for the improvement of patient's global satisfaction as well as positive assessment by the physician.[7]

Furthermore a study of the thermo physiological comfort on TEPSO® fabrics by means of a skin model apparatus [8] was conducted as shown in Table 1.

These results show clearly that the fabrics containing more PTFE fiber have a higher thermal conductivity, visible in the thermal resistance (R(ct)) values of Skin protector and Skin active sample, composed by, respectively, 100% and 95% PTFE fiber. They have a negligible thermal resistance, which is a very important point as it allows the fabric to very quickly absorb and dissipate the body heat. The thermal resistance slightly increases in that samples cotton is present in the blend (Skin bed and Skin comfort). The same tendency can be seen in the values of Evaporative resistance (R(et)). The samples tested are all very breathable, as all show a R(et) <6 m²Pa/W, so based on categorization of the Hohenstein institute they are considered "extremely breathable" fabrics. Again Skin protector and Skin active with their high content of PTFE fibers have the lowest Evaporative resistance, probably a result of the hydrophobic PTFE fibers. The excellent hydrophobia allows a better water vapour crossing through the fabric, whereas the samples containing cotton show a slight increase of resistance caused by the high absorption capacity of cotton.

As conclusion it can be said, that the analysis of the different fabrics highlighted two very important features for garments for Psoriasis patients:

1) The fabrics offer a high thermal conductivity that permits to gather and dissipate very quickly the body heat, which fosters the body temperature regulation.
2) The excellent breathability facilitates the body sweat removal, maintaining the body always dry and in comfort conditions.

Figure 4. *TEPSO® garment for Psoriasis.*

Bed Sheets for Decubitus / Pressure Ulcer Prevention

Decubitus or pressure ulcers, also known as bedsores, are localized injuries to the skin and/ or underlying tissue as a result, beside other influencing factors, of pressure in combination with shear and/or friction. Especially in hospitals treating immobile patients this is a major challenge for nursing staff taking a lot of actions to prevent. According to the US Agency for Healthcare Research and Quality the hospital costs related to pressure ulcer were USD 11 billion in 2006. As it is also a mayor cost factor, medical technology has recognized the problem. There are many approaches to increasing the comfort of those at risk of developing pressure ulcers. But some of these methods are not sufficiently effective, while others – such as mattresses with changing areas of pressure – are still very expensive.

Therefore the Swiss company Schöller Medical AG developed together with Swiss EMPA and the Swiss paraplegic centre bed sheets that reduce friction and enhance the wellbeing of patients. Core component of this fabric are Lenzing PROFILEN® yarns. The new fabric was tested extensively in the lab scale to show the better friction behaviour compared to standard hospital bed sheets against a skin model (Figure 5).

The conclusion of these experiments was that the textile composed of PTFE fibers showed a factor of three lower friction coefficient than normal hospital bed sheets under both dry and wet conditions when tested in vitro against a mechanical skin model. By absorbing and distributing interfacial water within the textile structure, the prototype also exhibited beneficial water transport properties during mechanical contacts. The observed properties suggest that the textile is a promising candidate for a skin protective hospital bed sheet which might be applied for the prevention of decubitus.[9]

Later on a clinical study on 20 patients was conducted, all with a sub acute spinal cord injury during the last period of the in-patient rehabilitation. Summarized the new bed sheet was favoured to the conventional one by patients and physiological skin examinations showed certain tendencies that underline the positive effects of the new bed sheet.[10, 11] Currently some hospitals specialized on paraplegic patients are equipped with the bed sheets to also get some long term data on a big number of patients. In the relevant group of physicians and textile specialists the new product was received very positively and even presented in the Swiss television as important innovation within the medical technology. In June 2013 the product receired the "TECHTEXTIL INNOVATION AWARD".

Conclusions

The above three market areas with their clinical studies show clearly the positive impact of PTFE for medical textiles in certain areas. The low friction as well as the absolute hydrophobia of the fiber proved especially in the last two applications to be valuable in a fabric used to protect the human skin.

Additional to that there are R&D projects in the field of wound dressings containing PTFE yarns. Beside the other mentioned benefits the "non-stick effect" can lead here to a faster healing as recovering skin will not be damaged during exchange of wound dressing.

Lenzing Plastics with its specialized PTFE multifilament yarns is continuing to work hard to support customers who are developing or already selling products in this very promising but also challenging area of medical textiles.

Acknowledgement

We would like to thank Lenzi Egisto s.p.a./ Prato, owner of Tepso brand as well as Schöller Medical AG/ Sevelen for their efforts and their perseverance on working with PTFE fibers in their projects described in this article.

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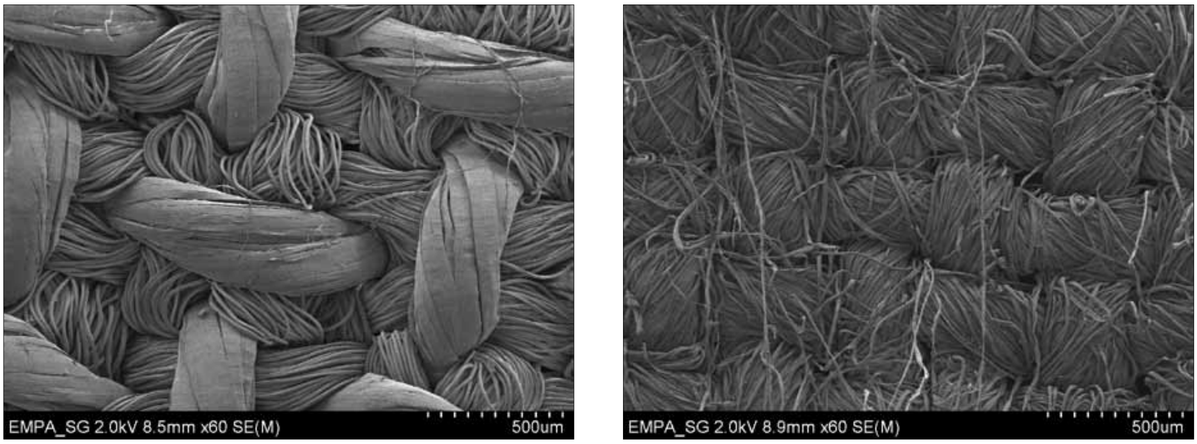

Figure 5. *SA scanning electron microscope (SEM) image of the new bed linen showing the dot-matrix like structure (PTFE on the surface) in comparison with a standard cotton bed sheet currently used in hospitals.*

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Viscose Fibres for Enhanced Fluid Management

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Abstract

The reason for the high appreciation of cellulosic fibres in different fields of application like textiles, nonwovens and hygiene products is not only the fact that they are natural and have a comfortable haptics. The main reason is their water absorbency which is much higher than the water absorbency of most synthetic non-cellulosic fibres.

Whenever a higher absorbency is needed, for example for hygiene and medical applications, viscose fibres can be functionalized to further increase their water absorbency.

There are also applications where cellulosic fibres with lowered or even suppressed water absorbency are required.

Ways how to regulate the water absorbency of viscose fibres into both directions, higher and lower absorbency, are shown. Furthermore the viscose fibre Olea is presented, a fibre which merges intrinsic water repellence and the comfort criteria of viscose fibres such as haptics and the ability to retain water vapour. The water repellence of Olea is using natural mechanisms without fluorinated chemicals and silicones in production.

Keywords: *viscose fibres, hydrophobic, repellence, absorbency, Olea*

Introduction

The viscose fibre was the first man made fibre the chemical industry produced. Even though the basics of viscose fibre production, spinning a xanthogenate solution into a sulphuric acid bath, did not change during the last 120 years [1] viscose fibres are far away from being “old fashioned”.

The high versatility of the viscose process and their positive environmental balance also compared to natural fibres like cotton make them even more modern than ever before.

In contrast to cotton the raw material wood does not require any fertilisers and pesticides for growth. Process chemicals of the viscose process and the upstream pulp process are circulated in closed systems and not distributed into nature like pesticides on cotton plantations.

Secondary products are no waste; they are sold to other industries as raw materials.

The positive environmental and social balance compared to cotton also becomes obvious when the surface and water consumption is compared. Compared to cotton 40% less surface and even 98.5% less water are needed for viscose fibre production [2]. Furthermore cotton is grown on farmland which could also be used for food production [2]. Farming and export subsidies make growing cotton more attractive than growing food plants and create a massive imparity between rich cotton growing countries like the US and third world countries which already led to disputes at the WTO [3].

Besides the cellulosic fibres other components of the cotton plant and the tree need to be handled and used. In case of the pulp process the non-cellulosic components are mainly used for energy production leaving even excess energy due to the high energy efficiency of the process. A big research topic at the moment is the material usage of lignin components which will increase the raw material usage and will further enhance the environmental advantage of viscose versus cotton.

Viscose fibres are biodegradable just as the natural cellulosic fibres which distinguishes them from most other man-made fibres.

The main difference of viscose fibres compared to most other man-made fibres, however, is their haptics which is soft and natural but not plastic-like and their ability to absorb and release water.

The supramolecular, nanoporous structure of cellulose allows the storage of humidity inside the fibre which then is exchanged with the fibre environment giving a high wearer comfort by moisture regulation. This wearer comfort cannot be achieved by thermoplastic fibres like PA, PES or PP which consist of compact hydrophobic material and are unable to regulate any humidity which leads to a reduced wearer comfort and bad smell as bacteria growth between the fibres.

Viscose fibres are preferred for hygiene products as their absorbency is approximately twice as much as for the natural fibres like flax or cotton [4]. As viscose fibres are manufactured without the use of pesticides their use not only guarantees performance but also safety.

Viscose fibres can be tailored using the "viscose fibres toolbox" which allows the selective emphasis or suppression of the functionalities of viscose fibres or the creation of new functionalities.

It will be shown how the absorbency of viscose fibres can be regulated using the "viscose fibres toolbox" going into the direction of higher water absorbencies as well as into the direction of lower water absorbencies down to intrinsic repellence like in the fibre Olea.

Materials, Markets and Methods

The absorbency range of fibres goes from zero for most thermoplastic fibres up to much more than 400% for superabsorbent fibres.

Regular cellulosic fibres cover the absorbency [5] range between 40 and 100%. Speciality fibres even go up to approx. 400% of reversible absorbency which predestines them for re-usable products.

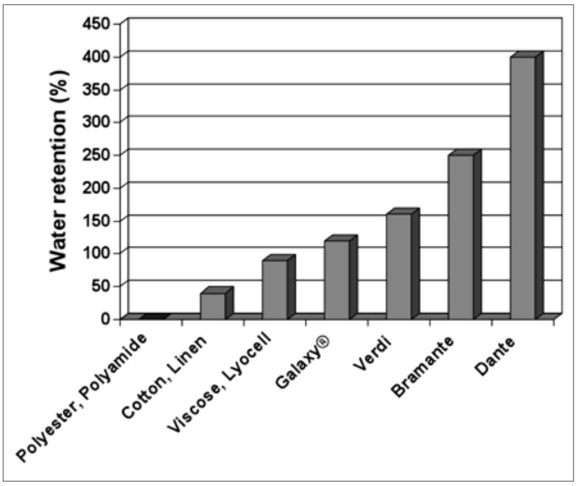

Figure 1. *Comparison of the absorbency of different fibres.*

The specific requirements of every market and application determine which region of absorbency is preferred. Besides that all applications have the same wishes for their materials: renewable, biodegradable and very cheap. In reality the price is the most important criterion and biodegradable and renewable remain wishes which – to become true – may require another increase of the oil price of more than 500% [6].

Low absorbency markets are dominated by thermoplastic fibres, mainly polyester and very few bio-based PLA. These fibres do not absorb water and are typically used for sportswear or nonwovens as they can be molten and therefore easily bind to other fibres or themselves.

For cover- and backsheets of hygiene products they are used as they have good wet-back behaviour. As liquids need to pass through the material a hydrophobic post-treatment with surfactants is necessary.

Though natural cellulosic fibres like cotton, hemp or flax have an absorbency of only 40% which is much lower than for man-made cellulosics they are widely used for apparel and nonwovens as the basic requirements of comfort are fulfilled and the cotton price is still very low.

Man-made cellulosics cover the entire absorbency range of above 50%. They do not only have the advantage of a high absorbency as in contrast to natural fibres they can be tailored, functionalised and produced reproducibly.

Standard viscose is appreciated for comfortable apparel like underwear and for wipes which need to be soft and highly absorbent. The speciality short-cut allows the adjustment of porosity and touch in special papers like filter and document papers.

A first step towards higher absorbency and different properties is the modification of fibre cross-sections. Viloft®, a flat fibre, is giving insulating properties to textiles. The trilobal fibre Galaxy® has an about 30% higher absorbency than standard viscose due to its specially designed cross-section and is therefore the number one fibre for Tampons.

Higher absorbencies than approx. 100 to 110% require chemical or important structural modifications of the fibres.

Hollow fibres like Bramante are produced using special spinning techniques. Bramante is collapsed at dry state but the cavity fills itself with water if the fibre gets in contact with moisture. The stored water can only be released by slow diffusion or evaporation but cannot be squeezed out by applying pressure. Wipes can store an additional quantity of skincare liquids if Bramante is used. The absorbency of hollow fibres is around 250%.

Verdi is an example for a chemically modified fibre using natural additives which modify the fibre struc-

***Figure 2.** Danufil® / Teabag with short-cut; Galaxy® / Tampon.*

ture to allow the absorption of 160% or even more humidity depending on the additive and its amount. Furthermore Verdi can absorb more vapour than normal viscose and has a non-sticking effect when the fibres are wet.

This makes Verdi particularly suitable for wound care applications as the removal of wound dressings is getting less painful.

Both fibres, Bramante as well as Verdi, can be used for semi-professional underwear and functional apparel giving a high wearer comfort under extreme conditions.

Verdi furthermore can be processed into nonwovens which offer additional comfort for insulating workwear [7] as it is used in frozen storages, especially if the wearer frequently changes between different temperature zones.

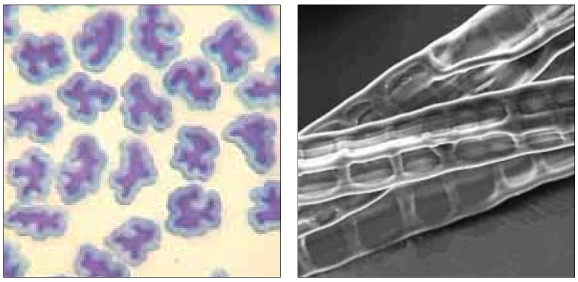

***Figure 3.** Modified fibre Verdi, hollow fibre Bramante.*

If single modifications using the "viscose fibres toolbox" are not sufficient to achieve the desired absorbency it is also possible to use two tools at the same time which leads for example to chemically modified hollow fibres like Dante which has an absorbency of around 400%, a non-sticking effect if wet and a high humidity absorbency.

With Dante it is possible to produce wound dressings for weeping wounds which do not stick to the wounds. Another market for Dante is the incontinence market where growing environmental consciousness and an aging society create a demand for washable incontinence products with a high absorbency even for medium to strong incontinence.

This fibre even allows the manufacture of washable products for medium to strong incontinence.

***Figure 4.** Modified hollow fibre Dante.*

It was demonstrated that the "viscose fibre toolbox" can be used to obtain a large range of fibres with different absorbencies.

It is even possible to obtain fibres having an absorbency of much more than 400% using the toolbox to incorporate superabsorbent particles (SAP). These fibres are not biodegradable as the SAP are not biodegradable. Furthermore SAP swell upon absorption and shrink upon desorption which leads to mechanical stress and gradual fibre degradation with release of SAP from the material. In addition to this re-usable products need to have reasonable drying times to be attractive which becomes very difficult at extremely high absorbencies above 400%. This makes them unsuitable for re-usable products but also for most disposable products where fluff pulp with SAP is the current and very cheap standard.

It became obvious that the region for "biodegradable absorbency" ends at around 400% where the hollow fibres still have a sufficient strength for processing and use and drying times become no obstacle.

Till now only methods to increase absorbency was shown but there is also a demand for fibres having a lower or even no absorbency.

One way to modify the absorbency of cellulosic fibes is to change their crystallinity. It is known that most of the absorbed water is absorbed in amorpheous fibre areas whereas crystalline areas do absorb much less water. [1]

The decrease of crystallinity allows obtaining absorbencies of around 150% when spinning baths without coagulation – delaying components like Glauber's salt are used and the fibres are not stretched. Using spinning baths with delayed coagulation and high stretching of the fibres allows manufacturing fibres with reduced absorbency like TENCEL® / Lyocell, Modal and cording fibres. Usually those fibres have absorbencies of around 60 to 70% which is still higher than the value for cotton.

Absorbency can be reduced much more if particles which do not absorb water themselves are incorporated into the fibres. Known examples are inorganic materials like heavy metal sulfides [8], other dense inorganic fillers [9] and hydrophobic organic particles or combinations of these materials. In this case the reduction of absorbency which can easily be controlled by the amount of material added to the fibre.

The fillers themselves do usually not absorb any water. Their influence in the fibre is the substitution of absorbing by non-absorbing material which alters the fibre absorbency but not the absorbency from the cellulosic backbone. Most efficient are heavy metal salts as they have high densities and put on a lot of weight which leads to a considerable reduction of absorbency measured in percent of fibre weight though the fibre volume was changed only very little.

If hydrophobic fillers are used it could be expected that they will repel water from the viscose backbone making the fibres hydrophobic. In most cases, however, they are not as finely distributed as it would be necessary which allows wicking of the viscose fibres, a process where strong hydrogen bonds between cellulose and water are formed.

Some examples exist where hydrophobicity was created after heating incorporated hydrophobic polymer particles above their glass temperature making them spread onto the fibres as a kind of impregnation [10].

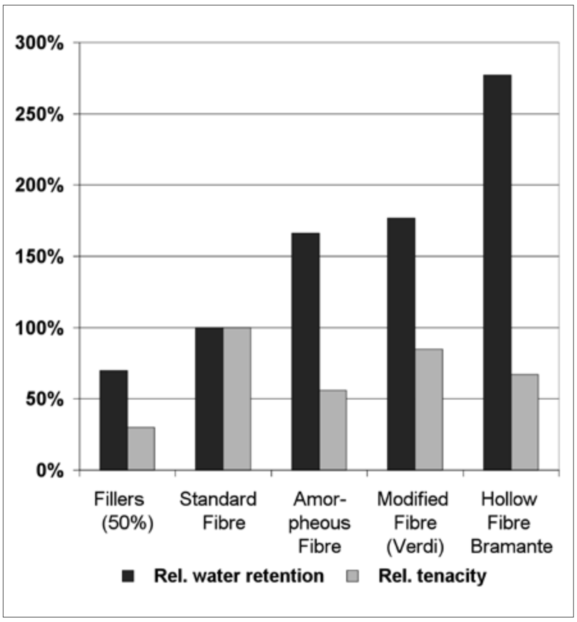

__Figure 5.__ Comparison of fibre strength after different modifications of absorbency.

Figure 5 shows the influence of some absorbency modifications on tenacity. Most modifications lead to a certain loss of tenacity which depends on the modification which was applied but is independent from the absorbency level which was reached. In case of modifications leading to higher absorbency the absorbency increase often predominates the undesired tenacity decrease which is often small compared to the absorbency change.

If the absorbency is reduced using fillers they are unable to stabilise the fibre structure which leads to a strong decrease in tenacity, accelerating with higher filler content. This effect is much stronger than the absorbency decrease and makes the fibres unsuitable for many applications like for example textile applications.

A New Way to Intrinsically Hydrophobic Viscose Fibres

It was shown that it is difficult or even impossible to reduce absorbency gradually down to zero using for example fillers because at a certain point the fibre strength gets lost.

It must therefore be questioned whether zero absorbency and hydrophobicity are equivalent and whether it is possible to make a viscose fibre hydrophobic by reducing its absorbency.

Absorbency is a volume property whereas hydrophobicity is a surface property defined by the contact angle from water with a surface of the hydrophobic material. Materials are hydrophobic if their contact angle is > 90° independent from their absorbency and hydrophilic if it is < 90° also independent from their absorbency.

The comparison of the definitions clearly shows that hydrophobicity and zero absorbency are not identical and must not be confused.

Hydrophobic, porous materials have the ability to absorb liquids, under certain conditions even water, whereas hydrophilic, unporous materials like glass will not absorb any water though they are hydrophilic.

As porosity is one of the basic structural properties of cellulose it is obvious that reducing the absorbency down to zero would also destroy the basic structure of viscose. The path to a hydrophobic viscose seems still possible if the fibre is modified in an appropriate way leaving the basic viscose properties unchanged.

Different methods to obtain hydrophobic cellulose derivatives are known. Acetylation of cellulose leads to hydrophobic cellulose acetate which is used in cigarette filters. Acetate is hydrophobic and has a very low water absorbency but it must be questioned whether acetate is still real cellulose? Cellulose acetate has lost quite a lot of the cellulose properties so that even though the basic polymer chain is still the same we have completely different monomer units and changed the polymer.

Another method is the use of coatings or finishes to make cellulose hydrophobic. This treatment always bears the risk of inhomogeneous distribution of the activity within the fibres, especially when yarns or fabrics are treated and some fibres are not accessible very well to the agents. Treatments which cover or impregnate the fibres hide the fibre properties behind the coating's or the impregnation's properties which means that the fibre properties are lost.

The challenge was to develop a viscose fibre which is permanently hydrophobic but still keeps the basic advantageous properties of viscose fibres.

To achieve this goal Kelheim Fibres used the "viscose fibres toolbox" with special additives to generate hydrophobicity on viscose fibres.

From a vast range of additives we identified substances containing neither silicones nor fluorinated agents as these substances are likely to be refused by demanding customers and may generate problems in some tests for hygiene and medical products.

FDA approved additives were preferably tested as it was expected that products manufactured using these additives would be suitable also for hygiene and food applications which would increase the number of applications that can be targeted using the hydrophobic fibre.

The additives were used in the viscose process which itself guarantees a homogeneous distribution of functional additives within the fibres even if the additives are not injected into the spinning dope but at different process steps.

As a result of the use of a special additive preparation we obtained hydrophobic fibres.

Figure 6 shows a comparison of the hydrophobic viscose fibres with standard viscose fibres given onto water. The standard viscose sank into the water quicker than the time needed to press the shutter of the camera whereas the Olea fibres were floating on the water surface like a water strider on a pond and did not sink into the water for more than 24 hours.

***Figure 6.** Olea fibres swimming on water compared to standard viscose.*

A comparison of the fibre properties between standard viscose and Olea shows that the fibres are within the same order of magnitude of tenacity and elongation (Table 1).

***Table 1.** Fibre properties of Olea compared to standard viscose.*

Viscose fibre	Standard viscose 1.7 dtex	Olea 1.7 dtex
Tenacity	26 cN/tex	> 20 cN/tex
Elongation at break	21 %	> 16%
Water holding capacity[11]	> 18 g/g	0 g/g

Already after the first tests it became obvious from the values of tenacity and elongation that textile and nonwovens processing could be targeted by this fibres.

In the meantime the mechanical parameters further approached the values of standard viscose and first internal tests showed that carding, OE and ring spinning are possible.

The Olea fibres are not only hydrophobic, they are also soft, have a pleasant touch and they still preserved one of the basic properties of viscose fibres, the ability to absorb and release humidity as it is shown in Figure 7.

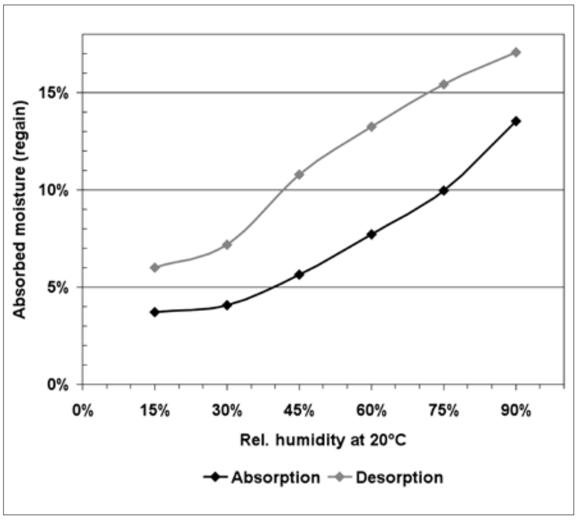

***Figure 7.** Absorption and desorption of humidity from Olea at 20° C.*

The absorption and desorption of gaseous water is one of the comfort criteria of viscose fibres which means that we can expect from Olea to have a similar wearer comfort than standard viscose.

The resistence of Olea's hydrophobicity towards extraction with organic solvents was proven. The resistance towards household washing is under investigation.

As Olea's base material viscose is biodegradable, the additive combination which was used produce Olea is also based on a biodegradable raw material we can expect that Olea is also fully biodegradable and therefore is a sustainable alternative to other fibres.

Summary and Outlook

It was shown that managing the water absorbency of viscose fibres opens the door to further applications of cellulosic fibres reaching from applications where high to very high absorbency is needed to applications where repellence with preserved basic viscose properties like the humidity management is demanded.

Up to now the range of 40% to 400% absorbency was covered with cellulose, viscose and speciality viscose fibres.

The development of Olea, a repellent fibre which does not absorb water under regular conditions, opens the pathway for cellulosic fibres to new applications like for example the sportswear and apparel market; back-and coversheets for hygiene products; filter media; hydrophobic wound dressings; wetlaids and other applications. For these applications Olea may become a renewable, biodegradable alternative to oil-based synthetic fibres which furthermore do not offer the comfort parameters of a viscose fibre.

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TENCEL® – A High-Performance Sustainable Cellulose Fiber for the Construction Industry

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Abstract

Fibers are used in construction materials already for a long time for reinforcement and improving the product properties. Normally, synthetic and steel fibers are used for this purpose; in plaster often pulp is used. The ever increasing demand in better construction materials requires the optimization of all components, there TENCEL®, the modern sustainable man-made cellulosic from Lenzing AG plays an important role.

The manufacturing process of TENCEL® leading to constant fiber diameters ranging from 9-12μm opens area of application which are not possible with conventional fibers used in the construction material industry nowadays. Already the addition of only 0.04% (per weight) fibers changes the properties of concrete substantially, like a decreased crack formation, excellent stability (filter press test) and reduced shrinkage showing an excellent fiber dispersion.

In addition a life cycle assessment [1] has shown that the production of TENCEL® out of wood shows a high level of sustainability. Mainly, the carbon footprint and the water consumption are lower than for other fibers.

Keywords: *TENCEL®, cellulosic fiber, concrete, plaster, sustainability*

Introduction

Fibers have been used in composite materials already for centuries as technological needs demand fibers for reinforcement and improvement of various construction materials. Concrete is a typical example where the addition of fibers plays an important role as concrete shows an excellent compressive strength but is lacking tensile strength. Modern buildings would not be possible without reinforced concrete as steel has an excellent tensile strength and in combination this composite material has changed the way of building completely. However, the installation of the steel construction for the reinforced concrete is time-consuming. Therefore there is an ongoing search for fibers to be mixed into concrete for reinforcement purposes. Commonly used are steel fibers in various forms, but also synthetic macro-fibers are employed in concrete. Macro-fibers are mainly used for reinforcement purposes having fiber length up to 60 mm and diameters bigger than 30 μm. In case of thinner concrete layers, mainly for decorative purposes, glass fibers and carbon fibers are used as they show better reinforcing values than steel but at much higher price which prevents the use in all applications.

In concrete also so-called micro-fibers are used, which have fiber lengths up to 20 mm and fiber diameters up to 30 μm. These fibers are used for different purposes like shrinkage reduction [2] or spalling prevention in case of fire [3], but cannot be used for reinforcement for structural parts like macro-fibers. Currently, the micro-fiber type used most for concrete is polypropylene (PP).

Already for a while and more recently strongly fuelled by the increasing importance of sustainability there is ongoing research about the use of natural fibers in concrete [4, 5]. The main problem to overcome when using natural fibers is the lacking alkali and temperature stability [6] and the varying fiber dimensions due to changing climate conditions.

Lenzing AG has developed TENCEL® – a sustainable fiber overcoming all these issues. Due to the manufacturing process of TENCEL® the diameter is kept constant, thus mechanical properties like tensile strength or elongation vary only very little from one lot to the next. The various types of TENCEL® fibers are produced in a diameter range of 9-12 μm which is at least 2 times lower than the diameter of natural fibers giving at least 4 times the fiber amount per weight unit thus enhancing the positive effect of the fiber addition to concrete.

Materials and Methods

Due to the production process TENCEL® fibers are obtained as a tow which is then cut to the required length, i.e. either 6 or 12 mm as standard length for microfibers in concrete.

All experiments were made first in a laboratory having precise control during the experiment and then the experiments were performed in concrete mixing plants or directly at construction sites to evaluate the practical implications of TENCEL® on the product quality and the workability of concrete. In the first series of experiments always two types of concrete, one with TENCEL® and one without were prepared and evaluated. In the more advanced experiments three concrete types, one without fibers (reference concrete), one with TENCEL® and one with polypropylene (PP) fibers were compared.

TENCEL® fibers are cellulosic fibers and therefore one of the properties of TENCEL® is the moisture management, i.e the fast water uptake and slower release during the curing period of the concrete. Therefore the first experiments were designed to evaluate the influence of TENCEL® on the cohesiveness of concrete, the tendency to segregate and bleed under static pressure as exerted by loads on the freshly-cast foundation piles. In this work the cohesiveness was measured according to the guidelines of the Austrian society for construction technology (ÖBV) for soft concretes. The experiment is carried out by placing the fresh concrete in a container of known volume and applying a pressure of 3 bar for the period of an hour collecting the filter press water into a measuring cylinder (Figure 1). The amount of water is recorded every 5 minutes and compared to other concrete types. The measurement was carried out with a TENCEL® content of 0.5, 1 and 1.5 kg/m³ concrete, equaling 0.02%, 0.04% and 0.06% per weight respectively. The amounts of TENCEL® were chosen based on the recommendations for the usage of PP in concrete and to minimize the reduction in compression strength.

Figure 1. Filter press for testing concrete stability.

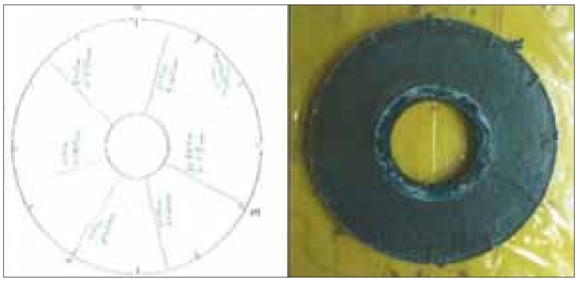

***Figure 2.** Shrinking of concrete; left side: crack formation; right side: test apparatus.*

Crack formation during the curing of the concrete (early crack formation) is an issue for concrete constructions, mainly for large concrete slabs as the cracks in the concrete simplify corrosion attacks on the whole concrete slab and thus are to be prevented. An experiment designed to evaluate the potential of TENCEL® to mitigate the early crack formation are so-called shrinkage rings (Figure 2) where the fresh concrete is stored for 8 hours while subjected to a draught of 4 m/s (simulating a breeze) at 20° C. After this curing time the length of the formed cracks is measured and an overall length is calculated as sum of the formed cracks. The average width is calculated by measuring the crack width at defined intervals and averaging the values. The crack area is defined as the product of the crack length and the average crack width. For this experiment three different concrete types were prepared, one without any fibers (reference concrete), one concrete with 1.2 kg/m³ PP fibers and one concrete with 1.2 kg/m³ TENCEL® based on the guideline "Fibre concrete" of the ÖBV. All three concrete types were filled into the rings and analyzed according to the procedure described above. The strength of concrete is based on the curing of cement with water thus in hardened concrete some water remains. This water changes to water vapor when the concrete is subjected to temperatures high enough (e.g. fire in a tunnel). The volume increase in the concrete due to the formation of the water vapor very often leads to spalling of the concrete which in turn can cause the collapse of the whole building when the steel reinforcement melts. To prevent these events a common procedure in some European countries is the addition of PP fibers to concrete as these fibers melt during a fire leaving open pore space where the water vapor can expand [3]. Again, three kinds of concrete were tested, a reference concrete and two concrete types with 1.2 kg/m³ TENCEL® and PP, respectively as 1.2 kg/m³ is the usual fiber dosage based on the recommendations of the ÖBV. Then concrete slabs measuring 30 x 25 x 10 cm were cast containing thermo elements at defined intervals. The slabs were put in an oven in such a way that only one side was subjected to the fire while the other side was at room temperature. The temperature was increased until 1153° C in 4 hours based on the EN 1363-1 unless a spalling event occurred before.

Results and Discussion

The results from the filter press (cohesiveness) are summarized in Figure 3 as obtained from concretes mixed in the lab as well as from large scale trials carried out in concrete mixing plants. As the filter press tests simulates the pressure of the surrounding areas on the concrete filled into holes for piling purposes, the less water is collected, the better the performance of the concrete in question. The loss of water in the concrete also leads to removal of the fine aggregates and thus can lead to a reduced stability of the concrete. The improved cohesiveness in comparison to reference concrete can be clearly seen as more water is collected from the reference concrete than from the concrete containing TENCEL®. The performance of TENCEL® is similar to a conventional stabilizer indicating that the sustainable TENCEL® fibers can be used as a replacement for a chemical stabilizer normally used in the concrete industry.

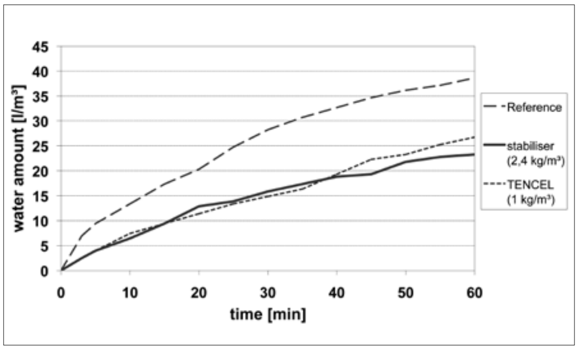

Figure 3. *Filter press results – TENCEL® showing same performance as conventional stabilizer.*

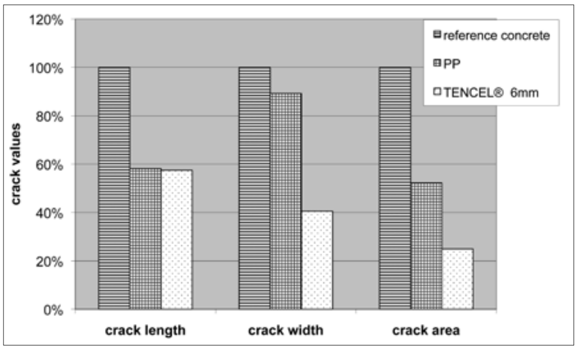

Figure 4. *Crack formation of concrete – comparison between PP and TENCEL®.*

In Figure 4 the effect of TENCEL® on the early crack formation is clearly visible. Although the crack length is the same for TENCEL® and PP, the crack width using TENCEL® is considerably reduced compared to PP fibers. The early crack formation is a common problem in concrete technology, mainly when building

Figure 5a. *Spalling of conventional concrete after fire testing.*

Figure 5b. *No spalling of concrete with TENCEL® after fire test.*

large floors (e.g. for industrial purposes). As these lab results are promising large concrete floors have been made using TENCEL®. The first results showed a low crack formation and an improved surface quality. Further studies will carried out during the lifetime of the floor as often cracks form after some time (1-2 years).

In Figure 5a the spalling effect of concrete exhibited to fire can be clearly seen, while in Figure 5b the positive effect of TENCEL® is evident. The results from the fire experiments show that TENCEL® performs as well as PP fibers commonly used in concrete for spalling prevention. Further studies with other fire curves like the Rijkswaterstaat (RWS) curve are planned as this fire curve simulates the worst case of an oil containing truck which starts to burn inside a tunnel where the temperature rises to 1140° C in only 5 minutes and the maximum temperatures reach 1340° C.

Conclusions and Outlook

The results obtained with TENCEL® in concrete show that a sustainable man-made cellulosic fiber can improve properties of concrete significantly, especially when compared to the conventionally used PP fibers.

However, there are still open questions remaining like the usage of TENCEL® at real construction sites needs to be studied in more detail. Other topics to be further investigated like the spalling prevention measured under more realistic circumstances or the positive impact of TENCEL® on the development of cracks over longer time periods (several years).

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Design of Viscose Fibres for Wetlaid Nonwovens

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Abstract

Cross-section, dimensions and functionality of viscose fibres can be modified to adapt the fibres to specific applications. With the Leonardo fibre a new extremely flat and smooth viscose fibre is available from Kelheim Fibres. Its unique structure makes the fibre transparent, a feature which can also be used to create wetlaid structures with improved transparency.

Flat viscose fibres also allow making of wetlaid nonwovens and paper from 100% viscose fibre. In these wetlaids and papers a low fibre thickness and an anionic modification are key parameters to improve tensile strength. But already with small percentages of viscose fibre incorporation, properties as porosity, tear resistance, tensile strength and double folds can be improved.

Keywords: *viscose fibres, wetlaid nonwoven, flat fibre, cross section, Kelheim fibres*

Introduction

Viscose fibres are 100% cellulosic fibres with a wide variety of applications. As short cut fibres they are also used in a range of wetlaid and paper applications. In these products their excellent dispersability, their chemical reactivity and their capability to form hydrogen bonds is an appreciated property. Since in many cases short-cut viscose fibres are used in applications where very specific product performance is required, there is a continuous need for new specialized viscose fibres in order to achieve the targeted product properties.

Materials and Methods

Materials

All viscose fibres in this study were produced by Kelheim Fibres and used in the cut length and fibre dtex as further indicated.

Methods

Laboratory sheets of 80g/m^2 were produced in the indicated composition without the use of any auxiliary chemicals. The obtained sheets were tested without seizing or other treatments. Lab testing was done following industry standard procedures at the CD-Laboratory for Surface Chemical and Physical Fundamentals of Paper Strength (TU Graz, Austria).

Results and Discussion

The Viscose Fibre Tool Box
Fibre Modifications for Improved Product Properties

Specific properties of wetlaid nonwovens can be controlled to a high extent through the modification of the fibres used for their manufacture. The viscose fibre process is very versatile and so fibre properties can be varied over a wide range, for example by adding additives to the viscose dope or by the use of different spinning conditions and aftertreatments. By application of these methods, for example fibres with functional additives, hollow fibres for extra absorbency or fibres with cationic or anionic modifications can be produced. As other man-

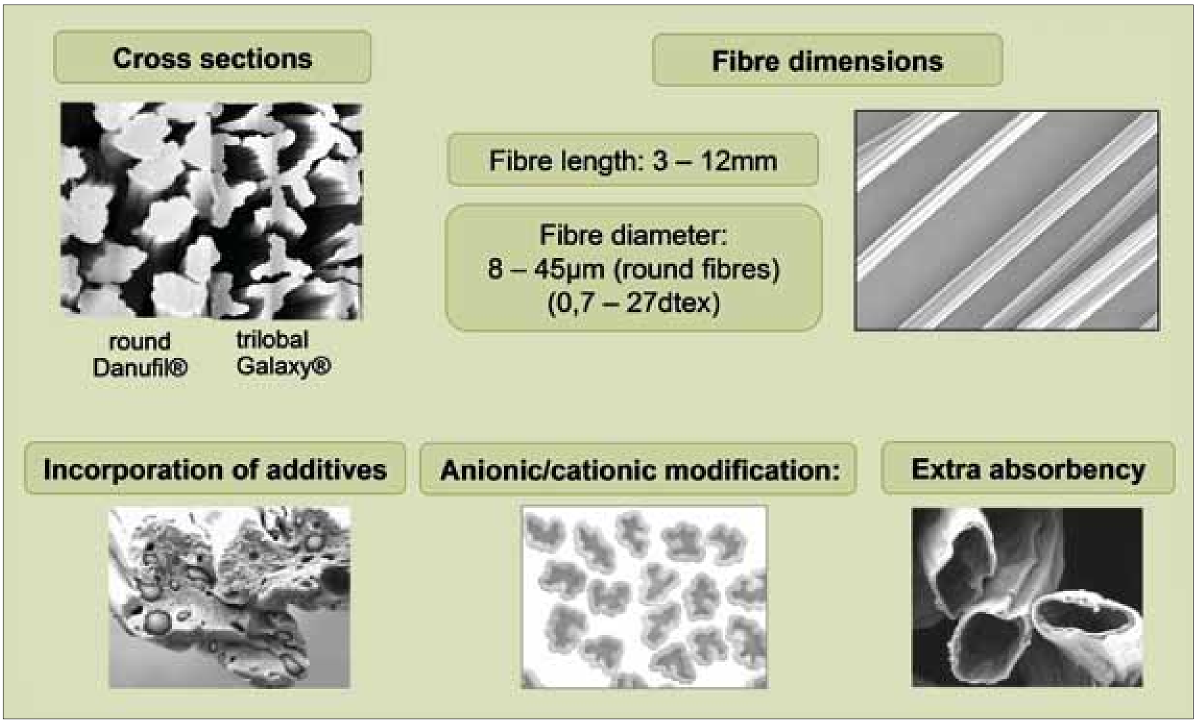

Figure 1. *Viscose fibre modifications.*

made fibres viscose fibres can be produced in very specific fibre dimensions and cross sections (Figure 1).

First samples of fibres with new properties can be produced at Kelheims pilot fibre spinning line. In a screening process fibre evaluation can be easily done on a labsheet former, but for the development of new products often several running meters of wetlaid nonwovens or paper are needed. Also the sheet formation will vary between a labsheet and a nonwoven produced in a continuous process. For these development cases, sample material can be produced on Kelheim Fibres inclined wire pilot line, where wetlaid nonwovens can be made from 20 to 250g/m^2 in 300mm width.

Leonardo – A new Flat Speciality Fibre

Viscose fibres can be produced in a variety of cross-sections. Fibres with flat cross sections are already widely known, the Viloft® fibre for example with a width to thickness ratio of 1:4 is mainly used in textile applications, where it gives very good thermal insulation properties.[1] The Bellini fibre, displaying a higher width to thickness ratio of 1:20 and a smooth surface, allows to produce papers from 100% short-cut viscose without the use of further additives.[2]

With the Leonardo fibre now a new viscose fibre with an even higher flatness was developed by Kelheim Fibres. The fibre is made by a special process, giving the fibre unique properties. Leonardo displays a width to thickness ratio of 1:40 and a very homogenous cross section with completely coplanar fibre surfaces. Contrary to regular viscose fibres, the Leonardo fibre does not show a crenulated cross-section, but displays an almost completely smooth fibre surface (Figure 2).

Its smooth surface gives the Leonardo fibre some distinctive properties, which can be of advantage in wetlaid or paper specialities. In Figure 3 (top) a 9dtex Leonardo fibre is compared to a 28dtex viscose flat fibre produced in a regular viscose process. The SEM-images show, that while the regular flat fibre displays the typical high number of crenels, the surface of the Leonardo

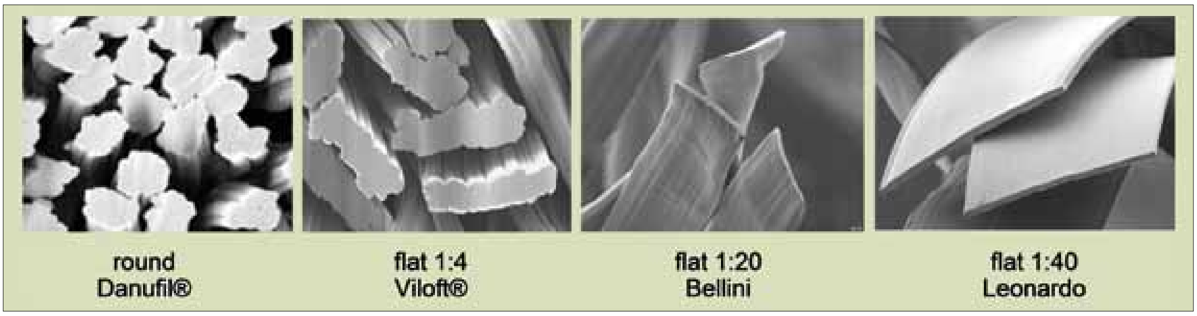

Figure 2. *Cross sections of viscose fibres.*

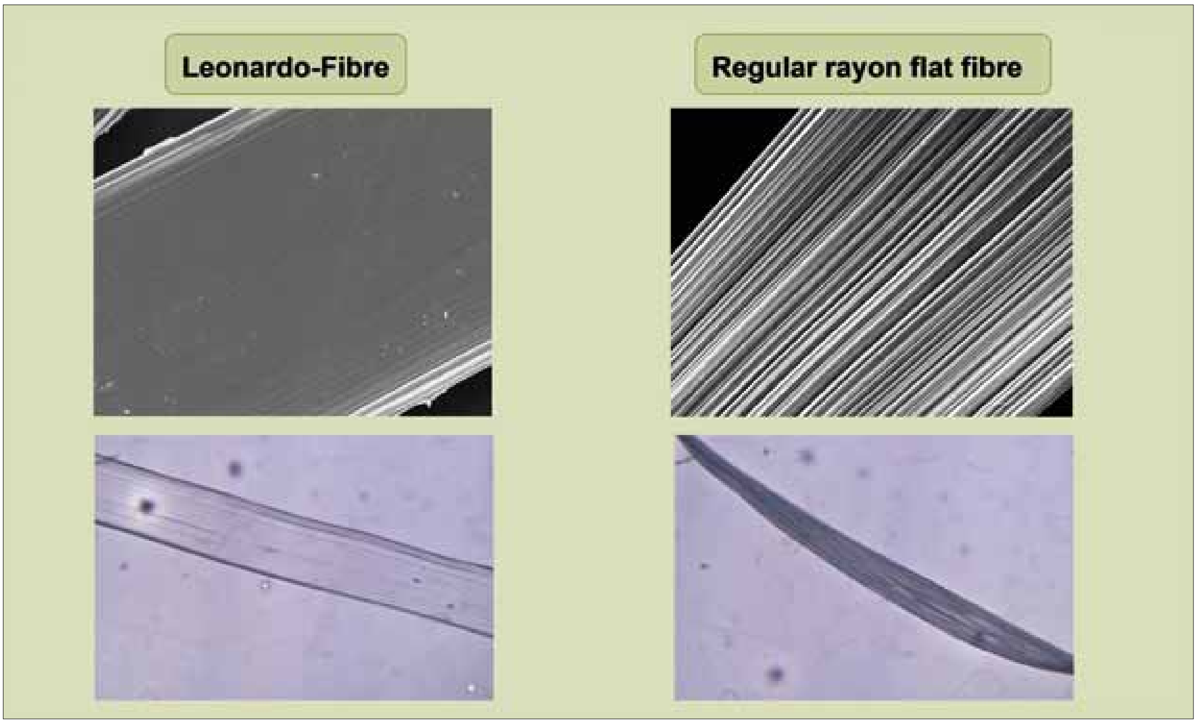

Figure 3. *Comparison of Leonardo and regular flat rayon fibre. top: SEM-Images, bottom: light microscopy.*

fibre appears nearly completely smooth. Both images were made at a five hundred fold magnification, the images thus also illustrate that the Leonardo fibres have the same width as the regular flat fibre of a three times lower fibre dtex.

The extremely flat and smooth fibre structure of Leonardo minimizes its light-scattering, which gives the Leonardo fibre a unique transparency. In Figure 3 (bottom), light microscopic images of a regular viscose flat fibre and a Leonardo fibre are shown. The images made under the same conditions highlight the transparent nature of the Leonardo fibre.

Using these translucent fibres, paper or wetlaid structures with improved transparencies can be achieved. But further to single fibre transparency, in a nonwoven or paper material it has to be considered that the numerous fibre-fibre interfaces in the paper structure are reducing the transparency of the sheet. To study this effect, 80g/m^2 lab sheets were produced from 100% viscose fibre. Laboratory testing showed that the opacity of the sheets made from Leonardo fibres is about thirty percent lower and the light scattering coefficient about seventy percent lower compared to sheets made out of viscose fibre with regular (round) cross-sections (Figure 4). As expected, transparency is slightly higher with increasing fibre dtex due to the reduced number of fibre-fibre interfaces, but this effect shows to be relatively small compared to the difference between sheets made from Leonardo and regular viscose fibre respectively.

Viscose Fibres in Wetlaid Nonwovens and Paper

Without the use of auxiliary additives paper sheets made only from regular viscose fibres are too weak to handle. Similarly to Bellini fibres, paper from 100% Leonardo fibre with considerable strength can be made due to the improved bonding properties of these fibres.

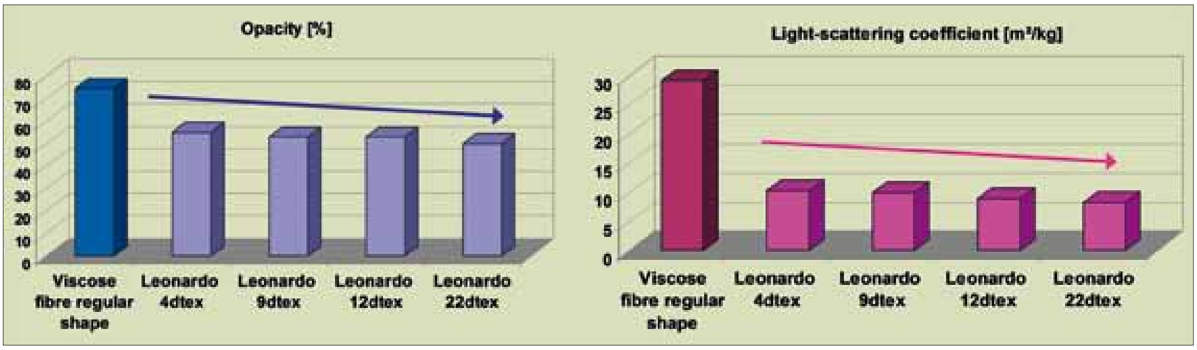

Figure 4. *Transparency of the Leonardo fibre.*

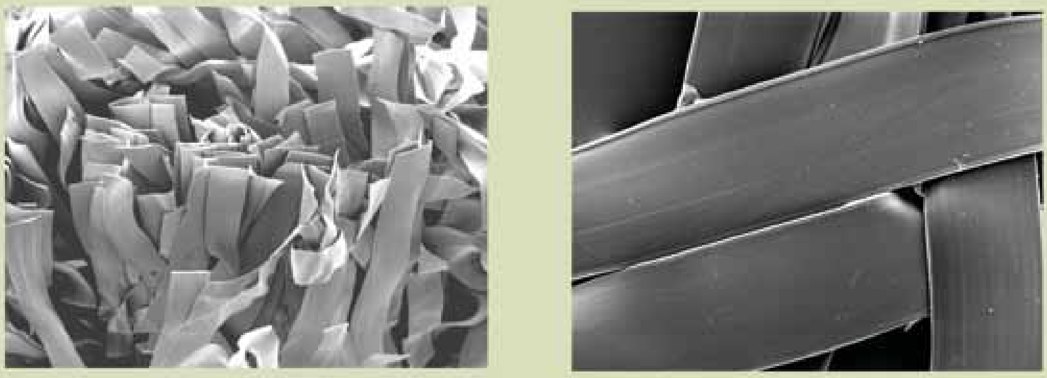

Figure 5. *SEM images of Leonardo fibres.*

The flat and smooth cross section of the fibres allows good fibre-fibre contact and so provides a higher area available for binding (Figure 5). In paper and wetlaid formation the flat side of the Leonardo fibres tends to get orientated with its wide side coplanar to the non-woven plane, which results in a good orientation of the fibre surface to form fibre-fibre bonds.

Influence of Fibre Dimensions

The very homogeneous structure of the Leonardo fibre makes it an ideal model to investigate the influence of the different single-fibre parameters on sheet parameters of the corresponding wetlaid or paper. To investigate the influence of fibre dimensions, sheets from 100% Leonardo fibre of different fibre length and coarseness were formed. Since the width-to-thickness ratio of Leonardo fibres is constant, Leonardo fibres with lower dtex also display a lower fibre thickness. The result of the testing shows that thinner and thus more flexible Leonardo fibres give sheets with increasingly higher tensile strength, the breaking length of a sheet made from a 4dtex fibre (2,5µm thickness) being four times higher than that made from a 28dtex fibre (7µm thickness). The number of double folds shows a similar trend: While the 28dtex fibres do not give foldable sheets, using 4dtex Leonardo fibres, sheets with close to two thousand doublefolds can be formed (Figure 6). It is also shown that longer fibres at a given dtex value give similar tensile strength in paper but lead to a correspondingly higher increase in tear resistance. For example Leonardo fibres of 9dtex in 6mm and 12mm give both the same tensile strength, but the sheet from the 6mm fibres has a tear resistance of about 830mN, while a sheet made from the 12mm fibres has a tear resistance of 1460mN.

Influence of Fibre Charge

Contrary to when regular viscose fibres are used, with the anionically modified Verdi fibres, which also display a standard round cross-section, paper from 100% viscose of some strength can be made.[3] The improved bonding properties can be attributed to the ionic modification of the fibre. Still the tensile strength of a 100% Verdi sheet is relatively low, but the anionic modification can also be used to further increase bonding strength of fibres with already good bonding ability. With the Leonardo fibre providing increased fibre-fibre contact a significant increase in tensile strength was expected. Effectively lab testing on sheets from 100% unmodified and modified Leonardo showed that an

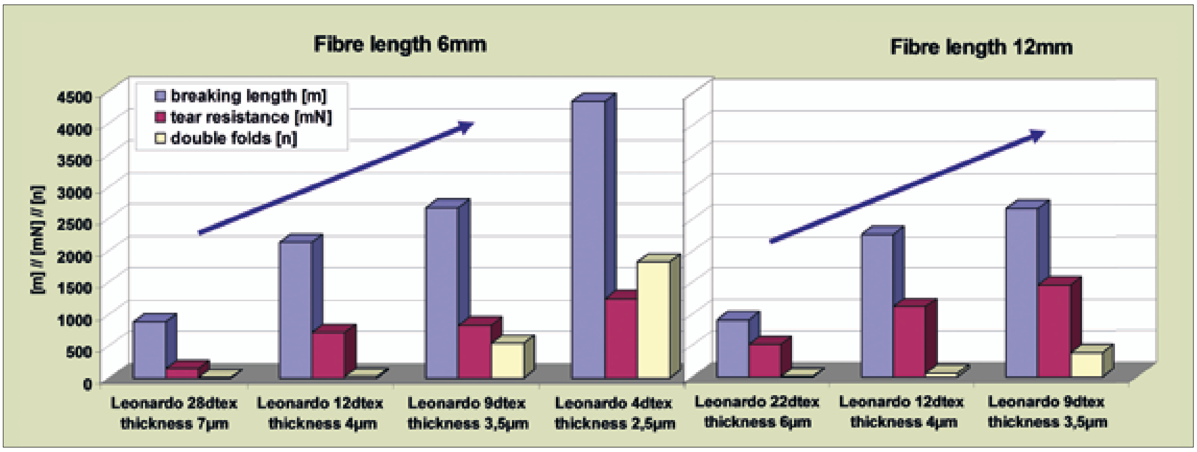

Figure 6. *Influence of fibre thickness and length on sheet strength and foldability.*

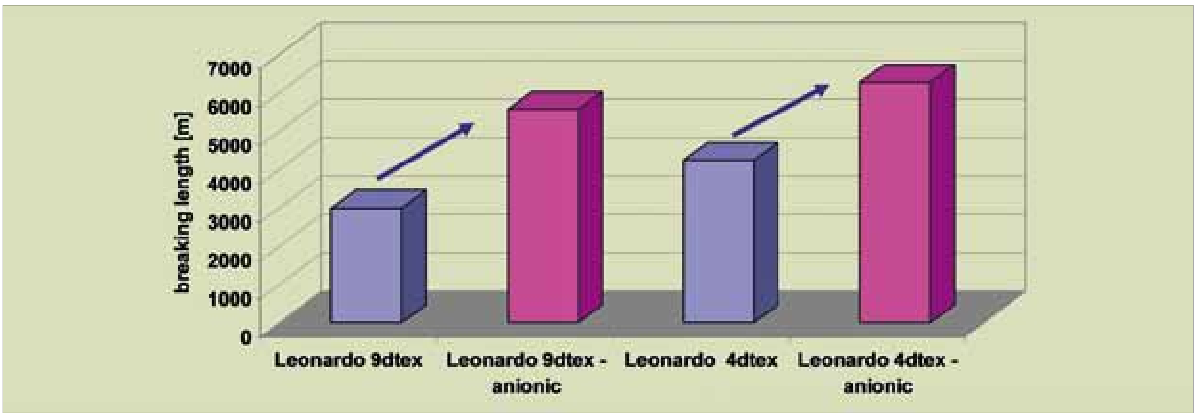

Figure 7. *Influence of anionic fibre modification on sheet strength.*

anionic modification of a Leonardo fibre significantly increases the tensile strength of the corresponding lab sheets (Figure 7). In the case of the 9dtex fibres, the breaking length of the sheets from modified fibres is about 85% higher, in the case of the 4dtex fibres the increase in strength is about 50%.

Blends With Viscose Fibres

As shown, single fibre parameters have a strong influence of on the sheet characteristics which can conveniently be studied in sheets made from 100% viscose fibre.

But also the incorporation of even small percentages of viscose fibres can be used to fine-tune wetlaid and paper characteristics. Here the choice of fibre cross-section plays an important role. While round Danufil fibres are mainly used to improve bulk and porosity of wetlaids and papers, flat viscose fibres do not increase the volume but do give a stronger improvement of tensile strength (Figure 8). When blending viscose fibres with pulp or into blends with other fibres, the resulting changes depend very much on the characteristics of the matrix used. Therefore in order to achieve the best possible effect, depending on the raw material composition, a viscose fibre of optimum length, dtex, cross section and chemical composition has to be selected individually in each case.

As an example 5% of Danufil (2,1dtex), Bellini (2,1 dtex) or Leonardo (4dtex) short-cut fibres in 6mm length were added to eucalyptus pulp refined to 26° SR. As expected, addition of round Danufil fibres increases the bulk by about 5%, whereas the addition of flat Bellini and Leonardo fibres does not give an increase in volume. Flat viscose fibres on the other hand give a higher rise in tensile strength, which can be attributed to their better bonding behaviour. In this example, Leonardo fibres give an improvement in breaking length of 25%. Additionally, in the given system, flat viscose fibres provide a much stronger enhancement of foldability (+200% in double folds) compared to round fibres.

Apart from a fine-tuning of properties, the addition of small amounts of viscose fibres to pulp can also achieve results, which are not possible with the single components alone.

In a further example, Bellini fibres in 1,9dtex with a variable cut-length (BelliniV) were added to Eucalyptus

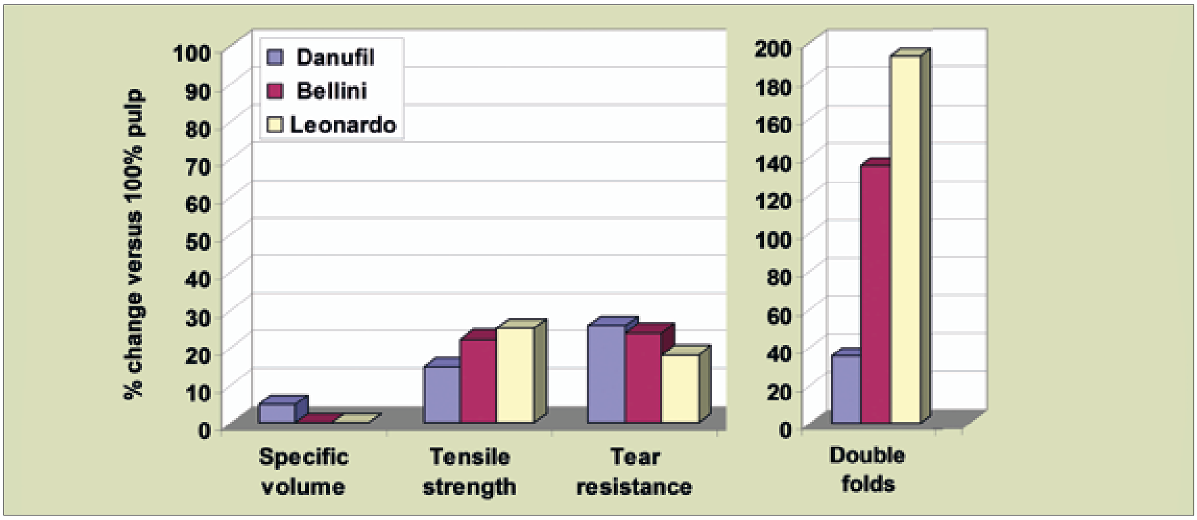

Figure 8. *Influence of cross-section in blends of pulp and viscose fibre.*

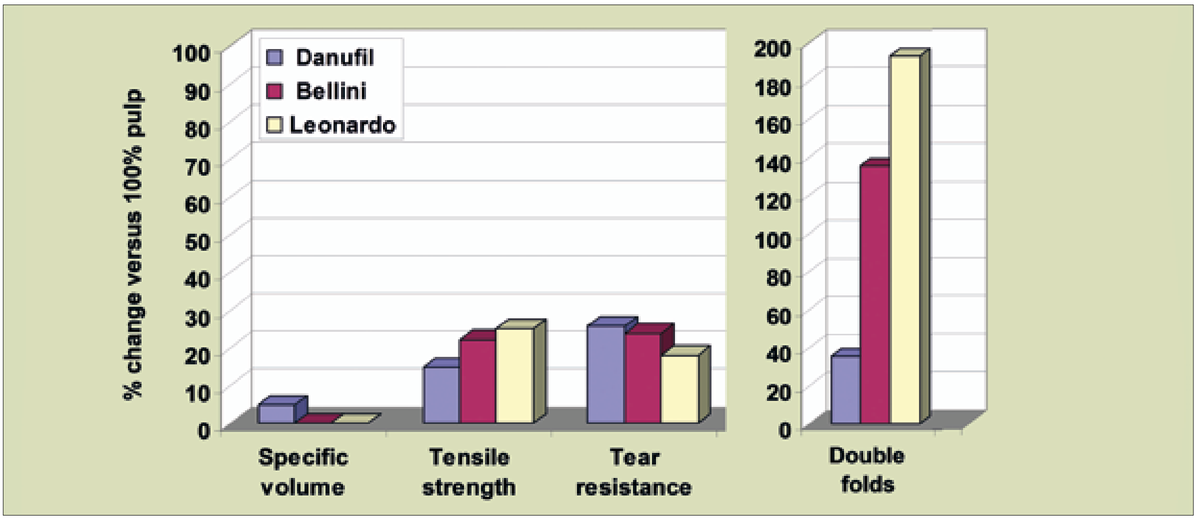

Figure 9. *Change of sheet properties after addition of 5% BelliniV fibre.*

pulp in 26° SR and the properties of the blended sheet was found to be quite different to those of sheets from either of the components alone.

While the air-permeability of the sheets made from only pulp or BelliniV respectively was around 1800ml/min, the sheet from the pulp/BelliniV blend had an air-permeability of 680mL/min. At the same time the blended sheet had a tensile strength that was 30% higher than that of the pulp sheet and about six times higher than the BelliniV sheets. Similarly the foldability of the blended sheet was much higher than in any of the single component sheets.

Conclusions

The viscose process allows the modification of functionality, fibre dimensions and cross section of the viscose fibres. The use of specially adapted fibres gives the possibility to introduce finished product properties through functionalized fibres.

Leonardo is a new viscose specialty with unique flatness and transparency, the influence of fibre dimensions on web strength in 100% Leonardo sheets was investigated. Furthermore it was shown in examples that air permeability, tear resistance, tensile strength and folding properties of wetlaid or paper sheets can be significantly influenced by addition of only small amounts of viscose fibres.

Acknowledgement

Labsheet testing was done CD-Laboratory for Surface Chemical and Physical Fundamentals of Paper Strength at the IPZ Graz.

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Novel Absorbing Fibres Based on Cellulose Acetate

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Abstract

Cellulose acetate having a degree of substitution (DS) of about 2.5 is known as a well-established technical product, which is processed to fibres, filter tow, membranes and thermoplastic materials. In general, the properties of this cellulose ester are strongly depending on the DS as it can be found for any cellulose derivative. Moreover, cellulose acetates cover a wider range of different properties that have not yet been used so far.

These materials remain cellulose-like at very low DS-values, but become more and more hydrophilic as DS reaches about 1.5, accompanied by an enhanced swellability and water adsorption as borderline case. When exceeding this DS, the solubility characteristic turn back to hydrophobicity and finally approach that of commercial cellulose-2.5-acetates (thermoplastic, soluble in organic solvents).

Nowadays, ionic liquids (IL), which have already attracted attention in cellulose research since a couple of years, provide the opportunity to combine both, chemical modification and physical shaping for the first time. With this cellulose acetate fibres with an adjustable DS-value are accessible without intermediate product isolation, because the used IL serves as solvent for reaction and shaping.

In particular, the preparation of biodegradable absorbing fibres is described characterised by high retention behaviour for water and electrolyte solutions.

Keywords: *celluloseacetate, absorbtion, ionic liquids*

Introduction

Since more than 100 years cellulose acetate is the driving force for innovations in different areas like aircraft, safety films, man-made fibres and many others [1]. Discovered by the German chemist Paul Schützenberger already in 1865 it became practicably for use as raw material for man-made fibres not until 1904, when the American chemist Georg Miles found that partially hydrolysed cellulose acetate could be dissolved in acetone. It was much cheaper than chloroform which had to be used for cellulose triacetate dissolution. Already in 1919 cellulose acetate plasticised by a softening agent was patented as the worldwide first injection moulding compound [2].

Consequently, cellulose acetate became an important technical material for use as man-made fibres, safety films and bulk artificial plastic. Nowadays, cellulose acetate with a degree of substitution (DS) of 2.5 is well-established industrial product with different applications dominated by filter tow or moulded padding.

Still as at the beginning of production in commercial scale the man-made fibres manufacturing procedure is subdivided into triacetate production step, partial hydrolyses, re-dissolving in acetone and fibres dry spinning process and hence more expensive than other man-made fibres (Figure 1) [3]. Therefore the amount of cellulose acetate fibres used for textile application is regressive.

As another fact, even though the properties of cellulose acetates changes dramatically with increasing DS, CA materials with lower DS than 2.5 are not commercially available yet, in spite of interesting properties. Very low DS values lead to more or less cellulose-like properties. DS values in the range from 0.4 - 0.6 result in strong swellable materials, because the hydrogen bond system is partially destroyed followed by an increased accessibility for water [4]. With further increasing DS the cellulose acetate becomes more and more hydrophobic as known from commercial secondary and triacetates.

As the third fact: All the different solvents which have been used for shaping of cellulose since decades, as for example cuoxam, carbon disulphide/NaOH and even N-Methylmorpholine-N-oxide, are not suitable for chemical modifications of cellulose. Not till the system N, N-dimethyl acetamide (DMA)/LiCl was discovered by Mc Cormick for use in cellulose dissolution and homogeneous derivatisation [5, 6] the opportunity for lower DS cellulose acetates became open. Both, etherification and esterification can be processed in DMA/LiCl without annoying side reactions. The most important drawback of this solvent system results from the high efforts for solvent components recovering. A process which includes acetylation and shaping is described in [7].

In the recent past ILs became more and more interesting for dissolution [8], shaping [9, 10] and derivatisation [11] of cellulose. Investigations about a one-pot process for the production of cellulose acetate fibres with controlled DS values and properties are described in [12]. After the dissolution of cellulose in the IL and the homogeneous modification of cellulose to cellulose acetate, a direct shaping of the cellulose acetate to fibres was carried out. Several ILs and different spinning parameters were tested, but only in laboratory scale, so far.

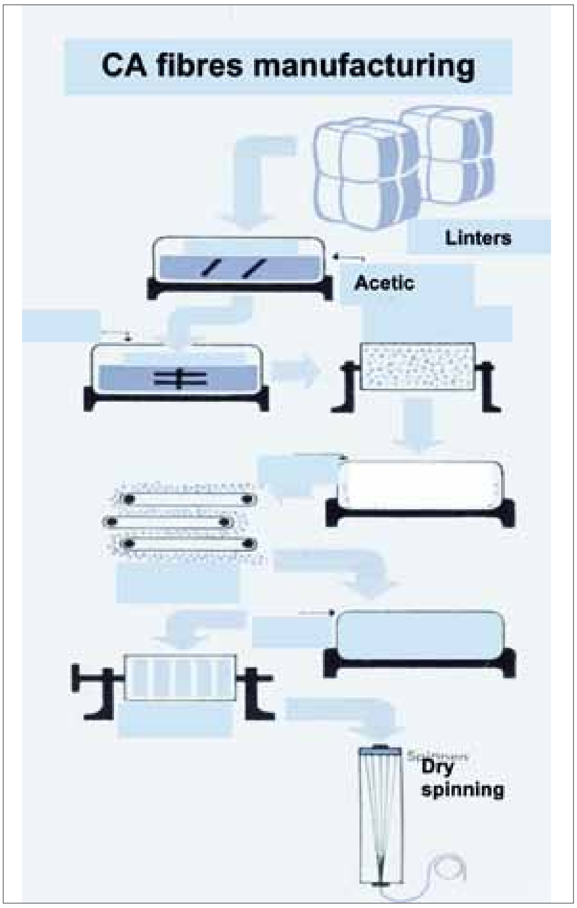


__Figure 1.__ Technological set-up for commercial CA fibres manufacturing as in the state of art (scheme resource: [13]).

In this paper we would like to demonstrate the technical potential of the IL based process for more economic efficient cellulose acetate fibres manufacturing in semi-technical scale and its broad variety of fibres properties.

Materials and Methods

MoDo 650 pulp from with the following analytical data was used: DP measured in cuoxam = 596; α-cellulose content = 92.9%.

The IL used, 1-Butyl-3-methylimidazolium chloride (BMIMCl) manufactured and supplied by Iolitec Co. was in analytical grade. It was used without any pre-treatment. Acetic anhydride was purchased from FLUKA and used as received.

Dissolution of cellulose in BMIMCl

531.7 g air dried cellulose (water content 7.2%) were added to 4,045 g of molten BMIMCl (99%) placed in a planetary paddle mixer. While stirring with a rotation speed of 60 rpm for 3 h at 98° C under vacuum (23 mbar) the cellulose dissolves completely [14].

Homogeneous Acetylation of Cellulose Solution

Directly after dissolution the esterification with acetic anhydride was carried out in the same type of reactor. After the solution was cooled down to 80° C, a certain amount of acetic anhydride was added quickly and the rotation speed of the stirrer was increased to 110 rpm. After a reaction time of 30 min at 80° C, unconsumed acetic anhydride and generated acetic acid were removed by vacuum (20 mbar) for 1 h.

Shaping of Cellulose Acetate Solution

A pilot plant piston spinning equipment, which consists of a heatable cylinder, a spin package, an air-conditioned air gap, a spinning bath, a turning round godet and a take-off godet, was used for the shaping trials. During the spinning test the acetate dope was tempered in the cylinder. The spinning dope was fed definitely to the spin package. The capillaries which leaked from the nozzle were shaped in the air gap and passed the spinning bath. A turning round godet collected the capillary skein and transported it over a traverse to the take-off godet. The finishing was carried out discontinuously after cutting the initial wet fibres into staples of uniform length.

Recycling of 1-Butyl-3-methyl-imidazolium chloride

The spinning bath, which consists of 20% IL and 80% water, was distilled under reduced pressure resulting in a mixture of 60% IL and 40% water.

The residual water was removed by a two-step treatment (135° C, 35 mbar, evaporation face 0.15 m^2, throughput 5 - 10 l/h) using a thin film vaporizer (Normag, Germany). The IL was concentrated up to 97 - 98% and could be reused several times.

Analytical Characterisation of the Cellulose and Cellulose Acetate Solutions

The solid content of the cellulose solutions was determined gravimetrically by precipitation in water followed by washing, drying and weighing of the precipitated films.

Its DP_{Cuoxam} was determined in cuoxam solution according to an internal house standard. For this purpose the intrinsic viscosity in cuoxam was detected by means of an automatic measuring capillary viscometer (Schott AVS 360).

The DP_{Cuoxam} was calculated according to Equation (1):

$$DP_{Cuoxam} = 2 \bullet \eta_{Cuoxam} \quad (1)$$

The α-content of the used pulp was determined as such part of pulp that is not dissolvable in a 17.5 wt.% aqueous sodium hydroxide solution at 20° C.

The rheological characterisation of cellulose solutions and cellulose acetate solutions was carried out with a rheometer of Haake MARS type containing cone/plate measuring system.

Zero shear viscosities (η_0) had been calculated from creep attempts in the rotation mode. Oscillation tests at three different temperatures have been used for calculation of the master curves of the cellulose solutions by means of a Williams-Landel-Ferry (WLF) transformation. Details of the rheological cellulose dope characterisation had been described in a former publication [14].

Fibre Characterisation

The determination of the water retention values (WRVs) of the cellulose fibres has been carried out according to DIN 53814.

The characterisation of the wet fibrillation tendency of the fibres was measured by the determination of the wet abrasion tendency (WAT). The WAT was detected by the investigation of the abrasion number of a wet fibre in opposite to an abrasion shaft. The shaft is covered by a fabric tube.

The experiment runs by using a defined pretension weight until the fibre is breaking [15]. The textile-physical fibre parameters were determined according to the following methods:

(i) single fibre fineness according to DIN EN ISO 1973,
(ii) fibres tenacity and elongation according to DIN EN ISO 5079 and
(iii) fibres loop tenacity according to DIN 53843, part 2

X-ray Diffraction

All measurements were performed by means of a BRUKER D8-Advance system equipped with a closed-cycled Eulerian cradle and a one-dimensional detector type LynxEye. The X-ray tube was operated at 40 kV voltage and 40 mA current generating a Ni-filtered radiation of $\lambda = 1{,}542$ Å wave length.

Sample preparation comprised cutting dried and conditioned fibres into short staples, and preparing a pecimen of about 2.5 mm thickness after randomising the fibres using an amorphous binder.

NMR Spectroscopy

^1H NMR spectra were measured with a Bruker Avance 250 spectrometer running at 250 MHz after perpropionylation of the cellulose acetate samples and dissolution in $CDCl_3$.

The ^{13}C NMR spectra of cellulose acetate samples dissolved in DMSO-d6 were measured on a Bruker DPX 400 spectrometer running at 100 MHz at room temperature.

Results and Discussions

Since a couple of years ionic liquids are used as solvents for cellulose, for alternative cellulose man-made fibres moulding, cellulose film manufacturing and homogeneous chemical derivatisation, respectively [16].

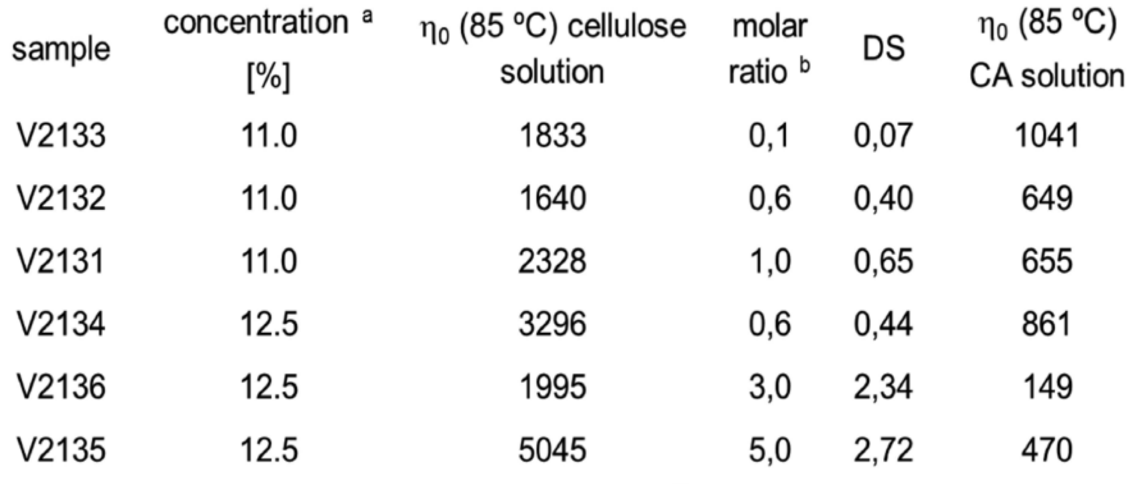
In case of derivatisation a lot of chemical reactions support a degradation of the IL or cause by-products, which are not completely removable again from the IL. In this regard acetylation represents an exception.

The use of IL as reaction medium leads to very pure and high substituted products, which can be attained by precipitation of cellulose acetates in water (very low or higher DS) or short chain alcohols (DS around 0.5) very simple [4]. The one and only by-product of the esterification is acetic acid, which could be easily removed together with unconsumed acetic anhydride by a simple vacuum distillation procedure.

The leading thought to use IL for combined polymer analogous chemical reaction and shaping of the resulting cellulose derivative was realised first by Kosan et al. in laboratory scale [11]. Based on theirs results we tried now to realise a scale-up of the process into the semi technical scale. As in the previous studies BMIMCl was exclusively used as solvent of choice in this study. It was identified as the most stable and most suitable solvent for acetylation and subsequent shaping [11].

In a first technological step the cellulose pulps were dispersed in used IL. 11 and 12.5% of cellulose was dissolved, respectively, by shearing at constant revolution speed.

***Table 1.** cellulose concentration, dopes viscosities, molar ratio and zero shear viscosity of cellulose dopes homogeneous derivatized by acetic anhydride.*



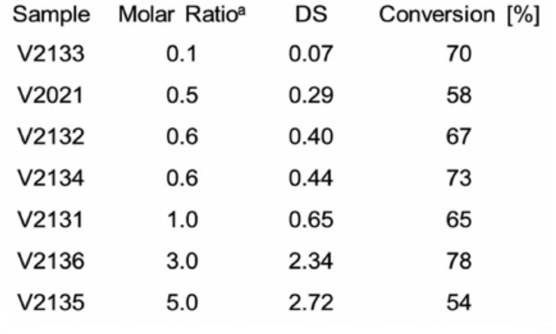
sample	concentration [a] [%]	η_0 (85 °C) cellulose solution	molar ratio [b]	DS	η_0 (85 °C) CA solution
V2133	11.0	1833	0,1	0,07	1041
V2132	11.0	1640	0,6	0,40	649
V2131	11.0	2328	1,0	0,65	655
V2134	12.5	3296	0,6	0,44	861
V2136	12.5	1995	3,0	2,34	149
V2135	12.5	5045	5,0	2,72	470

[a] pulp, DP 650 [b] acetic anhydride : cellulose

While dissolution state in BMIMCl was somewhat satisfactory in case of lower cellulose concentration, states of dissolution were not equally enough at higher cellulose amounts (compare to Table 1). The reason for strong changes in zero shear viscosities of the samples containing higher amounts of cellulose are not well understand so far. The use of too small-scaled, discontinuous dissolution procedures could be possibly one reason.

Nevertheless, in the following step dissolved cellulose was converted into cellulose acetate by homogeneous reaction with acetic anhydride. The cellulose dopes were converted at 80° C for 2 hours using a stirring reactor. The DS could be easily controlled by adjustment of the molar ratio of acetic anhydride to AGU (see Table 2). Effects of different polymer concentration regarding the CA yield were irrelevant. CA yield does also not depend on cellulose dope viscosity.

***Table 2.** Adjustable CA fibres DS regarding the used acetic anhydride to AGU molar ratio.*



Sample	Molar Ratio[a]	DS	Conversion [%]
V2133	0.1	0.07	70
V2021	0.5	0.29	58
V2132	0.6	0.40	67
V2134	0.6	0.44	73
V2131	1.0	0.65	65
V2136	3.0	2.34	78
V2135	5.0	2.72	54

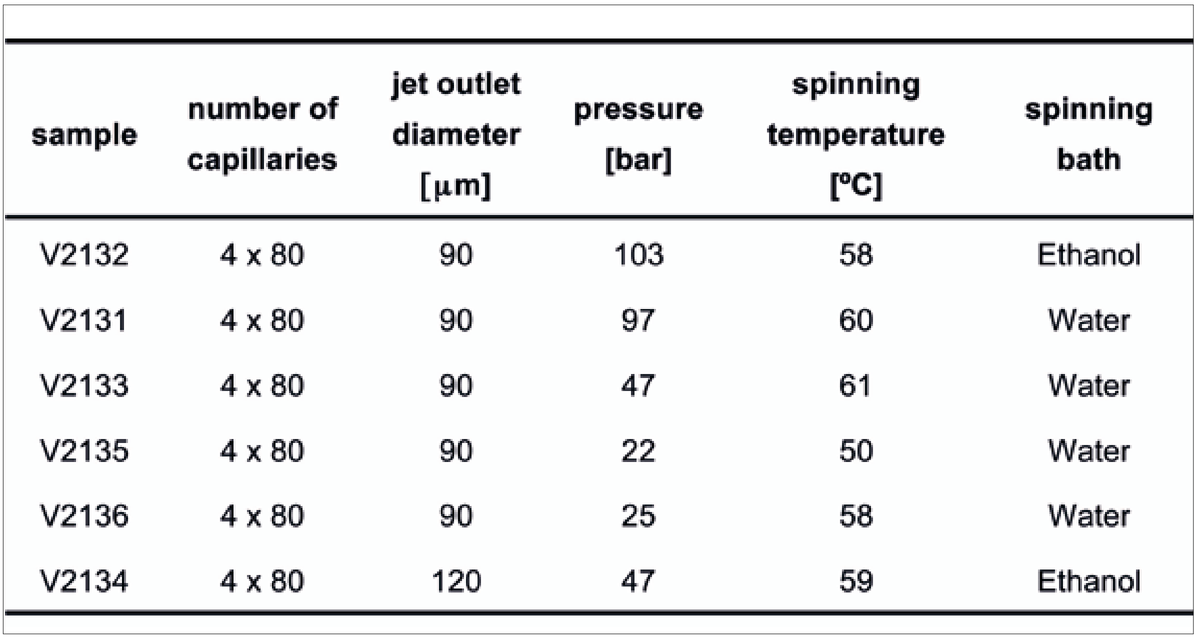
[a] acetic anhydride : cellulose

The CA dope viscosity after removing of excess acetic anhydride and generated acetic acid was strongly declined as a function of DS and initial cellulose concentration. Even at a very low DS of 0.1 the CA dope viscosity was fallen down to about 60% of the unreacted cellulose dopes. At the highest acetate DS the viscosity drop down to less than 10% of cellulose dope. The steady viscosity decline could be interpreted by the steady degradation of the H-bond bridges of the cellulose and provides a need to adjust the spinning parameter as needed for secure fibres spinning.

After reaction was finished not reacted acetic anhydride and generated acetic acid were removed from the solution and fibres were subsequently shaped by a dry-jet-wet spinning process. Spinning temperatures, drawing ratio, air gap length and spinning bath temperatures were tried to adjust to the characteristics of used dope (see Table 3). CA solutions having higher DS indicated poorer spinnability because of the very low zero shear viscosities. Further investigations for adjustment of most suitable initial cellulose concentration are under progress.

Regarding the adjusted DS the manufactured CA fibres exhibit different water adsorption ability. At very low DS the fibres exhibit low water retention, only, comparable with pure cellulose fibres manufactured according to direct dissolution process. If the fibres DS is increased to 0.5 up to 0.8 the water retention value is increased up to 300%. It was surprisingly that water retention was constant or further slightly increased up to 400% if electrolytes were added to aqueous media (Figure 2). This is totally in contrast to the well-known behaviour of super adsorbing polymers (SAP), where already small increase in electrolyte concentration strongly decreased

Table 3. *Spinning condition used for CA fibres manufacturing.*



sample	number of capillaries	jet outlet diameter [µm]	pressure [bar]	spinning temperature [°C]	spinning bath
V2132	4 x 80	90	103	58	Ethanol
V2131	4 x 80	90	97	60	Water
V2133	4 x 80	90	47	61	Water
V2135	4 x 80	90	22	50	Water
V2136	4 x 80	90	25	58	Water
V2134	4 x 80	120	47	59	Ethanol

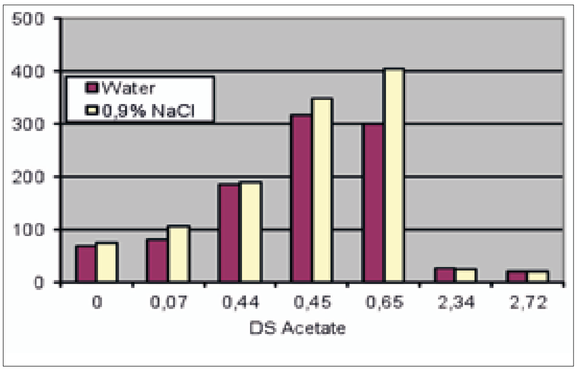


Figure 2. *Water retention values of CA fibres at different DS.*

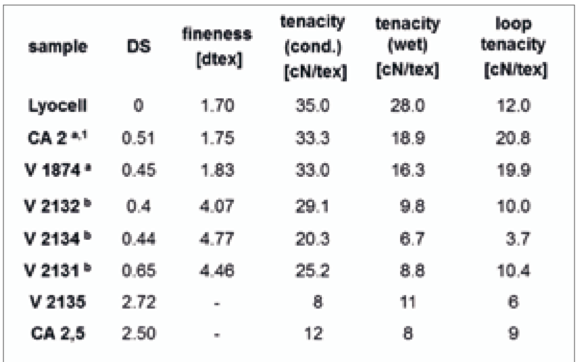
water retention values. The reason for such behaviour may be the increase of flexibility of macromolecule chains by added electrolytes.

At higher DS hydrophobic acetyl group becomes dominantly, CA fibres change to hydrophobic behaviour again and exhibit a strong decrease of water retention.

Textile fibres properties (see Table 4)

CA fibres with fineness of 1.8 to 7 dtex could be spun. Theirs single fibres tenacity at conditioned state is in the range of 30 (at DS = 0.4) down to 8 cN/tex (at highest DS of 2.7). The values correlate to the structural changes of cellulose macro molecule when converted to CA. At highest DS interaction of polymer chains is strongly reduced and degradation of cellulose intermolecular structure seems to be almost eroded (compare to results of x-ray diffraction studies). Loop tenacity of developed CA fibres is about 10 cN/tex for lower substituted types and about 6 cN/tex for fibres having higher DS. For higher substituted CA they are in the same order of magnitude as commercial samples of secondary acetate.

Table 4. *Textile-physical properties of manufactured CA samples in comparison to commercial (CA 2,5) and small laboratory scale (CA 2, V 1874).*



sample	DS	fineness [dtex]	tenacity (cond.) [cN/tex]	tenacity (wet) [cN/tex]	loop tenacity [cN/tex]
Lyocell	0	1.70	35.0	28.0	12.0
CA 2 [a,1]	0.51	1.75	33.3	18.9	20.8
V 1874 [a]	0.45	1.83	33.0	16.3	19.9
V 2132 [b]	0.4	4.07	29.1	9.8	10.0
V 2134 [b]	0.44	4.77	20.3	6.7	3.7
V 2131 [b]	0.65	4.46	25.2	8.8	10.4
V 2135	2.72	-	8	11	6
CA 2,5	2.50	-	12	8	9

[a] shapes on laboratory equipment
[b] shaped on pilot spinning equipment
[c] commercial secondary acetate fibre
[1] B. Kosan, S. Dorn, F. Meister, T. Heinze, *Macromol. Mater. Eng.*, **2010**, 295, 676-681

Compared to manufactured CA of this study, samples manufactured in small laboratory scale [4, 11] exhibit somewhat higher textile-mechanical characteristics. The reason could be more defined shaping conditions because of lower number of spinning capillaries in smaller scale. Investigation of more optimised spinning and coagulation conditions are still in progress.

X-Ray Diffraction / NMR

X-ray diffraction showed interesting details of these homogeneously synthesised cellulose acetates. The solvent was recycled using a thin film vaporizer. The following general conclusions can be deduced form the X-ray diffraction measurements. In general, signals detected by X-ray diffraction disappear or undergo flattening as

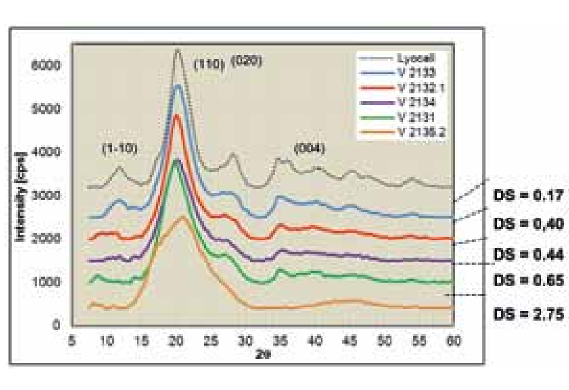


Figure 3. *Results of X-ray diffraction measurements using cellulose acetate fibres comprise different DS.*

the degree of substitution increases as shown in Figure 3. When comparing the structural features in that series of samples it becomes obvious that the intensive signals of the (10-1) and (002)-plane are less subjected to, for instance, broadening, as long as the DS-value remains moderate, where proceeding H-bonding blockage is accompanied by pronounced changes and loss of fine structure.

Although signals of the (101) scattering plane at $2\theta \approx 12°$ are generally less intensive, but always detectable in non-substituted cellulose regenerates, this particular feature is missing in almost all of the investigated samples.

Since these signals are also considered to be a measure of the crystallite width, it has to be assumed that increasing substitution causes advancing chain deterioration on the crystallite edges in first place, especially as the remaining scattering pattern retains its similarities with that of the pre-dominating cellulose-II-structure at DS-values not exceeding 0,5 significantly. There is further no distinctive DS-value definable at which the basic structure is definitely changing from partly crystalline to completely amorphous, so that even at values as high as 2,5 a certain degree of molecular short-range order is still present (see Figure 3 orange graph).

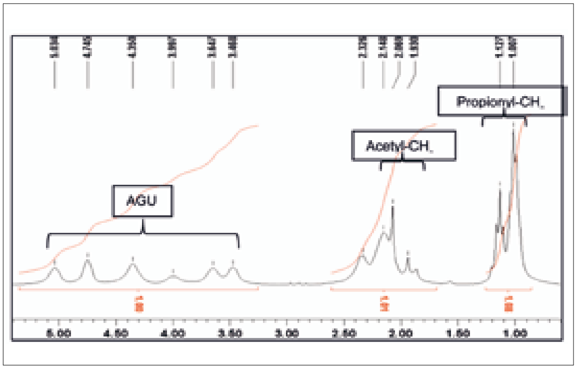


Figure 4. *^{1}H-NMR spectrum of perpropionylated CA (DSacetyl = 0.48) manufactured homogeneously in BMIMCl.*

NMR Spectroscopy

Determination of acetyl DS was carried-out by ^{1}H-NMR spectroscopy after perpropionylation of CA samples [17]. The AGU protons are located between $\delta = 3.3$ and $\delta = 5.2$, next to the signals of the propionate groups.

From the ratio of propionate protons to AGU protons the $DS_{propionyl}$ can be calculated. The DS of acetyl groups results from difference of the maximum DS of AGU groups (= 3) and DS of propionyl group, respectively.

In Figure 4 a $DS_{propionyl}$ of 2.52 and DS_{acetyl} of 0.48 is received, respectively. The DS of acetyl groups is fairly consisted with the $DS_{acetyl} = 0.66$, as determined by acid-base-titration of the cellulose acetates.

The frequency of acetyl group substitution in the cellulose AGU can be received from the ^{13}C-NMR spectrum (see Figure 5). The spectrum shows the highest degree of substitution at C 6, followed at C 2 and C 3. Perpropionylation pattern is inversed with it. Such a distribution is in accordance with the reactivity sequence at homogeneous reaction conditions, $OH_{primary} > OH_{secondary}$ and finally C 6 > C 2 > C 3, which is in contrast to heterogeneous reaction where C 2 is most reactive AGU position.

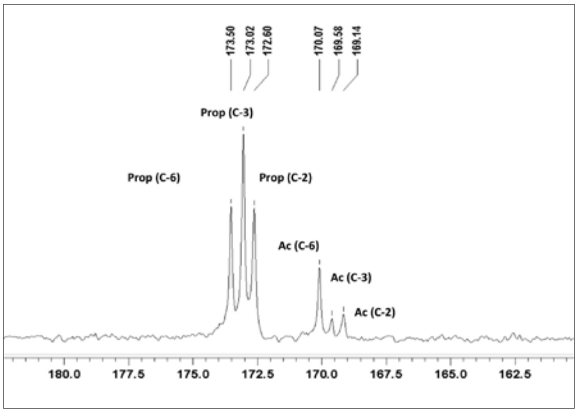


Figure 5. *^{13}C-NMR spectrum of perpropionylated CA ($DS_{acetyl} = 0.48$).*

Recycling of 1-Butyl-3-methyl-imidazolium chloride

The acetylation of cellulose in 1-Butyl-3-methyl-imidazolium acetate solely forms acetic acid as by-product. It is continuously distilled off from the reacting mixture under reduced pressure according to its rate of formation.

The non-volatile ionic liquid itself accumulates in aqueous spinning baths, while the concentration is usually kept at 20 wt.% for technological reasons. In the course of recycling those spinning baths are re-concentrated to about 60% by common vacuum distillation in a first step followed by treatment in a thin film vaporiser. There IL degradation is largely avoided by properly adjusted settings such as short residence times and higher throughputs. For intensifying the purification effect the IL is allowed to pass through the falling film evaporator twice.

This second step is intended to remove residual water and yields IL's having concentrations as high as 97 - 98% that might repeatedly be returned to the synthesis and spinning process.

Conclusions

The homogeneous acetylation and consecutive spinning of CA fibres using suitable solvents like ionic liquids offers an one step process without need of intermediate CA separation and additional re-dissolving. Not reacted acetylation agent as well as generated acetic acid could be fully separated by simple distillation procedure.

The degree of substitution (DS) of manufactured cellulose acetates up to 2.7 is adjustable regarding the molar ratio of cellulose and acetylating agent used. Cellulose acetate fibres having a DS of about 0.4 to 0.6 exhibit a water retention value of about 300%. It could further increased and adjusted at about 400% if small amounts of salts (NaCl) are added into the adsorbed aqueous liquid.

This is more or less in the same order of magnitude as for super adsorbing polymers when treated by diluted aqueous salt solutions.

With increasing DS the cellulose acetate crystallinity degreases and material hydrophobicity increases, repectively.

The substitution pattern also of low substituted celluloses which was determined by ^{1}H and ^{13}C NMR spectroscopy fairly correlates with results of acid-base titration evaluation. Most of the acetate substituents are located, as expected, at C 6.

In contrast to heterogeneous substitution the maximum reactivity of AGU carbons is in the order C 6 > C 2 > C 3.

The used ionic liquids could be effectifely purifieded in pilot plant scale by continuous thin film distillation.

Low substituted fibres may be biodegradable. Further process development is strongly needed for achievement of more stationary DS, product quality and CA fibres processing conditions.

Acknowledgements

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Functionalisation of Viscose Fibres

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Abstract

Growing fibre market and demand for bio-based products asks for cellulosic fibres with improved properties. For that purpose we aim in finding a chemical modification method that allows versatile applications. In the first step aldehyde groups were introduced into the cellulose chain by oxidation. These groups serve as anchor groups for attachment of functional molecules in a subsequent second reaction step. Application of such anchor groups was demonstrated by covalent attachment of the fluorophore dansyl hydrazine and by reduction of silver ions and deposition of silver on the fibre surface.

Keywords: *viscose, oxidation, aldehyde, antimicrobial finish, silver*

Introduction

It is expected that the market for fibres will grow in the future; especially bio-based manmade cellulosic fibres such as Viscose (rayon) or Lyocell might become more important. New bio-based fibres with altered properties are required to open new fields of applications and to allow a replacement of synthetic fibres. Especially changing hydrophobicity, dyeing capacities, antimicrobial or electrical properties are of interest for industrial applications.

In our work we are investigating possible anchor groups that can easily be introduced into cellulose and thus can serve as binding sites for further modifications. Our focus is based on generation of aldehyde groups by periodate oxidation of Viscose fibres similar to experiments described by Kostic et al. [1]. Metaperiodate is an oxidation reagent that selectively attacks vicinal hydroxyl groups. The fast formation of an intermediate complex is followed by a slower decomposition step, where the carbon-carbon bond is broken and an aldehyde group is formed on each of the carbon atoms. Periodate oxidation of cellulose attacks hydroxyl groups on carbon atom C2 and C3 of an anhydroglucose unit (AGU) which leads to ring opening and formation of dialdehyde cellulose without side reactions [2-4], see reaction scheme in Figure 1. Aldehyde groups undergo inter- or intramolecular hemi-acetal formation with hydroxyl groups of the same or neighbour cellulose chain leading to compact and insoluble molecules [5]. Reaction is performed under mild acidic conditions which prevents depolymerisa-tion of carbon chains.

2,3-dialdehyde cellulose can be further modified by oxidation to dicarboxylcellulose by chlorite oxidation (see Figure 1) or by reduction of aldehyde to the corresponding alcohol groups [5, 6]. Additionally, aldehydes can react with N-nucleophiles like amines, hydrazides or semicarbazides. Röhrling et al. [7] investigated the reaction of aldehydes of cellulose with the oxy-amine compound carbazole-9-carboxylic acid (CCOA). Fibres with antimicrobial activity are of special interest for wound dressings or textiles that prevent odour formation. Silver is a promising agent for such applications as it has antibacterial and antifungal activity. Different methods for production of silver coated fibres were published. One option is sorption of silver ions by carboxyl groups created by oxidation as described by Praskalo-Milanovic et al. [8]. Another option is the generation of silver particles by reduction of silver ions, either by reducing groups present in cellulose chain [9] or by

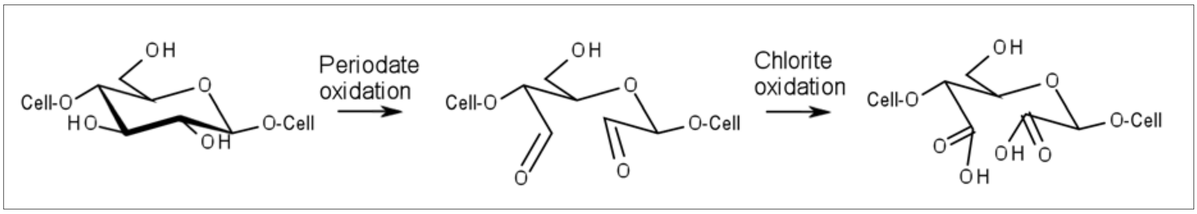

Figure 1. *Periodate oxidation of cellulose leading to dialdehyde cellulose and subsequent chlorite oxidation to carboxyl cellulose.*

use of external reducing agents such as ascorbic acid [10]. Prysiazhnyi et al. [11] used dielectric barrier discharge plasma pretreatment of Viscose and cotton and found silver particles after reaction with silver nitrate.

Materials and Methods

Viscose fibres

Never dried, washed fibres without finish were supplied by Kelheim Fibres GmbH.

Periodate Oxidation

Oxidation was done with excess sodium metaperiodate ($NaIO_4$) solutions under mild acidic conditions. Aqueous sodium metaperiodate solutions had a pH of ~4.5 and were applied without buffering. Temperature was varied between 25 and 70° C, periodate concentration was between 0.01 and 0.4 mol/L and cellulose concentration was between 0.25 and 100 g/L. Fibres were cut into short pieces to allow better suspension and stirring. Oxidation was stopped at different time points by filtration in a Büchner funnel, and thorough washing with water and ethanol; samples were frozen without drying and analysed by gel permeation chromatography (GPC).

Mechanical fibre properties were measured by Kelheim Fibres GmbH with a Fafegraph HR tensile tester from Textechno Herbert Stein GmbH & Co. KG. 20 single fibres per sample were measured with a clamping length of 20 mm.

Gel Permeation Chromatography (GPC)

10-20 mg of cellulose samples were activated in 4 ml N,N-dimethylacetamide (DMAc) overnight on a shaker (or for longer periods up to a week in case of samples with low solubility), and then dissolved in the appropriate amount of 9% w/v lithium chloride in DMAc (1 mL per 10 mg of cellulose) at 40° C in a shaking water bath. Dissolved samples were diluted 1:4 with DMAc, filtered through 0.45 μm polytetrafluoroethylene syringe filters and analysed by GPC as described by Henniges et al. [12]. Carbonyl group content and profiles were determined by heterogeneous fluorescence labelling with fluorophore CCOA (carbazole-9-carboxylic acid [2-(2-aminooxyethoxy)ethoxy]amide) as described by Röhrling et al. [7].

Dansyl Hydrazine

Dansyl hydrazine (CAS: 33008-06-9) was dissolved in ethanol and used as 3.4 mM aqueous solution in 0.02 M zinc acetate buffer (pH 4). Cellulose samples (5 mg/mL) were labelled at 40° C overnight. Analysis was done with fluorescence microscope Olympus IX81 with filter settings for fluorescein isothiocyanate.

Silver Ion Reduction

Periodate oxidized and non-oxidized Viscose samples were reacted at ambient temperature for 1 h with 1% Tollens' reagent (10 mL per 1 g of cellulose): 1% silver nitrate $AgNO_3$ was dissolved, some drops of dilute sodium hydroxide solution was added, then ammonia solution was added drop wise until precipitate re-dissolved completely, solution was then diluted to final volume. Reaction was stopped by removal of reaction solution by filtration and 3 washing steps with deionised water (40 mL per g sample, 15 min each) on a shaker to remove excess reagent solution and samples were then air dried.

Silver contents of depleted reaction- and washing- solutions were determined by Volhard titration as described in literature [13]. Silver deposited on Viscose fibres was dissolved by 30% nitric acid (HNO_3, washed out, diluted and analysed by Volhard titration. Scanning Electron Microscope (SEM) and energy dispersive X-ray spectroscopy (EDX) analysis was done with Inspect S50 by FEI Company with 'xT microscope control' software and gold sputtering with Leica EM SCD 005.

Results and Discussions

Oxidation (1st step)

We aimed at finding suitable reaction conditions for periodate oxidation that allow online integration of the reaction into Viscose fibre production process. Variation of reaction parameters showed high influence of periodate concentration and temperature on the reaction velocity. GPC measurements showed that molecular weight distribution did not change significantly at low degrees of oxidation as shown in figure 2. Carbonyl groups were introduced in all molecular weight fractions. Carbonyl group contents of several 100 μmol/g can be reached within some minutes of oxidation even

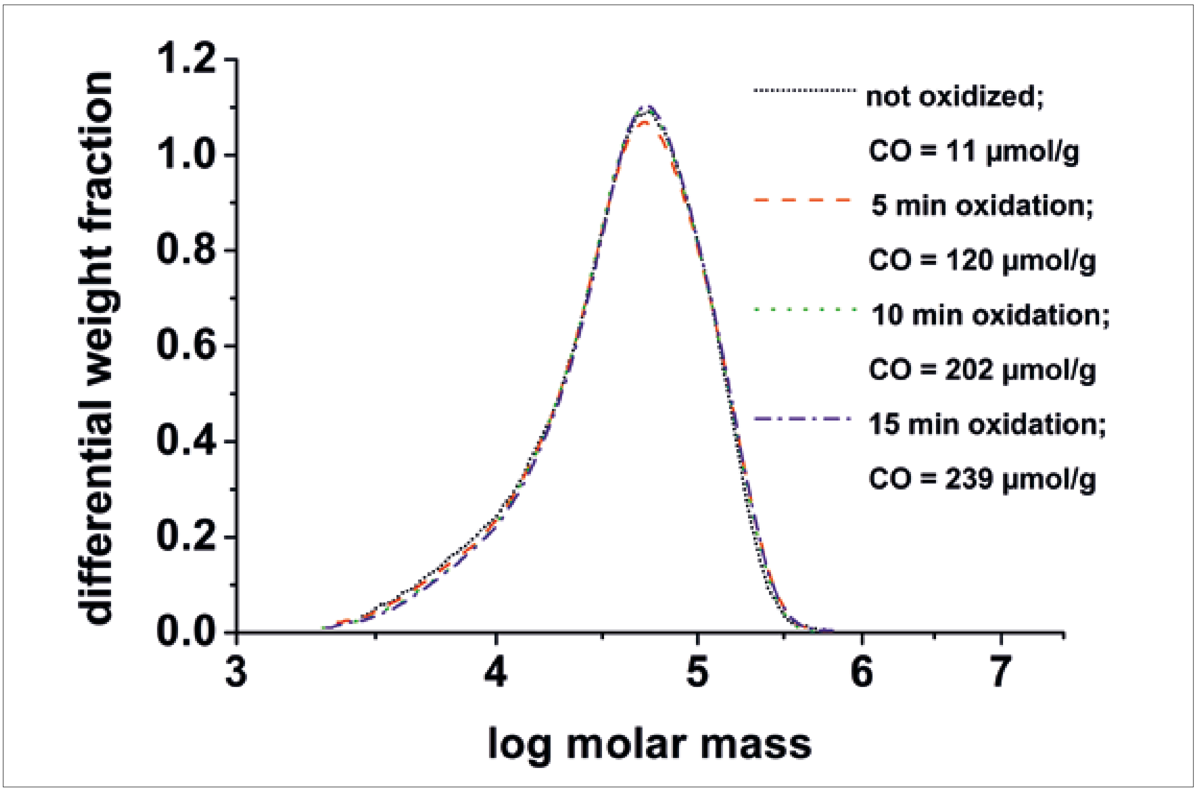

***Figure 2.** Molecular weight distribution for periodate oxidation series of Viscose fibres.*

at room temperature when a large excess of a concentrated periodate solution is used.

Data of mechanical fibre properties measurements showed high standard deviation and large variations between the samples. No clear trend could be recognized, observed variations are within the tolerance threshold for fibre production. Therefore slightly oxidized fibres with carbonyl group contents up to several 100 μmol/g should be applicable for further industrial processes.

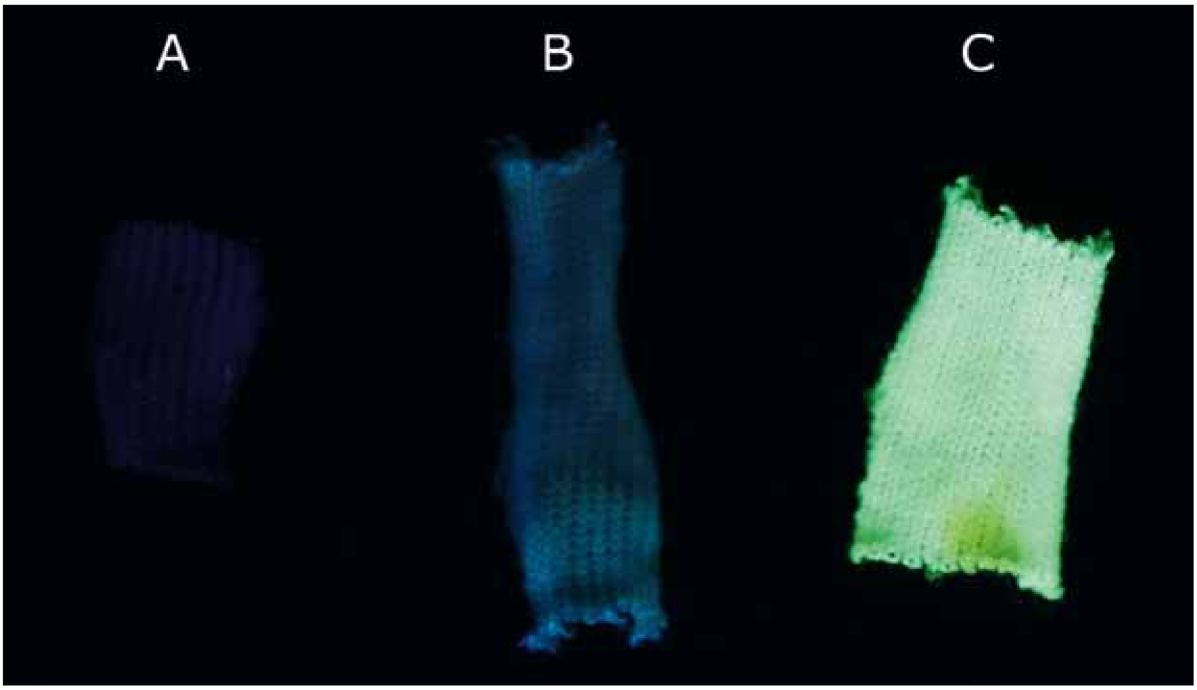

***Figure 3.** Reaction with fluorophore dansyl hydrazine: A) negative control not labelled, B) labelled, non-oxidized fabric, C) labelled oxidized fabric.*

Subsequent Reactions (2nd step)

Dansyl hydrazine was chosen as a model compound to demonstrate the reaction of aldehyde groups of cellulose with amine compounds. Fluorescence images of dansyl hydrazine labelled Viscose fibres showed highly increased fluorescence in case of periodate oxidized sample (carbonyl content ~ 140 µmol/g by periodate oxidation) compared to non-oxidized sample (carbonyl content ~ 23 µmol/g), see figure 3. This clearly shows the applicability of aldehydes as anchor groups for attachment of functional molecules.

Additionally we investigated effectiveness of reductive activity of aldehyde groups for the reduction of metal ions and subsequent deposition of metallic particles on fibres. We tested this with silver by use of Tollens' reagent that contains diamine silver(I) complex. During the reaction the colour of Viscose fibres turned to yellow or brown, moreover the reaction – and washing solutions – showed a yellow colour indicating loss of silver particles.

A fiber (sample A) with an initial carbonyl group content of ~18 µmol/g was periodate oxidized resulting in sample B with a carbonyl content of ~69 µmol/g. Oxidized and non-oxidized samples (A + B) were reacted with 1% Tollens' reagent at room temperature for 1 h: silver content of fibres reached ~ 0.5% for the non-oxidized sample C and ~ 1% for the oxidized sample D (see figure 4).

No silver particles could be detected by SEM and EDX measurements and yielded only minor amounts of silver. Further studies will be done with higher degrees of oxidation.

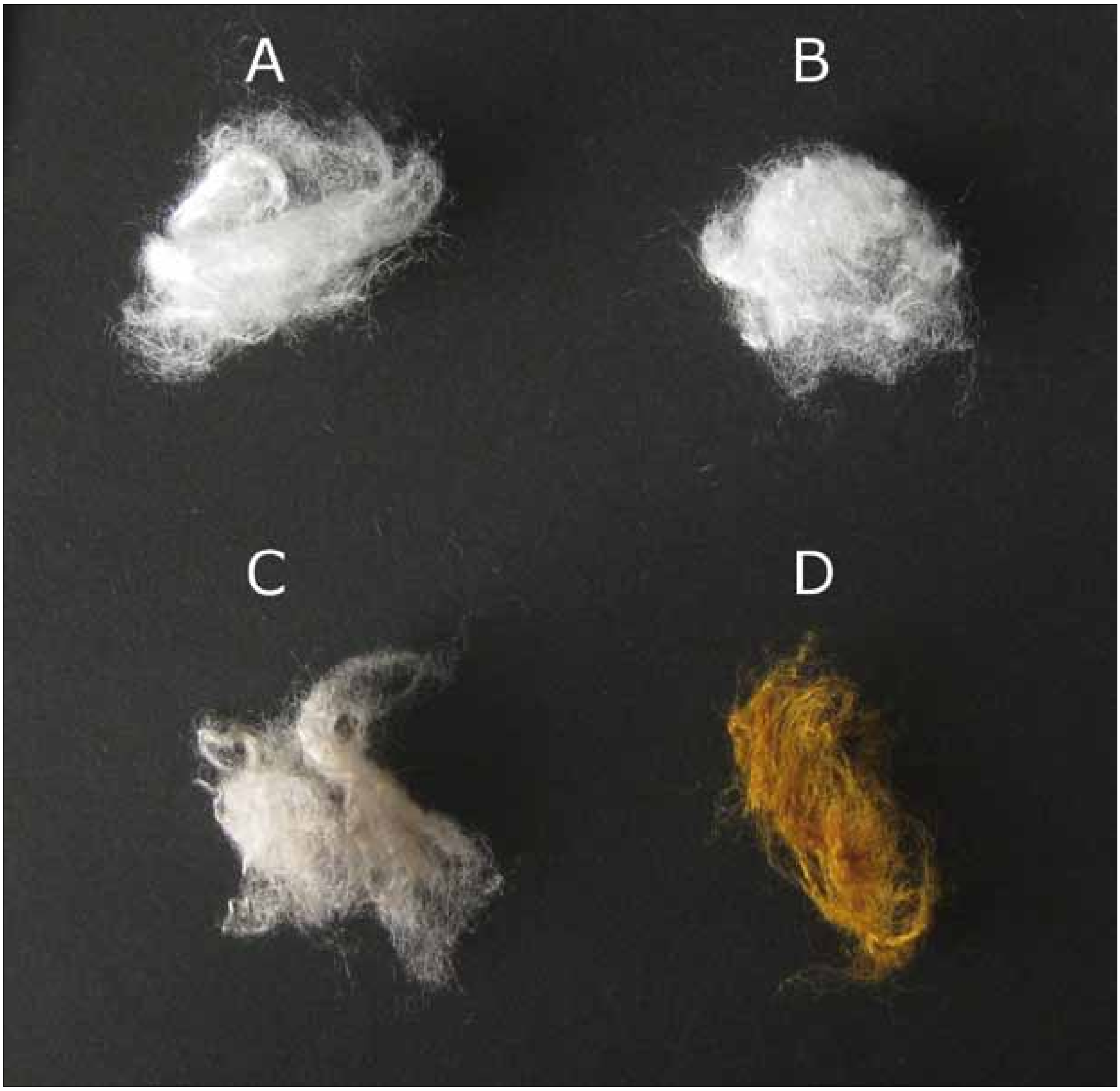

Figure 4. *Raw material (A + B: without silver) and silver containing fibres C (non-oxidized, ~ 0.5% silver) and D (oxidized, ~ 1% silver).*

Conclusions

We could show that periodate oxidation is a promising way to introduce aldehyde groups into Viscose fibres as the reaction proceeds in a sufficiently fast way for integration in the industrial fibre production process. The modification shows only minor effects on molecular weight distribution or mechanical fibre properties.

Aldehyde groups can be used for subsequent attachment of functional molecules for instance via a hydrazone linkage as shown with dansyl hydrazine. Additionally we have shown that reducing activity of aldehydes can be used for reduction and deposition of metal ions, like silver, on Viscose fibres.

Acknowledgements

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LENZINGER BERICHTE 91 (2013) 89 – 92

TENCEL® Gel – A Novel Cellulose Micro Suspension

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Abstract

Cellulose gels (micro- or nano fibrillated cellulose, MFC/NFC) derived from pulp have lately been propelled into the focus of scientific and industrial research. They show a fibrous character and are mainly studied as additives or as a reinforcing matrix. These unique materials are able to bind high amounts of water and can therefore form stable gels with a low amount of solid content. Applications include but are not limited to food, cosmetic and pharmaceutical industry, medical technology and material engineering.

The novel TENCEL® micro suspensions presented in this paper are obtained out of the Lyocell-process forming a three-dimensional network whereby fibrous and non-fibrous gels can be formed. Thus we are able to produce a broad range of different gels, which adjust perfectly to their field of application.

These TENCEL® gels are characterized as pure cellulose gels, without any additives or derivatization steps during their production. Properties of these gels regarding rheology, water retention value, incorporation potential, coating- and film-forming behaviour and possible applications are discussed in this paper.

***Keywords:** TENCEL®, celluslose, gel*

Introduction

Nanocellulose present unique materials having improved functionalities and outstanding performances. These cellulosic materials are divided into two groups – microfibrillated (or nanofibrillated) cellulose and cellulose nanocrystals – depending on the way of extraction from the precursor they are derived from. In the following just MFC will be mentioned. NFC is produced by extensive mechanical treatment of MFC.

In 1983 Turbak et al.[1,2] and Herrick et al.[3] invented the first cellulose gel by high-shear milling of a softwood-pulp slurry. For many years these gels counted as academic curiosities. With the start of the new millennium huge interest in these gels arose and grew exponentially. Not only academic research was interested in these novel gels any more, also industry got more and more curious about these unique materials. This rising interest can be seen in Figure 1 showing the increasing number of patents and papers over the past few years.

Cellulose gels are defined as stable, thixotropic gels having a low solid content (2-10%). After a chemical purification step to isolate cellulose from its natural source, either mechanical treatment leads to microfibrillated cellulose (MFC), or a hydrolyzing step results in nanocrystalline cellulose. In nature bacterial cellulose [4] is produced by the gramnegative bacteria Acetobacter xylinum under specific conditions as a fine,

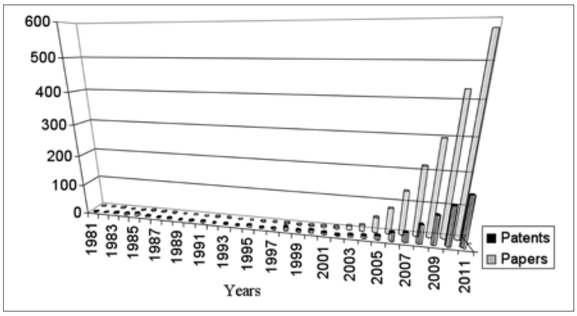

__Figure 1.__ Patents and papers concerning cellulose gels.

fibrous network or tunicate cellulose [5] (rod-like shape) can be isolated from marine filter feeders. In this paper only the topic of MFC will be covered, cellulosic nanowhiskers and bacterial cellulose are not discussed.

In the literature numerous precursors are named for producing MFC (corn corbs [6], potatoes [7,8], sugar beet [9], rice [8]- and wheat straw [10]), generally wood pulp is used. These precursors can either be used directly or after a purification step and undergo a mechanical treatment to obtain MFC. The mechanical treatment can be conducted using different methods or a combination of them [11]: high pressure homogenization, grinding, cryo-crushing, high-intensity ultrasonication or electrospinning. Nowadays high pressure homogenizers are the preferred aggregates used.

The cellulose gels mentioned above all show a fibrous character due to their appearance in nature. The TENCEL® gel presented shows no fibrous character any more, its appearance is sponge-like and it forms a 3-D network.

The TENCEL® gels [12] are obtained out of the Lyocell process. After precipitation of a low cellulose-content spin dope followed by a high-shear mechanical treatment the TENCEL® gels can be gained. Well-defined precipitation parameters allow shaping a precursor having a high surface area and an open structure, not showing any fibrous characteristics any more. This precursor can be treated using only a high-shear milling aggregate, no high-pressure homogenizer is needed for producing these gels.

Due to different precipitation parameters different TENCEL® gels can be produced – fibrous as well as 3-D ones. When precipitated as a fibrous gel the diameter, length and fibrillation degree of the precursor can be accurately adjusted.

Materials and Methods

For all experiments Saiccor pulp was used as precursor. The gels were prepared according to the descriptions mentioned above.

To obtain pulp gel, a pulp slurry was treated in a high pressure homogenizer.

After precipitating low cellulose-content spin dope, washing the precursor and high-shear milling, the TENCEL® gel was obtained, which in this case had a 3-D, non-fibrous appearance. The different production pathways are shown in Figure 3.

Even though it seems that the production of TENCEL® gel is more complicated, the milling efforts are reduced significantly. When milling pulp gel a high pressure homogenizer is required, consuming huge amounts of energy. Whereas the TENCEL® gel can be obtained by applying only high-shear. This reduces the energy consumption by a multiple.

Results and Discussions

Properties

TENCEL® gels are neutral in taste and smell having a white colour. No particles can be felt when rubbing between fingers; the appearance of these gels is creamy. Its high water affinity achieves stable, viscous suspensions having a low solid content. The gels show a thixotropic (shear-thinning) behaviour (Figure 2), making these gels pump- and sprayable. They are pH- and temperature-stable and they form dense and plain films. During the dissolution of the pulp numerous different substances (organic as well as inorganic ones) can be incorporated into the spin dope – implying the substance is stable during the dissolution. During the precipitation process the incorporated substance is evenly distributed and embedded within the gel-network.

The TENCEL® fibre is known to show excellent water management and a very high water adsorption capacity. The same properties can be found in its gel form. Having a high water retention value the gel shows a shear-thinning behaviour. The TENCEL® gel features a good workability due to its prominent rheological and absorption properties.

The turbidity of these gels can be observed by a simple visual inspection. With increasing the mechanical treatment the homogeneity and viscosity of the suspensions increase as well. The porosity and density of the films formed depend on the mechanical treatment applied and on which kind of gel used. Comparing the TENCEL®

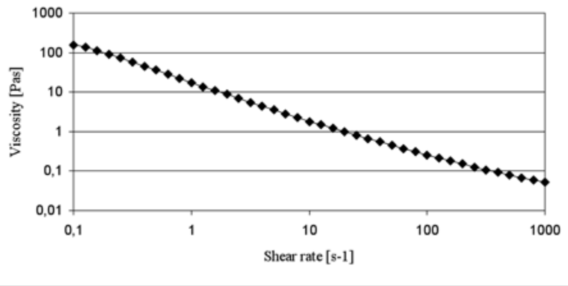

***Figure 2.** Thixotropic behaviour of the TENCEL® gel.*

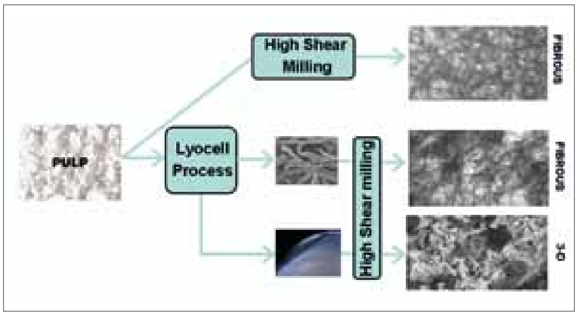

***Figure 3.** Different pathways for producing cellulose gels.*

Figure 4. Different film formation behaviour (optical microscopic images). Left TENCEL® gel, right pulp gel.

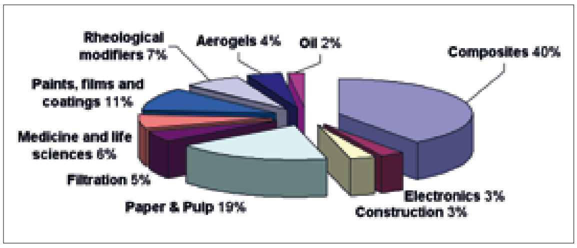

Figure 5. Possible application areas for cellulose gels.

gel with the pulp gel, the properties of these films are significantly different. Whereas the pulp gel forms a film having pores and a rough surface due to its fibrous character, the TENCEL® film shows no cracks or pores and the surface is smooth (Figure 4). Also different adhesion behaviours can be recognized on different surfaces. The TENCEL® gel forms a dense and well-sticking coating on PES, whereas the pulp gel forms a film which shows no grip on the surface and can be easily torn off. This can be explained by the high surface area formed within the TENCEL® gel. A similar pattern can be observed using glass as a surface, although the pulp gel shows a higher affinity to glass then to PES.

Applications

In 2012 Future Market Inc. published a report [13] concerning the global nanocellulose market and its development until 2017. It predicted a growth of this market being worth 500% and the market value of 250 Mio US$. Possible applications for these cellulose gels are numerous (Figure 5). Until today no commercial application for these gels is known – this field of research is still in the development phase and the application possibilities are boundless.

The most promising application area seems to be coating of various materials (Figure 6). On the left side of Figure 6 you can see a film formed from TENCEL® gel. No pores or cracks can be observed, the surface is even and a very continuous film is formed. On the right side of Figure 6 the same film made of pulp gel can be seen. The fibrous character immediately catches ones eye and pores and holes can be found all over the surface of the film. No continuous film can be formed. TENCEL® gels can be used to form very dense and smooth films being applied as membranes or barriers for food, tex-tiles, papers or pharmaceuticals.

With the well-sticking coating formed on PES foils nearly transparent films (Figure 7, left) can be generated, making this surface printable and it can be easily written on. Coating textiles opens up new opportunities to hydrophilize textile surfaces like polyester. For these coatings crosslinking would be necessary for fixation of the film on the surface of the fibre.

When coating paper (Figure 7, right) the tensile strength, porosity, density and printability are improved.

Also applications in the food industry are imaginable. Due to the creamy structure of the TENCEL® gel, where no particles can be felt, it could be used as fat replacer, adding no calories to the food, while mimicking the inherent texture of the fat. It could also be used as a flavour carrier, it stabilizes emulsions and foams and most obviously it could be used as viscosity modifier. Vegetables and fruits could be preserved during their transport and storage by coating with these gels.

A lot of research is done in the pharmaceutical and biomedical sector. Cellulose gels could be used as binder or coating for active substances. By adjusting these coatings a slow release-effect of the active substances could be achieved or the substances can be released at a certain point within the body (drug delivery system). Biomedicals are also a huge field of interest. Different research groups are studying the application potential of these gels. Researchers from Chalmers and University of Gothenburg [14] were able to grow nerve cells on a nanocellulose matrix - a first step in creating an artificial brain, whereby diseases like Alzheimer or Parkinson could be studied on a totally new level. On the other

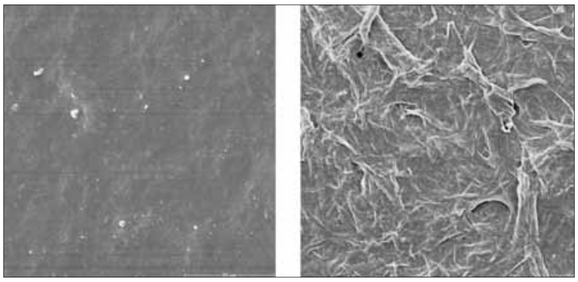

Figure 6. Applications – films & membranes (REM images). Left TENCEL® gel, right pulp gel.

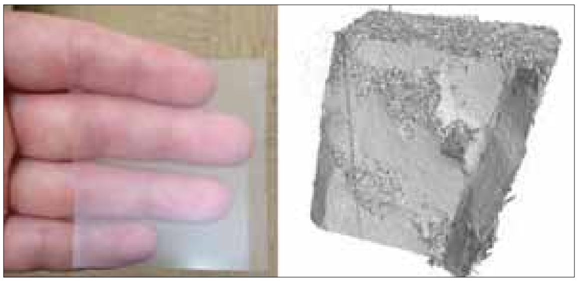

Figure 7. TENCEL® gel coatings on PES foil (left) and pulp paper (right, CT image, 1µm voxelsize).

hand toxic silicones could be replaced in implants by using these cellulose-based gels.

Artificial heart valves fail over long-term due to tearing and calcification effects. These problems can be overcome by formation of bionanocomposites using cellulose hydrogels as additives [15]. Formation of bionanocomposites using nanocellulose is not only of great interest in biomedicals, it can also be implemented in technical applications. The gels could be used as rheology modifier, reinforcement, for weight reduction or as stabilizer. Possible applications can be found but are not limited to plastic, construction, paints and furnishes.

Conclusions

Out of the Lyocell process tailor-made gels – with well-defined fibrous and non-fibrous structures – can be produced, which set these gels apart from conventional pulp-milled gels. Using this manufacturing process the gels can be adjusted to their specific tasks (e.g., appearance, incorporation potential). Numerous possible applications can be found in many industrial value chains.

Acknowledgements

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Cellulosic Fibers for Alkaline Battery Separators

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Abstract

This article reports on a study which was carried out to compare different fibers properties and their influence on the battery separators performance. Amongst cellulosic fibers, Lenzing's TENCEL® has a unique "fibrillation ability" and utilising the long and submicron "fibrils" it is possible to manufacture separators with small and uniform pores. In addition, the fibrils "interlace" together and create a 3D structure that ensures high dimensional stability.
Work to improve TENCEL®'s properties is also described which has optimized the fiber for alkaline battery separators.

Keywords: *Lyocell, cellulose, separator, battery, alkaline, fibrillation*

Introduction

Batteries play an important role in our everyday life. They supply energy to a wide range of devices from small portable music players to substantial power tools and electric vehicles.

A battery separator is a nonwoven fabric (or a membrane) that acts as a barrier between the positive and negative electrodes. Despite being an electrical insulator, it has to be porous to allow ion mobility [1,2]. Depending on the battery type and on the specific performance required, it can be manufactured using different production technologies and from a range of raw materials (fibers, polymers, binders, inorganic particles). Components are selected according to chemical properties, physical properties and economic factors.

Separators should exhibit good chemical resistance, shouldn't shrink or degrade when soaked with the electrolyte and should retain their integrity during the whole battery life (including shelf storage prior to sale).

Separators for alkaline batteries widely employ cellulosic fibers due to their ability to both absorb and retain the liquid electrolyte which is usually an aqueous solution of potassium hydroxide.

One of the preferred processes for making alkaline battery separators is "wet-laid" technology, where the cellulosic fibers can be mechanically "refined". This reduces their diameter and produces thin and uniform papers.

Materials and Methods

Materials

Lenzing AG carried out a study to investigate how different cellulosic fibers behave in alkaline battery separators and how they comply with separators requirements.

Several cellulosic fibers were taken into consideration including TENCEL®, Viscose and Pulp. Those fibers were used in blend with synthetic PVA fibers and water-soluble PVA binders.

Separator Basic Properties [1, 2]

Despite being a "passive" component of the battery (since it does not participate to the chemical reactions), the separator has a critical influence on battery performance.

First of all, it must physically divide the anode and the cathode, avoiding the so called "short circuiting" and resultant battery failure. This function is directly related to batteries safety and efficiency.

The separator has to be dimensionally stable during the battery manufacturing and the whole battery shelf-life, therefore good mechanical resistance and chemical resistance are both required.
Batteries are characterised by two basic properties that depend on their chemistry but are also influenced by the separator:

- Energy Density: the amount of energy that can be stored (capacity) and determines the battery life;
- Power Density: the ability to deliver a desired amount of energy in a certain time period.

Separator thickness is very important as, when the separator is thin, it occupies less space and creates more space within the active components (anode and cathode). This leads to a battery with higher energy density.
Power Density is related to the mobility of the ions and specifically the flow rate through the separator.
The separator porosity must be tuned to enable rapid absorption of the electrolyte on impregnation lines. Conversely it must retain the electrolyte as the drying of the separator will compromise battery performance.
In summary, the separator must have two functions that can seem contradictory:

- Electrical Insulation. To ensure the "Barrier Effect", it requires small pores and high Density.
- Ions Conductivity. To ensure the ions mobility, it requires high Porosity and low Thickness.

In order to optimise efficiency, it is strongly desired to have a separator where Electrical Insulation and Ions Conductivity are balanced.
Figure 1 shows that separators having Air Permeability within a certain range have also a good compromise between Density and Porosity.

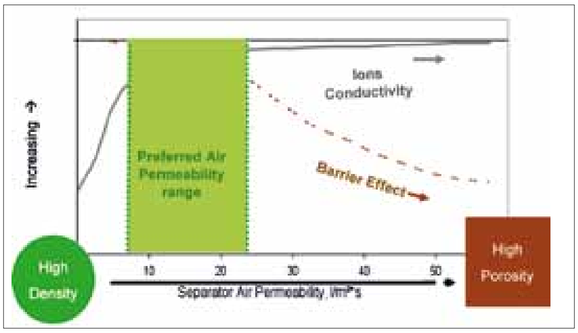

Figure 1. *Example of Ions Conductivity and Barrier Effect trends in relation to Air Permeability.*

Porosity

When we look at porosity, it is necessary to distinguish between Porosity % and pore size. The Porosity % of a separator is defined as the ratio of void volume to apparent geometric volume 2 . It is calculated with the following formula:
Porosity % = [1- (basis weight / thickness) / density of the polymers] x 100
Separator Basis Weight and Thickness are readily to measured with standard methods employed for nonwovens. Pores Size can be measured with different instruments such as a mercury porosimeter.
Figure 2 shows SEM pictures of two paper prototypes having similar Porosity % but very different Pores Size. Pores size is usually tuned according to the paper end use.
Figure 3 shows how porosity and pore size can vary according to the paper composition.
Results refer to blends of TENCEL® and Eucalyptus Pulp.

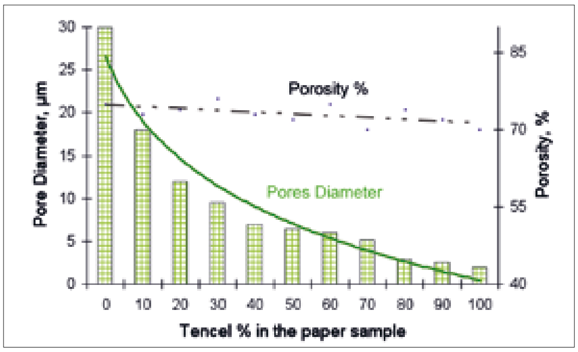

Figure 3. *Paper pores size in relation to the amount of TENCEL® in the blend.*

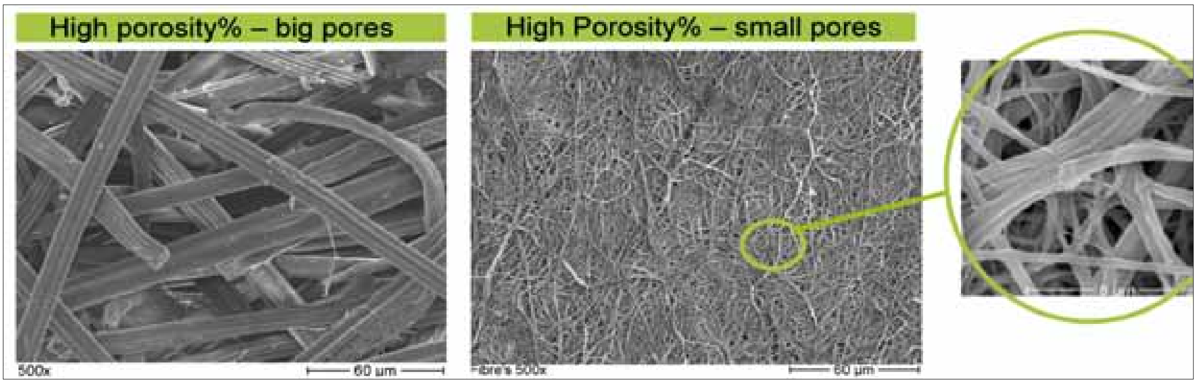

Figure 2. *Paper samples having different morphology.*

Dendritic Formation

In the specific case of alkaline battery there is a remarkable issue due to the so called “dendrites”. The anode is made with Zinc and on its surface there could be the formation of solid particles (dendrites) that are a threat for the battery. If the dendrites pass through the separator and contact the cathode the resultant short circuit causes battery failure (Figure 4).

For this reason the separator needs not only small pores but also “tortuous” pores.

Tortuosity is the ratio of mean effective capillary length* (L) to separator thickness (D), according to the following formula [2]:

Tortuosity= L / D

(* where L corresponds also to the ions path through the separator).

Fibrillating Fibers and Refining

As seen above, the morphological structure of the separator is directly linked to the battery performance. Accordingly, the selection of the fibers for producing the separator is of primary importance. In order to control Porosity % and pores size it is necessary to use fine fibers and, in particular, “fibrillating” fibers. Among fibrillating fibers it is recommended to use ones that are readily able to absorb the liquid electrolyte.

TENCEL® fibers, when are submitted to a mechanical refining process, show a morphological modification in terms of length and diameter. Each single fiber develops sub-micron fibrils that are particularly suitable for the production of thin and uniform separators (Figure 5)

Starting from TENCEL® fibers having a diameter of 10-12μm, it is possible to obtain fine fibrils having an average diameter of less than 1μm. (Figure 6 shows how TENCEL® fibers diameters change after refining).

To this extent is possible to state that TENCEL® is a “Precursor to Microfibers”.

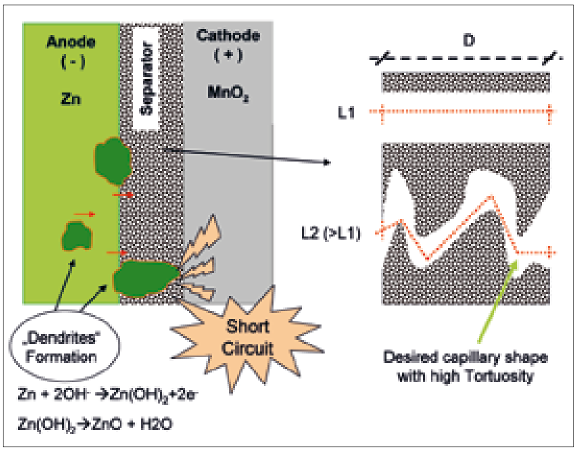

Figure 4. *Dendrite formation and separator Tortuosity.*

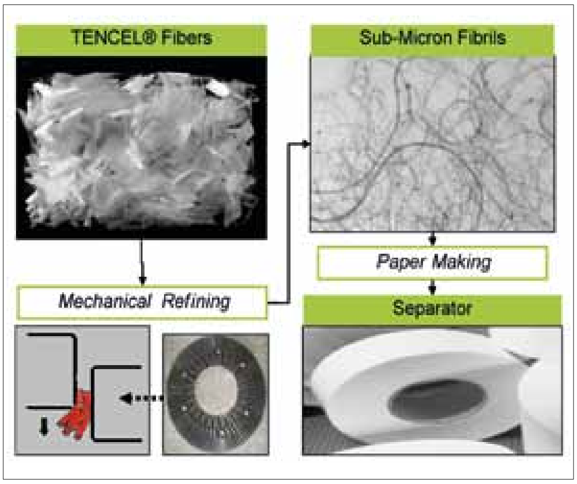

Figure 5. *Simplified layout of the separator production process.*

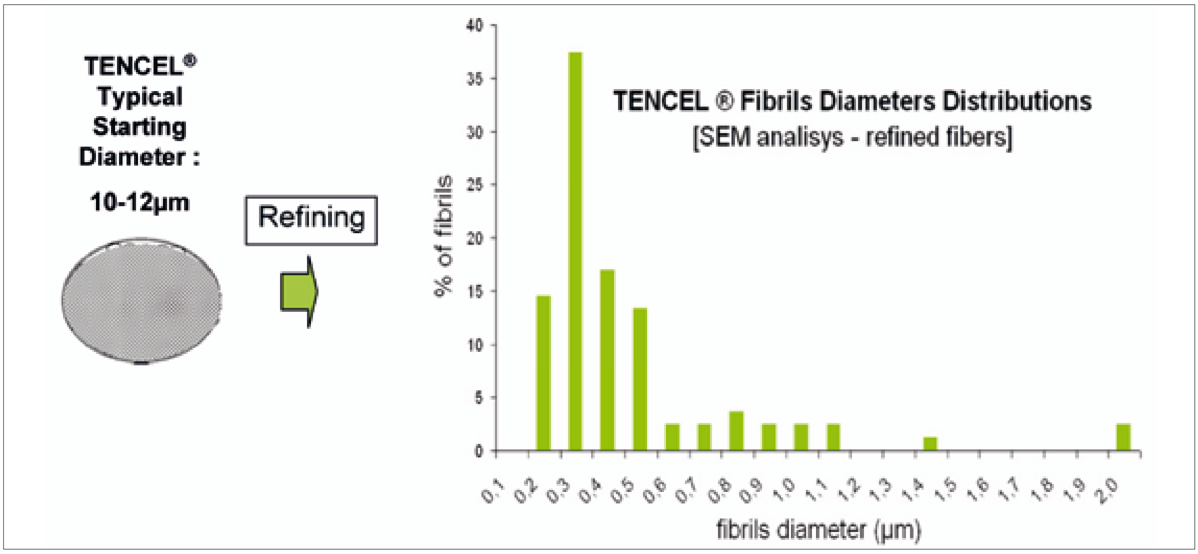

Figure 6. *TENCEL® diameter distribution after refining.*

Separator Behaviour With Alkaline Electrolytes

In alkaline batteries, the separator is required to have a good chemical stability in the presence of strong electrolytes (such as 30-40% KOH aqueous solutions). Two separator properties are very important during battery manufacturing and shelf-life: high dimensional stability and low deterioration in alkali. It is possible to evaluate these properties carrying out the following lab tests: "Area Shrinkage Rate in KOH" and "Weight Reduction Rate in KOH" [3,4]. Area Shrinkage Rate is measured according to the following procedure: cut a square sheet 120 mm x 120 mm (A1); immerse it in 40% KOH solution at 70° C; keep in the bath for 8 hours; measure the area of the wet sample (A2).

Area Shrinkage Rate (%) = (A1-A2)/A1 x 100

Weight reduction rate is measured according to the following procedure: cut one or more pieces of separator with a weight of approximately 5 g; dry the sample at 80° C for 1 hour; weigh the dried sample (W1); immerse it in 40% KOH solution at 70° C; keep in the bath for 8 hours; wash the sample with water; dry the sample at 80° C for 1 hour; weigh the dried sample (W2).

Weight Reduction Rate (%) = (W1-W2)/W1 x 100

Paper Prototypes

Paper samples have been prepared with a RAPID-KÖTHEN sheet former, according to EN ISO 5269/2. All prototypes contained approx 50% of synthetic components (PVA fibers and PVA soluble binder) and approx 50% of cellulosic fibers. The latter represented the so called "variable cellulosic fraction" of the blend, as showed in Figure7.

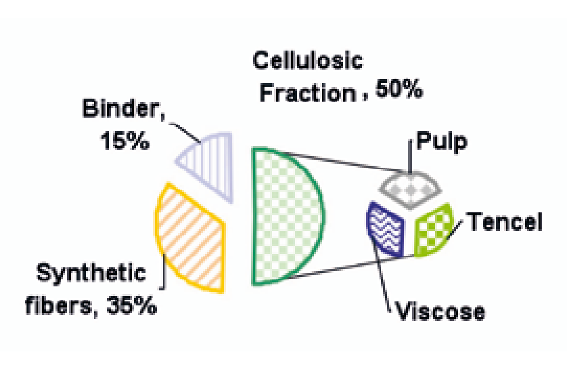

Figure 7. *Prototype composition.*

Under the "variable cellulosic fraction" the following materials have been compared: TENCEL® 1,7dtex/4mm, Viscose 1,7dtex/5mm, Eucalyptus Pulp and Cotton Linter Pulp. TENCEL® fibres has been refined with a Valley Beater according to ISO 5264-1 to CSF=150ml. Eucalyptus pulp fibers has been refined with a PFI U3000 mill according to ISO 5264-2 to CSF=400. PVA fibers, Cotton Linters and Viscose fibers were not refined. All samples have been prepared in the Basis Weight range 40-50g/m².

Results and Discussion

Figure 8 shows the results of the Area Shrinkage Rate test performed on the above mentioned prototypes. In the left part of the chart (samples made with cellulosic fibers in variable proportions and 0% TENCEL®), the shrinkage of the paper is above 8%.

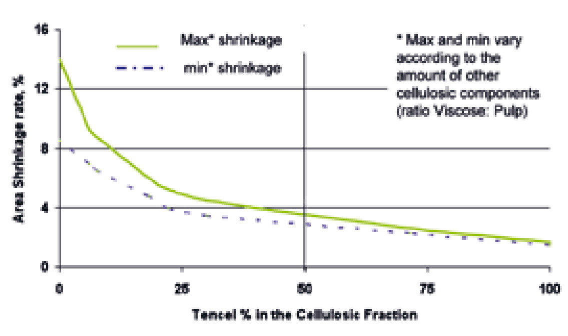

Figure 8. *Area Shrinkage Rate in relation to the amount of TENCEL® in the blend.*

Moving to the right, and adding TENCEL® in the blend there is a remarkable reduction of the shrinkage. With 50% TENCEL® the shrinkage of the paper is reduced to less than 4%. These positive results can be explained when examining the detailed paper structure under electron microscopy (Figure 9).

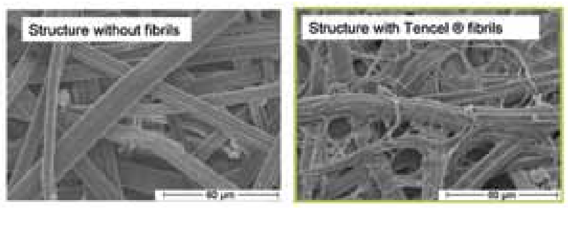

Figure 9. *Paper samples with and without TENCEL® microfibrils*

The extensive, long and fine fibrils of TENCEL® interlace efficiently during paper making and, enhanced by their swelling (preferentially in the radial direction), they "lock" together the paper structure.

In this way the paper has a dense structure with high dimensional stability.

Weight Reduction Rate in KOH of the paper prototypes varies significantly depending on the cellulosic fiber type used in the paper blend (Figure 10).

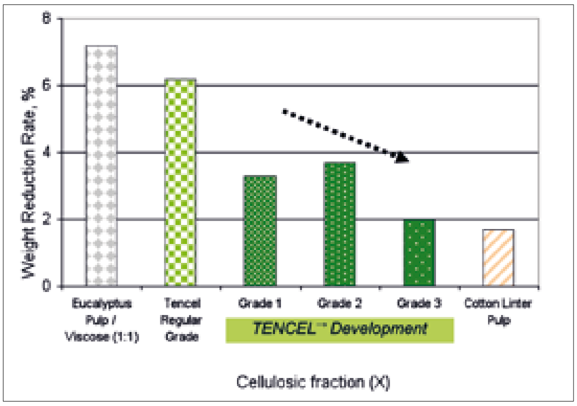

Figure 10. *Weight Reduction Rate of paper prototypes.*

Lenzing has specifically developed new TENCEL® grades with enhanced alkali resistance in order to increase the separator integrity as required by the latest generation batteries.

The developmental fibers maintain all TENCEL® key properties, including fibrillation ability, but they exhibit a considerably lower degradation in alkali. When considering the two key properties together, Dimensional Stability (linked to Area Shrinkage Rate) and Deterioration Resistance (linked to Weight Reduction Rate), we can see that the TENCEL® developmental grades offer outstanding performances for both requirements (Figure 11).

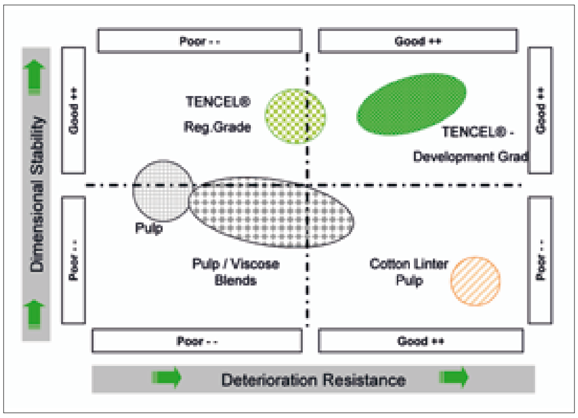

Figure 11. *Overview on paper integrity in relation to the fibers used in the variable cellulosic fraction.*

Other competitive fibers have good deterioration resistance but, due the fact that they do no fibrillate, they cannot ensure high dimensional stability.

Conclusions

TENCEL® fibers showed superior properties for the use in alkaline battery separators. Long and fine (sub-micron) fibrils give suitable porosity and dimensional stability.

TENCEL® developmental grades having higher alkali resistance enhance the separator integrity.

It has been proven that the combination of those properties has a positive impact on alkaline batteries performances and reliability (Figure 12).

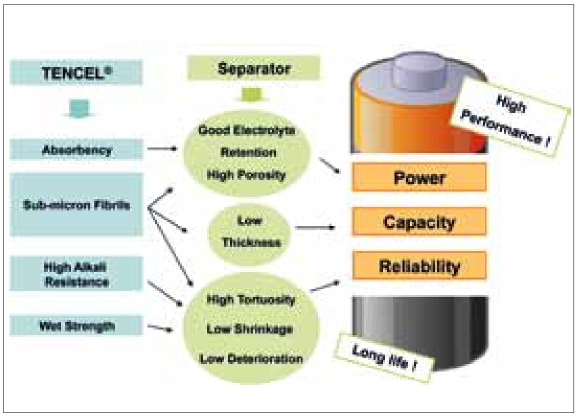

Figure 12. *Summary of TENCEL® peculiar properties and their impact on separators and alkaline batteries.*

Lenzing continues to carry out new activities in the field of electrical devices to provide effective solutions for the new generation of batteries (including lithium-ion), Aluminium Electrolytic Capacitors and EDLC.

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Polysaccharide Applications in Textiles and Materials Technologies

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Abstract

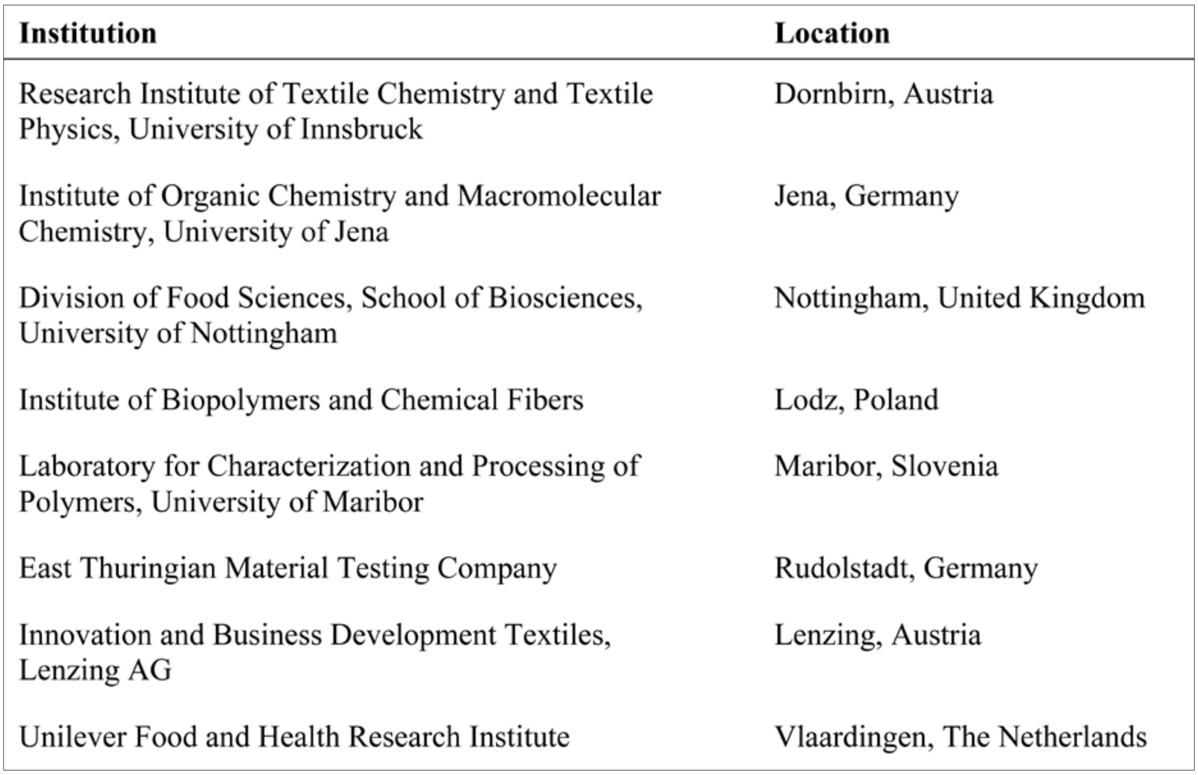
The paper presents a summary overview of the research investigations undertaken in the four-year European Commission funded Marie Curie Initial Training Network: “STEP”.

Introduction

Polysaccharides, e.g. cellulose, starch, chitin, are among the polymers that make up the fundamental components of life and constitute a major proportion of the earth’s biomass. These carbohydrate polymers constitute the largest segment of all available polymers, and hence exhibit the greatest potential as alternative sources of raw material in efforts to replace petroleum-based polymers with those obtained in sustainable modes from renewable resources.

A primary challenge in sourcing of materials/products from renewable resources is the development of “selective efficient separation and conversion proces-

Table 1. *The consortium in the Initial Training Network “STEP”.*



Institution	Location
Research Institute of Textile Chemistry and Textile Physics, University of Innsbruck	Dornbirn, Austria
Institute of Organic Chemistry and Macromolecular Chemistry, University of Jena	Jena, Germany
Division of Food Sciences, School of Biosciences, University of Nottingham	Nottingham, United Kingdom
Institute of Biopolymers and Chemical Fibers	Lodz, Poland
Laboratory for Characterization and Processing of Polymers, University of Maribor	Maribor, Slovenia
East Thuringian Material Testing Company	Rudolstadt, Germany
Innovation and Business Development Textiles, Lenzing AG	Lenzing, Austria
Unilever Food and Health Research Institute	Vlaardingen, The Netherlands

ses" [1]. 'Separation' processes involve isolation of the polymer from the matrix in which it exists in its natural state. 'Conversion' processes involve transformation and/or shaping of the isolated polymer to suit the desired end-use. Transformations are broadly defined to be changes in the intrinsic properties of polymers (e.g. changes of chemical structure), while shaping is defined to be changes of polymer extrinsic properties (e.g. morphology or form).

There exist viable, sustainable industrial-scale processes for the separation of polysaccharides (especially for cellulose and starch – two of the most abundant polymers in this category) from wood-pulp and crops among the forestry and agricultural sectors. However, existing conversion processes are limited in scope by the predominant intra- and inter-molecular non-covalent interactions that characterize the supramolecular structures of polysaccharides. The non-covalent interactions impose constraints on polysaccharide conversion by restricting polymer solubility in solvents, limiting thermal processability and dictating the feasibility and extent of functionalization.

To gain understanding of these constraints and to utilize the knowledge in finding solutions for polysaccharide coversion to overcome them, was the focus of the joint research-training program of the Marie Curie Initial Training Network "Shaping and Transformation in the Engineering of Polysaccharides (STEP)", formed by a consortium of industry and academic institutions (see Table I), and funded from the European Community's Seventh Framework Program from October 2008 – September 2012.

Research Activities of the Network

Two major areas of polysaccharide application, foods and materials, were represented in the consortium. In both, conversions typically involve swelling or dissolution of polysaccharides in solvent; and hence, polysaccharide-solvent interactions are of vital interest. In foods, the focus is on polysaccharide influence on solution structure and properties; while in materials, attention is paid to solvent influence on polysaccharide structure and properties. These two perspectives were integrated in the research investigations of the network. In this paper, we present an overview of the project's results pertaining to materials applications. The work was divided into the following broad categories:

- polysaccharide derivatization,
- mixing or blending polysaccharides with other components,
- polysaccharide shaping (i.e. dissolution and regeneration from solvents), and
- structure-property relationships in polysaccharides along with methods for their characterization.

The derivatization modes ranged from regioselective to non-specific reactions. 3-mono-O-alkyl cellulose bearing two different ether groups (methyl/ethyl, methyl/n-propyl or ethyl/n-propyl) were regioselectively synthesized with varying ratios of the two alkyl groups [2]. The mixed derivatives exhibit heat-induced self-association (i.e. thermogelation) in aqueous solutions at temperatures that vary with composition and proportions of the alkyl substituents [3-4], which is of interest as a means of controlling rheology in food and pharmaceutical formulations. Novel amino cellulose esters were synthesized through ring-opening reactions of lactam in BMIMCl with or without co-solvent, or in NMP/LiCl. Good yields of the derivative were obtained even with low molar ratio of reagent to cellulose, over a wide range of cellulose DPs [5]. Some derivatives were investigated for their utility as flocculants or thickeners as they have environmentally advantageous fate-after-use profiles [6], as well as surface-coating agents to modify properties of cellulose films [7]. Amino cellulose sulfate derivatives were synthesized in a novel route through tosyl cellulose intermediates [8]. The products are polyampholytic, exhibit pH dependent solubility and some antibacterial activity [9]. The derivatives could be added onto viscose to impart amphoteric properties to the fibers [10]. A method of introducing carbamate groups on woven cellulosics in a continuous pad-dry-cure process was devised [11]. The reagents are inexpensive, non-toxic and commonly used in the textile and paper processing and pad–dry–cure treatments are routinely employed at both industries. Hence, the process may be adopted in existing commercial-scale operations without additional capital investment. The treated substrates, paper or fabrics, may be utilized as adsorbents for heavy metals from waste water or in the creation of flame retardant products. An additional use is in the creation of all-cellulose composites or membranes, by further treatment with alkali [12].

A method of improving polysaccharide properties is by mixing or blending with a second component. In ideal cases, the resulting combinations exhibit properties not available in either component individually, i.e. synergies are created. In STEP, investigations were conducted on combinations of polysaccharides with another polysaccharide, an organic component or an inorganic component. It was found possible to achieve sorption of anionic polysaccharides (pectin, alginate, xanthan) on cellulosic fibers by first treating the cellulosics with calcium salts [13]. Copper ions were inserted in cellulosic fibers from alkaline conditions of copper–D-gluconate complexes [14]. Copper salts precipitate in alkaline conditions, but copper complexes with D-gluconate remain soluble. The sorption of copper by cellulose from complexes is believed to occur through ligand-exchange reactions, to extents depending on the strength of copper complexation with D-gluconate relative to that with cellulose. In experiments conducted to determine sorption profiles of silver ions on cellulosic fibers, the ions were found to reduce and form particles on substrates [15]. The treated substrates exhibited antimicrobial activity comparable to that reported for silver-nanoparticle-treated substrates – suggesting efforts towards nanoparticle synthesis may not be necessary to utilize the antimicrobial activity of silver on clothing and textiles. Methods were devised to incorporate calcium phosphates (hydroxyapatite powder, tricalcium phosphate nanoparticles) in chitosan fibers and sponges [16-17]. Composite fibers were produced with tenacity similar to that of pure-chitosan fibers. The composites also proved susceptible to enzymatic degradation. These properties are important in the envisaged utilization of the composites as scaffolds for cell-growth.

A significant stage in the preparing polysaccharides for use in materials applications is the creation of appropriate shapes or forms, e.g. creating cellulosic fibers or films from wood pulp. The process, termed "shaping", for polysaccharides is based predominantly on dissolving the purified polymer in solvent and then re-precipitating it in desired shapes. The investigations in STEP focused on the solvent (toxicity, thermal stability), polymer solubility, and potential for solvent recovery and reuse in processes. Ionic liquids – essentially ionic, salt-like materials that are liquid below 100° C – exhibit promise as solvents in cellulose processing. The safety and viability of their industrial-scale application were investigated for a wide range of ionic liquids [18-19]. The thermal stability of cellulose solutions in ionic liquids was determined to be comparable to that of the existing NMMO-system. Efficient recycling and reuse of ionic liquids, deemed necessary for achieving cost-competitiveness, remains a challenge. The difficulties arise due to high affinity of ionic liquids for cellulose as well as reduction of their thermal stability. It was found possible to blend cellulose with secondary components in NMMO or ionic liquids, but the latter are believed to possess advantages over NMMO for selected components [19-21]. There were indications that mechanical grinding renders cellulose susceptible to "cold-melting", i.e. plasticization in absence of high temperature [22]. If confirmed in further work, these results point to potential for thermo-mechanical shaping processes for cellulose similar to those used for thermoplastic polymers. Localized, limited swelling operations, although not categorized as shaping, are used as activation pretreatments. Concentrated urea-salt mixtures were investigated for the purpose as alternatives to the traditional alkali-based treatments [23-24].

In addition to the identity of chemical species' present in the chemical structure of polysaccharides, the physical arrangement of the long-chain molecules (i.e. supramolecular architecture) is also significant in determining the properties of these polymers. The determination of such structure-property relationships was the subject of some investigations in STEP, including the development or refinement of characterization methods. Model cellulose films were created from spun-coated trimethylsilyl cellulose for use in understanding mechanisms of biomolecule immobilization, water-cellulose interactions and structural rearrangement of cellulose on drying, as well as of enzymatic hydrolysis of cellulose [25-29]. By applying paramagnetic relaxation enhancement techniques in solid-state NMR spectroscopy of cellulose, it was found possible to obtain separable spectral contributions for crystallite cores, accessible and inaccessible surfaces of crystallites as well as solvent-accessible non-crystalline cellulose [30]. It was found possible, with a single fitting procedure, to simultaneously determine particle charges, polydispersity indices and intra-, inter-particle interactions in aqueous suspensions of nanocrystalline cellulose through small-angle x-ray scattering measurements with generalized indirect Fourier transformation [31]. The utility of perichromism was demonstrated in determining application-oriented properties of cellulose and its derivatives, e.g. solvent-polymer interactions and degrees of substitution [32-33].

An additional goal, of equal importance as the research, was the training of young researchers. A total of 16 PhD students and 6 postdoctoral researchers were recruited and trained in technical skills (instrumentation, analytical methodologies), on critical problem-solving, best-practice in management of Intellectual Property Rights, and on communicating research concepts and the results of investigations to a diverse audience by a variety of means (lectures, written reports, scientific publications etc.). More details on the project are available on its website: www.stepitn.eu

Acknowledgements

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Nano Cellulosics: The Impact of Water on Their Dissolution

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Abstract

The dissolution behaviour of dissociated cellulosic materials – nanocrystalline, nanofibrillated, and microfibrillated specimen – in the analytically important system N,N-dimethylacetamide/ lithium chloride (DMAc/ LiCl) was investigated by means of gel permeation chromatography (GPC) with multiple detection. The impact of water present in the samples was addressed by Karl Fischer titration and solvent exchange experiments. Generally, dissolution of dissociated cellulosics is severely impeded as compared to their starting materials. This is most likely a consequence of the high-surface-area fibrils or crystals that are capable of retaining comparatively high amounts of water. With the increased understanding of the forces that hinder cellulose dissolution in DMAc/ LiCl and how to overcome them provided by this study, future molecular analysis of dissociated cellulosics are expected to become more reliable facilitating quality control of production procedures.

Keywords: *cellulose, accessibility, dissolution, gel permeation chromatography, water content*

Introduction

The dissolution of different types of cellulose in the DMAc/ LiCl system is associated with a significant variation of required conditions as a function of fibre morphology, chemical composition, and cellulose allomorphism [1,2]. In this respect, there are demanding samples such as pulps that are rich in lignin, softwood kraft pulps [3], and to some extent also pulps from annual plants [4]. The complex dissolution of these materials is attributed either to poor accessibility of cellulose chains or special fibre morphology. Most of all, it is reflected in a significantly prolonged dissolution process, for example more than one week is reported for cotton linters [5]. Another group of difficult-to-dissolve cellulosic materials requiring long dissolution times and a special sample preparation procedure are dissociated celluloses (nanocrystalline, nanofibrillated, and microfibrillated specimen). During the preparation of these dissociated cellulosic materials, the original substrates are disassembled into micro- and nano-elements of different characters: entangled networks of microfibrils or suspensions of highly crystalline nanoparticles respectively. The most prominent effect of these fragmentations is a dramatic increase in specific surface area [6]. As a direct consequence, the interaction with water is increased leading to high water retention. This is suspected to be one of the driving forces of hindered dissolution of these materials.

Materials and Methods

The analytical set-up for dissolution of cellulosic materials and their determination of molar mass distribution by gel permeation chromatography, multi angle laser light scattering, and refractive index detector (GPC-MALLS-RI) is described elsewhere [4].
The relative water content was determined using a V20 volumetric Karl Fischer titrator (Mettler Toledo) with dry methanol and Hydranal composite 5 (both supplied from Sigma Aldrich). Alternatively, some water content determinations were performed using a moisture analyzer MA35 (Sartorius) that is based on infrared heating up to 105° C of the sample. In this system, no

Table 1. Cellulose substrates and their abbreviations, starting materials are in bold print.

Description of the cellulosic materials	Abbreviations
Dissolving pulp from Eucalytus	EDP
Nanocrystalline cellulose from EDP	NCCe
Cotton cellulose filter aid	WFP
Nanocrystalline cellulose from WFP	NCCw
Bleached softwood kraft pulp, used for mechanically prepared MFC	SWKP
Microfibrillated cellulose from SWKP	MFCs
Microfibrillated cellulose from SWKP with extended solvent exchange	MFCsx
Bleached softwood kraft pulp, used for TEMPO-oxidized nanofibrillated cellulose	toSWKP
TEMPO-oxidized nanofibrillated cellulose from toSWKP	toNFCs

specific determination of the water content is possible; any substance that evaporates above the given temperature will be monitored as weight loss.

Four different cellulose substrates were studied in terms of dissolution in DMAc/ LiCl and compared to disassociated materials obtained from them (Table 1).

Results and Discussion

The processing from the cotton cellulose filter aid starting material (WFP) to the nanocrystalline cellulose (NCCw) clearly decreases the molar mass of the cellulosic material and additionally alters the molar mass distribution (Figure 1). Note the appearance of a peak in the very low molar mass area and an additional shoulder in the molar mass area that elutes between 22 and 26 minutes in the NCCw sample. This peak contains molar mass molecules that are actually larger than those contained in the molar mass distribution of the starting material. The precise character of this observation is not fully understood yet, but some indications hint towards intact nanocrystals that are small enough to actually slip through the PTFE filters with 0.45 µm pore size used before sample injection.

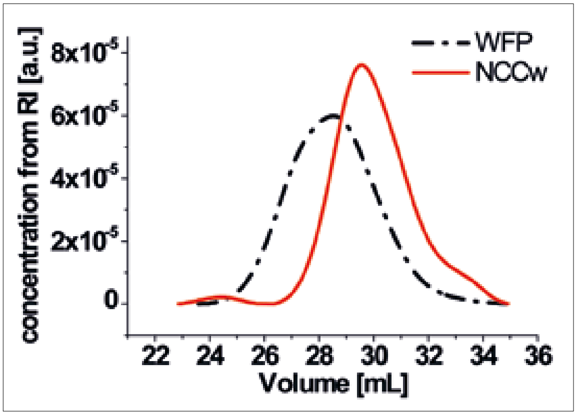

Figure 1. Volume versus concentration of WFP (black) and NCCw prepared from WFP (red).

The comparison of the mass recovery values for the dissolved starting pulps and the NCC materials prepared from them shows a dramatic difference between these two materials. For example, the total mass recovery for the dissolving pulp (EDP) was around 250 µg, while the corresponding amount for the resulting NCC was less than 20 µg, reflecting extremely slow dissolution process of NCCe as opposed to its starting material. The two possible explanations for this include differences in the surface area and morphological changes. Conversion of pulp to NCC is associated with an increase of the surface area leading to a significantly higher water content and hence severely impeded dissolution. The preparation of NCC comprises a significant removal of the amorphous regions of the starting material; increased crystallinity might play a superior role in these samples. Increased crystallinity is, for instance, expected to additionally retard the dissolution process, whereas morphological changes might have varied impact depending on the characteristics of the starting material.

In order to further study the impact of the surface area and the presence of water on the course of dissolution, the water content of the dissociated cellulosics and their starting materials was analysed taking fibrillated materials as an example. Since the sample composition after the DMAc-activation is decisive for the subsequent dissolution in the DMAc/ LiCl, the water content of the DMAc-activated samples was determined by Karl Fischer titration. According to the titration results the fibrillated celluloses show significantly higher water content after DMAc-activation compared to their starting materials, reflecting more porous fibrillated networks prone to bind and retain relatively high amounts of water. A single solvent exchange with DMAc obviously fails to sufficiently dehydrate these networks leaving them with the water content too high to allow unhindered dissolution in DMAc/ LiCl. Further solvent exchange however, decreases the amount of water in the samples (Figure 2).

The impact on dissolution is especially drastic in the case of toNFC, retaining more than 4 times more water compared to its starting pulp. This behaviour originates from the liberation of the thinnest nanofibrils with highly hydrophilic surface and is the reason behind the extremely poor solubility of this material in the DMAc/ LiCl.

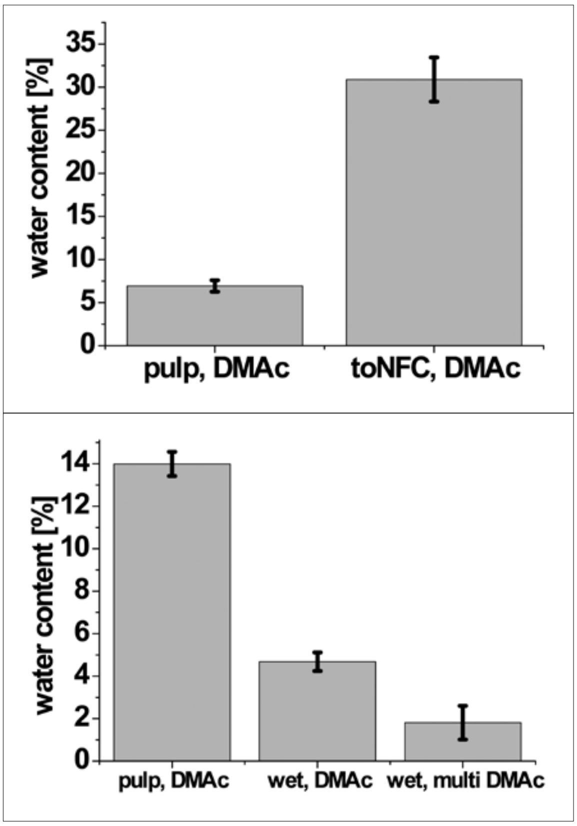

Figure 2. *Water content determined by Karl Fischer titration. Left: starting material and toNFC prepared thereof, both after single solvent exchange. Right: Starting material (pulp, DMAc), MFC sample prepared thereof after a single (wet, DMAc) and repeated (wet, multi DMAc) solvent exchange in DMAc. Error bars represent the standard deviation of at least three repetitions.*

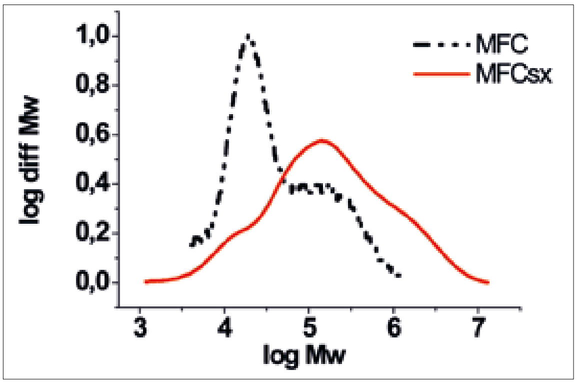

Figure 3. *Molar mass distribution of MFC before (MFC) and after multiple solvent-exchange (MFCsx) treatment.*

The features of dissolution were even more changed upon fibrillation. A drastic difference in dissolution behaviour between the fibrillated pulp and its starting material is evident reflecting the very poor solubility of MFC. Subjecting the repeatedly solvent-exchanged MFC samples to the usual solvent peeling analysis by GPC, improved dissolution behaviour was revealed (Figure 3). In contrast to the previously studied samples subjected to a single solvent exchange, the repeatedly solvent-exchanged MFC shows an even MMD profile. Moreover, the calculated mass recovery rate is significantly raised from less than 25 μg to more than 150 μg, exceeding that of the starting pulp.

Interestingly, applying the repeated solvent-exchange procedure on toNFC did not manage to improve solubility of this material, emphasizing once again the level of fibrillation and the morphology of the obtained material as decisive factors. In contrast to fibrillated celluloses, the DMAc-exchanged NCC samples show significantly lower water content than their non-dissociated counterparts. The NCC samples consist of highly crystalline particles showing very limited network building. This absence of entangled networks and a relatively high crystallinity, facilitating water removal by DMAc, contribute probably to the low amounts of water detected by Karl Fischer in case of these materials.

Conclusions

The dissolution behaviour of dissociated cellulosic materials in DMAc/ LiCl is principally determined by the morphology and the exposed surface area generated upon fragmentation and is thus strongly affected by the type of disintegration process and in some cases by the choice of starting material. Generally, fragmentation is associated with a severely impeded dissolution due to liberation of huge water-covered surface areas. The generation of entangled networks prone to retain water can be an additional obstacle.

For instance, highly porous networks of fibrillated cellulosic materials contain a high percentage of monomolecular and multilayered water attracted by hydrogen bonds both within the fibrillar network and at the large fibrillar surface. A single solvent exchange with DMAc employed in common dissolution procedures is insufficient in removing this water. As a result, fibrillated cellulosic materials show extremely poor solubility. Instead, repeated solvent exchanges are required as an efficient dewatering step in order to achieve satisfactory dissolution kinetics. As shown for microfibrillated cellulose, a dewatering through repeated solvent exchange both increased the dissolution rate and erased heterogeneities originating from variations in surface areas (and thus hydration) of the MFC fragments.

However, this dewatering treatment proved not to be feasible with materials hindering solvent exchange by strong gelling in water, such as toNFC. The low solubility of this material together with the pronounced resistance to solvent-exchange emphasises even further the importance of the extent of entanglement, its exposed surface area, and its degree of hydrophilicity. The impact of the surface bound water (and thus the surface area) of the material are particularly underlined by our studies of the two nanocrystalline celluloses. Due to the absence of entangled networks under solvent exchange conditions, these materials essentially retain only water bound at the surface of the NCC-particles, indicative of both the exposed surface area and solubility. Accordingly, the small cellulose nanoparticles extracted from dissolving pulp show significantly lower solubility compared to the large NCC particles from cotton.

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Novel Vegetable Oil Based Paper Sizing Agents as Substitutes for Crude Oil Based ASA

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Abstract

This paper presents a newly developed, green paper sizing agent. While for conventional ASA production crude oil based olefins are the main raw material source, for the presented material natural vegetable oils can be utilized. Especially vegetable oils having only monounsaturated fatty acid residues (oleic acid) in the triglycerides gave favorable products with low viscosity and high yield. Thus the most promising raw material was high oleic sunflower oil. The maleated product called MSOHO (maleated high oleic sunflower oil) was subjected to various tests comparing its hydrolytic stability to ASA, with the results proofing the higher resistance of this newly developed sizing agent against hydrolysis. Another set of experiments focused on the sizing characteristics of MSOHO. Ways for improving the sizing efficiency of MSOHO as to be able to compete with the very effective state of the art sizing agent ASA are discussed. As a result of the presented studies a high-quality internal paper sizing agent is available which is based on plant oils as renewable resources.

Keywords: *alkenyl succinic anhydride (ASA), high oleic sunflower oil, maleated vegetable oils, paper sizing, renewable resources*

Introduction

Sizing of paper is one prominent method to modify cellulose fibers in order to control the penetration of liquids into a paper sheets. According the concept of internal sizing the used chemicals are added in the wet end of the paper machine. The goal is to adsorb the sizing agent, or sizing agent emulsion on the cellulose fibers. At the same time interaction of sizing agents and fillers should be limited. For this purpose, amphiphilic molecules are used which are able to attach to the cellulosic fiber surface with their hydrophilic, polar side, whereas their hydrophobic, apolar side is directed away from the surface and repels water and thus hinders water penetration into the paper sheet. Today, alkenyl succinic anhydrides (ASA) and alkyl ketene dimers (AKD) are the most common chemicals used for this purpose in neutral to slightly alkaline paper production [1]. Frequently, ASA is the preferred option, especially when a short curing time is required. ASA is based on internal alkenes that react with maleic anhydride (MAA) at high temperatures around 200° C in an ene-reaction. The internal olefins have to be prepared by isomerization from alpha-olefins.

So far the conventionally used C_{16} or C_{18} olefins for ASA production have been exclusively provided by the petrochemical industry, but the demand for sizing agents based on renewable resources has increased considerably. This demand was also the central impetus for our research towards a suitable ASA-substitute based on renewable raw materials, such as natural vegetable oils.

During the last 30 years scientists came up with several alternative sizing agents that are based on renewable raw materials. The oldest ones were developed around 1980 and comprise the use of maleated vegetable oils [2-4]. Because they were rather viscous and lacked efficiency, when compared to ASA, in later publications the focus lay on maleated fatty acid esters [5-9]. As second class of new sizing agents anhydrides based on long chain fatty acids and rosin acids were discussed [10,11]. Another substance proposed to size paper was fatty acid, which is applied like ASA [12]. The aim of our research was the development of a novel paper sizing agent based on natural vegetable oils. Their unsaturated fatty acids, as part of triglycerides, were the co-reacting moieties in the ene-reaction with MAA [13]. Using vegetable oil as raw material eliminates the additional isomerization step needed in the case of olefins, and it gives additional benefit by reducing logistic efforts and transportation costs, but above all it meets the general demand for greener products.

The starting point for the development of maleated vegetable oils was the selection of the appropriate raw material. Therefore oils from different sources were maleated and analytically characterized [13]. The results clearly indicated that oils with high amounts of polyunsaturated fatty acid residues, such as linseed or soybean oil, tend to give overly viscous products when maleated, and are thus less qualified. Promising results were obtained for oils with a high content of monounsaturated fatty acid (oleic-). Rapeseed oil (RSO) and in particular sunflower oil high-oleic (SOHO) were the preferred raw materials for the new sizing agents. The products gained from these two oils are less likely to form polymeric by-products during the maleation step, and a higher yield of maleated triglycerides can be reached. The focus of further investigations lay on the use of high oleic sunflower oil (SOHO) as the raw material of choice giving maleated high oleic sunflower oil (MSOHO).

Results and Discussion

Investigation of hydrolytic stability

Based on their molecular structure containing the reactive anhydride moiety (Figure 1a), ASA and MSOHO are prone to hydrolysis when in contact with water. In this process, the succinic anhydride group is converted into succinic acid (Figure 1b). In applications related to internal paper sizing, the reactive sizing agents are dispersed in a cationic polymer solution, e.g. cationic starch, prior to their addition to the paper stock. In the case of conventional ASA, it is well-known that the resulting emulsions have to be used within minutes – otherwise the sizing efficiency will decrease significantly and eventually even be lost due to an increasing content of hydrolyzed sizing agent, which does not contribute to sizing [14, 15]. Accordingly, ASA emulsions must be continuously prepared on-site and have to be added to the stock immediately after preparation. In a related account, Isogai and Morimoto [16] reported sizing efficiency and hydrolysis behavior of different alkyl oleate succinic anhydrides to be enhanced as compared to ASA.

Partly hydrolyzed ASA also has the tendency to form detrimental deposits. As paper machines do not retain fibers and chemical additives completely, some of the added ASA will be released into the white water, where it circulates, hydrolyzes completely, and accumulates. Then it forms sticky calcium salt deposits, with the cation calcium being derived from calcium carbonate as the most commonly used filler [1].

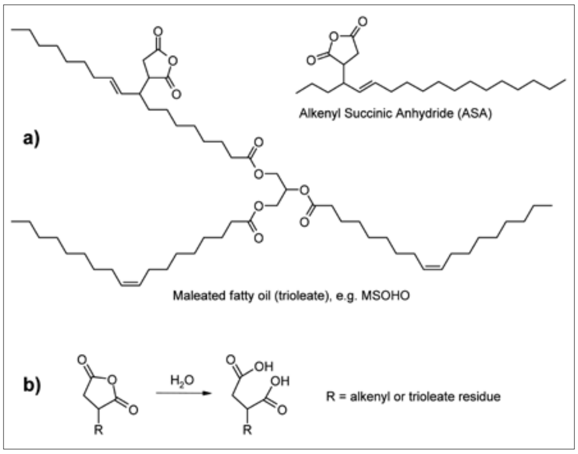

Figure 1. *a) Molecular structures of maleated fatty oil and alkenyl succinic anhydride. b) Hydrolysis of the succinic anhydride group.*

Internal sizing agents that are used according their application are added to the paper stock as aqueous emulsions. Therefore earlier studies focused on the emulsion stability of MSOHO in comparison to ASA [17]. Zero-order reaction rates were found, pointing out, that these hydrolysis rates are only influenced by diffusion of water into emulsion droplets. Conducting hydrolysis in its emulsion state MSOHO was considerably more stable than ASA, especially under conditions where a high Ca2+ ion concentration was present.

A more detailed investigation was conducted to clarify the differences found for the hydrolytic stability of MSOHO and ASA. The new, renewables-based sizing agent also has a succinic anhydride moiety as reactive group, similar to conventional ASA sizes. In general, it will also be affected by the same hydrolysis mechanisms as ASA.

In a first experiment the hydrolysis rates of ASA and MSOHO were determined in pure water in a 1:5 (w/w) ratio. This setting was chosen to eliminate possible effects originating from the cationic starch. These mixtures were emulsified at 70° C and then stirred at this temperature, while taking samples for the determination of the actual concentration of active sizing agent which was conducted using an HPLC-method described by Lackinger et al. [18] From 80% down to 20% active sizing agent an approximated zero order reaction rate was found for the measured hydrolysis curves of both sizing agents (Figure 2). Thus the hydrolysis rate is also dependent on diffusion phenomena as was the case for the emulsion stability tests mentioned above.

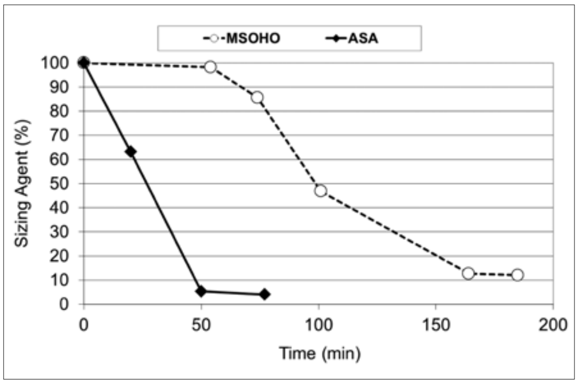

Figure 2. *Hydrolysis of the sizing agents MSOHO and ASA after dispersing them in water at 70° C.*

As the reactants are immiscible, water molecules are only able to react with the anhydride groups after having diffused into the emulsion droplets. This may be increasingly hindered by higher viscosity and higher hydrophobicity. While MSOHO has a rather high viscosity (>1000 mPas) ASA tends to have a rather low one (100-250 mPas). This provides an easy but sturdy explanation why maleated oils are hydrolytically far more stable in an aqueous environment than ASA. The half-times of the hydrolysis reaction were calculated from the linear regression fits in the range of 20-80% active size. They varied from 46 min for ASA to 105 min for MSOHO.

To exclude all effects that could result from different viscosities of the sizing agents as well as from diffusion phenomena the reaction was studied in organic solution. [18] Tetrahydrofuran (THF) proved to be the most suitable solvent, as THF and water are miscible and all sizing agents are properly soluble in a THF-water mixture. The concentration of sizing agents was set to give the same molar concentration (0.14 mmol/l) of reactive anhydride groups in solution. Figure 3 compares the results for the hydrolysis rates in THF solution measured for MSOHO and ASA. The observed pseudo first order reaction rates, that were almost the same for ASA and MSOHO, are governed by the reactive group (succinic anhydride) only. Based on the linear regression of the ln (c/c_0) versus time plot the half-life times were calculated for MSOHO (86 min) and ASA (80 min). Using this experimental setting the reaction rate is now exclusively determined by the chemical reactivity of the reaction center, which in all cases is the succinic anhydride moiety.

Sizing Efficiency of Maleated Vegetable Oils vs. ASA

When it comes to applicability of a new paper sizing agent the most important characteristic to test is its sizing efficiency. As MSOHO will be applied in the same manner as ASA (on-site emulsification with cationic starch) its efficiency was tested against standard ASA.

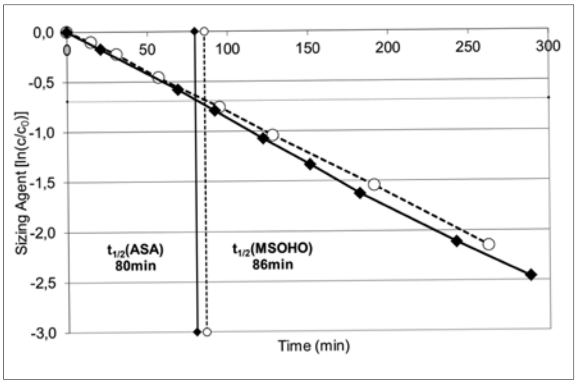

Figure 3. *Hydrolysis of ♦○ASA and ○ MSOHO in THF-water solution at 70° C.*

Hand sheets with commercial bleached kraft pulp (30/70 short/long fibre, 30° SR) containing a standard amount of 20% ground calcium carbonate were produced on a Rapid-Köthen sheet former at 45° C. For the detailed description of the test setting see [19].

The standard test to measure sizing efficiency is the Cobb60-Test [20]. The resulting value (Eq.1) is an expression of the water absorption over the time period of 60s given in g/m². Sizing efficiency is increasing when Cobb values are decreasing.

$$Cobb\left[g/m^2\right] = \frac{(m_2 - m_1)[g]}{0.01\left[m^2\right]} \qquad (1)$$

m_1 ..... mass of the sample before Cobb determination [g]
m_2 ..... mass of the sample after Cobb determination [g]

In a first series blends with 30% and 50% MSOHO in a commercial ASA type were tested against pure ASA. Almost no difference in efficiency was observed (Figure 4).

One outstanding characteristic of MSOHO in comparison to ASA is its higher viscosity. Common ASA has a viscosity ranging from 100 to 250 mPas, while for MSOHO it can be considerably higher. While the high viscosity positively influences the stability of MSOHO in an aqueous environment (hydrolytic stability),

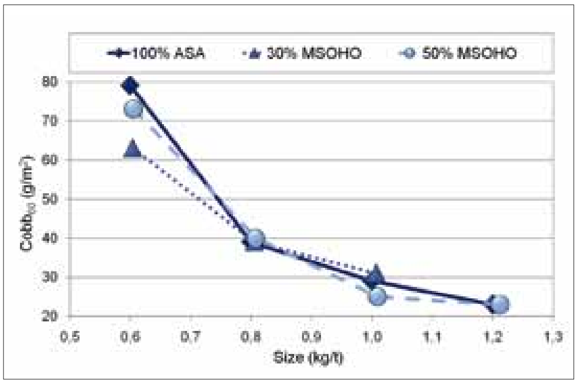

Figure 4. *Sizing efficiency for MSOHO-ASA blends.*

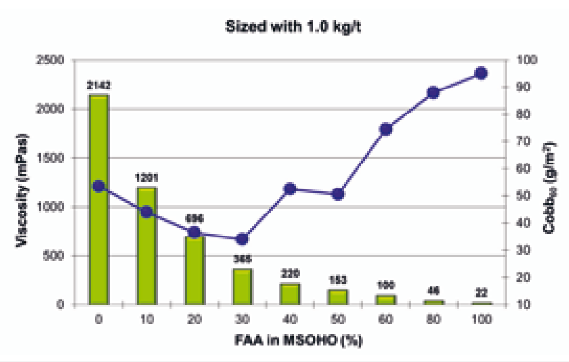

Figure 5. *Sizing efficiency for MSOHO-FAA blends.*

it is detrimental to sizing, because it makes spreading on cellulose fibers more difficult. A very convenient way was invented to overcome this problem: Another green sizing chemical with a very low viscosity (fatty acid anhydride – FAA [11]) can be blended into MSOHO. MSOHO and FAA are miscible at any ratio and already the exchange of 30% MSOHO for FAA reduces the viscosity from above 2000 to 365 mPas. As intended the sizing efficiency improves with small amounts of FAA blended into MSOHO (Figure 5). Whereas additions of over 40% FAA decrease the sizing efficiency as pure FAA is a weaker sizing agent compared to MSOHO.

For a better comparison of the found synergy of MSOHO and FAA and its benefits when these green sizing agents have to compete against ASA's efficiency a new test was conducted: An MSOHO – FAA blend (75/25 MSOHO/FAA) was measured against pure MSOHO, pure FAA, and ASA (Figure 6). The results prove the earlier findings. With the optimized MSOHO-FAA blend ASA sizing efficiency could almost be reached.

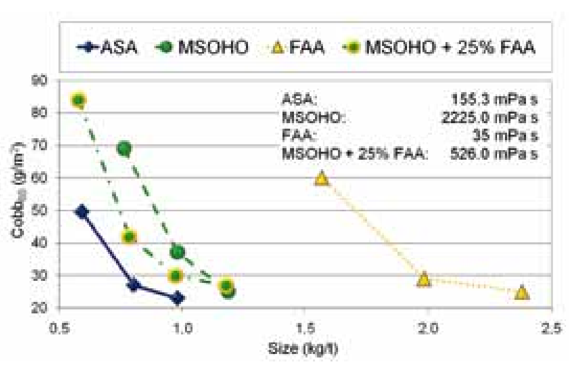

Figure 6. *Synergistic effect of MSOHO blended with FAA in paper sizing: A comparison to MSOHO, FAA, and ASA.*

Conclusions

The results presented clearly demonstrate that MSOHO performs similar to ASA with regard to many properties relevant to the papermaker; with regard to the other properties it is even superior. Since MSOHO is more stable against hydrolysis harmful deposits in the paper machines are reduced which means decreased maintenance times.

The other utmost important characteristic is MSOHO's sizing efficiency. The investigations of this parameter in relation to results gained with ASA were promising. There are two possibilities for first application tests where MSOHO has to compete against ASA: Either use an MOSHO-FAA (75/25) blend or blend 30% MSOHO into ASA.

The applicability of the new product is extremely wide, reaching to all paper producers which currently use ASA.

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A Novel Route to Obtaining Stable Quaternary Ammonium Fluoride Solutions in DMSO: Application in Microwave-Assisted Acylation of Cellulose

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Abstract

Previously, solutions of quaternary ammonium fluoride hydrates (R_4NF-xH_2O) in DMSO have been employed for cellulose dissolution and subsequent derivatization, by using "conventional", i.e., convection heating. Side reactions that limit the applicability of these solvent systems include polymerization of- and elimination reactions in the electrolyte proper, and fluoride ion-mediated cellulose ester deacylation. In the present work, these side reactions have been suppressed by preparing the electrolyte- tetraallylammonium fluoride (TAAF) and tetra(1-butyl)ammonium fluoride (TBAF)- directly in DMSO by a novel, expedient method. The resulting solvent systems dissolve microcrystalline- and cotton cellulose, the dissolved biopolymers can be efficiently acylated by acid anhydrides; thanks to the use of microwave heating. The degree of product substitution, DS, is higher than that obtained by convection heating in the same solvent system, being comparable to that obtained when imidazole-based ionic liquids are employed as solvents. The novel approach is attractive because of its efficiency, low cost, and potential application to the derivatization of other polymers.

Keywords: *tetraallylammonium fluoride, tetra(1-butyl)ammonium fluoride, DMSO, ionic liquids, cellulose carboxylic esters, cellulose acylation in homogeneous solutions*

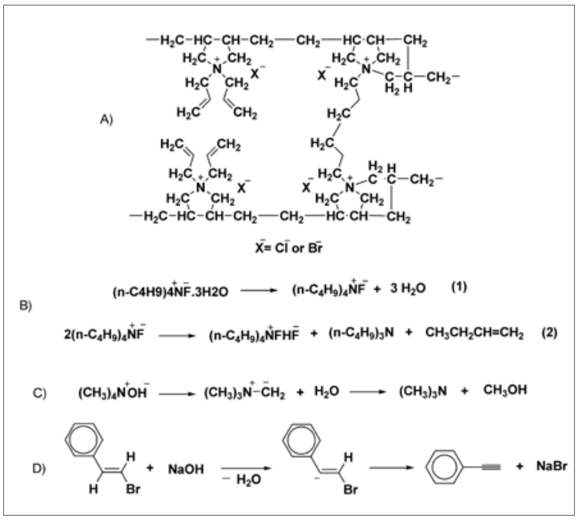
Introduction

Cellulose is the most abundant biopolymer and is the source of many important derivatives, including esters and ethers that are used as fibers, films, membranes, etc.[1,2] In the industrial processes, e.g., acetylation, cellulose reacts with the derivatizing agent (acetic anhydride/ solvent/catalyst) under heterogeneous conditions.[3] Alternatively, acylation can be carried out under homogenous conditions, where the biopolymer is first dissolved in an appropriate solvent, followed by its derivatization. This approach offers a series of advantages including, most importantly, a better control of the degree of product substitution, DS, within the anhydroglucose unit, AGU, and along the biopolymer backbone. This results in better control/reproducibility of the properties of the products, hence their applications.[4]

The semi-crystalline nature of cellulose is the results of strong inter- and intra-molecular hydrogen bonding;[5-7] disruption of these interactions is required for biopolymer dissolution. Single- and multi-component solvents have been employed for this purpose. Examples of the former include N-methylmorpholine-N-oxide and ionic liquids.[4,8] Solutions of electrolytes in dipolar aprotic solvents, e.g., LiCl/N,N-dimethylacetamide, DMAc [9,10] and quaternary ammonium fluoride hydrates, e.g., tetraallylammonium-H_2O (TAAF-H_2O) and tetra(1-butyl) ammonium-$3H_2O$ (TBAF-$3H_2O$) in DMSO, are examples of the latter.[11,12] In these solvent systems, biopolymer dissolution results essentially from the formation of hydrogen bonds between the OH groups of the AGU and the anion present;[13] this being the reason for the efficiency of electrolytes whose anions are relatively small with large charge density, in particular F^- and Cl^-. The present work is concerned with the use of the above-mentioned fluorides in DMSO. These solutions have been successfully employed as media for cellulose derivatization; the reaction mixtures have been heated by conventional, i.e., convection heating.[11,12,14-18]

Although efficient, the multi-component systems have some limitations/ drawbacks. For example, depending on the reaction temperature, derivatization in LiCl/DMAc may result in degradation of the biopolymer by the extremely reactive electrophilic species N,N-dimethylketeniminium ion (CH_2=C=$N^+(Me)_2$), whose precursor is the enol tautomer of DMAc, CH_2=C(OH)N$(Me)_2$.[19] In principle, the electrolytes TAAF and TBAF are subject to side reactions. Although Hofmann elimination is not operative with TAAF, it may undergo polymerization to form linear- as well as cross-linked cyclopolymers (Scheme 1a).[12,20,21] TBAF is known to undergo Hofmann elimination (Scheme 1b);[22,23] both fluorides may undergo degradation via an ylide intermediate (Scheme 1c), akin to the E1cB pathway (Scheme 1d), except that the species generated is a zwitterion, and not an anion.[24,25] In this regard, it is noteworthy that imidazole-based ionic liquids, ILs, may also undergo base-induced elimination of the relatively acidic C2-H of the heterocyclic ring.[26-30]

In the synthesis of TAAF, the final stage involves neutralization of the methanolic solution of the corresponding hydroxide with HF solution, followed by evaporation of the alcohol. In order to avoid electrolyte polymerization, solvent evaporation has been carried out under reduced pressure, at room temperature, or at higher temperature in the presence of a free radical inhibitor, propyl gallate.[12] Hydrated TBAF is available commercially, and can be obtained in anhydrous state from hexafluorobenzene and tetra(1-butyl)ammonium cyanide in THF, acetonitrile, or DMSO.[31,32]



Scheme 1. *A) Molecular structure of the (cross-linked) product that is formed by free radical polymerization of TAACl or TAABr in the presence of tert-butyl hydroperoxide initiator. B) Hofmann elimination of TBAF, C) degradation mechanism of tetramethylammonium cation by an ylide pathway, and D) E1cB elimination of trans-β-bromostyrene.*

The values of DS obtained for cellulose carboxylic esters in TAAF-H_2O/DMSO or TBAF-3H_2O/DMSO are relatively low. This is attributed to a combination of the consumption of part of the acylating agent by the electrolyte water of hydration,[33-35] and fluoride-ion mediated ester-hydrolysis, e.g., by a general-base mechanism. [12,36] In summary, the reason for the potential efficiency of the R_4NF-hydrate/DMSO solvent system (the small volume and high charge density of F^-) is also responsible for the obtained (relatively low) DS; this predicament calls for a suitable solution.

We report here on a novel approach, including the production of both TAAF-hydrate or TBAF-hydrate directly in DMSO with suppressed side reactions, and the use of these solvent systems as media for microwave(MW)-assisted acylation of cellulose. By adding DMSO before methanol evaporation, i.e., after ($Br^- \rightarrow OH^-$) ion-exchange and neutralization with HF, vide Experimental, alcohol removal can be carried out at higher temperatures (50-60° C) with negligible side reactions. The use of MW as source of heating led to cellulose carboxylic esters with higher DS values, as compared with those obtained in the same solvent systems, by using convection heating. To our knowledge, this is the first report on MW-assisted cellulose derivatization of cellulose in R_4NF-hydrate/DMSO. Noticeably, the product DS values are comparable to those obtained in imidazole-based ILs, under MW-irradiation. This favorable outcome is attributed to several factors: suppression/elimination of the side reactions due to attenuation of the strength of (F^-) as a base; decrease of the water content of the solvent system; enhanced biopolymer accessibility, due to cellulose-electrolyte-DMSO interactions.

Experimental

Materials

The reagents were purchased from Acros, Aldrich, or Merck and were purified, as described elsewhere.[37] Microcrystalline cellulose, MCC; Avicel PH 101 was from FMC (Philadelphia; viscosimetric degree of polymerization, DPv = 175). Cotton sheets (Nitro Química S.A., São Paulo) were cut into stripes, grounded, and sieved (100-200 mesh); DPv = 920.

Equipment

The value of DP_v was determined by using shear-dilution Cannon-Fenske viscosimeter (Schott), inserted in Schott AVS 360 automatic viscosity determination equipment. ^{1}H NMR measurements were recorded with Varian Innova-300 spectrometer (300 MHz).

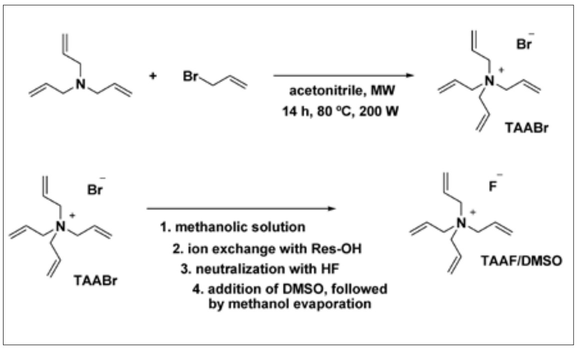
Material Characterization

The DS of cellulose carboxylic esters was determined by either the solvatochromic indicator method, [38] or by ester saponifaction followed by back titration of the residual base[39]; the results of both methods agree within ± 0.05. DPv was determined (25° C) from the intrinsic viscosity of cellulose solution in CUEN/ water (1:1, v/v) according to the recommended procedure.[40]

Synthesis of R_4NF-hydrates (as Solutions in DMSO)

Scheme 2 depicts the preparation of TAAF-hydrate/ DMSO; a similar route has been employed for obtaining TBAF-hydrate/DMSO.

The synthesis of TAABr was carried out as follows: A mixture of triallylamine (36.5 mL; 0.21 mol), allyl bromide (27.3 mL; 0.32 mol), and acetonitrile (84 mL) was heated under reflux in the cavity of a MW reactor (Mars, CEM, Matthews) for 14 h, at 80° C and 200 W; magnetic stirring. After removal of the volatiles under reduced pressure (2 mmHg), toluene was added, the solid reaction product filtered off, suspended several times in the same solvent and the solid filtered. The product was dried in a vacuum-oven at room temperature, in the presence of P_4O_{10}. Yield 95%; pale yellow powder; mp= 179-180° C (Electrothermal IA 6304); literature mp = 183-184° C [41]. Figure (1A) shows the ^{1}H NMR spectrum of TAABr and designation of the discrete hydrogens. Elemental analysis (Perkin-Elmer Elemental Analyzer CHN 2400) after additional drying under reduced pressure (48 h at 40° C, in the presence of P_4O_{10}): Anal. Calcd. for C12H20NBr: C, 55.8; H, 7.8; N, 5.4%. Found: C, 55.6; H, 8.0; N, 5.3%.



Scheme 2. *Steps of the synthesis of TAAF/DMSO.*

A similar procedure has been employed for obtaining TBABr from tri(1-butyl)amine (50.0 mL; 0.21 mol), 1-butyl bromide (33.8 mL; 0.32 mol), acetonitrile (84 mL). Yield 70%; white powder; mp = 102-103° C; literature mp = 101-103° C [42, 43]. The product gave the expected ^{1}H NMR spectrum (spectrum not shown) and the following elemental analysis results (after additional drying under reduced pressure for 48 h at 40° C, in the presence of P_4O_{10}): Anal. Calcd. for C16H36NBr: C, 59.6; H, 11.3; N, 4.3%. Found: C, 59.8; H, 11.3; N, 4.4%.

Figure (1A) shows the ^{1}H NMR spectrum of TAABr. From the relative areas of the peaks the composition of this sample is TAABr-0.4H_2O. A similar determination has indicated that the composition of corresponding tetra(1-butyl) electrolyte (spectrum not shown) is TBABr-1.4 H_2O

The counter-ion of TAABr or TBABr was then converted into the corresponding hydroxide by ion-exchange on a macro-porous resin (Purolite SGA55OOH, 1.10 eq OH^-/L), as follows: One liter of a methanolic solution of TAABr or TBABr (0.25 mol) was passed through a column containing the resin (400 mL). The completeness of the (Br^-/OH^-) ion-exchange was checked by treating a sample of the eluent with acidified $AgNO_3$ solution. The pH of the methanolic hydroxide solution (ca. 2 L) was brought to ca. 7 (expanded-scale pH-paper) by adding methanolic HF solution. DMSO was then added and methanol was removed under reduced pressure, from 200- to 10 mmHg at 50° C, then to 2 mmHg, at 60° C for ca. 4 h. [44]

Determination of theComposition of the R_4NF-hydrate/DMSO Solvent System

During evaporation, some DMSO was entrained along with methanol. The composition of the solution (electrolyte; water of hydration; DMSO) was determined by ^{1}H NMR spectroscopy; 1,4-dioxane was used as internal standard. A sample of R_4NF-hydrate/ DMSO was diluted with DMSO-d_6 whose water content has been previously determined (by comparing the integration of water peak with that of internal dioxane). Figure (1B) shows the ^{1}H NMR spectrum of TAAF-hydrate, along with peak attribution. Integration of the areas of the discrete hydrogens has indicated that this compound is TAAF-H_2O; the corresponding tetra(1-butyl) electrolyte is TBAF-2H_2O (spectrum not shown).

The concentration of the electrolyte in DMSO was calculated (by peak integration) from the same experiment. In what follows, the solvent system composition is given on the mole fraction scale. For example, $TAAF_{0.16}/DMSO_{0.76}$ means a solution of 0.16 and 0.76 mole fraction of TAAF and DMSO, respectively; the

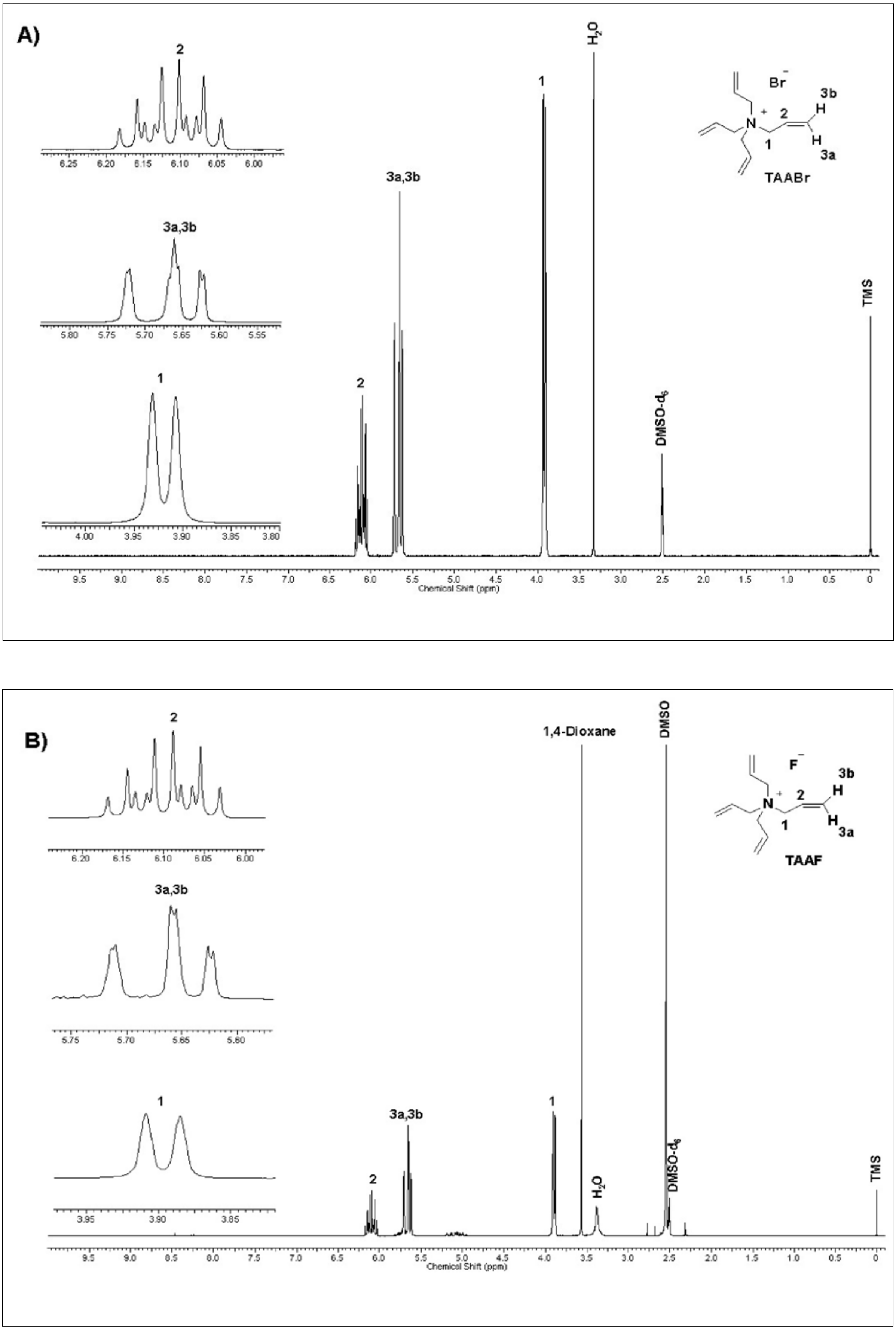
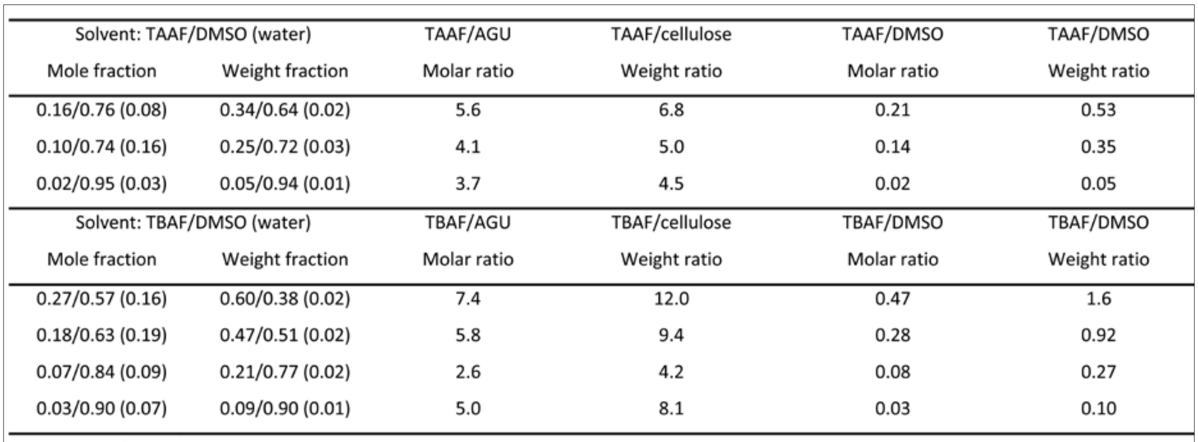


Figure 1. *^{1}H NMR spectra of A) TAABr-0.4 H_2O/DMSO-d_6 and B) TAAF$_{0.16}$/-DMSO-DMSO$_{0.76}$ in the presence of added 1,4-dioxane as internal reference. The subscripts stand for the respective mole fraction.*

***Table 1.** Solvent system composition.*[a]



Solvent: TAAF/DMSO (water)		TAAF/AGU	TAAF/cellulose	TAAF/DMSO	TAAF/DMSO
Mole fraction	Weight fraction	Molar ratio	Weight ratio	Molar ratio	Weight ratio
0.16/0.76 (0.08)	0.34/0.64 (0.02)	5.6	6.8	0.21	0.53
0.10/0.74 (0.16)	0.25/0.72 (0.03)	4.1	5.0	0.14	0.35
0.02/0.95 (0.03)	0.05/0.94 (0.01)	3.7	4.5	0.02	0.05
Solvent: TBAF/DMSO (water)		**TBAF/AGU**	**TBAF/cellulose**	**TBAF/DMSO**	**TBAF/DMSO**
Mole fraction	Weight fraction	Molar ratio	Weight ratio	Molar ratio	Weight ratio
0.27/0.57 (0.16)	0.60/0.38 (0.02)	7.4	12.0	0.47	1.6
0.18/0.63 (0.19)	0.47/0.51 (0.02)	5.8	9.4	0.28	0.92
0.07/0.84 (0.09)	0.21/0.77 (0.02)	2.6	4.2	0.08	0.27
0.03/0.90 (0.07)	0.09/0.90 (0.01)	5.0	8.1	0.03	0.10

[a] Determined from 1H NMR, using 1,4-dioxane as internal standard.

remaining, 0.08, corresponds to water of hydration. Table 1 shows the mixtures that have been studied, along with their compositions.

Effect of Heating Cellulose Triethanoate With TAAF-H_2O/DMSO on the Degree of Substitution (DS) of the Ester

A solution of a commercial cellulose triethanoate (CTA; CA 398-6; DS = 2.7; Eastman) was prepared by mixing the ester (0.55 g; 2.0 mmol) with 11 g of TAAF$_{0.16}$/DMSO$_{0.76}$ (molar ratio TAAF-H_2O/CTA = 9.5) in a round-bottom flask, equipped with a reflux condenser, protected from humidity. The solution was stirred mechanically at 570 rpm for 3h, at 80° C, by employing MW irradiation (30 W). The resulting solution was poured into ethanol (400 mL); the suspension was stirred for 30-60 min; the solid precipitated was centrifuged at 3500g (IEC Centra 244 MP4R). This procedure was repeated three more times, the product was dried under reduced pressure at 50-60° C, for 48 h, in the presence of P_4O_{10}, and its DS determined.

Dissolution and Acylation of Cellulose in TAAF-H_2O/DMSO or TBAF-2H_2O/DMSO

Cellulose (0.50 g; 3.09 mmol) was added to the corresponding amount of TAAF/DMSO or TBAF/DMSO (10 g, for the mixtures with (final) mole fraction of DMSO ≥ 0.84, see Table 1). The mixture was mechanically stirred (570 rpm) at 80° C, for 20-40 min, by applying MW-radiation (30 W). Cellulose dissolution was followed visually by employing a lamp placed behind the reaction flask. Cellulose samples dissolved readily in TBAF-2H_2O/DMSO to give clear solutions. On the other hand, solutions of these celluloses in TAAF-H_2O/DMSO were only translucent. Addition of the carboxylic acid anhydride to the cellulose solution in the latter solvent resulted in almost instantaneous (MCC), or slow formation of clear solution (cotton). After addition of the acid anhydride the mixture was kept under the above-mentioned experimental conditions during the required length of time, vide Tables 2 and 3. The workup of the products was similar to that given above (heating cellulose triethanoate with TAAF-H_2O/DMSO).

Results and Discussion

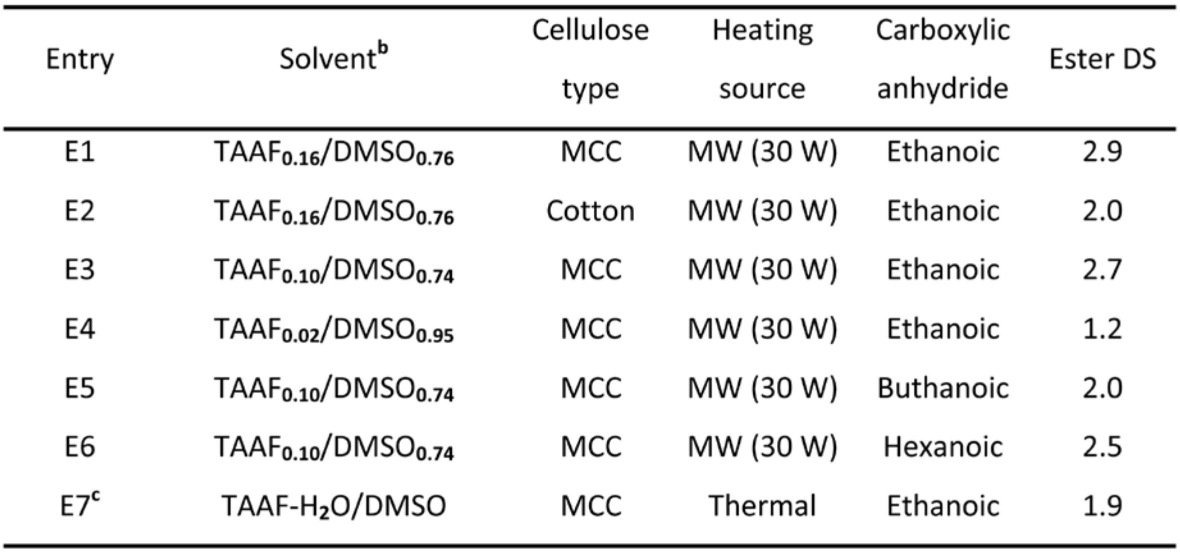
Comments on the Synthesis of R_4NF and Problems Associated With the "Conventional" Approach to Obtain Their Solutions in DMSO

Tetra(1-butyl)ammonium hydroxide is sold as concentrated aqueous solution; this can be converted into the fluoride by neutralization with HF. TAAOH is not commercially available and should be synthesized, e.g., from the corresponding halide. We have opted, however, for the synthesis of both compounds by the same route because evaporation of water from aqueous TBAF solution may lead to Hofmann elimination.

As given in Introduction, DMSO is added to TAAF after methanol evaporation. Unless alcohol removal is carried out at room temperature, or an antioxidant is added, electrolyte polymerization occurs. Cross-linked poly-TAAF is insoluble in DMSO and the suspension does not dissolve cellulose.[12] Although Hofmann elimination during the acylation experiment in TBAF-3H_2O/DMSO is not serious,[22,23] the molar ratio (water/AGU) in the resulting solution is ca. 9.[33] This relatively large amount of water is problematic, because it consumes a part of the acylating agent, and decreases cellulose-electrolyte interactions as has been demonstrated by ^{19}F and ^{1}H NMR.[45]

In principle, two approaches can be employed: reduction of the water content of TBAF without causing

***Table 2.** Results of acylation of MCC, or cotton cellulose, in TAAF-H_2O/DMSO.*[a]



Entry	Solvent[b]	Cellulose type	Heating source	Carboxylic anhydride	Ester DS
E1	$TAAF_{0.16}/DMSO_{0.76}$	MCC	MW (30 W)	Ethanoic	2.9
E2	$TAAF_{0.16}/DMSO_{0.76}$	Cotton	MW (30 W)	Ethanoic	2.0
E3	$TAAF_{0.10}/DMSO_{0.74}$	MCC	MW (30 W)	Ethanoic	2.7
E4	$TAAF_{0.02}/DMSO_{0.95}$	MCC	MW (30 W)	Ethanoic	1.2
E5	$TAAF_{0.10}/DMSO_{0.74}$	MCC	MW (30 W)	Buthanoic	2.0
E6	$TAAF_{0.10}/DMSO_{0.74}$	MCC	MW (30 W)	Hexanoic	2.5
E7[c]	TAAF-H_2O/DMSO	MCC	Thermal	Ethanoic	1.9

[a] Experimental conditions: 3 h, 80° C, and carboxylic anhydride/AGU molar ratio of 6; MCC, DPV = 175; cotton cellulose, DP_v, v is sub-index. The electrolyte is present as monohydrate.

[b] See Table 1.

[c] From literature; conditions: 15.33 mmol of TAAF; 0.56 mol of DMSO; TAAF/AGU mole ratio of 5.0; 3 h, 80° C, and ethanoic anhydride/AGU mole ratio of 6; MCC, DP_V = 175.[12]

Hofmann elimination, or use of anhydrous TBAF. Whereas the former is tedious and time consuming, the latter is not a satisfactory solution to the water-mediated side reactions. The reason is that one of the reagents is expensive (US$ 25.6/g $(C_4H_9)_4NCN$, Sigma Aldrich); the resulting solution in DMSO (a mixture of $C_6(CN)_6$ and anhydrous TBAF) is not stable; it does not dissolve cellulose after storage for 28 h at room temperature, due to Hofmann elimination and the concomitant formation of HF^{2-}.[32] Finally, it is worth mentioning that heating a cellulose ester with either TAAF-H_2O or TBAF-$3H_2O$ in DMSO leads to de-acylation.[12,36]

The Novel Approach: Problem-Free Production of Hydrated TAAF or TBAF in DMSO and Their Use in MW-Assisted Acylation of Cellulose

We raised the following questions: Can the side reactions be eliminated/suppressed? Does MW-radiation improve the DS values of the cellulose carboxylic esters as compared with those obtained by using convection heating? With regard to the first question, we decided to investigate the effect of adding DMSO to the methanolic solution of R_4NF, before evaporation of the alcohol. Our reasoning for using this approach rests on the ability of DMSO to associate with electrolytes in general, especially those with hard acid/base ions.[46] Strong solvation of the fluoride ion should decrease its basicity, hence eliminates/suppress Hofmann elimination (for TBAF) and degradation by the ylide pathway (for both electrolytes). This expectation is corroborated by several pieces of evidence. For example, all TAAF-H_2O/DMSO solutions were clear, with no visual sign of (insoluble) polymer formation. No gas evolution (1-butene from Hofmann elimination) has been observed during the evaporation of the alcohol from TBAF/methanol/DMSO, provided that the final mole fraction of DMSO ≥ 0.84. Another point in favor of using DMSO is that the concomitant removal of this dipolar aprotic solvent during methanol evaporation should not be appreciable, because of the large difference of the boiling points of the two solvents (124° C). Additionally, cellulose dissolution in the resulting R_4NF-hydrate/DMSO should be favorable because of the high capacity of the DMSO in causing biopolymer swelling (DMSO ranks second only to water).[47,48]

We have employed ^1H NMR spectroscopy in order to assess the occurrence/extent of side reactions. For example, the spectrum of TAAF-H_2O/DMSO (Figure 1B) shows a few additional peaks in comparison with that of TAABr-$0.4H_2O$ (Figure 1A). The same result has been observed for the pair TBAF-$2H_2O$/DMSO and TBABr-1.4 H_2O/DMSO (spectra not shown). Al-though a detailed characterization of these side products is beyond the scope of the present work, their concentration can be calculated from peak areas. Assuming that the additional peaks observed in

Table 3. *Results of acetylation of MCC in TBAF-hydrate/DMSO.*[a]

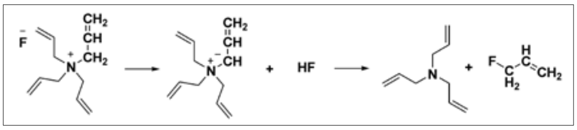
Entry	Solvent[b]	Cellulose type	Heating source	Carboxylic anhydride	Ester DS
E8	$TBAF_{0.27}/DMSO_{0.57}$	MCC	MW (30 W)	Ethanoic	0.9
9E	$TBAF_{0.18}/DMSO_{0.63}$	MCC	MW (30 W)	Ethanoic	1.4
E10	$TBAF_{0.07}/DMSO_{0.84}$	Cotton	MW (30 W)	Ethanoic	2.5
E11	$TBAF_{0.03}/DMSO_{0.90}$	MCC	MW (30 W)	Ethanoic	2.8
E12	$TBAF_{0.03}/DMSO_{0.90}$	Cotton	MW (30 W)	Ethanoic	2.5
E13[c]	TBAF-$3H_2O$/DMSO	Cotton	Convection	Ethanoic	1.6-2.3
E14[d]	AlMeImCl	MCC	MW (30 W)	Ethanoic	2.95
E15[d]	AlMeImCl	Eucalyptus	MW (30 W)	Ethanoic	2.2
E16[d]	AlBuImCl	MCC	MW (30 W)	Ethanoic	2.25

[a] Unless specified, the electrolyte is TBAF-$2H_2O$. Experimental conditions: 3 h, 80° C, and ethanoic anhydride/AGU molar ratio of 6; MCC, DP_V = 175; cotton cellulose, DP_V = 920.

[b] See Table 1.

[c] From literature; conditions: 20.92 mmol of TBAF-$3H_2O$; 0.84 mol of DMSO; TBAF/AGU mole ratio of 3.4; 3 h, 60-100° C, and ethanoic anhydride/AGU mole ratio of 6; cotton cellulose, DPv = 440.[33]

[d] From literature; conditions: IL/AGU mole ratio of 16.1 or 20.4, for 1-allyl-3-(1-butyl)imidazolium chloride, AlBuImCl/AGU, or 1-allyl-3-methylimidazolium chloride, AlMeImCl/AGU; 3 h, 80° C, 30 W, ethanoic anhydride/AGU molar ratio of 6; eucalyptus cellulose, DP_V = 965.[44,65]



Scheme 3. *Proposed mechanism of side reactions that may occur via ylide mechanism during the preparation of* $TAAF_{0.16}/DMSO_{0.76}$.

Figure (1B) were produced by the ylide pathway, see Scheme 3, some side reaction products can be envisaged, e.g., triallylamine (δ = 5.24 (CH); 4.63 and 4.59 ($C=CH_2$); 2.76 ($N-CH_2$) ppm.[49] The other product is not expected to be observed because of the low b.p of 3-fluoropropene (-10° C). Provided that this is the main decomposition reaction for TAAF-H_2O, based on the area of the extra peak at 5.21-5.5.17 ppm (Figure 1B) then the molar ratio TAAF/elimination products (triallylamine, CH) is 0.95/0.05, i.e., the extent of side reactions is, by this criterion, ca. 5 mol%. A similar calculation has been performed for TBAF-2 H_2O/DMSO, based on the formation (by Hofmann elimination) of tri(1-butyl)amine (δ = 2.31 ($N-CH_2$); 1.34 ($N-CH_2-CH_2$), 1.26 (CH_2), and 0.87 (CH_3); [49-51] has indicated that the extent of this side reaction is ca. 19 mol%.

Published data have shown that MW-heating is more efficient than its convection counterpart, both for cellulose dissolution and subsequent derivatization in electrolyte/dipolar aprotic solvent and ILs. The reason may be due to the transient, and continuous formation of “hot-spots” in the reaction mixture whose temperature is higher than bulk solution temperature.[52-55] We have also recently shown that MW-assisted acylation of cellulose in ILs is faster than their counterparts where heating is by convection.[56] We have expected the same result with R_4NF-hydrate/DMSO, because the highly polar medium is able to absorb/dissipate this electromagnetic radiation efficiently.

MW-Assisted Dissolution and Acylation of Cellulose in R_4NF-hydrate/DMSO

In principle, the stabilizing effect of the electrolytes by DMSO is expected to increase the DS of the produced esters, provided that F^--mediated product deacylation, e.g., by the general-base mechanism is also suppressed. A combination of factors may lead to this favorable result: reduction of the basicity of the fluoride ion due to its efficient solvation (by DMSO) and suppression of the hydrolysis due to reduction of the water concentration in the medium. The following result (see Experimental) shows that this is indeed the case. The DS of the commercial CTA sample decreased from 2.70 to 2.55 after being heated at 80° C (30 W) for 3 h in $TAAF_{0.16}/DMSO_{0.76}$. For comparison, heating the same CTA for 6 h at 60° C with TAAF-H_2O/DMSO gave an ester with DS = 1.7;[12] heating cellulose acetate with DS = 2.42 with TBAF-$3H_2O$ for 24 h at 50° C gave ester with DS = 0.92.[36] There-fore, the fluoride-ion mediated ester hydrolysis is suppressed.

We now address the results of cellulose acylation in the two solvent systems. Table 2 shows the data of acylation of MCC, and cotton cellulose, in TAAF-H_2O/DMSO. The best results, in terms of DS, were obtained by using mole fraction of TAAF of 0.10-0.16 and MW-radiation (E1 and E3). The average DS obtained (2.8) is much higher than that reported for the same solvent system, DS = 1.9, when convection heating was used, E7 [12]. The DS values for acetylation of cotton (E2) is lower than the corresponding value for MCC (E1) most probably due to differences in DP_v, v is sub-index and accessibility of two types of cellulose.[57] The same difference in DS has been observed for the reaction in TAAF-H_2O/DMSO, with convection heating.[12]

TAAF-H_2O/DMSO has also been successfully employed for the synthesis of other esters, butanoate and hexanoate (E5 and E6). The dependence of DS on the anhydride used is similar to that observed elsewhere, i.e., ethanoic ≈ hexanoic > butanoic.[12,18,56,58] As recently shown, this dependence on the length of the acyl moiety of the anhydride is due to subtle changes in- and compensations of the enthalpy and entropy of activation.[59]

Table 3 shows the data obtained for cellulose acetylation in TBAF-$2H_2O$/DMSO. The highest DS value was obtained by using electrolyte mole fraction of 0.03 and MW-radiation (E11 and E12). Whereas the former DS is comparable to that shown in E1 of Table 2, the latter is larger than that reported elsewhere for TBAF-$3H_2O$/DMSO, but using convection heating, E13.[33] As expected, the same dependence of DS on the type of cellulose was observed in TBAF-$2H_2O$/DMSO (cf. E11 and E12).

Tables 2 and 3 show several interesting points. The mole fraction of TAAF (0.10 to 0.16; E1 and E3 of Table 2) and TBAF (0.03, E11 of Table 3) that give the largest DS are different. The results also show that the dependence of DS on the mole fraction of the electrolyte is relatively large. For TBAF, this is not an electrolyte concentration effect, because better results have been obtained at lower concentrations. It may be traced to the occurrence of Hofmann elimination, because gas bubbles (presumably 1-butene) have been observed during methanol evaporation for mixtures of TBAF/DMSO with mole fraction of DMSO < 0.84.

The results of the present study can be compared with those for the same reaction in ILs, in particular 1,3-dilakylimidazlium chlorides.[35,54,55,60-64] E11-E12, and E14 to E16 show that the efficiencies of the present solvent systems are comparable to those in the ILs with chloride counter-ion, for both MCC and fibrous cellulose, probably because of the above-mentioned strong biopolymer-fluoride ion interactions.[45]

Conclusions

Previously, the use of R_4; 4 s sub-index solvent system in cellulose dissolution/derivatization has been hindered due to side reactions that may occur during the synthesis of the electrolyte proper and/or the resulting ester. The former include polymerization and several eliminations; the cellulose ester produced may undergo F^-; the minus sign is super-index mediated deacylation. These problems are traced to the basicity of the fluoride ion (isoelectronic with the hydroxide ion).[66] In the present work, these problems have been suppressed by exploiting the efficient solvation of the fluoride ion by DMSO, and by reducing the water content of the electrolyte. An incremental increase in DS has been obtained by substituting MW-heating for its convection counterpart. The results, in terms of DS, are comparable to those obtained with ILs that are typically employed for cellulose derivatization. The difference in cost of the two solvents (R4NF/DMSO and ILs) is remarkable because the former is composed essentially of (relatively inexpensive) DMSO. Therefore, the scope of applications of R_4; 4 s sub-index for dissolution/derivatization of cellulose, as well as other natural and synthetic polymers, can be enhanced by using the present approach.

Acknowledgements

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