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A VISION FOR THE TEXTILE INDUSTRY IN EUROPE

Thomas Fahnemann

(Opening speech of the International Man-Made FIber Conference, Dornbirn 2005)

Ladies and Gentlemen, Distinguished Guests:

When representatives of the European chemical fiber industry got together in Dornbirn during the last few years, the focus has long since expanded beyond the confines of mere technical issues. It is true that the meetings have always served as one of the most important platforms for an exchange of ideas and innovations in our branch. However, what is the point of developing the most wonderful ideas when the markets for our products have disappeared and we no longer have the opportunity to implement these concepts? What is the point of it all when we are faced with dwindling cash flows, the basis for incorporating these ideas in our investments and production lines?

In recent months, the development of our branch has been dominated by one single issue. In fact, this topic has even filled the business pages of the daily newspapers, a rather rare phenomenon in our industry. It is a fact that today, here and now, all of us are witnesses to and are being impacted by a revolution in commercial and trading policies which is – one has to admit – unique and unheard of in the economic history of our modern age. The repercussions emanating from the expansion of the Asian and, in particular, the Chinese textile industry, to the European and American markets have by far exceeded all our previous expectations.

Today I would like to briefly touch upon several issues which have emerged as a result of this commercial cataclysm for the European chemical fiber industry and, in particular, for the textile sector linked to it. At the same time, it has to be emphasized that there are no easy solutions. Nevertheless, every today is followed by another tomorrow. It is our role and duty, in our capacity as managers, to actively shape this future. Even in times of far reaching changes, we should not give up, but remain at the helm to chart the future course of our industry.

Are we experiencing a structural transformation, or a magnitude 8 earthquake in commercial terms? If you look at the figures, there can hardly be any doubt as to the strength and sustainability of this eruption. Between the years 1995 and 2004, the exports of the Chinese textile industry catapulted from 36 billion dollars to 95 billion dollars. In the first five months of 2005 alone, Europe imported 36% more textile products than all of last year. At the same time, orders placed with Europe’s textile industry dramatically declined in the first half of 2005, and I am talking about a double-digit drop.

Ladies and Gentlemen, never before in modern economic history has such a dramatic and radical structural transformation in a crucial industry taken place in such a short time.

Could it be that we were not adequately prepared?

Well, this can hardly be the case. In the last five to eight years, the development of the Chinese textile industry took place with the help of textile machine manufacturers, which were predominantly European companies. Between 1994 and 2003, half of all the textile machines produced in the world were delivered to China. In this period, approximately a quarter of all the spinning machines manufactured in the world were also shipped to China. I assume that nobody was a victim of the erroneous belief that these wonderful machines would actually stay packed and unopened in their crates.

It must also be said that the elimination of import quotas took place according to a precisely developed time schedule, starting with the Uruguay talks already in 1995. Thus, in this case we can also say that this particular development also occurred without any real surprises. Any of you who are familiar with the principles of Physics can easily imagine the effects when, effective January 1, 2005, you open the stop valve separating – figuratively speaking – the vessels containing Chinese products being offered on the one hand, and the containers representing demand in Europe and the USA on the other hand. Let me illustrate this for you in numbers. For example, imports of pullovers from Asia leapfrogged by 534% in the first quarter of 2005. In several product groups which ultimately triggered implementation of the safeguard provisions, there was still a tripledigit growth of imports from Asia.

Would it be a viable solution to once again introduce import quotas, as the Europeans did through the WTO security clause, which hastily went into effect as an emergency measure? Is it at all possible to influence global structural changes in the long term by adapting commercial or trade policies? I believe that re-introducing temporary restrictions for Chinese textiles in Europe is certainly understandable when it comes to short-term political considerations, but in the long run, they are surely the wrong response.

Let me explain why.

- First, trade restrictions can easily be circumvented. This was also the case in the past, when, for example, companies transferred manufacturing operations to other Asian countries such as Thailand, Bangladesh or Vietnam, but also re-directed export flows through third countries. A good example is Russia. It is estimated that textile imports from China valued at 7.5 billion dollars are shipped across the border on back roads.
- Second, Europe and, naturally the USA would lose an enormous amount of political credibility vis a vis China. In regards to its membership in the World Trade Organization, remember that we made specific assurances to the Chinese, which must be seen in connection to the concessions made by China as the result of long-term negotiations.
- In addition, there are some fundamental considerations to keep in mind. When you get down to the nitty-gritty, the basis of our economic system is that ultimate success is only reserved for those who can offer products and services cheaper and better than their competitors. Those who operate

efficiently are rewarded with increases in their market share. Those who cannot keep pace are punished with a loss of market share. Our increasing prosperity is based on this principle. For this reason, in a world dominated by H&M, Zara and Mango, women who are fashion-conscious today can afford so much fashionable clothing for so little money in a way which has never existed before. Consumers do not mind at all if the products originate in Asia. The decisive parameters governing their choice are quality and price. Clothing has become an article of daily use, with a rather short life span.

- Furthermore, we should pose the question, whether in fact the wealthy industrial countries should actively encourage the outsourcing of products and services to emerging markets, as a means of ensuring that the people in these countries have jobs and their own income. Let us not forget that there are approximately 40,000 textile factories in China today, which provide employment for up to 19 million people. Most of these workers are women without much of an education, who have migrated to the cities from rural areas in order to find gainful employment. Of course, one can claim that the conditions in these textile plants are close to being exploitative, considering the fact that these people earn less than one dollar an hour for their labor. But what other alternative would there be for them? Either no work at all, work done under even more gruelling conditions or for even less pay than agricultural workers.
- We should also not forget that the children of these textile workers could already become customers for European-made products tomorrow. Increasing prosperity, the current explosive growth in the number of Chinese getting an education - as illustrated by the 4 million engineers who are currently being trained – and investments in the nation's infrastructure make this country unbelievably attractive as a potential sales market.

By the way, we also have to stop making the mistake in thinking that China has only been successful in the global textile industry because of its low labor costs. It is true that labor costs in China amount to about 100 Euro per month, a fraction of what Western industrialized countries pay. However, they are still approximately 30% higher than the poorer countries in Southeastern Asia, such as Laos or Vietnam. The success of the Chinese can be attributed to the way in which they combine the most advanced technologies with efficient logistics, a high level of productivity and the willingness of the population to work hard. Therefore, China has also managed to put pressure on the textile industry in other emerging economies, for example in Central or South America, or in Turkey. And that is the reason why experts definitely consider it a realistic possibility that every article of clothing in the world will be manufactured in China in the year 2010.

To sum up what I have said so far, I believe that the global structural transformation in the textile industry cannot be stopped, even if there must always be winners and losers in times of structural change. It is naturally the challenge of our political system to pay attention to the social aspects of change by passing regulations pertaining to abuse as well as taking accompanying measures. It is also necessary to politically take steps to ensure that society can manage the consequences of this structural change. However, in the long run, as the economic history of the world demonstrates, the final result is more prosperity for everyone through more efficient business operations.

Admittedly, what is different from earlier global outsourcing of production is the sheer speed of change. In previous centuries, national economies also underwent drastic revolutions in their manufacturing structures. However, this process took place much more slowly. One vivid example is Switzerland. Once upon a time, it was one of the world's most important business locations for textile production. In the middle of the 19th century, two-thirds of all Swiss exports were textile products. At the beginning of the 20th century, textiles still accounted for half of all exports. Today, this figure amounts to only 2.6%. In 2004, approximately 150,000 people in Germany were employed in the textile industry, a sharp decline compared to 900,000 workers back in 1970. Nevertheless, even if this structural change was quite a dramatic one, it required a quarter of a century.

The displacement of simple, labor-intensive production activities from Western to Eastern Europe in the steel and mechanical engineering industries or in the automotive sector in the second half of the 20th century lasted one to two decades. This structural transformation – which is still in progress – has been dealt with in a somewhat socially compatible manner. However, the latest opening of our markets for textile imports hit us like the wave of a tsunami. Above all, the textile industry in Southern and Eastern Europe has been impacted.

It must be emphasized that the European textile industry is not a marginal sector. After all, in 2003 the industry employed 2.5 million people in Europe. At the beginning of the 21st century, Europe still ranked among the biggest exporters of textile products in the world. However, in 2004 alone, 165,000 jobs were lost and over 10,000 companies disappeared from the marketplace. This trend will be accelerated dramatically in 2005. This is due to the fact that the remaining jobs are now in danger of being eliminated, particularly in the Southern and Eastern European countries.

There is no way in which we can avoid justifiably accusing European policy makers of not fulfilling their duty, and failing to warn us in due time. Which sociopolitical precautions were taken at a European level? None at all. Was any structural assistance provided to the textile industry, similar to the kind of support which has been and is still commonly granted to other sectors such as agriculture, or the iron and steel industries? The answer is no. Precisely these kinds of measures would be urgently required and I believe it is still not too late to implement them. In the Eastern European region, where labor costs are still attractive in European terms, the attempt is still being made to respond to the challenge of Asian manufacturers when it comes to efficiency, quality and pricing. In this case, assistance would be urgently needed.

But it would be wrong for companies to have to rely exclusively on our political system. European industry must find solutions to these challenges on its own, and it will manage to do so. Even if low labor costs in Asia translate into competitive advantages, we should not forget that labor costs in themselves do not represent the only decisive factor driving success or causing failure.

There are other factors which are absolutely crucial in connection with the success of a given facility or business location, such as the costs of capital, available know-how as well as flexibility in terms of proximity to the markets and how products are tailored to meet the demands of the marketplace.

There are cases in which the textile fiber industry has demonstrated that the globalisation of the value-added chain in the textile sector can be seen as an opportunity and not as a danger. The basis is achieving a maximum level of productivity, a high degree of specialization together with first-class service and delivery reliability. It is no secret that Lenzing AG, for example, has been quite successful in selling large quantities of special fibers to Asia for many years, naturally also on the Chinese market. The only admissible interpretation is that Europe as a manufacturing location can, in fact, compete against Asia when it comes to products which are capital-intensive and which require extensive know-how.

Similarly, there are examples in the downstream textile chain, provided that one does make an appropriate differentiation – that not only can products "Made in Europe" actually survive on the global marketplace, but that the booming economies of Asia can already serve as extremely attractive sales markets. This trend, which is being profitably exploited by Europe's luxury goods industry at the moment, is already evident.

Nevertheless, we should not make the mistake of going into denial about how reality is really shaping up. Because of the structural transformation in the textile industry, sales of the chemical fiber industry in Europe will significantly decline, at least in terms of overall volume.

In this case, the USA can serve as a warning to us. In effect, there is no longer a major market for textile fibers in the country. Since 1995, more than 900,000 jobs in the textile industry have been lost. Obsolete manufacturing facilities, a low level of investments, an unwillingness to embrace innovation along with far-reaching price reductions combined to pave the way for increased imports. It would be quite safe to say that the American textile industry has been downright obliterated by the purchasing managers of large U.S. retail chains such as Wal Mart, which obtain better and cheaper products in Asia.

This process should not be repeated in Europe! We must share the goal of maintaining a considerably smaller industrial structure in Europe's textile sector, but one which is capable of competing and surviving in the long run within the framework of a newly defined business environment.

Of course there are naturally no panaceas. However, there are several core elements of what I would term a new, long-term and future-oriented "cohabitation" between the chemical fiber industry and the European textile fiber industry.

From my point of view, I would like to list five cornerstones of this strategic partnership:

1. Product innovation instead of "more of the same"

2. Authentic creativity instead of facelifting
3. Small instead of large-scale batch sizes
4. Flexibility, not rigid production plans
5. Manufacturing of speciality goods and exploiting niche markets, instead of offering standards and commodities

In this case, the bottom-line is that the fiber industry will play a crucial role, in some areas, towards determining the future of the textile industry. With our innovative strength, we are the ones who embody the beginning of the value-creation chain. If we succeed in creating new ideas and new, high-performance "building materials", figuratively speaking, then the architects and builders who follow us will also be capable of effectively doing their jobs.

How can we achieve this?

- As a start, we should not make the mistake of cutting down on our research and development efforts. Europe has been the technological leader for the textile fiber industry, and still is. All important innovations in the last decades originated in Europe. It should stay this way, because if we give up on R&D, we give up on ourselves.
- On the contrary, we have to once more intensify our research and development work in our industry, in order to maintain this competitive edge in the long term.
- Furthermore, even closer cooperation within the value creation chain is required. We can only manufacture the right products if we, in our capacity as fiber producers, develop a sufficient understanding of the real needs of our end customers. This means that we have to work much more intensively with designers and product developers and also cooperate more closely with our sales people than we have in the past. Even if our customers are spinning companies and weaving mills, it is our responsibility to learn how to think in the way the end-customers do, and thus precisely evaluate the product value for the final consumers.
- Another key point is driving forward an opening of the fiber industry at all levels. We have to be increasingly open to technologies which are derived from other sectors and which can also be applied in our industry, for example in the field of bio-chemistry.
- Next, let me speak about an optimized transition from product development to the production process. The acceptance of innovations in our relatively conservative industry often fails because they are not optimally implemented in limited-lot production. However, those who do not take a risk and experiment will not be able to launch innovative products on the market. Even if it sometimes hurts, demonstrating the courage to fail will be much more in demand in the future.
- In addition, we need a more effective utilization of existing think tanks and above all, better coordination of how these think tanks are used. What I mean is that maybe we are not aware of everything that we actually know. In the future, a decisive factor will be to dialectically link academic and theoretical knowledge on the one

hand with the practical experiences and wishes of the textile chain on the other hand. This is the only way in which we can ensure that our "technological horsepower", so to speak, is efficiently used to drive our industry forward in Europe.

- Besides, we should make it a developmental priority in the fiber industry to improve the functionality of our products. Right now we are in the early stages of developing special fibers for specially-defined applications, for example through incorporation or special after treatments and finishing processes.
- If we succeed in doing this on a much broader level, then we will manage to create a stable basis for Europe's fiber industry to be able to quickly develop even more into a provider of speciality products. Even with small-size production batches, we can generate attractive, long-term returns on our investments. In addition, specially-made products can not be so easily copied and are not as interchangeable as standard products with low margins.
- My last point involves discovering new fields of application for textile fibers. We have already succeeded in opening new markets for textile fibers in the non-woven sector. We have been able to quickly observe the success of this strategy. It is precisely the markets in the developed industrialized countries which have opened up exciting growth opportunities in the nonwoven sector. Even in this respect, we have to already begin thinking about which markets we want to capture the day after tomorrow.

In conclusion, I would once again like to emphasize my view that the European textile fiber industry will only have the chance to persevere if it succeeds in maintaining its role as a trendsetter in the world. My vision of the future in ten years time is to have our industry emerge as a small but highly innovative and creative industry in Europe, one which manufactures more premium products. And it will continue to serve as a technological know-how provider for our "followers", no matter in which part of the world they live. This is quite a difficult path to tread, because it will definitely entail far-reaching adjustments in production capacity in Europe. Nevertheless, there is no real alternative.

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OVERVIEW ON LATEST DEVELOPMENTS IN VISCOSE INDUSTRY

Follow up of trends and prospective future developments in technology and equipment used in viscose industry.

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Summary:

The fast growing capacities in fiber raw material world wide, where viscose fiber is a part of it, is reflected by the international market of textile application and end uses to a immense extend.

This paper introduces the impact of the technologies and state of the art of equipment used for processing viscose / cellulose products, the innovative aspects and developments achieved in the past period to make the producers to stay competitive in the market. Some of them have made big efforts to cope up with demand of the market either from quality point of view or have increased capacities for the same reason or have been in the position to do both.

It shall also highlight the relation between the viscose producers and the suppliers of those innovative and advanced equipment to comply with the needs to challenge the future of both, producers and suppliers.

Lot of efforts have been spent by almost all of the viscose producing companies and their suppliers of equipment and technology to reach the status of today. The big achievement is looking into the fast growing capacities as well as the outcome in terms of range of fibers and qualities world wide.

This paper deals with the relationship between the producing companies and their suppliers of technology and equipment and how variable the benefits for both sides will be if they are doing the cooperation in different ways. This paper also gives space to elaborate on several approaches which have been used by the parties in the past . When we consider the results of those approaches, some of them can be taken as guidance for new and promising outlook as well.

This paper tries to find some aspects from the position of an engineering partner which is quite successfully active in the field of viscose / cellulose processing.

We are taking a look at the following main chapters:

1. Improvement in quality versus increase of capacity
2. Competition between innovativeness and imitation of design
3. Latest developments of equipment and technology
4. Environmental Solutions for Waste Gas Handling
5. Outlook into prospective equipment and systems for viscose production

Improvement in quality versus increase of capacity

A wide range of experts discussed already the issue of whether quality improvement is the first top aim of a producer to strengthen its position in the competition amongst regional and international producers. Or is capacity increase for the same product range the only way to lower the production cost sufficiently?

Both ways need to be considered carefully for individual decisions.

- In low price periodes only those manufacturers can survive who are able to offer better quality for cost competitive prices
- Cost competitive prices only can be achieved with well adopted technologies and best quality equipment.

The maximum possible capacity of a system depends on the capability and reliability of the equipment used. Capacity increase can not be achieved by just adding same equipment as already in use to a so called multiple arrangement. The reason for such an approach is sometimes to avoid changes in spare part and wear part handling. For sure there is an economical measure to some extend but it has a limitation which is simply calculateable. The cost / price relation is lost over a certain extension and handling limitations take place along with losses on chemicals, energy consumption, etc.. Even building space is limited as well.

The ideal advice is the aim to improve the quality first or at least not to accept a certain reduction or deviation of that. Second is to study the best project arrangement for capacity increase but to consider the innovations in equipment and technologies adopted by different sources in the market in meantime.

Competition between innovativeness and imitations in design

To summarize the numerous discussions regarding the issue of whether innovation will pay off against imitations of equipment or the local made developments, we found a very clear statement during our evaluation with the leading companies:

- Innovation is still the goal for all active producers to stay competitive with their own product in the market and to be close to the product chain up and downstream.
- Imitating of technology and equipment to reduce investment cost by saving cost for development of better quality of goods or technology does not pay off on long term.
- Imitations are simply copies of ways and measures which have been adopted by others. In meantime they are for sure ahead in terms of product range, quality and technology, etc., and run most probably a better business.
- The approach via innovation is based on a clear strategy with defined aims. Products are produced for a prospective future market and with expectable prices in order to ensure the efforts will become feasible.
- The key is a clear defined aim for a strong position within the range of competitors and the market demand and everybody does it - *Competition is all the time involved but need not to hurt all the time. At least when market is eager to get good products with good quality.*
- Innovative companies like those in Europe have met the demand of market by both, quality of products and cost competition. Same conception can be used by others as well who would like to compete the market instead of the competitors.
- The different approach via imitations is most of the time aiming to compete the prices of goods which are already introduced to the market. Different companies have thought about this approach as like: we know the market better, we can get the market share by increasing our output, we can invest cheaper than others can do, we can do everything better, a.s.o. At the end this approach will end up in price dumping which is not at all

good for quality products. Finally the market will lose its interest in cellulosic fibers.

- At the same time, and this is made evident, the interest for innovations is going to be reduced on long term. Further the approach via imitating competitors and technology leaders does not give an additional step in quality of the end product. The aim will be achieving simpler equipment or simpler technological solutions and both can not find the acceptance at the user end.
- Conclusion as above: in low price periodes only those manufacturers can survive who are able to offer better quality for cost competitive prices.

Latest developments of equipment and technology

The active suppliers of equipment and technology for the range of cellulose process plants like viscose staple fiber, viscose filament, sponge, films and casings, etc., can be divided into the major groups:

- **Local suppliers** in the producer´s countries, who have made their experiences there on their local market in the past.
- **Equipment suppliers** around the world who have been involved in the past because their capability to offer large project packages and equipment for process has been a sub contracting issue.
- **Engineering companies** around the world who are capable to offer only equipment
- **Engineering companies, like LENZING TECHNIK**, having their back up from their competence as engineers of an competitive fiber producer with active programs for innovation and development of process and equipment to cover the needs of future market demands. These kind of Engineering companies have a sincere interest to be involved in active projects. The main reason is for sure to make some business. The frame for such cooperation has been given earlier in this paper.

Local suppliers have their biggest advantage in their ability to compete the later one because of their cost structure. Their main disadvantage is the lack of any new innovations. as their focus goes for the more or less copy of existing systems rather than for new developments. The final result has been explained above.

Individual producers can organize project management by their own and financing issue is also no more a big problem. Everyone can call the suppliers directly and there is no need of a general contractor any longer, even not for spending additional risk money for the whole package.

Engineering companies do a very good job world wide. The implementation of new equipment needs some experience to make modifications more feasible for an active producer.

We would like to introduce the range of the newest developments on equipment and technology offered by Lenzing Technik to make the job easier for the respective producers. The following list represents just a short glance of the entire range of systems:

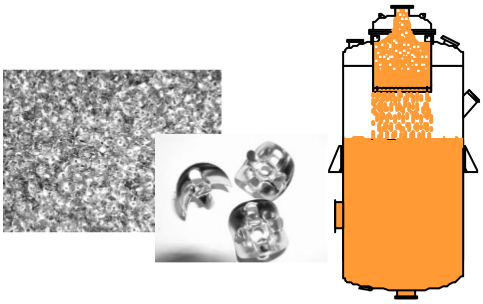
- **Homogenizers for Viscose (Staple and filament as well):**
  - Used within the viscose preparation process to homogenize the viscose for quality improvement. Many of our Homogenizers are in operation at viscose producers because of it´s low specific power consumption, the quality level and reliability. One further development concentrates on the attrition disks for further improvement of the existing LENZING TECHNIK systems.

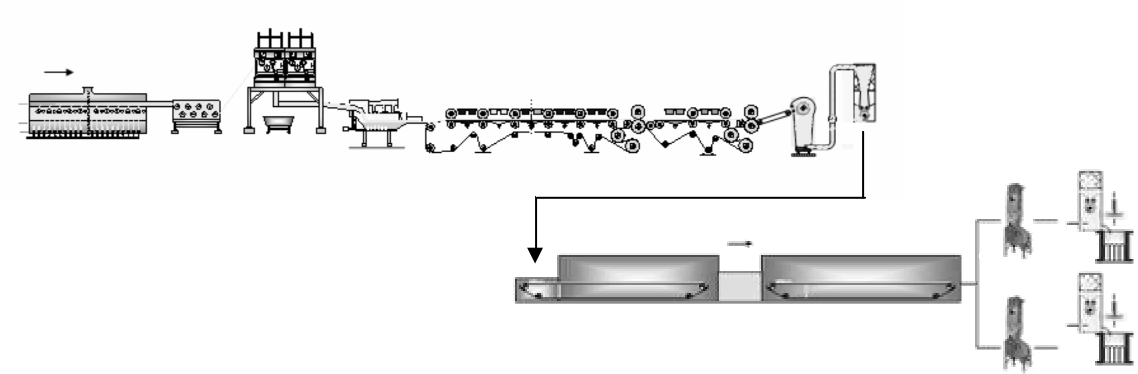
- **Wet Churn (Xanthator) (Staple and Filament as well):**
  - The Wet Churn by LENZING TECHNIK is a unique equipment for xanthogenation of alcali cellulose in the viscose preparation process.
  - We have proved a lot to the capability and reliability in the meantime. LENZING TECHNIK offers its equipment for any kind of viscose solutions required from several aspects of the process as per the experience of the producers. The range of standard equipment size is given in our brochures. Customized solutions can be offered on demand. Increasing the specific production capacity is an ongoing process, which shall not only be utilized on installing bigger equipment.

- **KKF 20 Viscose Filtration (Staple and Filament as well):**
  - The KKF-system is a fully automatic, continuous back flushing system using the principle of depth filtration.
  - The system introduced by LENZING TECHNIK has been accepted by the market of being the contribution to the demand for higher production capacities of the last period.
  - The position of our KKF Viscose Filtration system has been confirmed by the market now for many years to be the market leader in terms of quality and reliability and we are proud of that.

- **Deaerator for viscose (staple and filament as well):**

  The equipment is made to remove the dissolved air and small quantities of air bubbles containing in the viscose. Looking into the existing solutions which are already in operation there is still the demand for a more efficient equipment to eliminate / reduce the air bubbles from the dope. The system offered by LENZING TECHNIK has the capability to fulfill the target and can do it in the best economical way also.

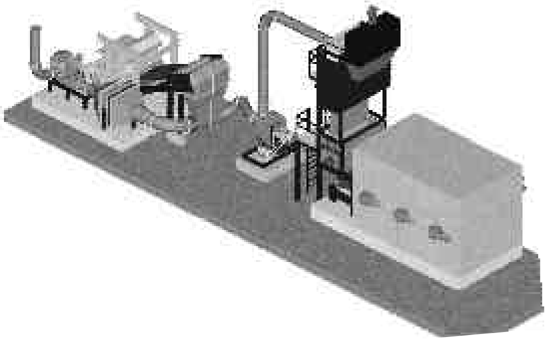


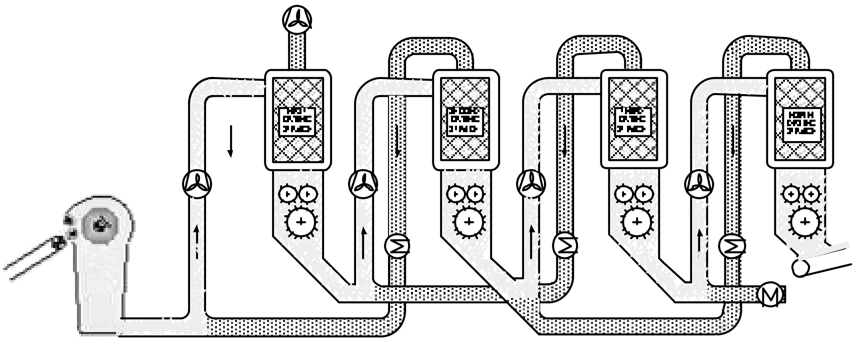


- **Staple Fiber Line 60000 t/y capacity:**
  - This new conception is made for viscose staple fiber spinning.
  - Specific highest capacity per unit offered at date for an economical investment approach.
  - A lot of advantages but the major advantage is the fast ROI and lower specific production cost.
  - For companies which are already settled in the market this line is a stable production with attractive fiber range and prices.
  - Further capacity increase might be possible but some debottle-necking or reengineering needs to be done in parallel in viscose preparation, spin bath circulation, etc. as only multiple arrangement of the involved equipment in these sections might not be the solution.

- **Blow Feed Dryer:**
  - This equipment was developed to simplify the wet opening step in the fiber process line including a drying step for the staple fiber before entering the final dryer.
  - The system provides the advantage of equal distribution of the fiber mat over the working width including reduction of wet spots.

- Simple in implementation but best result in terms of return of investment
- Improving the flexibility of those plants already on the peak of its capacity and space for additional dryer is limited.





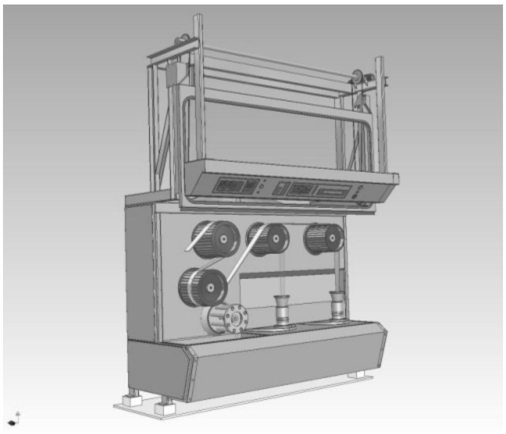
- **Multiple Stage Blow Dryer for Staple Fiber lines:**

  - This equipment will be a new innovation to replace existing drying systems for staple fiber.
  - On basis of the results from the Blow Feed Dryer an adequate fiber dryer will be the next step in our equipment range for the future.
  - Introducing 3-stage dryers in order to save building space and investment as well as to reduce handling costs (or make it simpler).
  - The results of our tests are encouraging enough to concentrate on such a track.
  - Innovations as introduced by other suppliers are going into the same direction.

- **Enlarged Spinning Heads for Staple Fiber Spinning:**

  - In parallel to the development of the line capacities studies have been made in order to have the right spinning heads available when the equipment for the line is ready.
  - In earlier speeches and papers we have already given an outlook into this direction and we can confirm that we are in the position to offer different sizes of spinning heads now.
  - The trend is going for larger capacities per unit. This is in line with the trend of enlarging the specific capacities of spinning lines as well.

- **Fiber Cutter for enlarged capacities:**
  - The new fiber cutter system is designed for highest cutting quality on wet cutting basis for viscose staple fiber processing.
  - This will be the answer to the demand of the market as to some extend the single line capacities have reached tow thickness of close to 12 Mio dtex. Some companies made trials in this range but the successful solution is still not yet offered.
  - LENZING TECHNIK shall keep its promises and will introduce a new design for that purpose in very short time.
  - A new design for such a new system is not the problem of the engineers on the job at all. The question mark is on the assemblies of a new design which should be compatible with the existing systems to reduce spare & wear parts stocks.



Environmental Soluition for Waste Gas Elimination

- **BioGat of LENZING TECHNIK:**
  - This system has already been introduced for several applications in processes containing CS2 and H2S in their off gases.
  - Experiences on our pilot plant as well as our BioGat reference plants have proved that a wide range of CS2 and H2S concentration can be handled and fluctuations of feed concentration and loading rates do not affect the viability of the biology.
  - Furthermore, shut down periods are not a big problem for the biological system.
  - Compared to other processes (e.g. catalytic adsorption), investment costs are significantly low. Additionally, the process works at temperatures between 28 and 35°C and average pressure drop doesn't require neutralisation of the acidic products. Hence this fact, the operating costs (running costs) are lower compared to other systems.
  - The exhaust gases are converted into non - toxic compounds.
  - Besides the excellent introduction of our waste air elimination system called „BioGat“ of Lenzing Technik we are on the way to cover other applications outside the cellulose field as well. Our joint and enhanced cooperation with leading universities will be the link

to those applications which might be

Dimethylsulfid, Dimethyldisulfid (DMS, DMDS)
Methamercaptanes (MM, Methanthiol)
VOCs (volatile organic compounds, e.g. solvents).
Alcohols, Ketones, Aldehydes, Hydrocarbons, etc.
Compounds containing reduced sulphur;

Please consider our fully equipped pilot plant for any principle tests to be done before a decision is made for a new large scale project.

Outlook into prospective equipment design and systems for viscose production

An outlook into prospective future for systems and equipment required for viscose production can be made in a very simple way:
There will be a demand for modification in existing productions all the time and also a demand for total production lines in order to cope up with strategic wish of the individual companies to strengthen their position.
The trend for the most economical approach but to consider the proper innovative equipment and technology will continue for a long term period.
So there will be an adequate space for innovations all the time and these will concentrate on:

- Enlarging further specific capacities per equipment unit / process section
- improvements in reliability of equipment and process for higher plant capacities
- local sourcing of adequate supplies

The contribution from the equipment suppliers will be to keep their awareness for the needs and to search for technical and technological solutions in order to satisfy the request from the producers.

The remaining aim is to have the suitable solutions ready all the time. The contribution of the market will be to encourage the suppliers to remain flexible and innovative as well.

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Hans Weber
Lenzing Technik GmbH

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Lenyinger Berichte, 84 (2005) 17-21

SCIENCE INNOVATION & ENVIRONMENTAL PROTECTION

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Profile of NCFC

Nanjing Chemical Fibre Co., Ltd (**NCFC**) is a middle-sized viscose fibre manufacturer. It was put into production in 1964. The shares of **NCFC** have been being listed in Shanghai Stock Exchange since 1996. Employing 2400 people and with an annual capacity close to 45,000 tons for fibres (and a relative sum for pulp), the company has all necessary utility and auxiliary facilities. These years, we have made great efforts to survive and grow near a famous and important city under a market-economic system.

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1. Viscose Fiber Production in China

China's rayon industry began in 1950s. It grew up in the later decades. Impacted by high growth of synthetic fibres, however, during the period from the middle of 1980s to the end of 1990s, the growth of rayon fibre in China is very low as the case in the world. Minus growth even occurred with the staple fibre. Fig.1 shows the production trend of cellulosic fibres (mainly rayon ones) in the world.

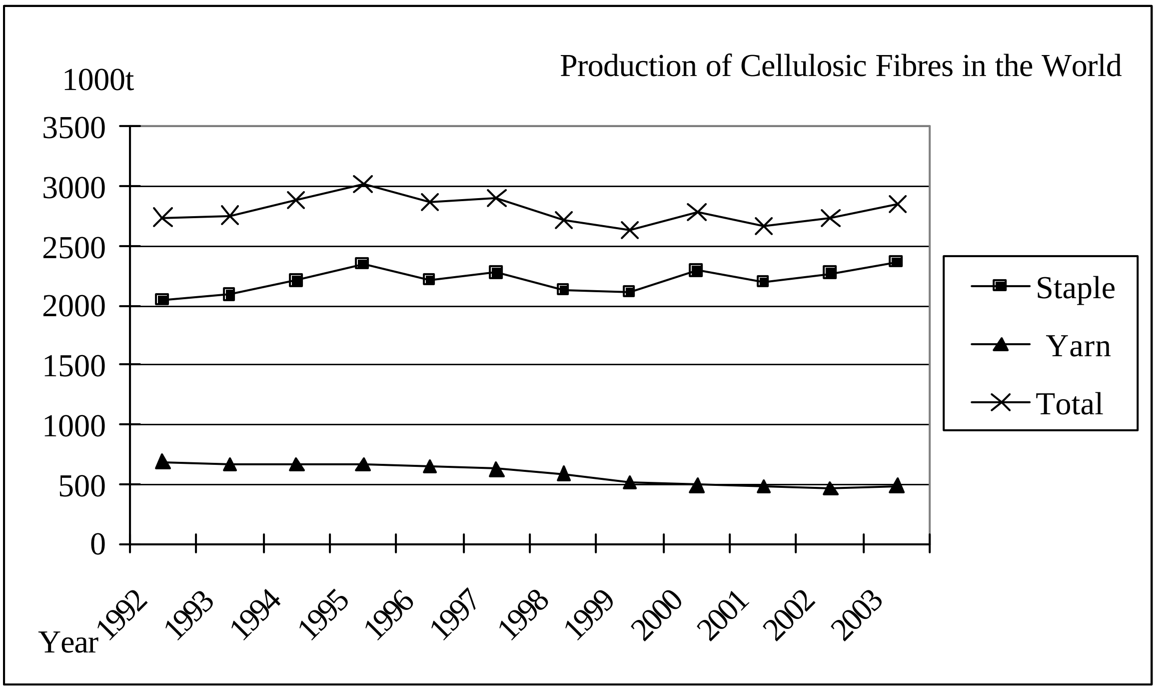

Figure 1. Cellulosic fibres yield in the world

Facing to puzzlement, enterprises in China strived hard to pave a rough road for their development. And rayon industry in China has got a rapid growth since the beginning of the new century. From 2000 to 2004, China has averaged 14.3% per annum growth with viscose fibre production. Fig.2 shows the total yields of viscose fibres in China for recent years.

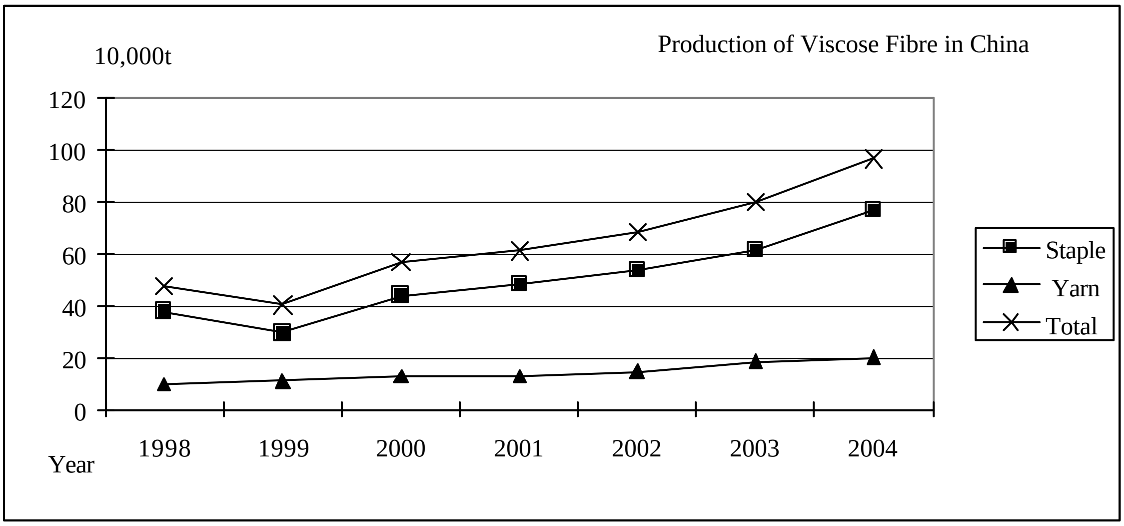

Figure 2. Viscose fibres production in China

How can we reach the situation? From the experience of NCFC, maybe you can comprehend the important role of innovation and environmental protection.

2. Science Innovation and Environmental Protection in NCFC

In the end of last century, turnover of NCFC is very limited. To progress in step with our country’s economy, great efforts were made.

2.1. Innovation of Viewing and Analyzing

- Viscose fibre is made from natural material; therefore it is excellent for comfort of wear. Another important fact is that its disadvantage can be covered by the combination with other synthetic fibres.

- Raw material for viscose fibre comes from the nature and is reproducible. So we don’t rely too much on crude oil for the fibre.

- Domestic fibre demand increases continuously because of the growth of GDP and population. The lure of more opportunities in the post-quota world market also leads to demand growth on chemical fibres. Fig.3 shows citizen consumption of chemical fibres in China.

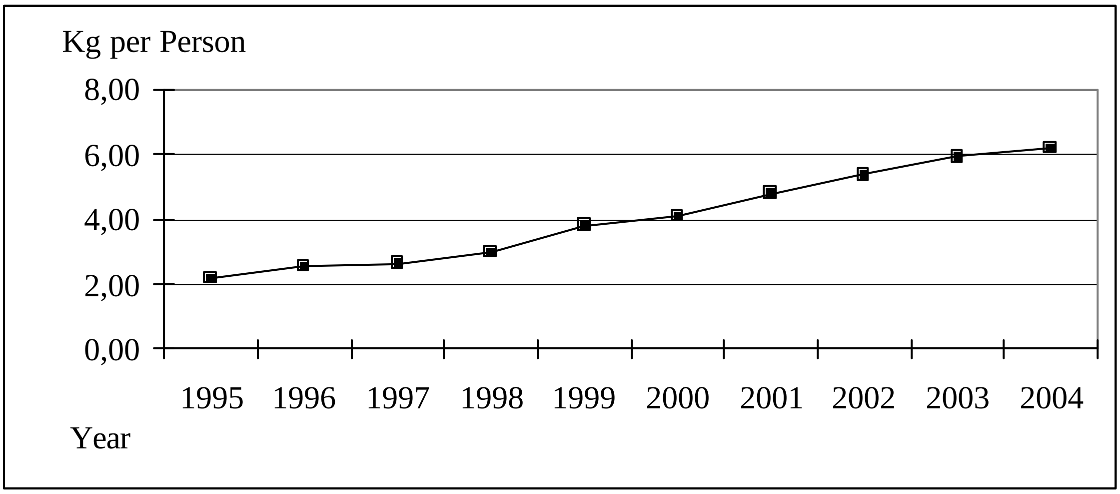

Figure 3. Citizen consumption of chemical fibres in China

- Profitability of viscose fibre was analyzed seriously. Around the end of year 2000, there was a price margin of about CNY5000 per ton between staple fibre and pulp. That is space for processing cost. Though many plants were operated in the red then, we thought we could do some things. We still have potential in costs of electricity power consumption, steam consumption and manpower. We've tapped the potential very well. Fig.4 and Fig.5 show the prices and price margin for viscose staple fibre in China.

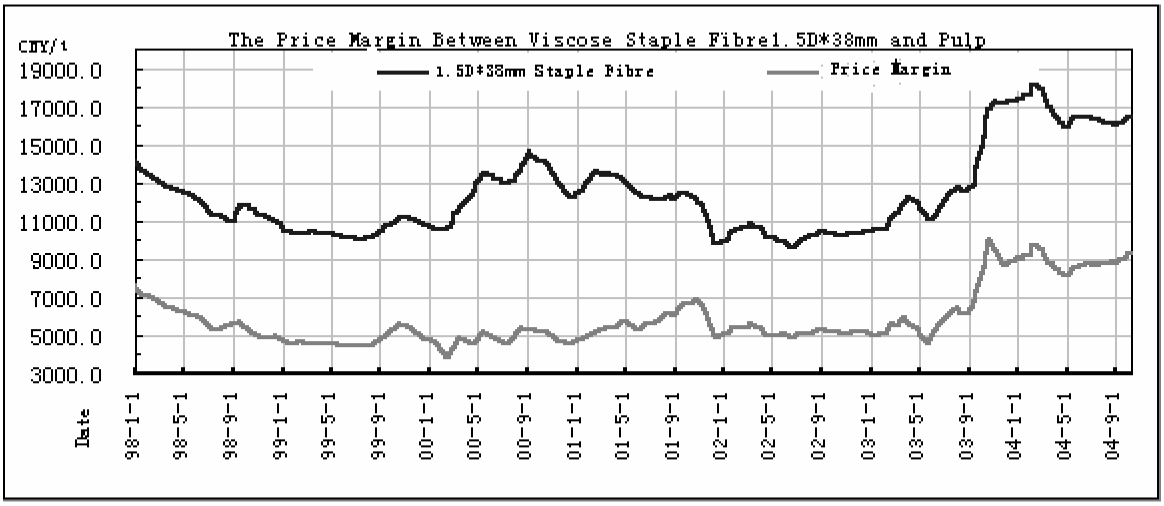

Figure 4. Fibre price and the price margin between staple fibre(1.5D×38mm) and pulp

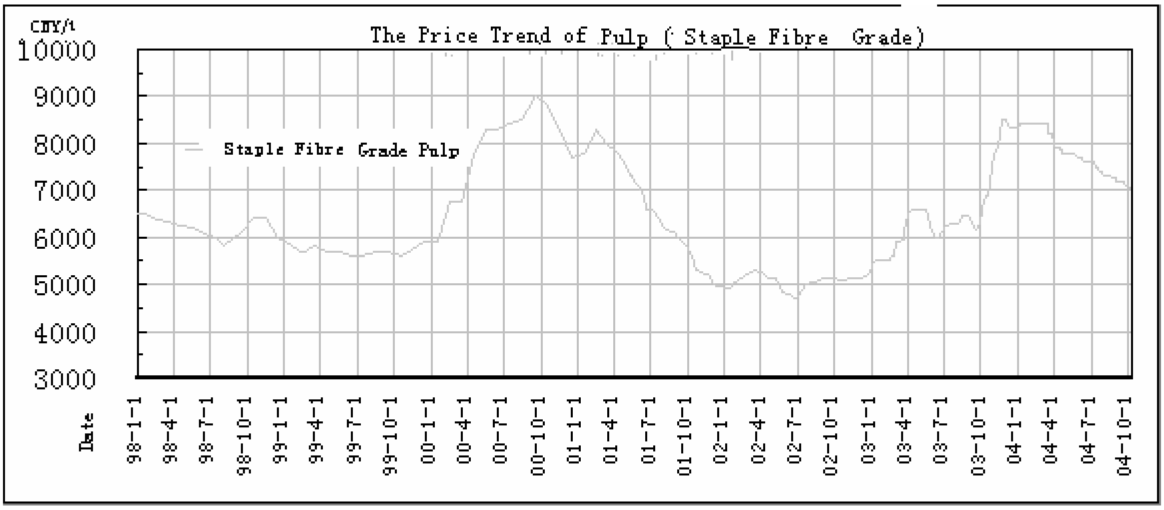

Figure 5. The price trend of pulp

2.2. Technical Innovation

It is key important to increase production capacity in the same time improve product quality so as to run a line with profit. In the end of year 2000, there were two production lines for staple fibre with capacity of 5000 t/a each in NCFC. Then one was shut down, the other was operated at 1000 t/a. We expanded the stopped line to a greater capacity of 30,000 t/a.

- Reconstruction was speeded up a great deal. In the May of 2001 we made the decision to expend the line, and we re-started the line with the new capacity in the November of 2002.

- Machines of high capacity were applied, some of them even be first use in China. For example, we made an AC press of 1800 width to get a high capacity of 15,000 t/a, a chain-plate type ageing box and a belt type dryer to 30,000 t/a. These machines were made in China, and therefore investment could be controlled to a low level. A 2-step continuous filtration system was an innovative philosophy to us then.

- Some key machines were imported from Lenzing Technik to guarantee high quality of product and lower cost for manpower. As a result, Lenzing's wet-churns, rough homogenizers, flash deaerator, KK filters and after-treatment machine have played an important role in our new line.
- A modern DCS control system was introduced in the new line so that outdated process-managing mode was improved.

2.3. Attach Importance to Environmental Protection

Environmental protection is an invariable theme, especially for viscose industry. Because of it, viscose industry has declined dramatically in many industrialized countries. There are so many difficulties to eliminate pollution to environment with viscose fibre production.
Chinese governments at all levels attach importance to environmental protection. Instead of riding the fence and playing at policies, NCFC has poured a large sum of money into treatment facilities for effluents these years. Treatment to waste water has been being intensified phase by phase. In the same time we concentrated on easing pollution to the air. We found some solutions:

- Water consumption per ton fibre is reduced more than 60% by means of more recycling of water. For example, there is very limited wastewater now in filtration sector because of the process innovation. Water from flash deaeration of viscose and flash evaporation of spin-bath is fully recycled.

- Off gas from degassing of spin-bath is treated within a wet desulfurating system for the filament lines. Purified sulphur is produced.

- With staple fibre plant, incinerating in incinerator and burning in boiler of power plant is implemented for rich and lean off gas respectively. It was not easy for us to find these solutions.

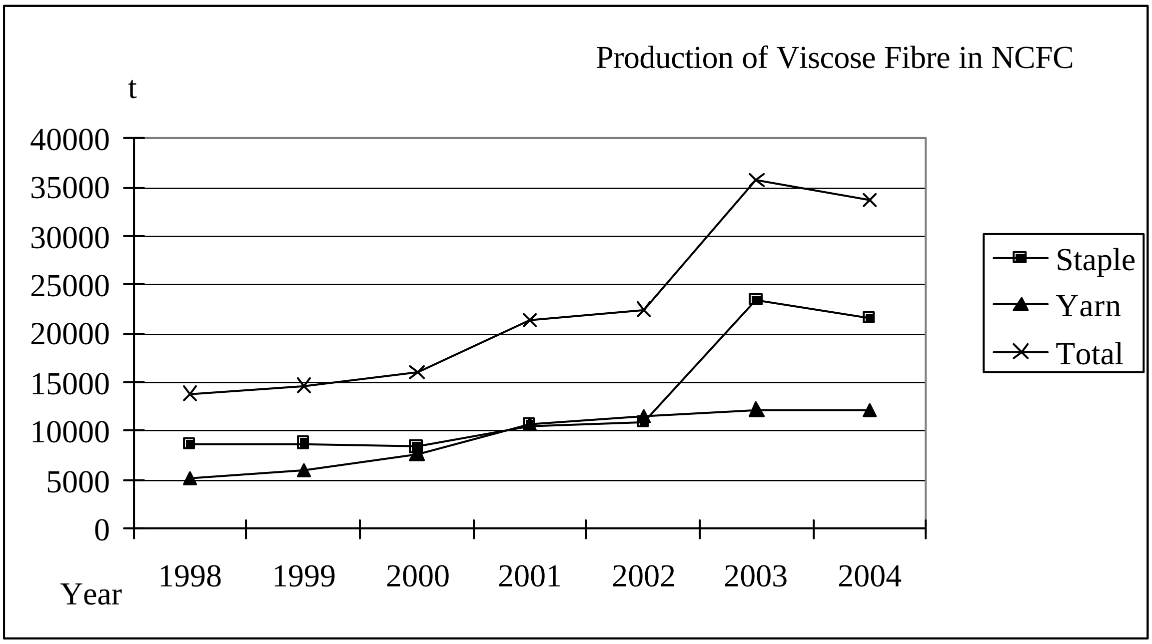

Figure 6. Production in NCFC

3. Conclusion

Science innovation and environmental protection bring NCFC possibility to survive and opportunities to develop. Fig.6 shows the production situation in NCFC for these years. What most important is that the comprehensive economic efficiency of NCFC is much better than before. We are now more confident of development to viscose fibre. The information should be aired to the world that China’s viscose industry is not developed in price of sacrifice of environment. Science innovation and environmental protection are source drivers for the development.

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NEW DEVELOPMENTS IN THE USE OF ADDITIVES IN THE VISCOSE INDUSTRY

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1. Introduction

Akzo Nobel has a strong tradition of close working relationships with rayon manufacturers. In the design of our additives, considerable attention is given to actual market requirements and feedback from customers and potential users. In this paper, we shall briefly describe two of our recent developments, one in the area of spin bath dispersants and another in the field of modifiers.

2. SPIN ADDITIVES – New Developments of the Berol Spin 668 Concept

Since some years ago, Berol Spin 668 was first introduced to the market as a stable spin bath dispersant, compared to traditional dispersants. Performing as an excellent dispersant in highly acidic and hot spin bath systems, Berol Spin 668 is stable towards hydrolysis in such conditions and remains soluble even under high temperature (like in evaporators), unlike most commonly-used surfactants.

As an amphoteric, Berol Spin 668 is cationic in the acidic spin bath systems but in the after-treatment steps where conditions are less acidic and even alkaline, it turns from cationic to nonionic (pH 1-3), and eventually becomes anionic (pH > 3).

Its properties vary with pH according to the table below:

pH		Dispersion Power	Foaming	Solubility	Wetting Speed
<1	Cationic	Very Good	High	High	Low
1-3	Non-ionic	Poor	Low	Low	Low
>3	Anionic	Moderate-Good	High	High	Low

Worth notice is that in the final washing steps, Berol Spin 668 becomes anionic. This should be beneficial for the washing processes of the regenerated celluloses. These negatively charged spin bath additives adsorb onto hydrophobic material, thus hindering their re-deposition onto negatively charged regenerated cellulose material.

The amphoteric nature of Berol Spin 668 also affords an improved environmental profile of wastewater discharged from rayon plants. Further details are reported in 2.1 below.

2.1 The Envinronmental Profile of Berol Spin 668 in Wastewater

As environmental regulations on wastewater released into natural water bodies become more stringent, we have heard increasing appeals for additives with improved environmental profiles. In cooperation with a viscose producer, Berol Spin 668 was analysed using various standard wastewater test methods, and compared against a conventional spin bath additive.

The following standard tests (modified) were run and results shown below:

Test (a) 5540 C: Anionic Surfactants as MBAS (Methyl Blue Active Substances)

For the diluted sample containing Berol Spin 668 (20 ppm), the MBAS equivalent content is 0.21 mg/l (= 0.21ppm). Traditional spin bath dispersants are not expected to be tested positive under this test.

Test (b) Cationic Detergents as Bromophenol Blue Active Substances

Product	Absorbency at 404nm
200 ppm Trad. Spin Additive	0.315
200ppm (active) Berol Spin 668	0.065
Blank	0.037

Test (c) 5540 D: Nonionic Surfactants as CTAS (Cobalt Thiocynate Active Substances)

Product	Absorbency at 620nm
200 ppm Trad. Spin Additive	1.531
200ppm (active) Berol Spin 668	0.01
Blank	0.004

As seen from the results above, Berol Spin 668 outperforms cationic spin additives traditionally used by rayon plants in the detection tests for cationic and non-ionic surfactants (tests b and c). In fact, Berol Spin 668 is almost non-detectable. In the test for anionic surfactants (test a), Berol Spin 668 is detectable only to a very small extent (1%).

2.2 Plant Experiences with Berol Spin 668

The multi-fold advantages of Berol Spin 668 stipulated above have motivated several full-scale plant trials over the past few years. Their experiences have mostly been positive and shall be discussed below.

(a) Staple Fiber Plant 1

This was one of the first plants to try to replace a conventional spin additive with Berol Spin 668 during a trial in the mid 1990s. After some efforts initially to cope with some issues (e.g. foaming and low wetting), the plant witnessed some changes over a few years. For one, the plant required far lesser dosage of Berol Spin 668 and found cleaner systems overall, including the spinning sections, evaporators and CS2 boxes.

In the initial trial period, even though fibre properties and spinning behaviour were unaffected, foaming was a problem in the evaporators, leading to difficulties in the gas scrubbers. This problem was later resolved with the use of Berol Visco 370 to control the foam.

Another prominent improvement seen was the drop in the number of black particles in a fibre product produced on the trial line over time as shown in the graph below:

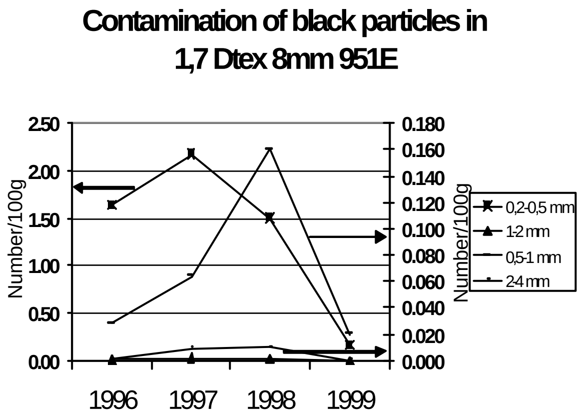


Figure 1. Number of black particles per 100g fibre of quality 1,7 Dtex 8 mm 951E.

(b) Rayon Cord Plant

In this plant, the changeover from the then-used spin additive to Berol Spin 668 took place in a few small steps over a few months. One clear observation was that hard deposits were found before the trial became softer and were easier to scrub off. There were also significantly less deposits in the spin bath pump suctions and pipe lines. Spin bath clarity showed some positive signs of improving.

The flip side to this high dispersion power of Berol Spin 668 was that particles were dislodged at a higher speed and as a result, sand filters were overloaded and had to be cleaned more religiously.

(c) Cellophane Plant

The plant has been using Berol Spin 668 for almost a year. The experience was unequivocally good — Spin baths on machines looked much better, with heating coils looking particularly clean. The period between evaporator cleaning extended from 10 days with the old spin additive to 5 weeks with the new Berol Spin 668 system. The deposits also became easier to remove.

The only negative observation has been excessive foaming, in the acid bath, but above all in the effluent water. With the use of suitable antifoam aids, the foaming problem subsided to a suitable extent.

(d) Staple Fiber Plant No. 2

This plant is still undergoing the trial and so far, no clear advantages/disadvantages could be observed with the use of Berol Spin 668 as opposed to the traditional spin additive. Foaming became more obvious and there were fluctuations in the spin bath clarity. However, due to fluctuations in several other plant parameters during the trial, their relationships to the use of Berol Spin 668 were not conclusive.

3. MODIFIERS – Stability and Solubility

In recent years, as the complaints of black coloured particles contaminating the viscose production system soared, we studied the stability and solubility of modifiers, which are sometimes added in substantial amounts to the viscose, especially in the production IT fibers.

3.1 The Stability and Solubility of Traditional Modifiers

Process surfactants are believed nowadays to degrade under certain conditions. Especially of interest are the literature reports that ethoxylate chains typically found in modifiers undergo thermal degradation (oxidation) under high temperature and acidic conditions (less than pH 6).

The extent of degradation of traditional modifiers was tested by refluxing the product for 6 days under sump zone conditions (100°C, mildly acidic). The results are reported below:

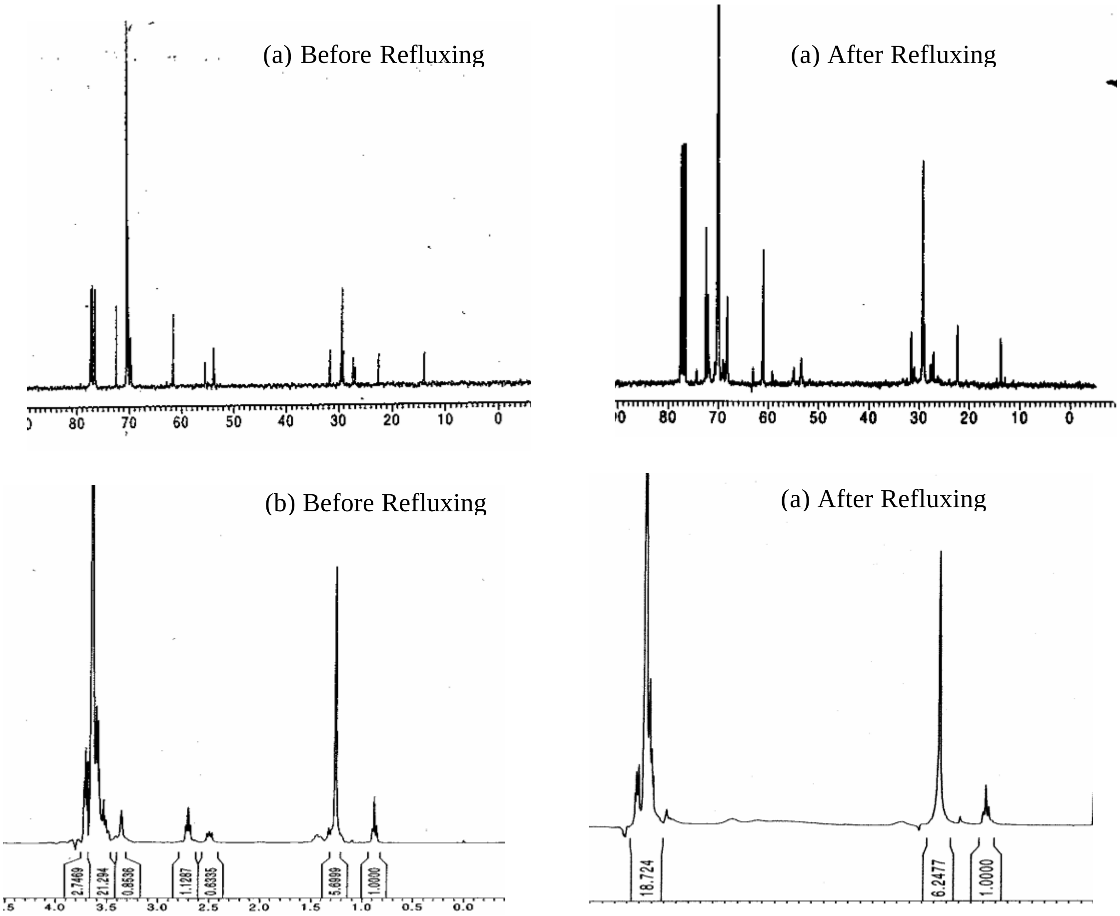


Figure 2. (a) C13-NMR and (b) H-NMR, profiles of a modifier before and after refluxing for 6 days under sump zone conditions (100°C, mildly acidic).

In Fig. 2, signs of structural degradation were apparent after the treatment, with a messier C13-NMR profile (with a drop of some peaks and the appearance of some small peaks), and a lost of 2 prominent peaks in the H-NMR profile.

Degradation of modifiers can lead to insoluble degradation products that could lead to clogging in the long run. This was demonstrated when a spin bath containing 100 ppm of a modifier turned cloudy upon 24 hour reflux and light-colored resinous material was found stuck to the sides of the glass flasks.

Further, we have also found that common modifiers have normally limited solubility in the spin bath. This aggravates the clogging and black particles situation.

3.2 Berol Visco 641 – A More Stable and Soluble Modifier

As discussed above, traditionally used modifiers have the disadvantages of being unstable in the long run and having limited solubility. Replacing the traditional additives (partially or fully) with a more stable and soluble modifier like Berol Visco 641 can avoid, to some degree, the formation of black particles. Fig. 3 below illustrates the higher solubility of Berol Visco 641 in spin bath against the traditionally used additive:

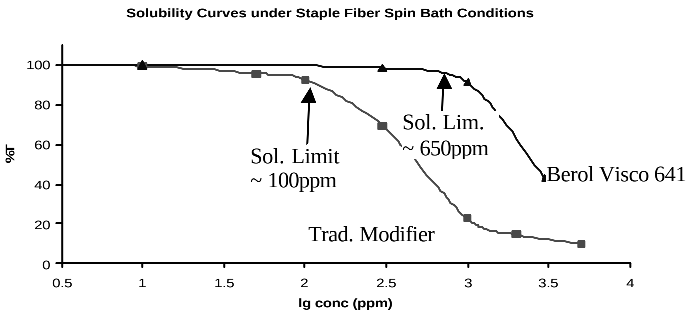
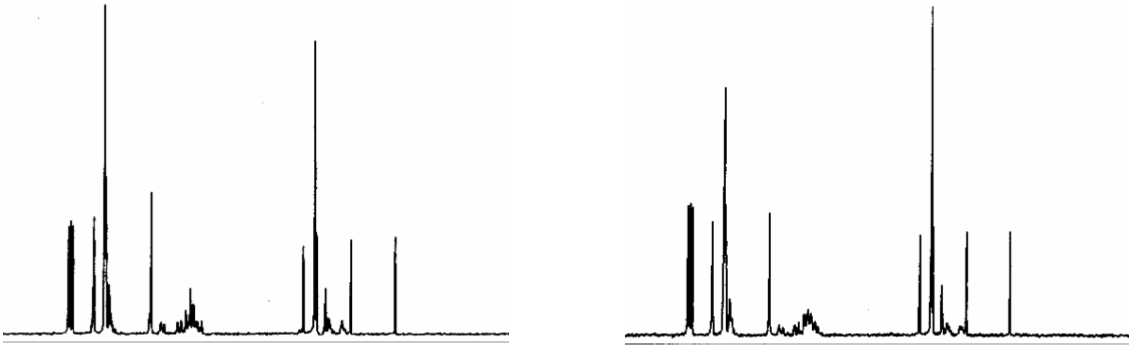


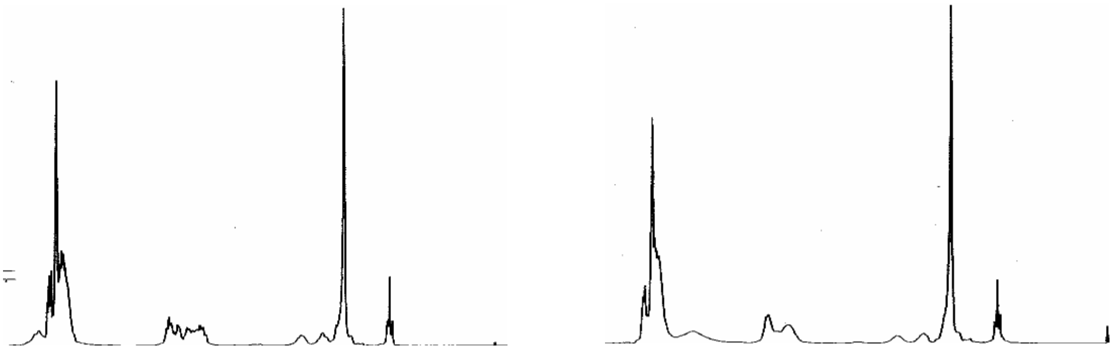
Figure 3. Comparing the Solubility of Traditional Modifiers vs. Berol Visco 641.

Another advantage of Berol Visco 641 over traditional surfactants is its relative stability, as illustrated by Fig. 4 below:



(a) Before Refluxing

(b) After Refluxing



(b) Before Refluxing

(b) After Refluxing

Figure 4. (a) C13-NMR and (b) H-NMR, profiles of Berol Visco 641 before and after refluxing for 6 days under sump zone conditions (100°C, mildly acidic).

Referring to Fig. 4, after refluxing for 6 days under sump zone conditions (100°C, mildly acidic) Berol Visco 641 appeared to have retained much of its structural integrity, unlike traditional modifiers which showed signs of degradation after the same treatment (See Section 3.1).

The relative stability of Berol Visco 641, when used to partially replace conventional modifiers, has two advantages:

1) Less insoluble degradation products will be formed,

2) Sulphurous particles released during harsh conditions (e.g. in evaporators) due to decomposition of traditional modifiers would be re-dispersed by Berol Visco 641 and not adhere much on equipment. In the experiment mentioned in Section 3.1 above in which a spin bath solution containing 100ppm of a traditional modifier was refluxed for 24 hours, the addition of 50ppm of Berol Visco 641 prior to reflux helped reduce the amount of clogging material on the glass surfaces, with particles more dispersed in the liquid.

4. Conclusions

Through co-operations and full-scale plant trials, we have learnt much about the practical use of the Berol Spin 668 system. In most of the plant trials cited above, the advantages of this system were apparent, and Berol Spin 668 has been used commercially since. On the other hand, the development of Berol Visco 641 as a modifier is still in its infancy. From our initial studies, we believe in its potential as a stable and soluble performance modifier, and are committed to its development over the next few years.

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OXIDATION OF REDUCING END GROUPS IN CELLULOSES ACCORDING TO DIFFERENT PROTOCOLS

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ABSTRACT

The recently established fluorescence-based CCOA method provides carbonyl group profiles, reporting both aldehyde and keto functionalities [1]. To assess the state of oxidation even better, a differentiation between aldehydes – mainly present as reducing end groups (REGs) – and keto groups would be very attractive. Our approach to distinguish those groups in cellulosics was based on the oxidation of the reducing end to the corresponding acids, leaving behind only keto groups for CCOA profiling. Hence, the overall carbonyl profile was monitored before oxidation, and a keto profile was obtained after the oxidation step. Two procedures for the oxidation of REGs have been tested: the formazane method [2] and the oxidation by silver ions [3]. Both approaches have been thoroughly evaluated to address the degree of conversion and the effect on the molecular weight

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Introduction

The main causes for the formation of carbonyl groups in cellulosics are isolation, processing, and purification procedures. In general, acidic pulping processes introduce more carbonyl groups than alkaline ones. Both, pulping of wood and especially bleaching of the resulting pulp – which mainly utilizes oxidative procedures – are responsible for generation and further conversion of oxidized groups in cellulose. Such functionalities represent sites of pronounced chemical instability, they must be considered as "hot spots" along the polymer chain, where subsequent chemical side reactions, such as chain cleavage, cross-linking or condensation, are likely to occur. It is therefore not surprising that these oxidized functions – despite their relatively low concentration in the µmol/g range – are crucial factors in governing properties and behavior of pulp samples, such as dissolution, chemical stability, bleachability, reactivity in derivatization reaction, aging behavior, and yellowing behavior and so on.

The CCOA method provides a good means to measure carbonyl groups in relation to the molecular weight, so-called carbonyl profiles. However, the CCOA procedure does not distinguish between keto and aldehyde groups; it moreover reports the overall amount of both functional groups. This includes the naturally occurring reducing end groups in cellulose, which are aldehydes masked as hemiacetals. To report additionally oxidized sites in cellulose a differentiation from the reducing ends is necessary. Different approaches are theoretically conceivable: a selective derivatization of either aldehyde and keto groups, a mathematical calculation of the reducing end groups and its subtraction from the molecular weight distribution data, or a selective "masking" of either of the two oxidized species by oxidation or reduction [1,2]. An elegant approach would employ a fluorophore, of which the wavelength depended strongly on the type of carbonyl it is attached to. So far, such a differentiation of keto and aldehyde groups by labeling is not available. The mathematical calculation of reducing end groups from the number average molecular weight data are theoretically possible, and would directly result in a distribution of keto and aldehyde groups relative to the molecular weight. Further chemical manipulation of the cellulose is not necessary here. However, the calculation approach also has considerable drawbacks: the error of the measurement of Mn is rather large and depends highly on the data evaluation of the GPC measurements, and so would the calculated REG content. In addition, pulp samples and also aged papers contain oxidized reducing end groups, since the REG is a primary site of oxidative attack. Such groups would finally be responsible for further inaccuracy of the data. The third approach consist in the conversion of one carbonyl species into an inert or “masked” form, which is not reported by the labeling procedure. We employed the latter approach, in particular the oxidation of aldehydes (REGs) to the corresponding acids, in our studies. After the oxidation, labeling reports exclusively the keto groups in the sample. Drawbacks are further chemical modification of the material, and the prerequisite of a quantitative reaction. In this paper, we wish to report investigations toward selective oxidation of reducing end groups in order to obtain keto group profiles which can be correlated to the overall carbonyl (keto + aldehyde) profiles and allow a differentiation of carbonyl structures in cellulosics.

Experimental

Chemicals were obtained from commercial sources and were of the highest purity available. Pulps from different origins and sources were used. The CCOA labeling was performed as described earlier [3-5]. Different pulps were used: hardwood magnesium bisulfite A, Hardwood sulfite B, Softwood sulfite, Eucalyptus Kraft pulp, cotton linters.

General analytics.

Gel permeation chromatography (GPC) measurements used the following components: online degasser, Dionex DG-2410; Kontron 420 pump, pulse damper; autosampler, HP 1100 column oven, Gynkotek STH 585, fluorescence detector TSP FL2000; multiple-angle laser light scattering (MALLS) detector, Wyatt Dawn DSP with argon ion laser (λ_0 = 488 nm); refractive index (RI) detector, Shodex RI-71; Data evaluation was performed with standard Chromeleon and Astra software. The pH value of the solutions in DMAc/LiCl was determined by pouring a defined amount into 100 ml of deionized water.

GPC method

The following parameters were used in the GPC measurements: flow, 1.00 ml min^{-1}; columns, four PL gel mixedA ALS, 20µm, 7.5 x 300 mm; fluorescence detection, ?$_{ex}$ = 290 nm, ? $_{em}$ =340 nm; injection volume, 100 µl; run time, 45 min. DMAc/LiCl (0.9% w/v), filtered through a 0.02 µm filter, was used as the eluant.

Silver ion oxidation.

Diamminsilver solution $[Ag(NH_3)_2]^+$ was prepared by dissolving 1 g of $AgNO_3$ in 7.5 ml water and adding 0.8 ml NH_3 conc. The initial brown precipitate was dissolved by further addition of conc. NH_3. The solution was then diluted with water to a volume of 75 ml. Air-dried pulp (50 mg) was disintegrated in a lab mixer. Excess water was removed and 8 ml of diamminsilver solution $[Ag(NH_3)_2]^+$ were added. Temperature and reaction time were varied (12; 24; 48 and 168 hours, r.t., 40° C; 80° C and 100° C). The oxidized pulp was thoroughly washed with H_2O and 0.1 M EDTA (pH = 10), and excess liquid was filtered off. Subsequently, CCOA labeling was performed: 4 ml of a solution of 1.25 mg CCOA in 4 ml of zinc acetate buffer (pH = 4) were added, and the suspension was shaken in a water bath at 40° C for 7d.

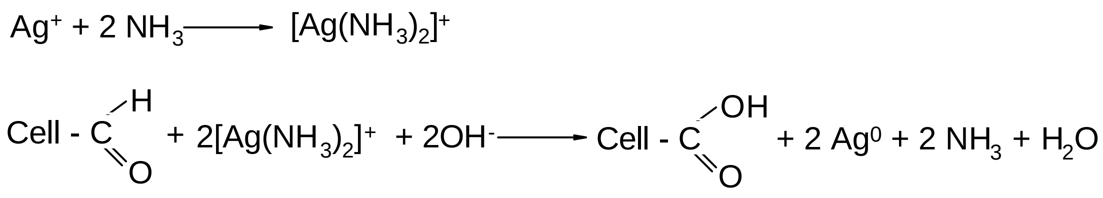
TTC oxidation.

Air- dried pulp (50 mg) was disintegrated in a lab mixer, and washed with H_2O and EtOH. DMAc (6 ml) was added, and the suspension was shaken overnight at r.t. Excess DMAc was filtered off and 4 ml of DMAc/LiCl (9 %) were added. After dissolution of the cellulose, the solution was diluted with DMAc (6 ml). Three stock solutions were prepared: solution A: 0.01 M TTC in DMAc/LiCl (3.6 %) (0.067 g TTC dissolved in 20 ml of DMAc/LiCl (3.6 %), solution B: 2 M t-$BuNH_2$ in DMAc/LiCl (3.6 %) (2.102 mL t-$BuNH_2$ in 10 ml of DMAc/LiCl (3.6 %), solution C: DMAc/LiCl (3.6 %). 1 ml of 0.5 % cellulose solution in DMAc/LiCl (3.6 %) and 2 ml of solution A were stirred in a 5 ml vial. 1 ml of solution B was added, and the vial is heated at 75° C for 10 min in a water bath and immediately cooled to r.t. The cellulose was reprecipitated in 150 ml of water/ethanol (v/v = 50:50), and labelled according to the CCOA procedure.

Results and Discussion

Oxidation with silver ions.

The silver ion oxidation converts the reducing ends to the corresponding acids according to the equations in Figure 1. This procedure was initially applied to label reducing ends in cellulose for visualization in microscopy [6, 7].



$$Ag^+ + 2\,NH_3 \longrightarrow [Ag(NH_3)_2]^+$$

$$\text{Cell - C}(=O)H + 2[Ag(NH_3)_2]^+ + 2OH^- \longrightarrow \text{Cell - C}(=O)OH + 2\,Ag^0 + 2\,NH_3 + H_2O$$

Figure 1. Oxidation of reducing ends of cellulose by diamminsilver cations.

Pulp	*Carbonyl content in µmol/g*	*Decrease of carbonyls DC=O*	*Reduction of Mw in %*
Hw Sulfite A	18.1	8.3 µmol/g	38.1
Hw Sulfite B	9.4	4.2 µmol/g	35.1
Sw Sulfite	12.3	3.3 µmol/g	47.0
Hw Kraft	5.5	1.5 µmol/g	32.7
Cotton Linters	3.9	0.8 µmol/g	11.5

Table 1. Removal of carbonyls and reduction of the molecular weight by oxidation with silver complex.

For most pulps, oxidation with complex silver ions caused the expected decrease in carbonyl group contents. Only cotton linters (CL) and eucalyptus kraft pulp (Hw Kraft pulp), which originally contained a low number of carbonyls, did not respond with a significant reduction in carbonyl groups. The decrease of carbonyl groups (?C=O) due to the silver oxidation at 100° C for 10 min is shown in Table1.

From Figure 2 and Figure 3 it was evident that the oxidation with the silverdiammin complex required elevated temperatures in order to significantly decrease the number of reducing end groups. While the aldehyde groups of the hardwood sulfite pulp were strongly consumed at the beginning of the treatment, the functional groups of the cotton linters were rather inert in this phase. Thus, pulps of different origin and provenience behaved quite differently during this oxidation step.

In order to complete, the oxidation with silver ions must be carried out under alkaline conditions (pH 10), which in most cases imposes a degradation of the cellulose sample due to beta-elimination processes at keto and aldehyde groups along the cellulose chains.

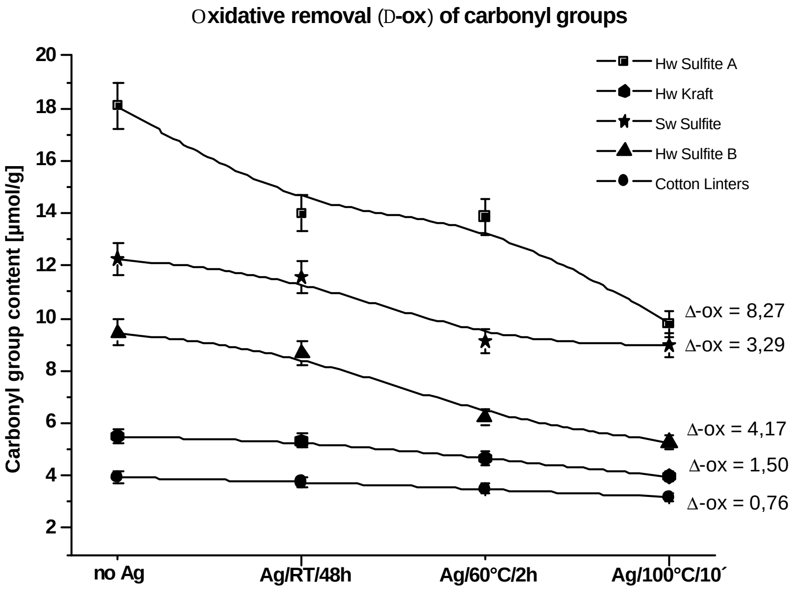


Figure 2. Effect of time and temperature on the oxidative removal of carbonyl groups in different pulps by oxidation with diamminsilver complex.

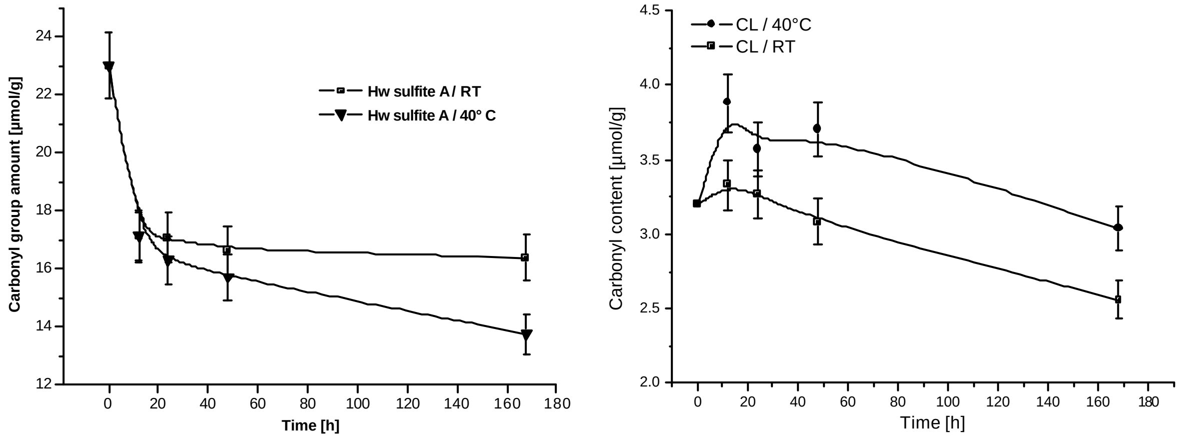


Figure 3. Reaction kinetics for Hw sulfite A pulp (left) and cotton linters (right) oxidation by diamminsilver complex at r.t. and 40°C.

The extent of the observed degradation again highly depended on the respective pulp sample and ranged between 3 – 47 % of the original Mw (Figure 4). While sulfite and kraft pulps showed a larger reduction in Mw (33 – 47 %), cotton linters was only degraded in range of 3 – 11 %..

In addition, a different dissolution behavior of the samples in DMAc/LiCl (9 %) was observed after oxidative treatment. A high temperature treatment (T > 60° C) with silver ions, which is more effective in reducing the carbonyl content, caused decreased solubility of the cellulose sample in DMAc/LiCl (9 %). Cotton Linters even became completely insoluble under these conditions. Only if the time of treatment at temperatures above 60° C was less then 2 hours, cellulose samples treated in DMAc/LiCl (9 %) could still be dissolved.

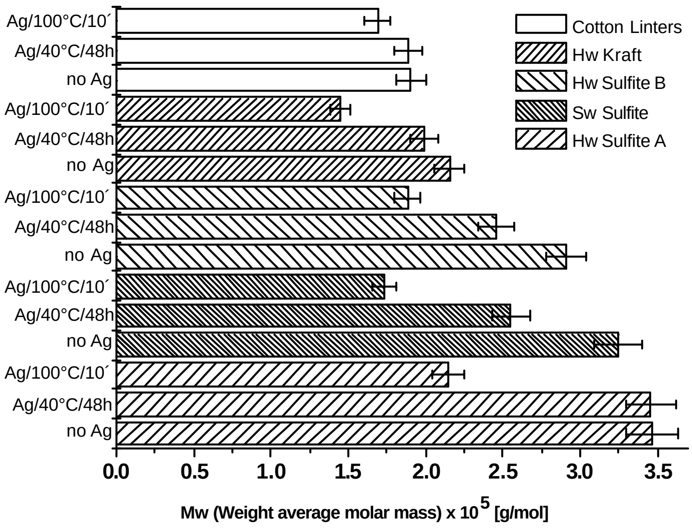


Figure 4. Reduction of the weight average molecular weight (Mw) upon oxidation with diamminsilver complex.

Oxidation with TTC.

Oxidation with TTC (2,3,5-triphenyltetrazolium chloride) has already been known for a long time in pulp analytics to determine the reducing end groups in paper materials [8]. Upon oxidation of the aldehyde groups in pulp to the corresponding acids, purple-colored triphenylformazane is formed, see the equations in Figure 5.

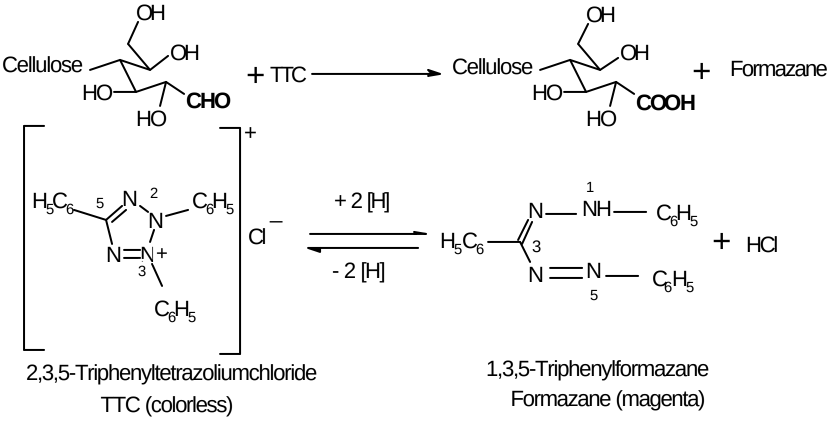


Figure 5. Oxidation of aldehydes in cellulose (REGs) by TTC.

According to the original procedure, a suspension of pulp in aqueous alkaline solution (KOH) had been used. Strlic and Pihlar [9] considerably improved the method by employing the cellulose in homogenous solution in DMAc/LiCl in the presence of *tert*-butylamine. In both cases the formation of formazane is followed spectrophotometrically at 546 nm or 524 nm, respectively. In our approach, we utilized TTC oxidation in homogeneous solution and followed the changes in the carbonyl content by standard CCOA analysis. This required a re-precipitation of the pulp sample in order to remove excess oxidant and byproducts prior to CCOA labeling, but afforded total carbonyl (keto) content and profiles (Figure 6).

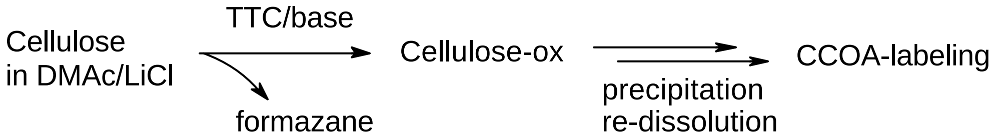


Figure 6. General approach for the oxidation of celluloses with TTC in combination with CCOA analysis.

This procedure was applied to different pulp samples. For most pulp samples a degradation of cellulose, as seen by a decrease in the molecular weight, was observed, which was severe in some cases (sulfite pulps). This reduction in molecular weight has to be considered when applying the simple spectroscopical method: novel REGs are formed during cellulose degradation, which add to the originally present ones. This might eventually lead to incorrect data of the measured reducing end groups, if the values are not corrected for sample degradation. From our previous investigations [10], we learned that a mere heating of pulp samples (also sulfite pulps) in DMAc/LiCl for 10 min at 75°C did not result in a strong degradation. Hence, other compounds in the mixture must have triggered the cellulose degradation. Therefore, we investigated different auxiliary bases, such as pyridine, *t*-butylamine (*tert*-BuNH$_2$), *N*-methylmorpholine (NMM), dicyclohexylethylamine (DCHEA), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and morpholine. All bases had a negative effect on the molecular weight, but not all of the auxiliaries were able to promote the oxidation with TTC. Especially DBU and morpholine as auxiliary bases in the oxidation with TTC did not result in a significant reduction of the amount of carbonyl groups (cf. Figure 7). *t*-Butylamine, morpholine and Hünig base, in contrast, had a pronounced effect.

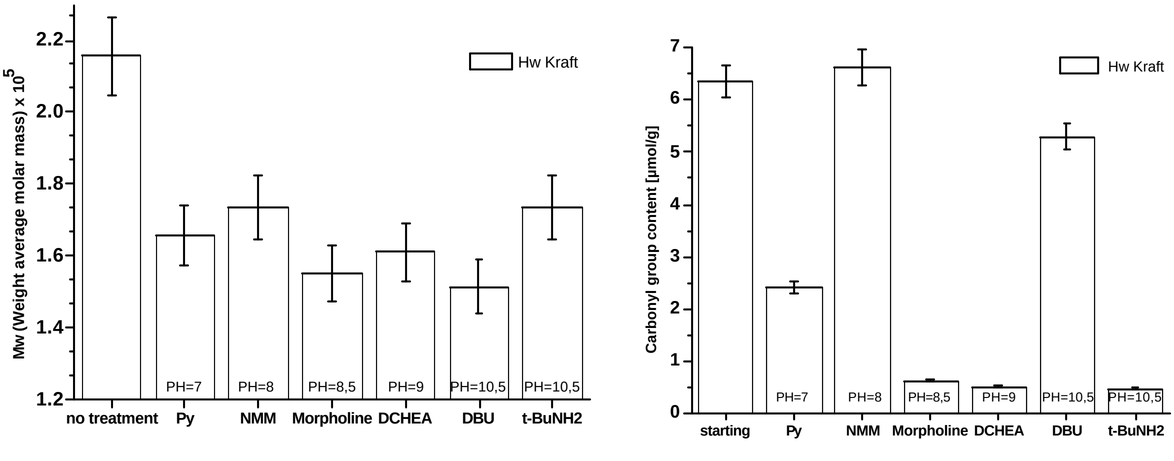


Figure 7. Effect of different auxiliary bases on the molecular weight (left) and on the oxidative removal of aldehyde groups (right) by oxidation with TTC.

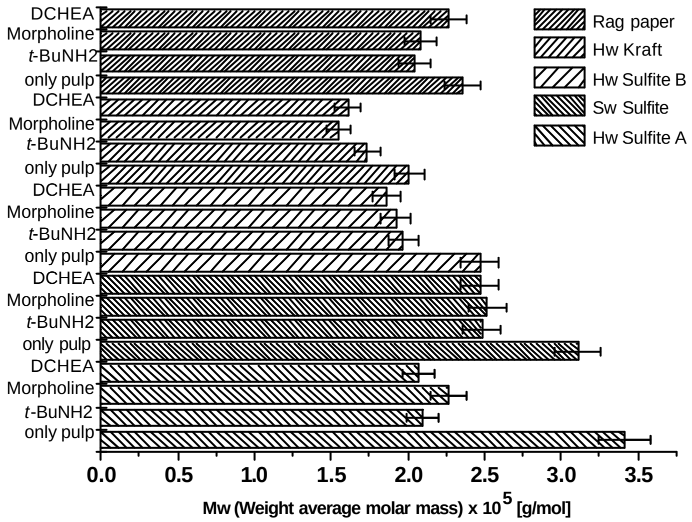


Figure 8. Effect of different auxiliary bases on the molecular weight of different pulp samples

Figure 8 depicts the effect of auxiliary bases on different pulp samples. It was evident that sulfite pulps were rather sensitive to the oxidative treatment in DMAc/LiCl independent of the base used. Hardwood kraft pulp and especially ancient rag paper showed much less degradation under the conditions applied. For such pulp samples, the TTC procedure appeared suitable to monitor keto group profiles with a tolerably small simultaneous degradation of the cellulose.
Such a keto group profile, a distribution of keto groups relative to the molecular weight distribution, is given in Figure 9 for a eucalyptus sulfite pulp and a rag paper. In general, the total amount of keto groups was rather low. According to the TTC method, approx. 10% of the carbonyl groups were attributed to keto functionalities. Figure 9 nicely demonstrates that oxidation to keto groups predominated in the bulk region (DP 200-2000) in both pulps. However, the keto group distribution differed significantly as expected (Figure 10).

Summary

Two chemical approaches have been tested to oxidize reducing end groups in cellulose to obtain keto group profiles after removing aldehyde groups oxidatively. The oxidation with diamminsilver complex gave only an insufficient reduction in the carbonyl content under mild conditions, but caused a severe degradation of cellulose under more drastic settings.

Oxidation with TTC under homogeneous conditions in DMAc/LiCl resulted in the expected reduction in carbonyl groups. However, also here a reduction in the molecular weight was observed, for some industrial pulps a drastic DP loss was found. There was no unambiguous correlation of MW reduction with the type of auxiliary base applied (neither base strength nor nucleophilicity). In case of rag paper and hardwood kraft pulp, keto group profiles were obtained, the loss in DP being tolerable in these cases.

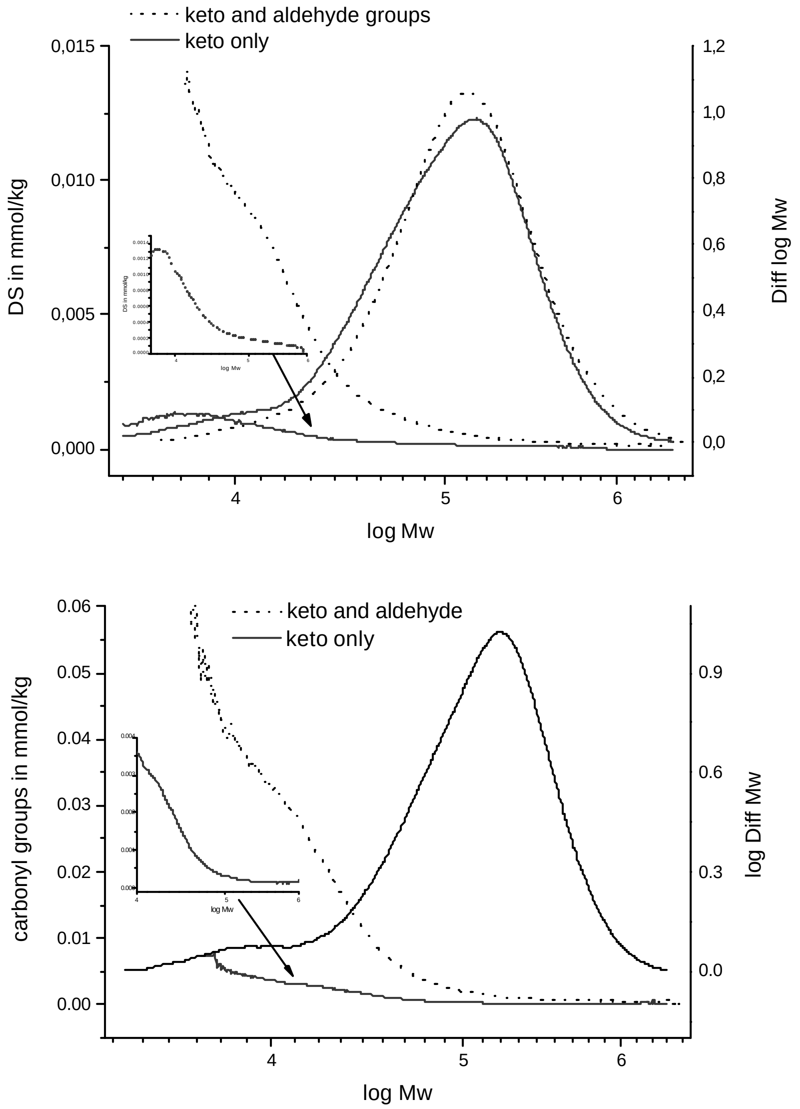


Figure 9. Carbonyl profile, keto profile and molecular weight distribution of a hardwood sulfite pulp (upper) and a rag paper from 1825 (lower).

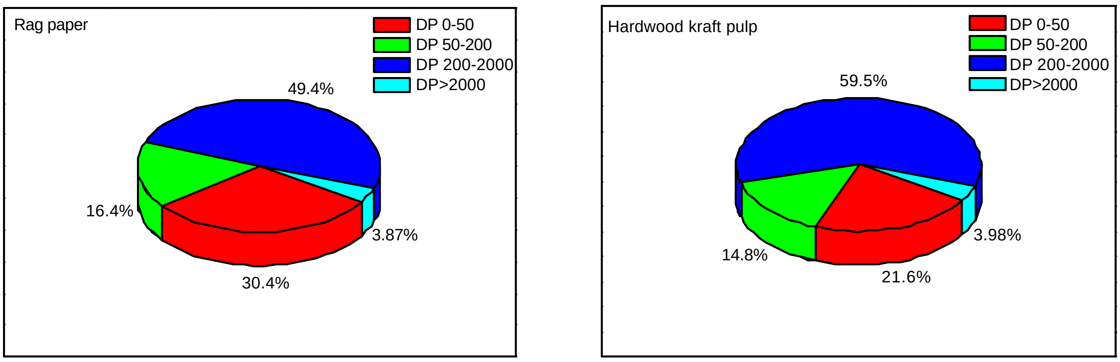


Figure 10. Numerical evaluation of the keto group distribution after TTC oxidation of rag paper (left) and hardwood kraft pulp (right).

Acknowledgements

The authors would like to thank Dr. Sonja Schiehser for practical assistance and GPC measurements. Financial support by the Austrian Christian-Doppler Research Society and by Lenzing AG, Austria, is gratefully acknowledged.

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TENCEL® - THE KEY TO HIGH PERFORMANCE NONWOVEN PRODUCTS

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Abstract

Lyocell fibres are commercially supplied by Lenzing Fibers under the trade names Tencel® and Lenzing Lyocell®. These constitute a family of fibre grades that are successfully used in a wide range of nonwovens products that require absorbency, purity, softness, strength and biodegradability. Perhaps best known for their use in carded and spunlaced nonwoven fabrics, additional lyocell fibre grades have been specifically developed for use in dry laid and wet laid applications where short fibre lengths, typically below 20mm, are required.

This paper reviews the fibre characteristics of these short staple grades and the properties of the resulting fabrics with specific emphasis on how these fibres can be used to engineer the key fabric attributes for high performance nonwoven products.

Introduction

Lyocell fibres are 100% cellulosic fibres, solvent spun from purified woodpulp. The lyocell fibres commercially manufactured and supplied by Lenzing Fibres are marketed under the Brand name Tencel® and incorporate the fibre grades from the established Tencel® and Lenzing Lyocell® product ranges.

Developed in the 1980's, these high purity, versatile and fully biodegradable fibres are manufactured using a highly eco-friendly process, designed from the outset to minimise its environmental impact.

Full scale commercial manufacture of lyocell fibres commenced in 1992 with the opening of the first Tencel® plant in Mobile, Alabama, USA. Although initially targeted at the fashion apparel sector, a niche business in nonwovens was developed through the late 1990's utilising the unique attributes of lyocell. During the first five years of the 21st Century, the growth of the nonwovens business for lyocell was targeted as a key strategic area for both the Tencel® and Lenzing Lyocell® product ranges. This strategy was reconfirmed during the merging of the Tencel and Lenzing businesses in 2004 and today, a significant proportion of Tencel® fibre sales are into nonwovens applications.

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Lenzing is the only commercial scale manufacturer of lyocell fibres, with production plants located in the USA, UK and Austria.

Key areas of success for Tencel® are in wipes, medical & hygiene and filtration applications. Within these sectors, the strong growth of the spunlaced wipes market has been well documented over recent years but the development of short staple length fibre grades (typically below 20mm) specifically tailored for airlaid and wetlaid applications has also been an important area for business growth. Fibre grades are produced for a range of converting technologies including papermaking, wetlaying and airlaying as well as for use as reinforcing fibres in polymeric or inorganic matrices.

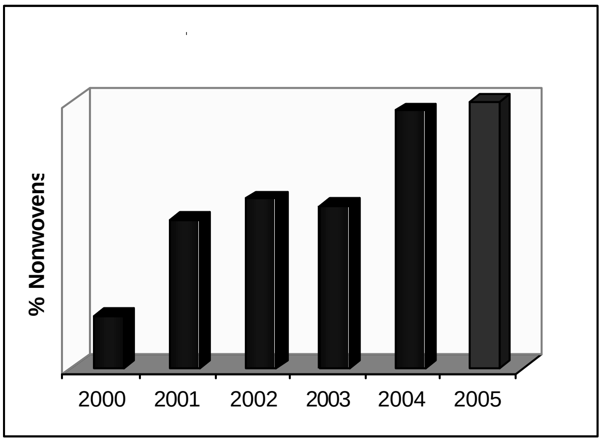

Figure. 1 – The development of Tencel® sales into nonwovens applications

Tencel Fibre Production and Filament Properties

The manufacture of Tencel® is based upon the dissolution of purified, dissolving grade woodpulp in an amine oxide solvent (N-methylmorpholine – N-oxide) to form a viscous spinning solution.

The woodpulp is a renewable raw material sourced from carefully managed forests and purified under tightly controlled conditions to ensure optimum performance in the Tencel® process.

Once the spinning solution has been formed, it is filtered and extruded through spinnerettes into a dilute solution of the spinning solvent to form continuous filaments. The filaments are washed to remove the solvent, which is recovered, purified and concentrated for re-use in the Tencel® process.

For short staple Tencel® production, the fibre is kept in continuous tow form throughout the washing, finishing and drying stages of the process. Only at the end of the production is the fibre cut into staple. Either reel cutting or off-line guillotine cutting is used, depending upon the cut length required. However, in some cases, the fibre is collected in tow form for special downstream processes. The clear distinction between the tow manufacture and the staple cutting processes maximises production flexibility and enables the optimisation of fibre grades to create an extensive portfolio of carefully tailored products.

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Tencel® fibre is characterised by its smooth, round cross-section, excellent filament tenacity and high modulus, which are retained to a very high degree in the wet state. Water imbibition approaches that of viscose fibre and far exceeds that of polyester (PET) and polypropylene fibres.

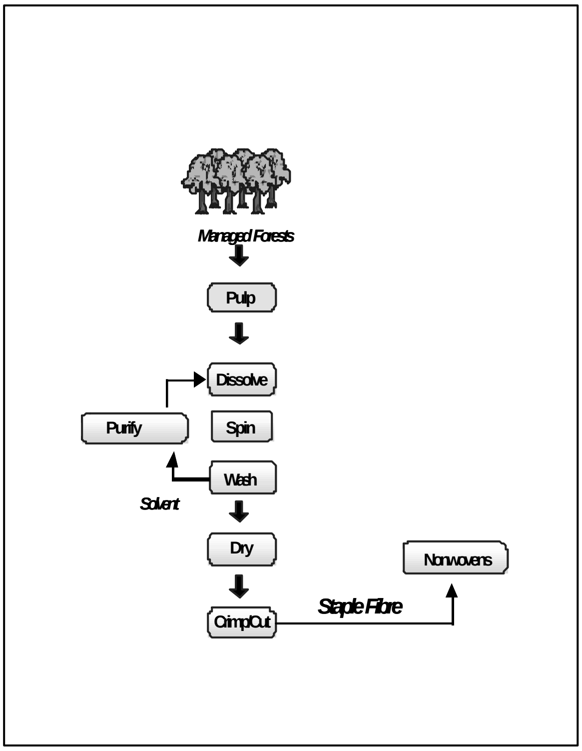

Figure. 2 - Tencel® Production Process

Property	Uniit	Tencel	Viscose	Polyester	Polypropylene
Dry Tenacity	(CN/tex)	30-40	20-25	40-50	25-35
Dry Extensability	%	10-16	20-25	15-55	200-300
Wet Tenacity	(CN/tex)	25-35	10-15	40-50	25-35
Wet Extensability	%	12-18	25-35	15-55	200-300
Initial Wet Modulus	(CN/tex)	200-270	40-60	-	-
Water Imbibition	%	60-70	90-100	<5	0
Cellulose DP		500-800	250-350	N/A	N/A

Figure. 3 – Filament Properties of Tencel® fibre

Tencel in Short Cut Fiber Applications

All of the applications for short cut grades of Tencel® are characterised by their requirement for fibre staple lengths below 20mm, for filaments that are easily opened and separated and that the fibre is dispersed easily in either air, aqueous or organic media. To fully optimise the fibre grades for each application, fibre variables such as cut length, fibre end cut quality, titre, finish type, finish level, lustre and crimp are tailored to match the processing and performance characteristics of the fibre to the product requirements.

Airlaying

Tencel® fibre grades for airlaying usually lie within the range of cut lengths from 4 to 10mm. Tencel® imparts a luxurious, soft hand feel to the fabric and this may be maximised by using the fibre in layered fabric structures in the outermost layers. Compared to pulp fibres, Tencel® gives a major increase in fabric thickness as well as an associated improvement in fabric absorbency.

The high filament strength and long fibre length, in comparison to pulp fibres, enables fabric strength to be maximised as the proportion of Tencel® is increased. The webs are consolidated and integrity is imparted by either chemical (resin) bonding, thermal bonding using meltable binder fibres, or by hydroentanglement (airlace). Studies(1) carried out in conjunction with the University of Leeds in the UK, identified how fibre variables such as cut length, finish type and fibre crimp affect filament dispersion in the air chamber. Fibre specifications have been developed to optimise web formation and hence maximise fabric quality and performance.

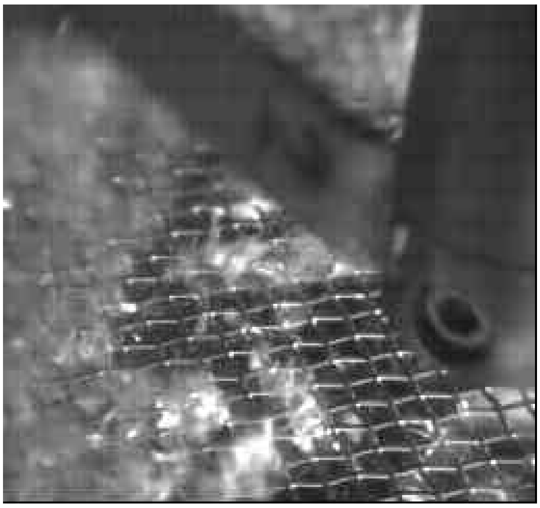

Figure. 4 - Tencel® Fibres in an Airlay Chamber

Applications for airlaid® Tencel fabrics include high performance wipes, food packaging and medical products.

Wetlaying

The parallel and untwisted filaments produced from the tow-based Tencel® process, combined with the high wet fibre modulus, promote good dispersion of the fibres in the mixing chest of wetlay systems, even at relatively long cut lengths. Typical cut lengths for such applications range from 5 to 12mm, although dispersion is possible at up to 16mm staple length using low stock concentrations.

The smooth fibre surface enables good inter-fibre contact in the web, thereby imparting high wet web cohesion and giving high efficiency transfer of the web prior to bonding. During drying, the fibre's high wet stability reduces fabric shrinkage and maintains fabric evenness. In use, the high fibre strength and excellent bonding efficiency of wetlaid Tencel® gives fabrics with excellent low linting characteristics utilised in critical task wipers for clean room environments.

In an interesting contrast to fabrics used in medical applications, in which fabric opacity and cover are required, bright luster grades of Tencel® fibre have been used in wetlaid fabrics to give excellent fabric transparency, where the quality of the product held within the nonwoven is a key marketing objective. In this instance, the smooth fibre surface and consistent refractive index promote reduced light scattering and hence maximises transmission of light through the fabric.

Ease of disposal is an increasingly important factor in the design of wetlaid, or indeed drylaid fabrics. For instance, fabric strength increases with the cut length of the Tencel® fibres but if the product is required to be dispersible upon disposal into domestic plumbing and sewerage systems, then shorter fibre lengths may be favored. A number of companies have developed dispersible fabrics using short cut Tencel® fibre in conjunction with water sensitive binder systems. Some of these are published in the patent literature (e.g Kimberly-Clark {USP 5,986,004} and Oji Seishi {JO9-228214}), whereas others are even more commercially sensitive. The concept of using Tencel® in such structures is to give sufficient strength to allow the fabrics to be used but to make fabrics lighter weight and bulkier by reducing consolidation to allow them to fold in flushing and then break up. Once immersed in water, Tencel® plasticizes and the fibre modulus decreases, potentially initiating the disentanglement process.

Tencel® is fully biodegradable, so when the fibre has entered the sewage or waste treatment system, it will break down into carbon dioxide and water under enzyme action. This is illustrated in the following micrographs for fibres degrading under the action of soil burial:

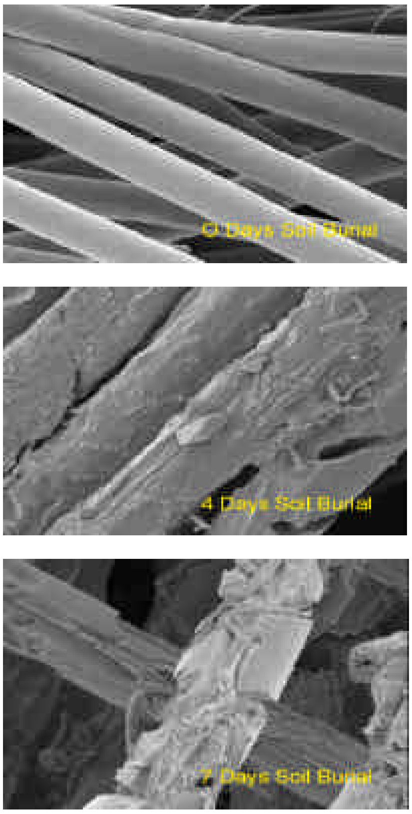

Figure. 5 - Biodegradation of Tencel®

Speciality Papers

The unique fibrillar, crystalline structure of Tencel® can be broken down through mechanical wet abrasion, for example at the beating stage of a traditional papermaking process. This wet abrasion generates submicron diameter round cross-section fibrils, which are retained within the fibre network, creating a micro-porous structure, ideal for fine filtration. In addition to controlling filtration characteristics and fabric permeability, manipulation of the fibrillation of Tencel® can be used to vary fabric opacity, tensile strength and tear strength.

By virtue of the nature of the papermaking process, the shortest staple lengths of Tencel® are used, with cut lengths typically of 4mm or less. Applications for papers comprising Tencel® include electronic component insulating papers, hot oil filtration for food contact and automotive end-uses, as well as cigarette filter papers. In all of these applications, the high purity of Tencel® and the controllability and reproducibility of its fibrillation are of key importances.

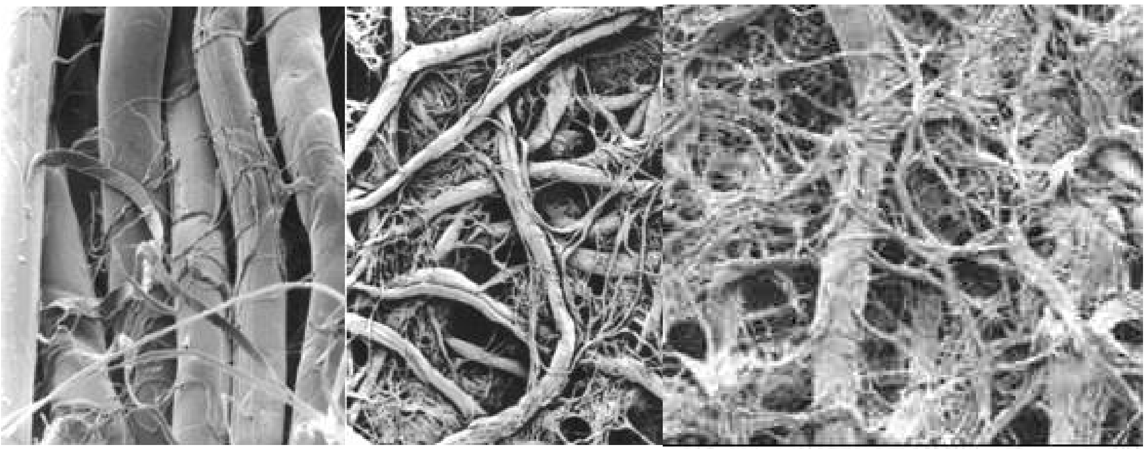

Figure. 6 – Increasing fibrillation of Tencel®

Composite Reinforcement

Tencel® fibre can be used as a reinforcement in polymeric or inorganic matrices in either short cut staple or continuous tow form. Dispersion of short cut, uncrimped fibre in polymeric matrices, such as polypropylene, gives composite properties comparable to glass reinforced materials.

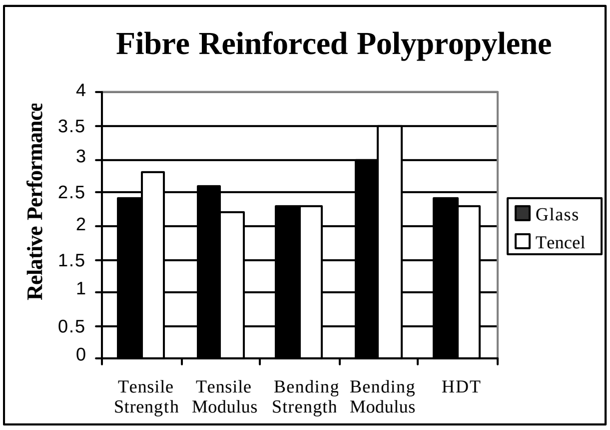

Figure. 7 –Tencel® for reinforcement of polypropylene(2)

In comparison to the glass-reinforced material, Tencel® reinforcement imparts better acoustic and thermal insulation and offers the possibility of improved recycleability.

Inorganic matrix materials such as ceramics or cements also benefit from Tencel® reinforcement. Compression and bending strength are improved at addition levels as low as 1kg/m3 but the greatest benefits are obtained in improved crack resistance against failure mechanisms such as dynamic fatigue, freeze-thaw action and extreme heat cracking. The non-melting nature of Tencel® means that it can be reliably used in autoclave cured or high exothermic cements in the production of high performance cement mouldings.

Summary

A plethora of exciting opportunities for product differentiation and market growth have been described where the incorporation of Tencel® short cut fibre grades gives improvements in:

- Fabric bulk, softness and strength
- Filtration performance
- Composite toughness and strength

These benefits are attained across a wide range of applications and Tencel® fibre grades have been tailored to give optimal performance in papermaking, wetlaid, airlaid and composite conversion technologies.

The rapid growth of Tencel® in nonwovens has been built on continuing market demand for absorbent fibres in wipes. This paper has illustrated that the fibre offers much wider opportunities to develop new products for diverse applications based on a unique combination of inherent fibre properties and progressive product development. It is a story in its early stages and one that is set to continue.

Acknowledgements

1. Dr S J Russell and M Osman, Nonwovens Research Group, School of Textile Industries, University of Leeds, UK – study of Tencel® in an airlaid process.

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TAILOR-MADE ABSORBENT CELULOSE FIBERS FOR NONWOVENS

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LENZING AG NONWOVEN INNOVATION

Abstract

In contrast to textile applications where cotton is the most commonly used cellulosic fibre, viscose and lyocell are the dominating fibre materials for absorbent nonwoven products. The particular advantages of man-made cellulosics are their exceptional purity, superior absorbency compared to cotton or pulp, and their softness and opacity. Depending on product and end-use the requirements regarding the sorption properties of the material are quite different: a dry wipe e.g. shall absorb a fluid rapidly and retain it, a wet wipe shall hold a lotion temporarily and release it on demand whereas a tampon shall expand immediately after wetting and retain a maximum amount of fluid even under pressure.

Viscose and lyocell fibres can be modified in their physical properties by various means in order to fulfil these different requirements. This paper gives an overview of various physical and chemical methods to design man-made cellulosic fibres with tailor-made sorption properties, it reviews useful test methods for characterisation of the sorption properties of fibres, nonwovens and tampons and assesses the performance of various fibres in absorbent nonwovens.

Introduction

In hygiene, medical and wipes applications nonwoven absorbency is the most significant property. It is controlled by both, structural parameters of the web and absorbency of the fibre.This paper will focus on the characterisation and modification of fibre absorbency, review various approaches to develop fibres with improved absorbency and include an assessment of the performance of the fibres in nonwovens by using spezialised test methods.

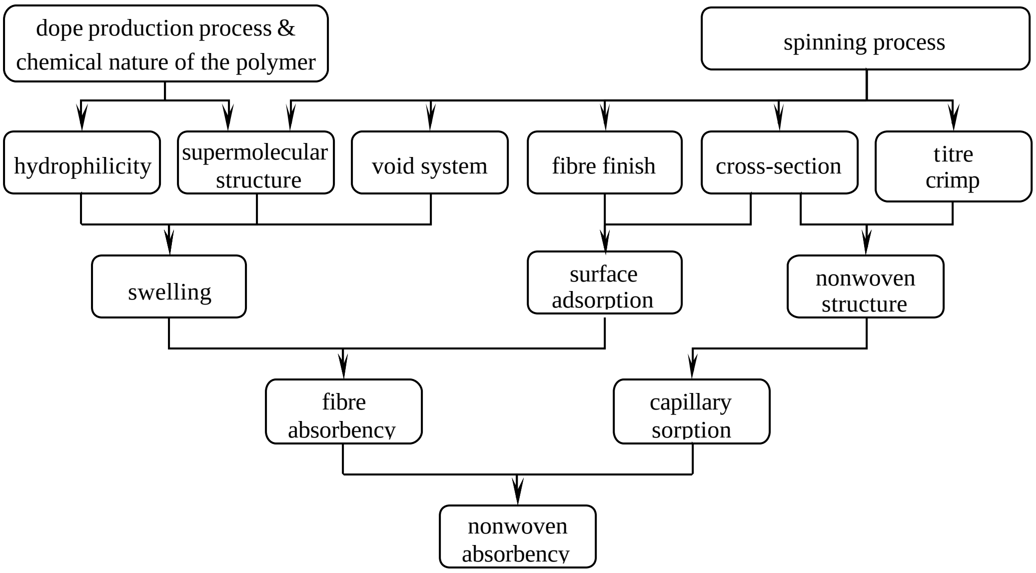

Figure 1. Physical influences controlling the absorbency of fibres and nonwoven fabrics

Swelling

As indicated in Fig. 1, sorption tendency of a fibre is generally influenced by the chemical nature of the polymer material, the production process of the dope and the spinning conditions. As the hydrophilicity of cellulosic materials is much higher than the hydrophilicity of synthetic polymers, sorption tendency dramatically decreases from cellulose fibres over polyamide fibres to polyester and polypropylene fibres. Within the limited spectrum of regenerated cellulose fibres the chemical composition of the polymer material is basically the same, and as water and aqueous solutions are not capable to penetrate highly ordered crystalline domains, sorption tendency of the regenerated cellulose fibres is strongly affected by parameters controlling the supermolecular fibre structure like size, arrangement and orientation of the crystallites. The investigation of selected cellulose standard fibres reveals an increasing degree of supermolecular order from viscose over modal to lyocell, expressed by the orientation factor and the crystallinity index. The most obvious reasons for this trend are the deliberate increase of the molecular weight during dope production and the higher stretching ratio of modal and lyocell fibres compared to viscose. With respect to lyocell, also a pre-orientation of the macromolecules in the dope by formation of a lyotropic solvent state is discussed.

Another aspect which strongly affects the sorption tendency of cellulose fibres is the formation of void volumes and their distribution over the fibre cross-section. In chemically regenerated viscose and modal fibres a distinct skin/core-structure is formed with primarily small pores in the skin and a sponge-like structure of small and large voids in the core. The solvent-spun lyocell fibres in contrast show a very homogeneous distribution of very small pores over the whole fibre cross-section

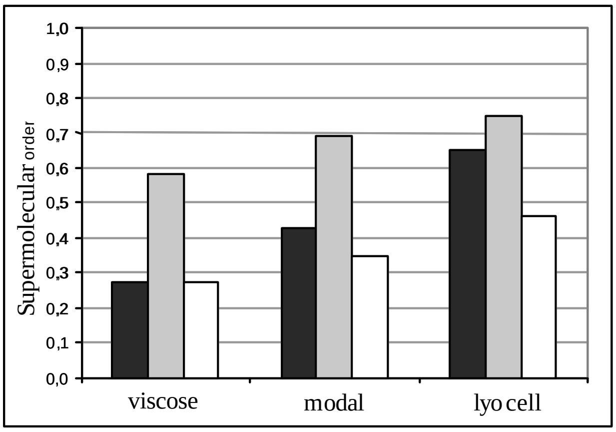

Figure 2. Degree of polymerisation [10^3 g/mol] (■), orientation factor (▒) and crystallinity index (□) in viscose, modal and lyocell fibres

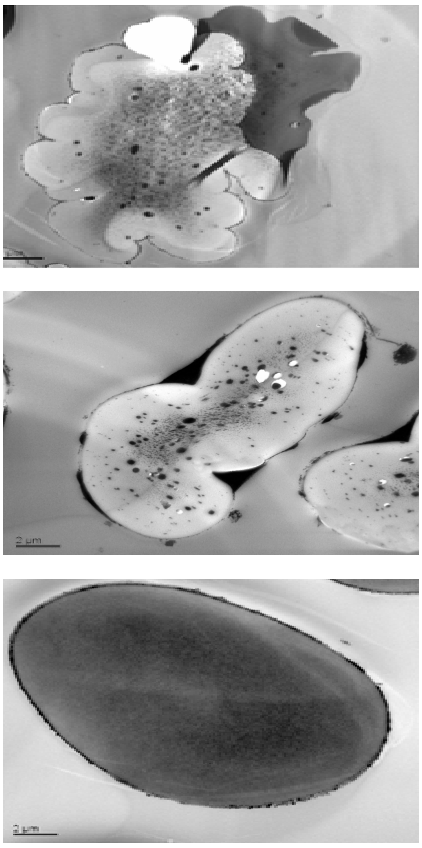

Figure 3. TEM investigations of wet viscose (upper), modal (middle) and lyocell (lower) fibres

A related aspect to be considered is the influence of the total void volume and the average pore diameter on fibre sorption. In both cases increasing sorption tendencies from modal fibre over lyocell to viscose fibre are observed when investigated by size exclusion chromatography.

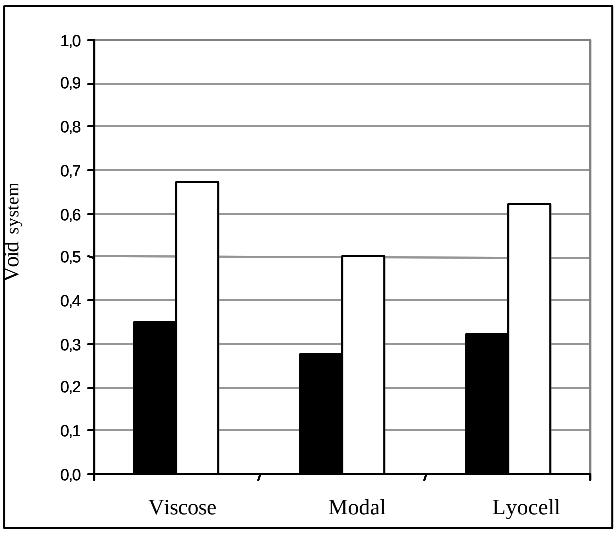

Figure 4. Pore diameter [10 nm] (■) and void volume [ml/g] (☐) in viscose, modal and lyocell fibres

The total swelling trend is given by superposition of all structural tendencies, whereas the void volume seems to be the dominating property. The effect of swelling can easily be visualized by microscopy in form of a cellulose fibre, brought in contact with water or an aqueous salt solution.

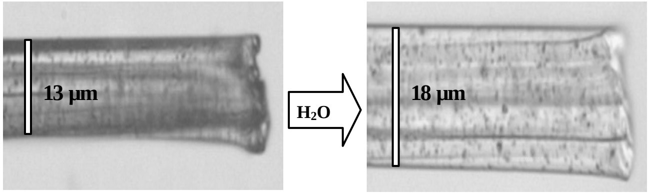

Figure 5. Typical diameter increase of a viscose fibre when wetted

Another test is the assessment of the water retention according to DIN 53814. The norm describes the controlled exposure of carded fibres to an aqueous environment and the subsequent removal of excess liquid by centrifugation. As only water held inside the fibre cavities is removed by the centrifugation process, the weight difference to the dried sample is a good measure for the liquid taken up by swelling. The low values observed with polyester and polypropylene result from the hydrophobic nature of the polymer materials.

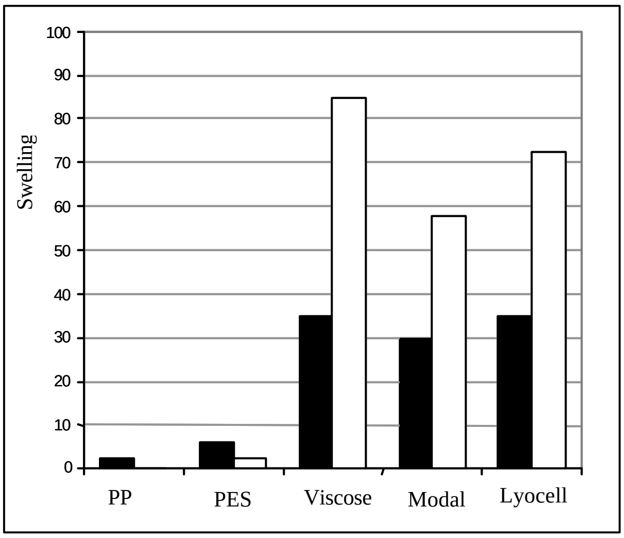

Figure 6. Diameter increase [%] (■) and water retention [%] (☐) of PP, PES, cotton, viscose, modal and lyocell fibres

Adsorption

Besides swelling the liquid adsorption on the outer surface of a fibre and the inclusion of water in the fibre cavities by capillary force are additional effects contributing to fibre and nonwoven absorbency. The first mechanism correlates with the geometrical surface area of a fibre and is directly related to the shape of the fibre cross-section, which in turn is mainly controlled by the dope additives, the spinneret geometry and the spin-bath composition. Another aspect is the hydrophilicity of the fibre finish and its adhesion on the fibre surface. The second mechanism exerts a much stronger influence on nonwoven absorbency. It mainly depends on the shape and volume of the cavities formed between the fibres and is solely controlled by the fibre crimp and the nonwoven production technology.

Fibre and Nonwoven Absorbency

As a separate investigation of adsorption is not of technical interest, water adsorption and swelling are assessed together. The most common test methods are the norm DIN 53923 and the closely related tests WSP 10.1 and WSP 10.2. All three methods describe the controlled exposure of a nonwoven sample to an aquous environment, the subsequent determination of the time it requires to get completely wetted (liquid absorbency time) and the assessment of the liquid mass retained inside the fabric after a specified time of drainage against gravity (water holding capacity). The main difference between these three test methods is the sample preparation: WSP 10.1 teaches the use of a stainless steel wire basket as a sample container, DIN 53923 reports the attachement of the nonwoven fabric to a metal grid and WSP 10.2 describes the application of a simple pile of nonwovens. The mutual basis for all these test methods is published in the European Pharmacopeia in form of an experimental description teaching the investigation of the water holding capacity of carded fibres.

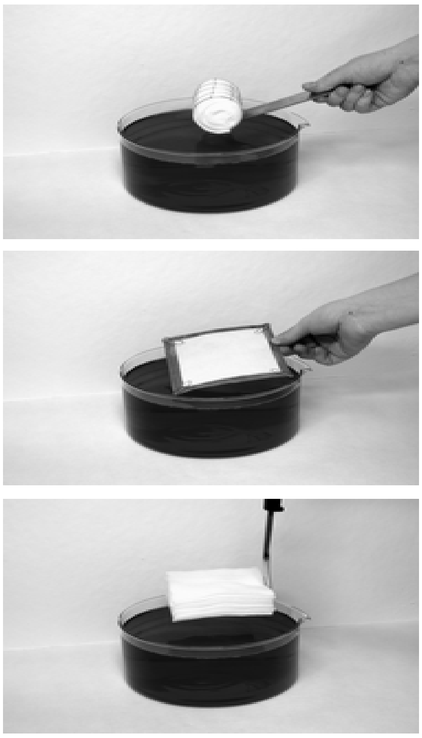

Figure 7. Experimental setup of the methods WSP 10.1 (upper), DIN 53923 (middle) and the downscaled WSP 10.2 (lower)

According to DIN 53923 the water holding capacity of standard cellulose fibres increases from modal over lyocell to viscose fibre, and follows nicely the sorption tendency discussed earlier.

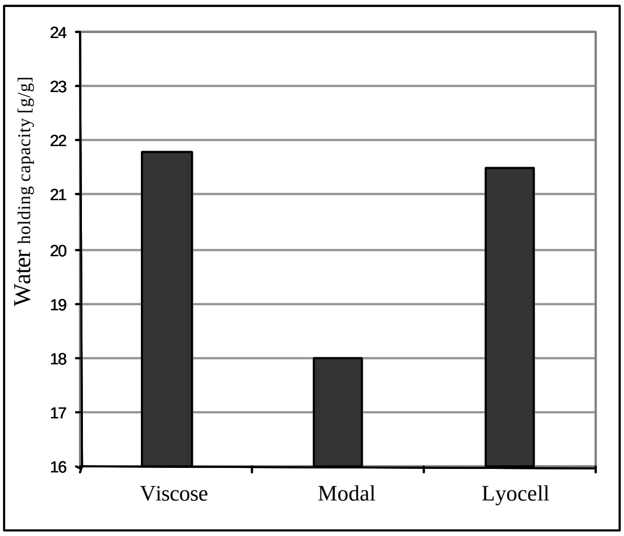

Figure 8. Water holding capacity [g/g] of viscose, modal and lyocell fibres

WSP 10.1 provides an additional test method (liquid wicking rate) which tells about a nonwoven sample fixed in a vertical position over a water basin. After the nonwoven is brought in touch with the liquid surface the rise of the liquid front within a specified time is monitored.

The investigation of nonwoven fabrics, which are manufactured from mixtures of polypropylene, polyester, viscose and lyocell fibres by spunlace technology reveal liquid wicking heights increasing with the cellulose fibre content. Due to the hydrophilicity of the polymer material all fabrics containing polypropylene show lower wicking heights than nonwoven products containing polyester. Both methods, the liquid wicking rate and the absorbency time are mainly controlled by capillary force and provide information about the nonwoven structure.

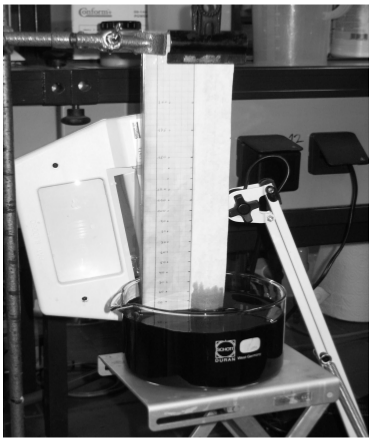

Figure 9. Experimental setup of test method WSP 10.1 / liquid wicking rate

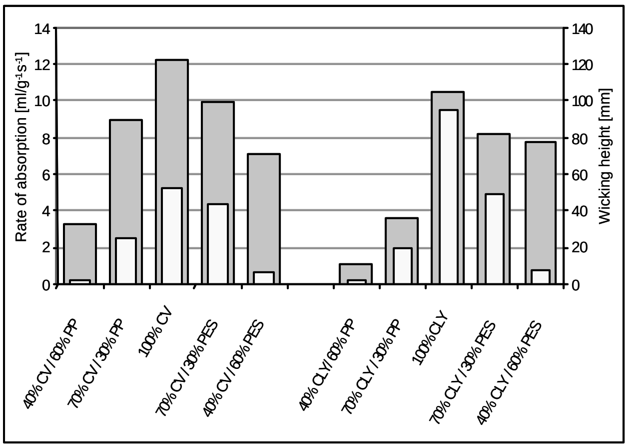

Figure 10. Rate of absorption [mlg^{-1}s^{-1})] (☐) and wicking height [mm] (▨)of spunlace fabrics from PP/PES/CV/CLY fibre blends

Test method WSP 10.3 describes the determination of the nonwoven absorbency when only one side of a nonwoven fabric is in contact with the aqueous liquid while the whole sample is kept under constant mechanical pressure. Physical values to be measured are the demand absorbency capacity and the maximum absorption rate.

Highly Absorbent Cellulose Fibres for Tampon and Hygiene Applications

A common approach to further increase the absorptive capacity of cellulosic fibres is the incorporation of hydrophilic polymers like starch, guar gum, carboxymethyl cellulose or alginate into the viscose dope. Due to an increased hydrophilicity of the fibre material the water retention rises from 86% up to 144%. The water holding capacity in contrast is not increased as titre, crimp and cross-section are only marginally affected. A very similar approach is followed when finely ground superabsorbent resins are incorporated into cellulose fibres. With a SAP content of only 10% the water retention of lyocell fibres can be raised to a maximum of 155%.

Viscose fibres modified by incorporation of cellulose carbamate however appear to have a completely different profile: water retention remains at the same level whereas water holding capacity is significantly improved. This can be explained by the fact, that most of the carbamate is regenerated during the spinning process and the fibre shows an exceptionally high level of crimp.

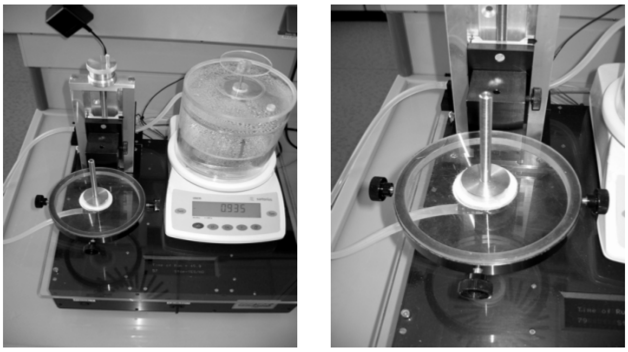

Figure 11: Modified experimental setup of the test method WSP 10.13 / GATS

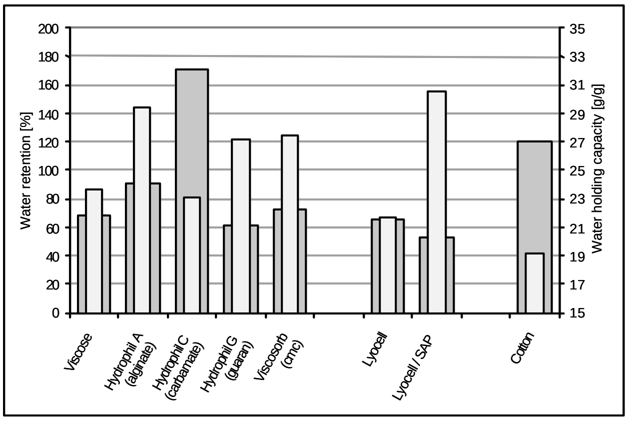

Figure 12. Water retention [%] (☐) and water holding capacity [g/g] (▨) of highly absorbent cellulose fibres

A completely different way to increase the absorption capacity of nonwoven products is to increase the capillary attraction by controlling size and shape of the cavities formed within the fabric. Due to the star-like shape of the cross-section and the higher rigidity, fibres manufactured via trilobal spinnerets (ViscoStar) show a very high absorptive capacity. When polyglycol is added to the spinning dope, the fibre cross-section changes gradually to a triangular shape. As a result, the water retention and the water holding capacity slightly rise due to an increasing hydrophilicity of the fibre material

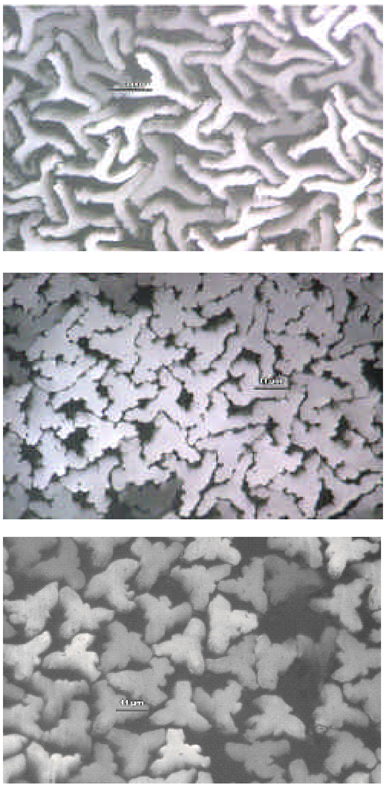

Figure 13. Modification of the fibre cross-section by addition of 0% (left), 2.5% (middle) and 5% (right) polyglycol to the spinning dope

Size and shape of the void volumes of a nonwoven fabric can also be influenced by the crimp of a fibre. In the special case of viscose, the crimp is strongly affected by a rise of the alkali content in the spinning dope. Even though the water retention stays unaffected, the resulting fibres (ViscoNova) reveal remarkable higher water holding capacities than Viscose due to their much higher crimp. The comparatively high water holding capacity observed with cotton has to be ascribed to the hollow fibre structure.

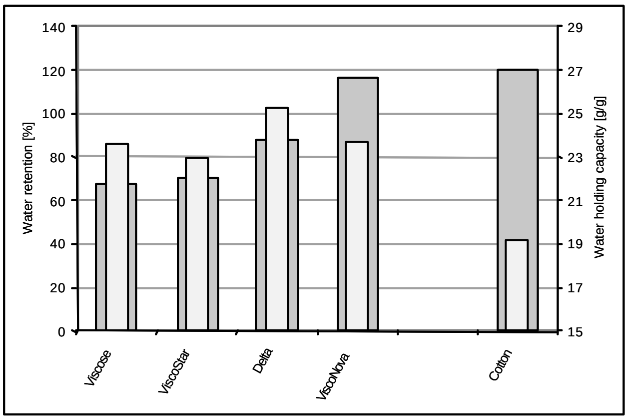

Figure 14.Water retention [%] (☐) and water holding capacity [g/g] (■) of highly absorbent cellulose fibres.

Typical end-products which highly rely on the outstanding absorbency of cellulose fibres are tampons. In this field of application, the very special syngina test method WSP 350.0 has proven valuable for determination of the absorptive capacity. The test describes the exposure of a tampon plug to an aqueous solution under a specified pressure and the subsequent measurement of the liquid mass retained within the product. In Lenzing a simplified version of this test using a vertical test chamber and water instead of saline solution is applied. Thus, the syngina values appear about 20% higher than those of the WSP test.

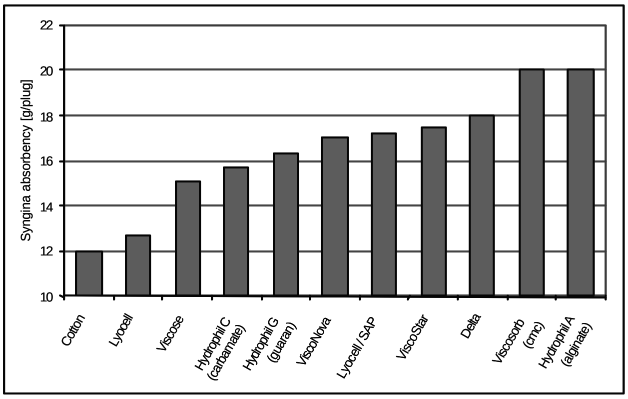

Figure 15. Syngina absorbency [g/plug] of highly absorbent cellulose fibres

Due to the completely different compression ratios in the nonwoven samples the syngina values follow other trends than the water holding capacities. From economical, technical and medical points of view the trilobal ViscoStar fibre and the highly crimped ViscoNova fibre have proven as the most suitable fibres for tampon applications.

In hygiene applications high absorbency under slight mechanical pressure is a very important demand. Within the spectrum of EDANA and INDA test methods the demand absorbency test WSP 10.3 is the closest approximation to simulate these end-uses. When spunlaced fabrics of different fibre types are compared, cellulose fibres generally show much higher absorbency than polyester or polypropylene fabrics under the same conditions. In addition, the test reveals a significant increase in absorbency with our superabsorbent lyocell fibre.

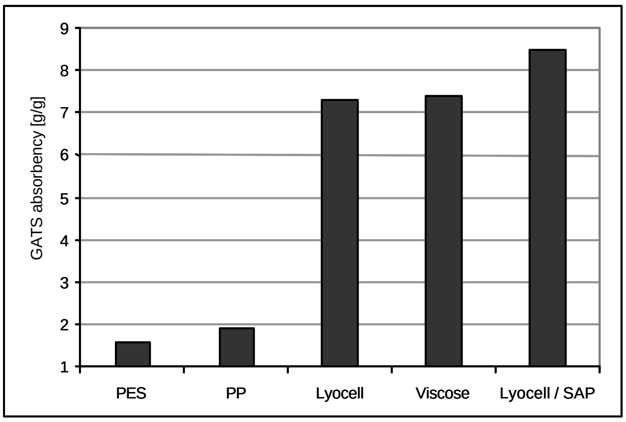

Figure 16. Demand absorbency [g/g] of spunlace fabrics from cellulose and synthetic fibres (50 g/m²)

Highly Absorbent Cellulose Fibres for Wipes Applications

A fundamental requirement to a common household wipe is the ability to take up aqueous liquids under moderate pressures. To a limited extent, this behaviour can also be simulated by the test WSP 10.3, which describes the determination of the nonwoven absorbency when one side of a fabric is brought in contact with an aqueous liquid while the whole sample is kept under a constant mechanical pressure.

Needlepunched fabrics with weights of 100 g/m² and densities of 0.05 g/cm³ clearly show increasing absorbency values when the fibre composition ratio is changed from 100% Viscose to 100% ViscoStar. Thus, the absorptive performance of a household wipe can be increased by 50% without remarkable influence on the mechanical properties when viscose is partially replaced by Viscostar fibre.

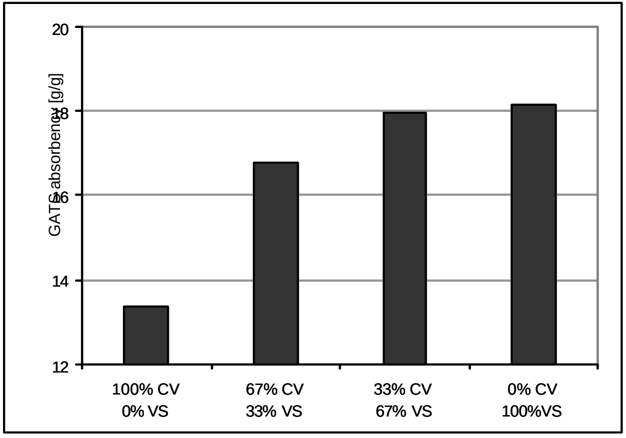

Figure 17. Demand absorbency [g/g] of needlepunched fabrics from CV/ViscoStar fibre blends (100 g/m²)

Conclusion

The sorption properties of man-made cellulose fibres are characterized by two different parameters: water retention and water holding capacity. The water retention of a fibre is mainly determined by its supermolecular structure and its void system. It has been shown that by incorporation of an additional hydrophilic polymer into the cellulose matrix the water retention can be significantly increased, whereas the water holding capacity is not affected because it is mainly driven by surface parameters and can be influenced by modification of the fibre titre, crimp, the shape of the cross section or the fibre finish. By chemical and physical modification of viscose and lyocell fibres prototype fibres with different profiles in water retention and water holding capacity can be obtained. The performance of such fibres in nonwovens is still difficult to predict, as manufacturing technology and structural parameters of the fabric have a significant influence on product performance.

Absorbent nonwoven products are designed to absorb, transport, distribute, retain or release fluids under different usage conditions. Some test methods have been presented which appear to be useful to assess the performance of a material under simulated usage conditions: a syngina test demonstrates the advantage of advanced cellulose fibres like Viscostar or polymer incorporated fibres in tampon applications, while the GATS test confirms the superior absorbency of viscose and lyocell fibres compared to polyester and polypropylene as well as the potential for further improvement of wiping materials by introduction of SAP-incorporated lyocell or trilobal Viscostar fibres.

Man-made cellulose fibres provide purity, softness and absorbency for a broad spectrum of nonwoven products. The capability to design tailor-made fibres with a certain absorbency profile will stimulate innovation in the nonwovens industry and foster the design of new and advanced nonwoven products.

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STRUCTURE-PROCESS-PROPERTY RELATIONSHIPS OF HYDROENTANGLED FABRICS

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The formation of hydroentangled fabrics relies on the impact of high-speed water jets to bond fibres (or filaments) in a web to produce a coherent fabric structure with the required properties. It is known that the influences of water pressure and specific energy influence the tensile properties of hydroentangled fabrics, but little is known about how the structure of hydroentangled fabrics determines the fabric properties and how both processing parameters and fibre properties influence the formation of the fabric structure. The limited information about the fundamental mechanisms involved in hydroentanglement hinders the engineering design of functional fabric structures. Therefore, it is desirable to have structure-process-property relationships for hydroentangled fabrics that links hydroentanglement processing parameters, fabric structure and fabric properties (e.g., tensile strength and permeability) in order to engineer hydroentangled fabrics to meet the requirements of specific product applications.

In this paper, modeling of the basic hydroentangled fabric formation process is summarized based on a consideration of the fibre deformations induced by water jet impact. A relationship between the fabric permeability and the deflection depth of fibre segments in hydroentangled fabrics is introduced.

1. Introduction

Hydroentangled fabrics with the required combination of physical properties are widely used in numerous technical applications, including wipes, napkins, sanitary, medical dressings, scaffolds[1], clothing interlining, filters, composites[2-4] and composite prepregs[5]. As the properties of these hydroentangled fabrics depend on both fibre properties and the water jetting process, a process-structure-property relationship will provide a tool to manipulate the hydroentangled fabric structure to achieve satisfactory product performance by both establishing appropriate manufacturing parameters and selecting proper fibre specifications. This requires quantification of the degree of bonding in hydroentangled fabrics (i.e., the hydroentanglement intensity) and the establishment of relationships between the hydroentanglement intensity and the corresponding fabric properties.

Earlier attempts to characterise the entanglement intensity or entanglement "completeness" in hydroentangled fabrics have relied on experimental measurements of fabric tensile properties and fibre dimensions[6,7]. These approaches have limited value in the prediction of the fabric structure and fabric properties. The fibre and polymer properties, fibre dimensions, web geometry and process-related settings known to influence the degree of bonding have been discussed[8-11]. Experiments have also demonstrated the effect of fibre type on tensile properties and therefore bonding developed during hydroentangled fabrics. However, these studies neither quantify the bonding of hydroentanglement nor establish a basic relationship between fabric structure, processing settings and fibre properties that considers the response of fibres to the jet impact. In our previous papers[12,13], an approach for determining the bonding intensity in hydroentangled fabrics was introduced based on a consideration of the deformation of fibres by the water jets during the process.

In this paper, a brief summary of the approach is presented to introduce the concept of the deflection of fibre segments in fabric bonding and to illustrate its influence on the permeability of a variety of hydroentangled fabrics.

2. The models of the formation of hydroentangled fabrics

2.1 The model of the fabric formation process

In respect of the interaction between fibres and the water jets, two important features of fibre displacement during hydroentanglement have been reported based on high speed photographic studies, (1) Parallelisation and preferential longitudinal reorientation of fibres commences some distance in front of the impinging water-jet and (2) Deflection of the web in a horizontal direction is accompanied by simultaneous compression of the web by 10-20 times the original web thickness as the web passes through the jet impingement zone. Ijaiya[14] and Qiao[15] studied the fibre segment deflections which take place in the web thickness as a result of water jet impingement. It has been observed that fibres with low bending rigidity are more easily deformed in to the shape of a "full loop" or into a curved form visible in the fabric cross-section. An increased number of "full loops" are obtained as the water pressure increases and fibre modulus is believed to be important in governing the formation of such loops.

Based on previous experimental and photographic observations of the jet impact area, three major changes in fabric structure with increasing water jet energy have been identified (Figure 3): (a) initial compression of the web, (b) the inducement of fibre entanglements, which depends on fibre bending and reorientation, and (c) the partial recovery from compression when the impacted areas of the web leave the jet impact area.

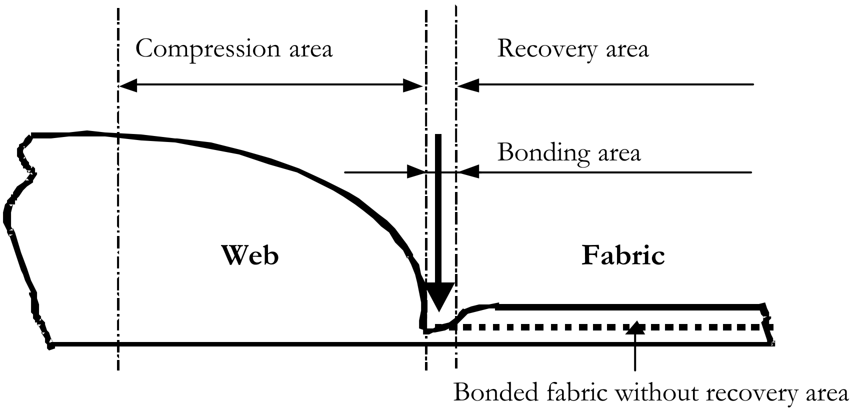
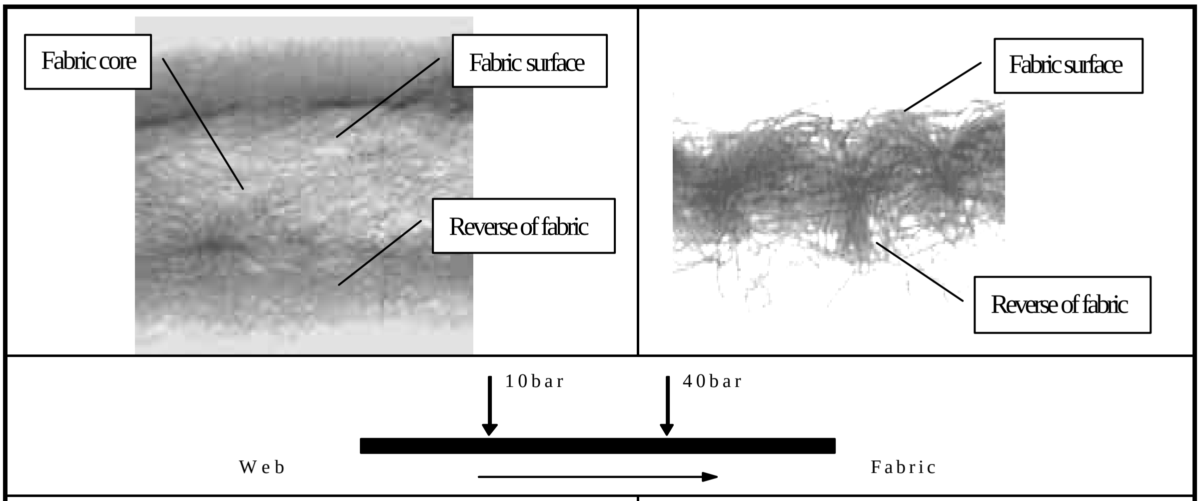


Figure 1. Schematic of the web compression and bonding areas during hydroentanglement.

2.2 Models of the bonding in hydroentanglement and the bending of fibre segments

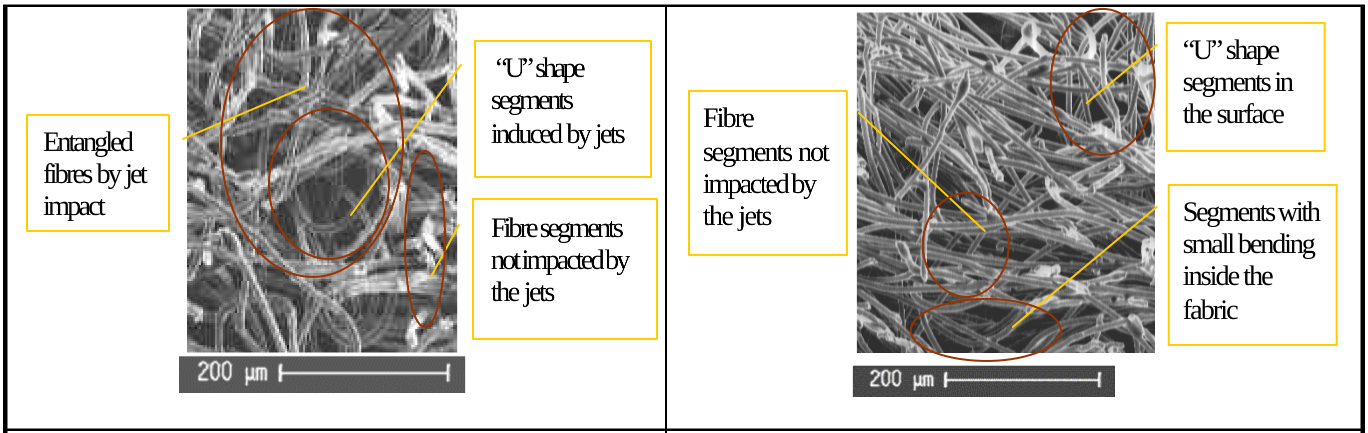
In the early stages of hydroentanglement using just a few injectors (see Figure 1), differences in the consolidation of hydroentangled fabrics made at low water jet pressure (30~40 bar) from polypropylene (PP) fibres and viscose rayon fibres have been examined[16]. The surface of the fabric containing PP fibres compacted more than the interior and a “core-skin” structure was formed that was easily delaminated (see Figure 1(a)). In contrast, throughout the cross-section of a viscose rayon fabric produced using the same jetting conditions and web weight, evidence of fibre segment bending and entanglement was observed throughout the cross-section and the “core-skin” effect was absent (see Figure 1(b)). The fibre deformations and entanglements in commercially produced hydroentangled fabrics (carded and cross-laid before hydroentanglement) of different packing densities have been examined using the SEM, and examples of two hydroentangled polyester fabrics are shown in Figure 2. In the thinner fabric (75g/m^2), many of the fibres within the jet impact area are bent into a "U" shape, and bonding takes place throughout the fabric thickness. In the jet impact areas of the thicker fabric (200g/m^2), it is mainly the fibres near the fabric surface that are bent into a "U" shape within the impact area, while the fibres in the centre of the fabric exhibit smaller deformations. The fabric bonding is poorer than in the 75g/m^2 sample. Of course, the shape of the deformed fibre depends on Many factors including the velocity of conveyor belt.



(a) Fabric composed of 100% PP fibre (1.7dtex X 50mm) (100g/m^2)

(b) Fabric Composed of 100% viscose rayon fibre (1.7dtex X 50mm) (100g/m^2)

Figure 2. Cross-section of two hydroentangled fabrics composed of different fibres showing variations in consideration.



U-shaped fibre segments in the cross-section of a thin fabric (75g/m^2) produced on an industrial production line

Fibre segments in the cross-section of a thick fabric (200g/m^2) produced on an industrial production line

Figure 3. Variations in the heterogeneity of hydroentangled fabrics composed of 1.7dtex polyester fibres.

Based on the model in Figure 3, the fibre bending and deformation induced by the water jet will be associated with the fibre entanglements and bonding. This gives rise to increased packing density, an increase in the penetration of individual fibre segments into the fabric cross-section (see Figure 4) and an increase in the frequency of deflected and looped fibres (see Figure 5). These structural features can reflect the intensity of entanglement (i.e. hydroentanglement intensity).

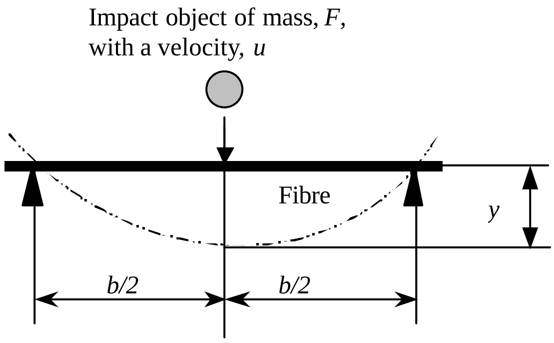


Figure 4. Schematic of a cylindrical fibre subjected to a dynamic impact

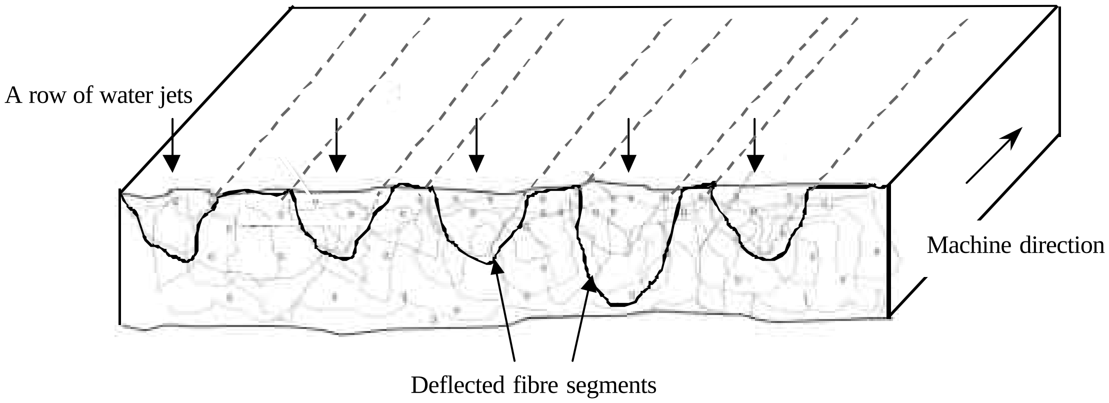


Figure 5. Schematic of fibre segment deflections in the fabric cross-section due to jet impact.

3. Prediction of the Fabric Bonding Prior to the Manufacture of Fabrics

Based on the models in section 2, the intensity of the hydroentanglement bonding in the hydroentangled fabrics are associated with the bending of the fibre segments induced by the water jets. It can be quantified by both the deflection depths of fibre segments and the hydroentanglement intensity, which depends on the effective water jet energy, the web structure and the fibre properties. Thus, the level of fabric bonding (i.e., the intensity of the fibre entanglements) can be predicted prior to the manufacture of the fabric based on manufacturing parameters, the web structure and the fibre properties. This approach is useful in the engineering of hydroentangled fabric structures.

3.1 The effective energy for entangling fibres

The applied energy introduced to the web during hydroentanglement is consumed in various ways, for example, there may be (1) energy losses due to absorption by standing water in the web, K_0; (2) compression of the web, K_1; (3) permanent deformation of the fibres, K_2; (4) temporary, recoverable deformation of fibres in the web, K_3; (5) frictional work resulting from fibre displacement and reorientation, K_4; (6) fluid drag resistance of fibres and capillary resistance of pores in hydrophobic web surfaces, K_5. Therefore, it is important to recognize that only part of the applied energy is available for the purpose of entangling fibres, which results from inducing permanent fibre displacements and bending deformations. The fibre entanglements in hydroentanglement process depend on the effective applied energy, K_2, which is used to displace and permanently deform the fibres in the fabric to produce entanglements.

3.2 The deflection depth of fibre segments

The deflection depth of a fibre segment in the z-direction, *y*, can be calculated based on the dynamic impact force of water jet on a fibre segment (see Figure 4) as shown as follows:

$$y=\frac{\sqrt{2}pgr_w^{0.5}}{12}\frac{r_f}{Ed_f^2}\frac{nC_dD^2p^{0.5}d_x^4}{mv_b}\left(1+\sqrt{1+\frac{48}{p^2g^2r_w}\frac{Ed_f^2}{r_f}\frac{mv_b^2K_2}{n^2C_d^2D^4d_x^4p}}\right) \qquad (1)$$

Where

r_w is the density of water (= 1000 *kgm*$^{-3}$);

r_f is the fibre density (*kgm*$^{-3}$);

C_d is the water flow discharge coefficient. A measured value of 0.66 is used (based on the current experimental set-up in our laboratory)

D is the diameter of the orifice (*m*)

d_f is the fibre diameter (*m*)

d_x is the diameter of a water jet stream on the surface of the web (*m*)

E is the Young's Modulus of the fibre (*Nm*$^{-2}$)

K_2 is the kinetic energy of the water jets applied to a fabric of unit area for the permanent deformation of constituent fibres (*J/m*^{2}). To simplify the problem in this paper, it is assumed that K_2 is thus the same as the total energy, i.e.,

$$K_2=\frac{1.11nC_d^3D^2p^{1.5}}{v_b r_w^{0.5}}$$

m is the area density of the web (*kgm*$^{-2}$)

n is the number of jets per unit length in a water jet strip (*ends/m*)

p is the hydrostatic pressure drop per jet (Nm^{-2})

v_b is the velocity of the conveyor belt (*m/s*)

y is the deflection depth of a fibre due to a dynamic impact (*m*)

3.3 The hydroentanglement intensity (H)

The hydroentanglement intensity, *H,* is defined as the sum of the deflection depths of all fibre segments impacted by the water jets in a unit area of fabric, or the product of the number of fibres hit by the water jets, *N*, and the deflection depth of each fibre segment in the z-direction, *y*, as given in equation 6.

$$H = yN \qquad (2)$$

Clearly, the number of impacted fibres is proportional to the total impact area of the water jets in the web and the deflection depth of each impacted fibre segment depends on both fibre properties and the effective applied energy.

$$N=\frac{mA_w}{\frac{p}{4}d_f^2d_xr_f}\frac{1}{nd_xv_b}=\frac{4m}{pd_xd_f^2r_f} \quad \text{(Number of fibre segments impacted/m}^2\text{)} \qquad (3)$$

Where

A_w is the impact area of a single water jet on the web per unit time (*m*^{2})

N is the number of fibres deformed in a unit area of the web during jet impact (*ends/m*^{2})

H is the hydroentanglement intensity (*m*)

$$H = yN \quad = \frac{\sqrt{2} g r_w^{0.5}}{3Ed_f^4} \frac{nC_d D^2 d_x^3 p^{0.5}}{v_b} \left(1+\sqrt{1+\frac{48}{p^2 g^2 r_w} \frac{Ed_f^2}{r_f} \frac{mv_b^3 K_2}{n^2 C_d^2 D^4 d_x^4 p}}\right) \qquad (4)$$

The influence of fiber rigidity on the hydroentanglement intensity is given in equation 5[14],

$$H \approx \frac{7.18}{\sqrt{R} r_f d_f} \frac{C_d^{1.5} D p^{0.75} m^{0.5} d_x}{r_w^{0.25}} \qquad \text{when} \sqrt{\frac{1.03*10^{-3} R}{d_f^2} \frac{mv_b^3 K_2}{n^2 C_d^2 D^4 d_x^4 p}} >>1 \qquad (5)$$

Where

R is the flexural rigidity of a fibre with a circular cross-section (Nm^2)

4. Linkage between the Fibre Entanglements and Fabric Properties

Traditionally, the influence of the hydroentanglement process on the fabric structure and fabric properties are shown on the tensile strength–applied energy graphs. In this section, a linkage between the fibre entanglements and the fabric properties (tensile strength and permeability) were shown.

Both hydroentanglement intensity (equation 4) and the deflection depths of individual fibre segment (equation 1) in a hydroentangled fabric are the quantifications of the levels of the fibre entanglements in a fabric in different aspects, and they can be linked to specific properties of the fabric. To establish the relationship between the levels of the entanglement of hydroentangled fabrics and their physical properties, the tensile strength and permeability of a series of hydroentangled fabrics composed of polypropylene and viscose rayon fibres respectively were measured (see Table 1).

It is noted that the modulus of wet fibres rather than that of dry fibres influences the fibre bending and the intensity of fibre entanglements, and it is known that the modulus of wet viscose fibres is about half that of dry viscose fibres. The modulus of polypropylene is constant during the hydroentanglement process. Fabrics were produced using two injectors and various water pressures according to the profile in Table 1 and the fibre properties are shown in Table 2.

Table 1. Processing parameters and fiber properties

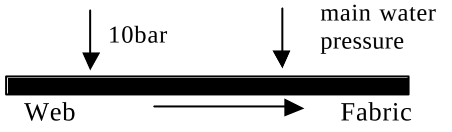
Fabric groups	Fabric weight (g/m²)	Fiber diameter (µm)	Fiber length (mm)	Fiber type & linear density	Main water pressure (bar)
					
1	100	11.9	40	Viscose 1.7dtex	10, 20, 30, 40, 50, 60, 70, 80
2	100	15.4	50	Polypropylene 1.7dtex	10, 20, 30, 40, 50, 60, 70, 80

Table 2. Fibre properties[1].

		Viscose rayon	Polypropylene
Young's Modulus (GNm^{-2})	Dry	3-4.5 (4)	0.5-5.5 (2.5)
	Wet	≈ 50% of the modulus of dry fibre	≈ 100% of the modulus of dry fibre
Density (Kgm^{-3})		1520	910
Rigidity ($*10^{-12}$ Nm^{-2})	1.7dtex	3.94	6.9
	3.3dtex	14.9	26.2
Fiber tenacity (cN/tex)		16-30	25-60

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[1] Fiber properties, http://www.dfv-fachmedien.com/dmmf/img/187_tab1.jpg

4.1 Relationship between fabric tensile strength and Hydroentanglement Intensity (H)

It was observed that the fabric tensile strength links to the hydroentanglement intensity, which depends on the variations in the applied energy, the fiber rigidity, water jetting conditions and the web density.

A traditional way to explain the effect of hydroentanglement on fabric bonding is to plot a graph of the applied energy and the fabric tensile strength. Such a graph for fabrics composed of polypropylene and viscose rayon fibers is shown in Figure 6 and a generalized trend of the effect of applied energy is shown in Figure 7.

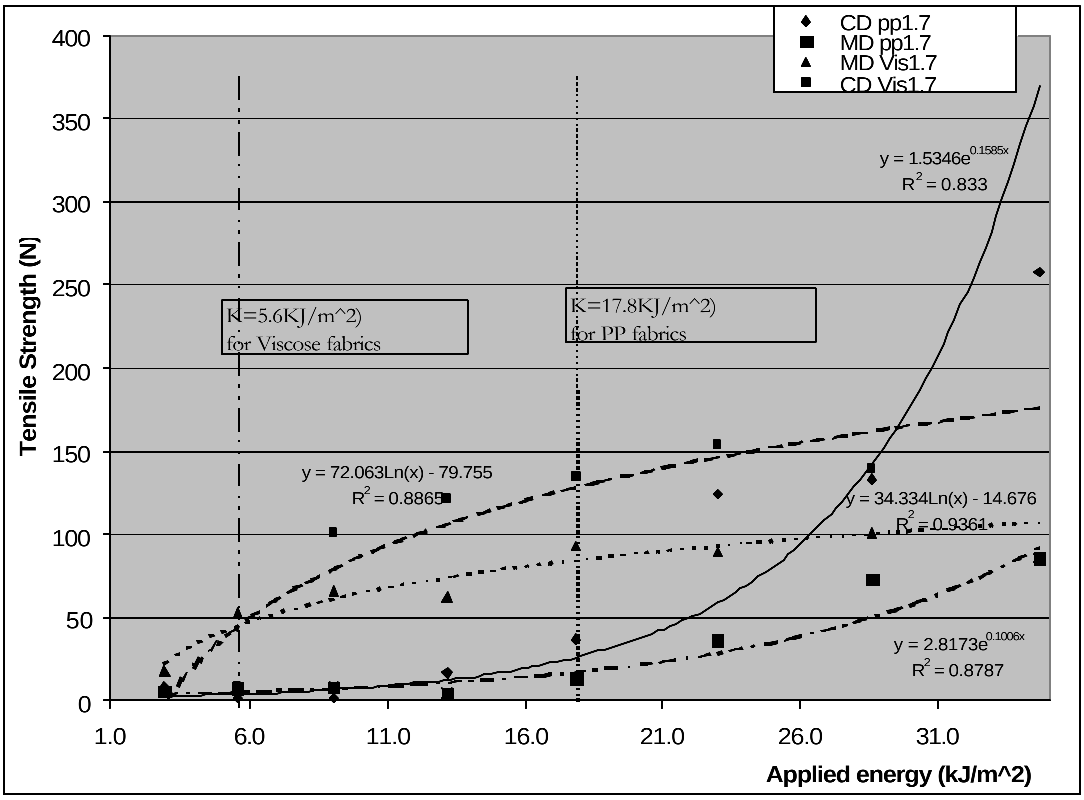

Figure 6. The influence of applied energy on the tensile strength of hydroentengled fabrics.

It is known that the tensile strength of hydroentangled fabrics generally increases with increasing applied energy to a peak level, but the precise relationship between fabric tensile strength and applied energy varies depending on fibre properties (see Figures 6 and 7). In Figure 6, the strength of hydroentangled polypropylene fabrics is comparatively insensitive to increases in energy until a threshold level is reached (around 17.8 KJ/m^2) in this particular example. In contrast, much higher increase in fabric strength is observed for the viscose rayon fabric at low energy and the threshold (turning) point (around 5.6KJ/m^2) is at a much lower energy compared to polypropylene. As the energy increases further, the strength of the polypropylene fabric increases markedly and ultimately and the fabric is stronger than the viscose rayon fabric (Figure 6).

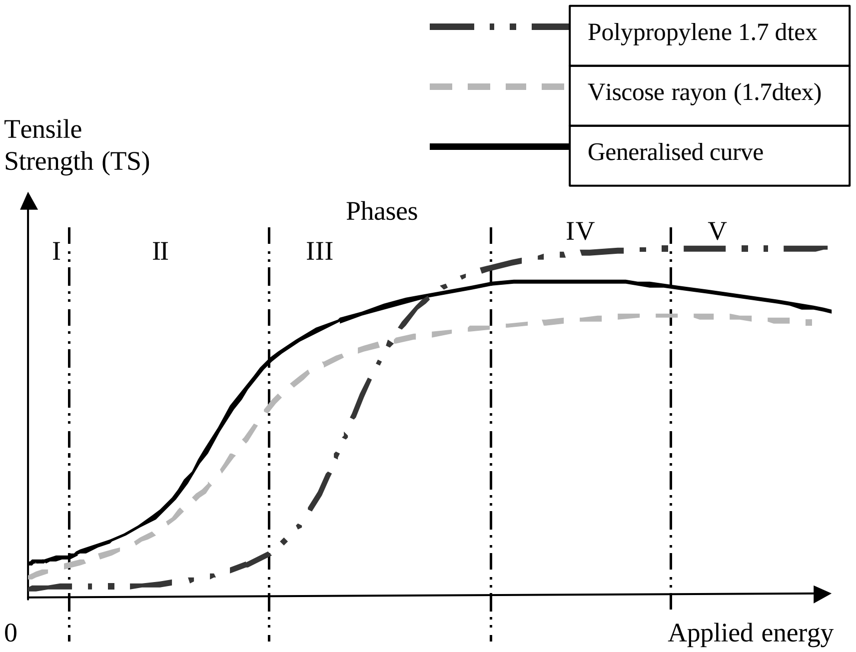

Figure 7. A generalised graph of fabric strength vs applied energy of the two fabrics.

The effect of hydroentanglement intensity (H) on the tensile strength is quite different from that of applied energy. A graph to show how the tensile strength varied with the hydroentanglement intensity is shown in Figure 8 and a generalized trend of the effect of hydoentanglement intensity (H) on the fabric tensile strength is shown in Figure 9. It is apparent that there is a threshold of hydroentanglement intensity, before which the strength changes little with the hydroentanglement intensity and after which the strength increased markedly with increases in hydroentanglement intensity. It is interesting to note that the threshold for both viscose rayon and polypropylene fibres are nearly at the same value (3600 ~ 3800km) (The modulus of both wet viscose rayon and wet polypropylene fibres are considered in these examples), and that the corresponding water jet pressures of the hydroentanglement intensity threshold for fabrics containing viscose and polypropylene fibres are different (the corresponding water jet pressures are 20bar and 50 bar for fabrics containing viscose and polypropylene fibres respectively).

The changes in fabric tensile strength associated with progressive increases in applied energy (i.e., the increase of the hydroentanglement intensity) have been described in five phases (see Figures 7). In phase I at low specific energy, only small increases in fabric strength are observed with increasing applied energy. In phase II, as the energy increases, the tensile strength increases following a threshold point at very low energy that depends on fibre properties (e.g. fibre rigidity) and web weight. In phase III, the tensile strength markedly increases as a function of energy. When the peak tensile strength of the hydroentangled fabric is reached, further increases in energy result in comparatively small changes in tensile strength (in phase IV). As the energy increases further, there may be a decrease of the tensile strength resulting from structural degradation of the constituent fibres due to the high impact energy. A similar description can be applied to the changes in fabric tensile strength with increase in hydroentanglement intensity (H), while the thresholds of hydroentanglement intensity for both fibres are nearly at the same value (see Figure 9).

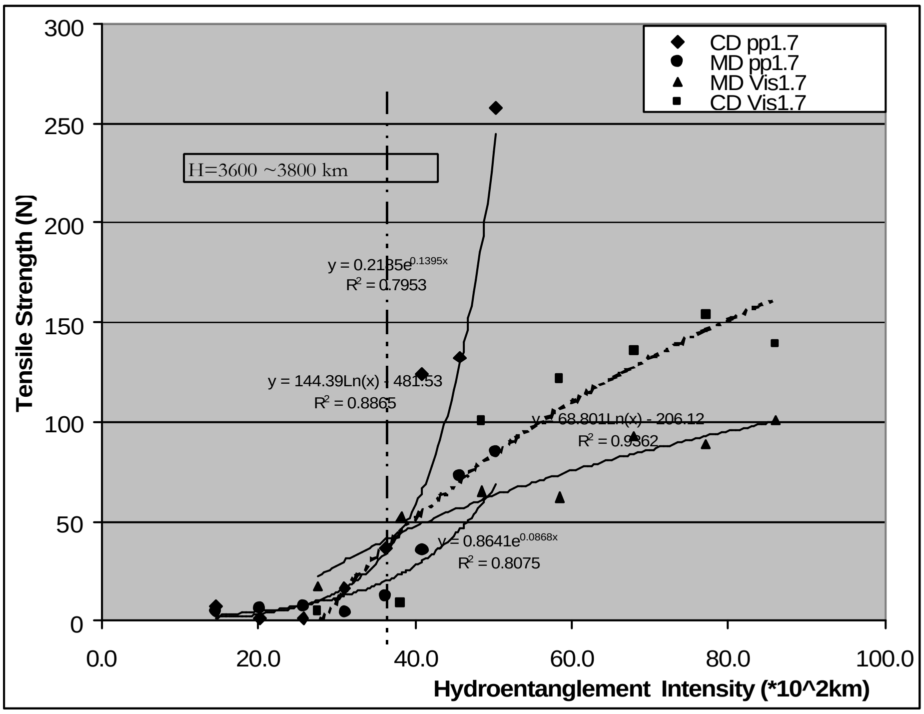

Figure 8. Relationship between the fabric tensile strength and hydroentanglement intensity with in-creasing applied energy (Fabrics composed of polypropylene (1.7dtex) and viscose rayon (1.7dtex) respectively).

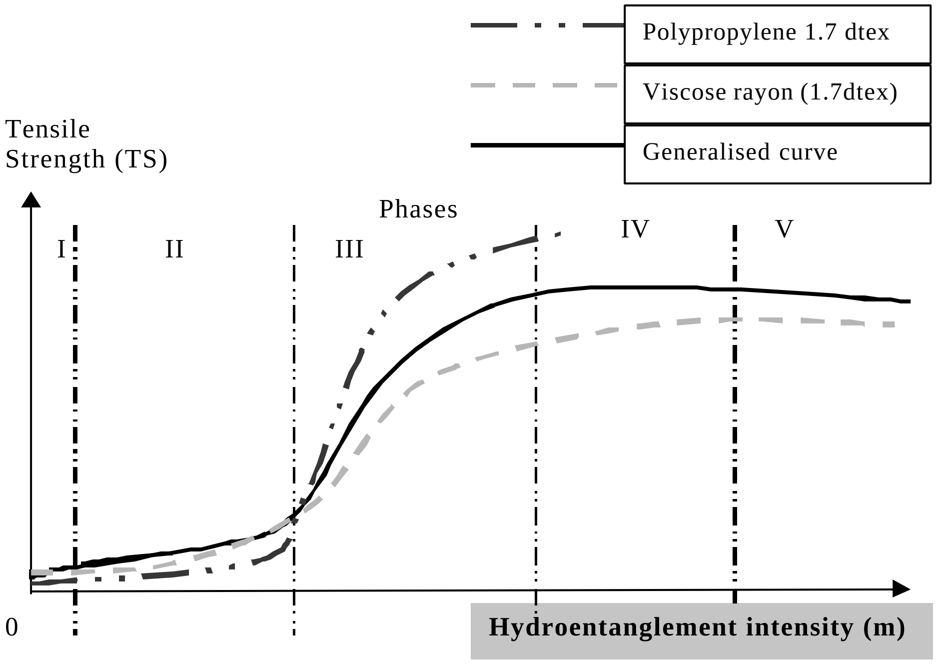

Figure 9. Generalized diagrammatic representations of the changes in tensile strength (*TS*) of hydroentangled fabrics as a function of applied energy.

4.2 The relationship between fabric permeability and deflection depth of fibre segment

It is also found that there is a link between the fabric permeability and the deflection depths of fibre segments obtained in bonding, which depends on the hydroentanglement processing parameters and fibre properties. This linkage will provide a basic tool to manipulate the fabric structure to obtain fabrics with a required permeability.

The permeabilities of hydroentangled fabrics containing polypropylene and viscose fibres respectively were measured and their relationship with the corresponding bending deflections of fibre segments is shown in Figure 10. It is apparent that the permeability of the fabrics is linearly related to the deflection of the fibre segments in the fabric containing viscose rayon fibres. However, there is a complex relationship between permeability and the deflection of the fibre segments in the fabric containing polypropylene fibres.

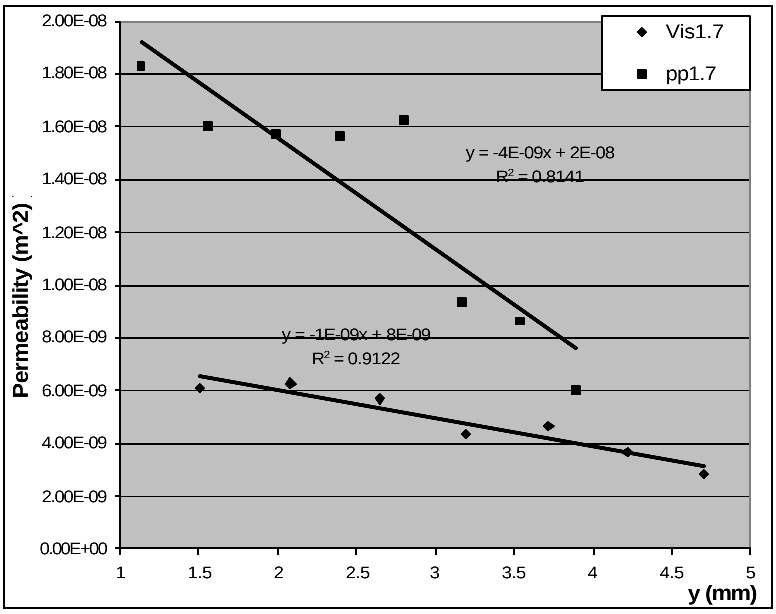

Figure 10. Relationship between the fabric permeability and the predicted deflection depths of fibre segments.

This difference in the trends for the two types of fabric is due to the variations in the fabric structure. In the polypropylene fabrics where small deflection depths are observed, the fabric structure is analogous to a two-layer fabric composite, and the fibre bending is principally restricted to the fabric surface layer and the fibres in the remaining layer are not deformed. In contrast, both the viscose fabrics and the polypropylene fabrics having the greater deflection depth have a uniform structure in the direction of fabric thickness, where the predicted deflection depths of the fibre segments are greater than the measured fabric thickness, and all the fibre segments are deformed.

Therefore, it is found that there is an improved linear relationship between the fabric permeability and the difference between the predicted deflection depths of the fibre segments and the measured fabric thickness, as shown in Figure 11.

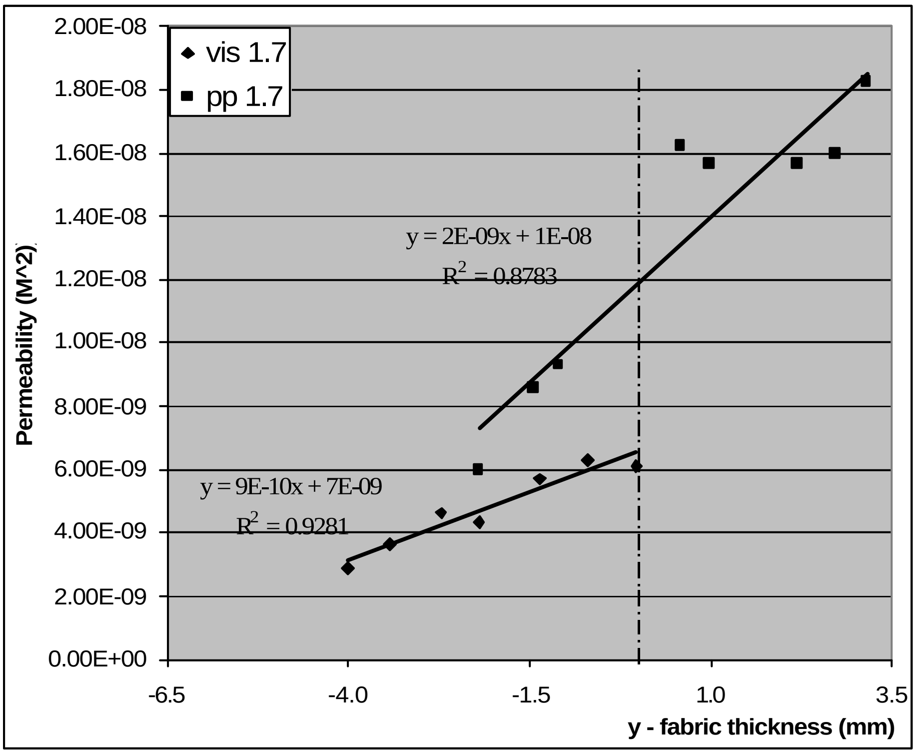

Figure 11. Relationship between the permeability and the difference between the predicted deflection depths of fibre segment and the measured fabric thickness.

5. Conclusions

1) The formation of a hydroentangled fabric from a web is considered to involve three basic mechanisms: (1) lateral compression of the original web, (2) bending deflections and reorientation of the constituent fibres, and (3) recovery of some of the compression and bending deflections. These mechanisms may occur independently or in combination depending on the applied jetting conditions.
2) Only part of the total energy applied to a web is absorbed by the entanglement of fibres arising from the bending deflections introduced by the impinging jets.
3) In the range of the applied energies and fiber types studied, the fabric tensile strength positively correlates with the hydroentanglement intensity (H).
4) Fabric permeability is related to the deflection of fibre segments in hydroentangled fabrics, in particular, it is linearly related to the difference between the predicted deflection depth of the fibre segments and the measured fabric thickness.

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CONTRIBUTION TO THE DISSOLUTION STATE OF CELLULOSE AND CELLULOSE DERIVATIVES

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Abstract

Basing on five industrial relevant systems, consisting of cellulose or its derivatives (organic or inorganic), in one- or multi-component systems with aqueous or anhydrous solvents, we discussed the transformation of cellulose I into II, the precipitation structures and the achievable dissolution state. Hereby a specific attention was turned to the dissolution and formation of Lyocell fibres in ionic liquids.

Keywords: Cellulose, Lyocell fibre, Dissolution state, Ionic liquids, Precipitation structures

Introduction

Subject of this paper are the results and comparison considerations of five cellulose derivatives and their solutions that are technically relevant for the formation of cellulose or have the potential to achieve technical relevance. An overview of the selected systems is shown in Table 1.

The selected systems vary in starting substance: stable (1) or metastable derivatives (2) of cellulose, or native cellulose (3-5); solvent type: organic (1, 4, 5) or inorganic (2, 3); number of components: one (1,5) or multi-component (2-4); solvent type: aqueous (2-4) or anhydrous (1,5); and in type of final product: cellulose derivative (1) or cellulose (2-5). The systems 1-4 are almost known, but the dissolution, formation and regeneration of cellulose from 1-butyl-3-methylimidazolium chloride (BMIMCl), an ionic liquid, is new.

The experiments were established under the aspects of the lyocell process and shall contribute to the clarification of the dissolution state and fibre formation. Thereby we focused on such questions like transformation of cellulose I into cellulose II, the influence of the component water on swelling, dissolution and fibre forming process, as well as the

	Cellulose (or its Derivative) / Solvent	Solvent			Final Product	
		Type	Components	H_2O	Type	Structure of Precipitate
1	Cell. Acetate / Acetone	Organic	1	-	Cell. Acetate	irregular
2	Cell. Xanthogenate / NaOH - Water	Inorganic	2	+	Cell.	irregular / fibre
3	Cellulose/ Cuoxam - Water	Inorganic	2	+	Cell.	fibre structure
4	Cellulose / NMMO - Water	Organic	2	+	Cell.	fibre structure
5	Cellulose / BMIMCl	Organic	1	-	Cell.	fibre structure

Table 1. Selected cellulose/cellulose derivative systems

evaluation of the dissolution state – plasticized cellulose, cellulose gel, or network solution.The dissolution, forming and regeneration of cellulose from ionic liquids is of special interest, since it leads by definition to Lyocell fibres too; but in difference to the amine oxide, the water is not involved in the dissolution but acts only as a swelling agent.

Test Results and Discussion

Transformation of Cellulose I / Hydrate Cellulose / Cellulose II The formation of alkaline cellulose is preliminary to the transformation of cellulose to its acetate or xanthogenate derivatives. According to Fink, Walenta and Philipp [1] a complete transformation of cellulose I into sodium-cellulose I is obtained with 12 or 18 wt % NaOH within 15 s, which is then transformed by washing and drying completely into thermodynamically stable cellulose II.

Earlier, we presented the results of the influence of aqueous N-methylmorpholine-N-oxide on the lattice transformation of cellulose I at 85°C (WAXS-curves, scattering angle 4-40°) [2]. According to that results the cellulose I is stable up to a water content of 76.5 wt-% (~ dihydrate), while a treatment from 81 wt-% (~1.5 hydrate) onwards, after washing and drying, will lead to a complete transformation into cellulose II. Although this process was accompanied by a more or less strong swelling, dissolution was not observed. These results were approved by works of Cibik [3].

In systems 1-4 the transformation of cellulose I into II always takes place in the presence of the swelling agent water. The question remains, what will happen to the cellulose after treatment with an ionic liquid. The WAXS-curves of cellulose after treatment with BMIMCl at 105°C and decreasing water contents, as well washing and drying are seen in Figure 1.

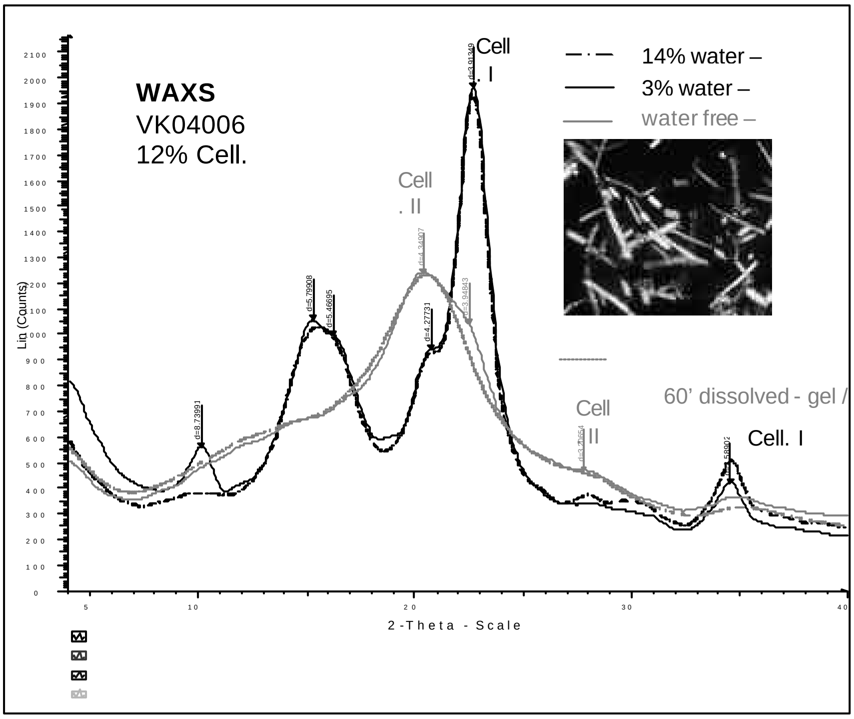


Figure 1. WAXS curves of cellulose in BMIMCl

The samples with 3 and 14 wt% water show obvious reflections of the cellulose I at 0.391 and 0.258 nm, while the anhydrous transformation suspension/solution (see picture in Figure 1) and the solution with the reflections at 0.436 and 0.320 nm document the complete transformation into cellulose II. Though at a water content of 3 wt% we can see under the microscope an obvious swelling, the lattice transformation will start only after a complete exclusion of water.

Dissolution State

The understanding and if possible quantitative measuring of the processes during dissolution and of the dissolution state is of great importance for technical processes of the cellulose deformation.

For its description various model simulations were developed. On the one hand it concerns the electron-donor-acceptor (EDA) concept of Nakao [4] and Philipp [5] respectively the acid-base-concept of Turbak [6] for description of the processes during dissolution and on the other hand the possible appearance forms between the ultimate states solid and molecular disperse solution formulated by Schurz [7] and Burchard [8].

In the ideal case we will get a complete solvatized network solution in preparation of concentrated spinning dopes. Between the solid and the homogenous network solution different transformation stages like „plasticized“ cellulose, gel states and network solution with gel parts can be classified. Hence the question arises whether the reachable dissolution state is stable or metastable and whether the cellulose structure will be destroyed completely during dissolution or will remain parts of that structure or is there any capacity for remembering.

For the „acetate process“ this seems to be clear, since a derivatization with a DS of 3 or 2.5 should destroy the cellulose structure completely and during precipitation there is not any regeneration to cellulose. Figure 2 shows the microscopic precipitation picture of cellulose acetate / acetone (~1 wt-% cell.) in water. As expected no fibre structure is formed but more or less spherical cellulose acetate particles.

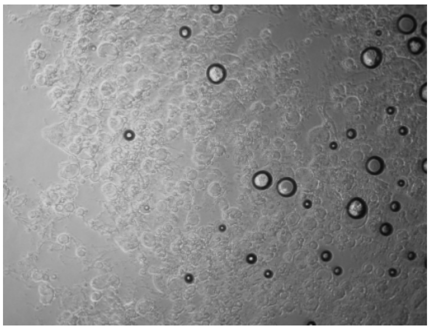
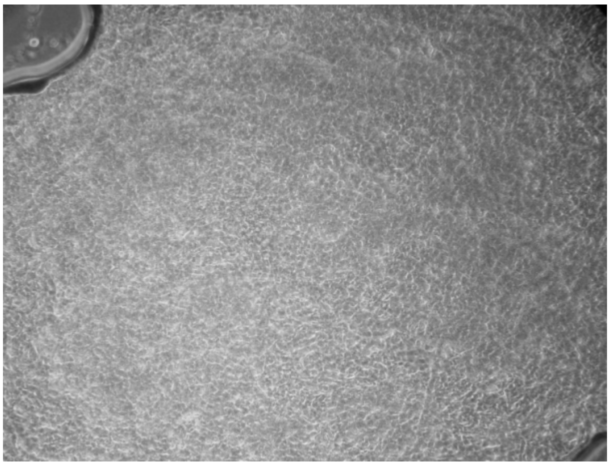


Figure 2. Microscopic picture of the precipitation of cellulose acetate / acetone in water

In case of dissolution of cellulose xanthogenate with a DS of ca. 0.5 in caustic soda in order to get „viscose“ a dissolution state is obtained which comprises all sizes from individual molecule to residual fibre structures [9]. It is not clear if at this DS a complete destruction of the cellulose structure was achieved. Figures 3(a) and 3(b) – show the microscopic picture of a precipitation of viscose (~1 wt-% cellulose) immediately after addition of diluted sulphuric acid / sodium sulfate solution and after a dwelling time of 60 minutes. Compared to Figure 2 we see in Figure 3(a) fibrous parts and in Figure. 3(b) a characteristic fibre structure of the cellulose.



(a) t → 0 min

(b) t = 60 min

Figure 3. Microscopic picture of the precipitation of viscose

The dissolution of cellulose in cuprammonium hydroxide [$Cu(NH_3)_4(OH)_2$, Cuoxam] does not require a derivatization but the complexing of the cellulose through the –OH groups on C2 and C3 nodes requires a break of the hydrogen bonding in such a way that according to Burchard, Seger and Klüfers [10,11] the dissolution can lead up to a molecular disperse solution. The cellulose in Cuoxam can be considered as a polymeric metal complex. In Figure 4 you see the microscopic picture of the precipitation of a Cuoxam solution (~1 wt% cellulose) in diluted sulphuric acid. The cellulose forms a characteristic fibrous structure but it is differing significantly from the one in Figure 3(b).

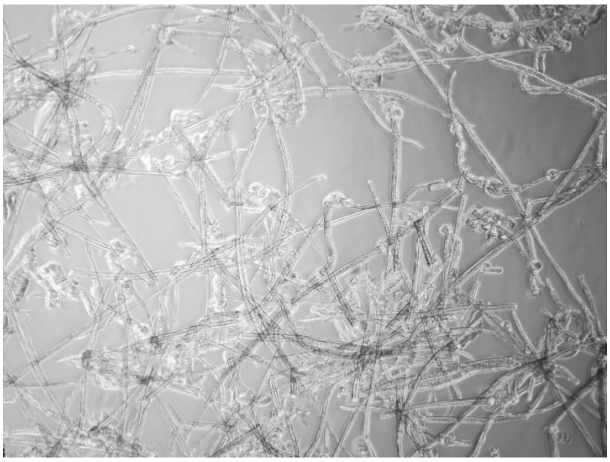


Figure 4. Microscopic picture of the precipitation of a Cuoxam solution

The dissolution of cellulose in amine oxide hydrate is not accompanied either by derivatization or by formation of stable complexes and can be explained by the EDA concept. The dissolution state of cellulose in amine oxide hydrates was studied by Weigel [12] by Wide Angle X-Ray Scattering. He observed that the melt of NMMO-monohydrate still shows a regularity corresponding to the crystal structure of solid monohydrate and that the addition of cellulose does not lead to a qualitative change of the melt structure but only to some damages. Static and dynamic light scattering measurements by Morgenstern [13] and Röder [14] of cellulose / NMMO-hydrate solutions showed, that also in diluted solution aggregates can be found consisting of up to 1000 cellulose molecules and that in case of large particles it concerns the residues of original structures. The improvement of dissolution state indicated by the surface area/volume ratio with increasing cellulose concentration [14] describes the metastable solution state and emphasises the significant influence of the manufacturing conditions like temperature and shear field and approves the order in dissolution, that means the transformation from the solid via the gel state and the homogenous network solution to the molecular disperse distribution. In the microscopic picture of the precipitation of a solution of cellulose (~1 wt%) in amine oxide hydrate in water, as represented in Figure 5, we can see a characteristic fibril structure of the celluloses comparable with that one in Figure 3(b).

Figure 5. Microscopic picture of the precipitation of a cellulose solution in NMMO hydrate in water

Remains the study of a solution of cellulose in ionic liquids, in our case the 1-Butyl-3-methylimidazolium chloride. Ionic liquids were mentioned already 1914 [15], an information about the use as a solvent for cellulose was first given in the patent literature in 1934 [16]. The BMIMCl is a transparent to slightly yellow liquid with a melting point between 60 - 70°C, possesses no measurable vapour pressure and is stable up to temperatures of at least 250°C. In opposition to the amine oxide hydrate the electrical conductivity of BMIMCl is with 60 mS at 25 wt% or 1.4 mS at 99.8 wt% BMIMCl 10,000 times higher. That means that the BMIMCl is not an electrical neutral inner dipole like the NMMO-hydrate, but posses a real ion conductivity.

The dissolution is not accompanied either by a derivatisation nor by a complex forming. An explanation through the EDA seems reasonable, whereas the chloride anion takes the donor- and the imidazolium cation the acceptor-function related to the hydrogen respectively the hydroxyl oxygen. The dissolution process conditions are similar to the dissolution of cellulose in amine oxide hydrates but with the difference, that the BMIMCl will gain its dissolution activity only at a complete absence of water. The solution is strong hygroscopic and with addition of water the cellulose is precipitated spontaneously. The microscopic picture of just precipitated cellulose shows Figure 6. The fibril structure of the cellulose is comparable with that one in amine oxide hydrates in Figure 5 or to the viscose in Figure 3(b).

Figure 6. Microscopic picture of the precipitation of a solution of cellulose in BMIMCl in water

If we want answer to the initial question about the achievable dissolution state of concentrated solutions we can assume that a solvent without derivatisation or complexation will lead through a strong swelling to a „plasticized“ cellulose with original structure features and/or a characteristic capacity for remembering of the structure. We have also to consider that for a spinning dope with for example 13 wt% cellulose we have a molecular ratio of 1 : 8 for cellulose / NMMO-MH or 1 : 6 for cellulose / BMIMCl and the swellability is significantly restricted. From rheologic measurements (viscosity, storage and losses moduli, relaxation time spectres) was concluded, that there is a metastable dissolution state depending strongly on the process conditions. The comparison of the zero shear viscosities of one and the same cellulose in NMMO-MH and BMIMCl shows at the same molar ratio equal values. For instance cellulose solutions with 10.8 or 13.3 wt% cellulose (Cuoxam-DP: 454) in BMIMCl and 13.3 or 16.4 wt-% of the same cellulose in NMMO-MH (molar ratios 1:8 or 1:6) have equal zero shear viscosities with values of 2500 or 12500 Pas at 85°C. This is a very interesting result because obviously the zero shear viscosity not depends on the chemistry and geometry of the solvent molecules, but depends on the number and mole volume of the solvent molecules. This backs our structure proposals up for the systems cellulose / NMMO-MH and cellulose / BMIMCl in Figure 7 (a and b).

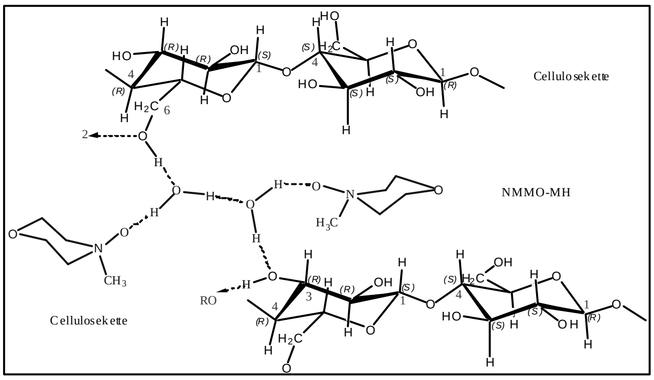


Figure 7(a). Draft of the structure of the system cellulose / NMMO-MH

In Figure 7(a), a draft of the structure of the system cellulose / NMMO-MH is presented. According to this idea the bondings between the OH-groups on C6 and C3 remain on principle and will be prolonged by incorporation of n x 2 NMMO-MH molecules resulting necessarily in an increased flexibility, reduced viscosity and improved deformability of the cellulose. This interpretation would also explain the preservation of original structure features and the great capacity for remembering.

Figure 7(b) shows an analogous draft for spinning masses of cellulose / BMIMCl. Also here the hydrogen bonds between the cellulose chains are elongated through the BMIMCl. This leads to a higher flexibility, lower viscosity and higher formability without complete loss of the original structure features.

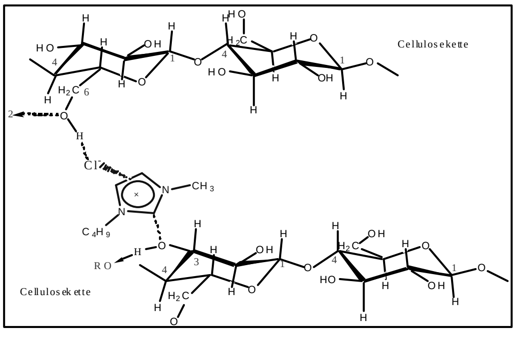


Figure 7(b). Draft of the structure of the system cellulose / BMIMCl

Dissolution of cellulose in BMIMCl and subsequent shaping

The two-component system cellulose / BMIMCl seems to be an interesting item for spinning of Lyocell fibres and is predestined for investigating the influence of water on dissolution, shaping and regeneration also in the amine oxide process.

As already mentioned, the higher stability represents an important advantage. Figure 8 shows the enthalpy change for pure BMIMCl and dope over the temperature. The pure solvent has an endothermic melting peak between 60-90°C and remains unchanged up to the limit of the investigation temperature of 250°C.

After dissolving 12.1 wt% cellulose (Cuoxam DP 530) the endothermic melting peak shifts to lower temperatures of about 45°C. That means the melting point of the dope is decreased significantly.

This will prevent dope crystallisation at room temperature. Starting at a temperature of 213°C an exothermic peak appears, that indicates the onset of cellulose decomposition. From the viewpoint of thermal stability the ionic liquid is clearly superior to amine oxide hydrate.

The dissolution of dry or conditioned cellulose in aqueous BMlMCl proceeds very slowly and does practically not yield any spinnable solution, as described elsewhere [17]. Swelling of cellulose in water and replacement by BMIMCl seems to be a required precondition to allow the solvent to penetrate the accessible sites of the cellulose. When considering some boundary conditions such as pH-value of the aqueous suspension, temperature, shearing field, concentration and time it is still conceivable to convert cotton linters (BWL), steeping sulphate-(VHS) and sulphite pulp having technically relevant molecular masses into very bright dopes.

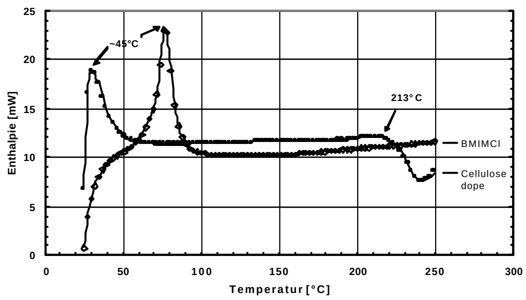


Figure 8. Enthalpy change for pure BMIMCl and dope over the temperature

The molecular mass degradation during dissolution remains clearly below 10 %. The images displayed in Figure 9 allow an assessment of the state of dissolution. The particle size distribution of two dopes with 11.5 wt.- CL (Cuoxam DP 650) or 12 wt.% VHS (Cuoxam DP 569) has been measured by means of laser diffraction [18], respectively. The particle content of 20 or 30 ppm and a particle distribution between 1.2 – 43 µm or 0.25 – 6.5 µm corresponds to a good dope quality comparable to that one of amine oxide solutions.

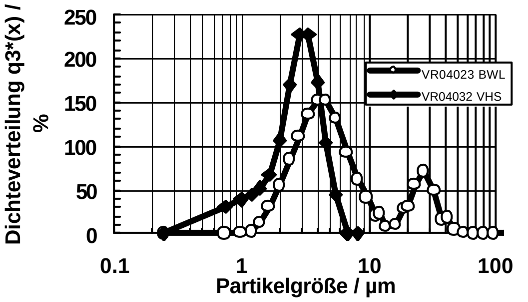


Figure 9. Particle size distribution of two cellulose dopes in BMIMCl

The rheological properties of these dopes, i.e. viscosity, storage- and loss modulus, are plotted versus shear rate in Figure 10.

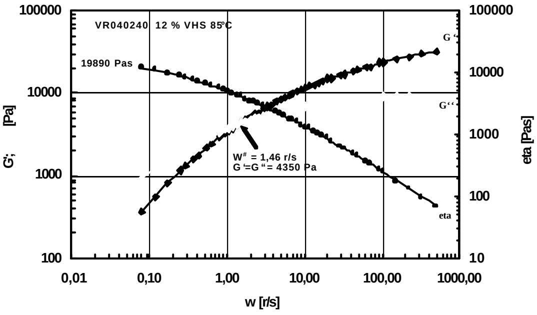


Figure 10. Rheological properties of a cellulose dope in BMIMCl (viscosity, storage- and loss modulus)

The zero shear viscosity determined by creeping test and the stress-strain curve calculated from the moduli are significantly above that ones of a amine oxide solution with the same cellulose concentration. The presence of super-molecular structures is indicated by the course of the dynamic moduli.

It was of further interest to gain knowledge regarding the fibre forming ability and regeneration of such solutions. A schematic presentation of the processes occurring at fibre formation is given in Figure 11.

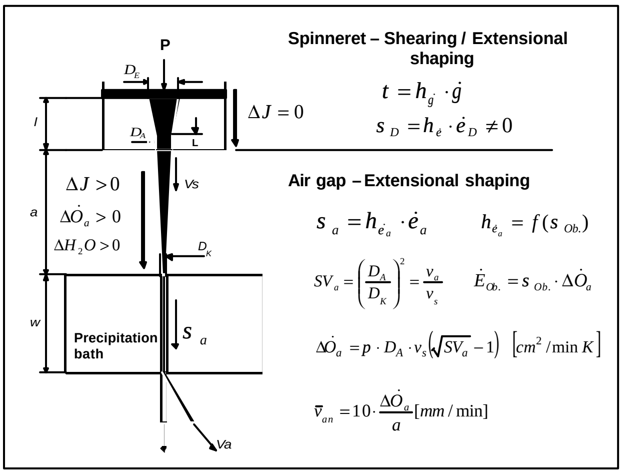


Figure 11. Fibre forming

Providing a capillary of the length l and a pressure p at constant temperature, the dope will be stretched from the capillary inlet diameter D_E to the outlet diameter D_A.

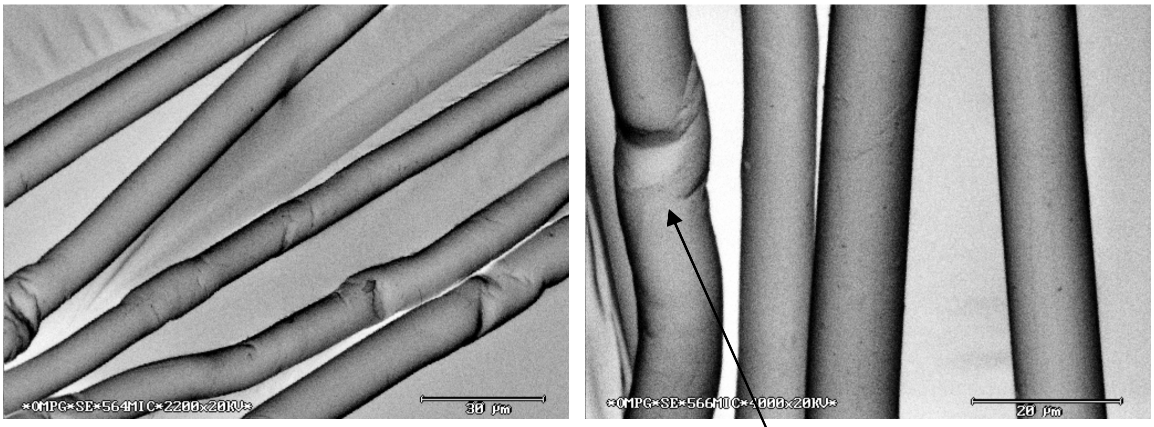
This shaping covers a portion of shearing- as well as elongation. Drafting in the air gap of length a represents the next step. There the liquid spinning jet will be tapered exclusively under the influence of the extensional stress (which is the product of elongation viscosity and elongation velocity) from the capillary outlet diameter D_A to the fibre diameter at the coagulation bath inlet D_K. The surface tension of the dope is one important measure of the elongation viscosity.

The extensional deformation along the gap is connected with a reduction of the temperature, a growth of the surface area and a water diffusion into the fibre boundary zones. The steady new formation of the fibre surface during the spinning draft causes on the one hand additional energy power given by the product of surface tension and surface growth and on the other hand it could lead to damages in the homogeneity of the fibre surface. The surface area growth per time unit and filament can be calculated by the diameter at the capillary exit, the injection rate and the spinning draft and can reach considerable values.

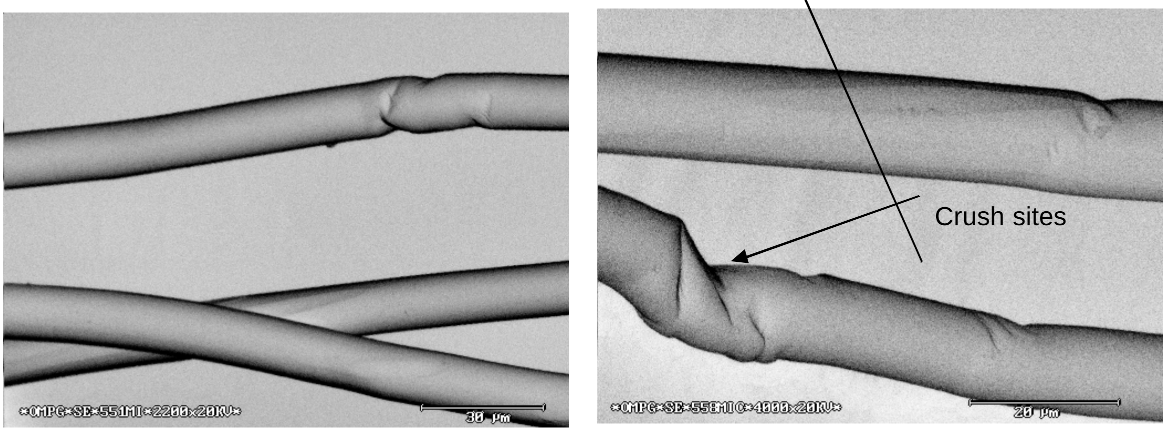
The growth of the surface area standardised to the gap a = 1 corresponds to the rate of the surface growth and was found to be an important criteria for evaluation of the fibre forming and fibre properties.

Since the surface tension of the spinning dopes has not a nonsignificant importance we determined the surface tensions of the solvent and of the dope by Digital Tensiometer (Gilbertini TSD). The surface tension of water with 72.4 mN/m is decreasing by addition of NMMO or BMIMCl and is gaining for the NMMO-monohydrate at 85°C ca. 44 mN/m or for the anhydrous BMIMCl ca. 40 mN/m, that means the difference between the two solvents is low. By dissolution of 11 wt-% VHS-pulp the surface tension of NMMO-monohydrate was increased to ca. 54 mN/m or for BMIMCl to values between 80 and 100 mN/m. This considerable difference should be an explanation for the worse deformability of cellulose / BMIMCl spinning masses beside the effects of the different molar ratio cellulose / solvent and the higher viscoelasticity.

The oriented solution jets are regenerated spontaneously under spinodal separation to a continuous cellulose phase which is riddled with a continuous solvent phase, the later pore system by precipitation of the cellulose during the passage of spinning bath, an aqueous BMIMCl-solution with adjusted pH-value, subsequent washing and drying. The obtained fibres are round and of a very smooth surface.



VK040071.5 1,62 dtex SV_a=12,4 v_a=30 m/min ? $\dot{O}_a$ = 25 cm^2 /min K v_{an}=114 mm/min



VK040071.1 1,70 dtex SV_a=3,4 v_a=50 m/min ? $\dot{O}_a$ = 27,3 cm^2 /min K v_{an}=68 mm/min

Figure 12. EM-pictures of spun fibres

Figure 12 shows the EM-pictures of the spun fibres of similar fineness but different spinning conditions with 2200 - 4000 times magnification. The spinning draft is different by 3.6 times and the rate of the new surface aftertreatment. But here influence on the mechanical fibre parameters is in the range of the measuring error.formation by 1.7 times. The „crush sites“ are typical for cellulose fibres and are a result of the aftertreatment. But here influence on the mechanical fibre parameters is in the range of the measuring error.

The mechanical fibre parameters of fibres of a VHS- and CL-pulp of a fineness of 1.3 dtex as well as the tendencies of the properties compared to Lyocell-fibres from amine oxides are represented in Table 2

We obtained stiff fibres with significantly increased strengths in conditioned and wet states, moduli and loop tenacity and reduced elongation at break. The wet abrasion resistance seems to be improved marginally.

Orienting measurements by X-ray wide angle scattering showed, that at comparable orienting angles the lengths of the crystallites will be by ca. 12 % longer and the crystallite cross section by ca. 14 % smaller, than for traditional Lyocell fibres. Further studies of the fine structure, the morphology and pore systems will have to be done.

The current state of knowledge allows the conclusion that with regard to dissolution and deformation the ionic liquids are inferior to amine oxide hydrate but with regard to the danger potential and achievable fibre properties they give very interesting new starting points.

Parameter		**VHS** VR040241.3	**CL** VR040231.1	**Comparison amine oxide**
Fineness	dtex	1.31	1.27	↘
Tensile strength $_{kond.}$	cN/tex	48.9	57.7	↗
rel. tenacity ratio	%	91.0	90.1	↗
Elongation at break $_{kond.}$	%	12.3	9.0	↘
Elongation at break $_{wet}$	%	13.1	9.0	↘
Loop tenacity	cN/tex	30.3	27.9	↗
Initial modulus	cN/tex	942	1166	↗
Wet modulus	cN/tex	327	511	↗
Wet abrasion resistance	T	50	43	↗

Table 2. Fibre parameters Lyocell fibres (IF)

but with regard to the danger potential and achievable fibre properties they give very interesting new starting points.

Conclusion

Basing on five industrial relevant systems, consisting of cellulose or its derivatives and organic or inorganic, one- or multicomponent, aqueous or anhydrous solvents we discussed the transformation of cellulose I into II, the precipitation structures and the achievable dissolution state. Hereby a specific attention was turned to the dissolution and fibre forming of Lyocell fibres of ionic liquids. A molecular disperse distribution even at low concentrations cannot be expected for solvents non-derivatizing or complexing the cellulose. Higher cellulose concentrations do not lead to homogenous solvatised network solutions, that means the dissolution state is metastable and corresponds more or less to a strong plasticized cellulose, which shear- and extensional viscosity is increasing and the deformability is decreasing with increasing surface tension.

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IONIC LIQUIDS: CURRENT DEVELOPMENTS, POTENTIAL AND DRAWBACKS FOR INDUSTRIAL APPLICATIONS

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Dedicated to the memory of Prof. Josef S. Gratzl [1]

There is an increasing willingness to develop new cellulose-based materials due to the fact that cellulose is the earth´s most abundant biorenewable macromolecular resource. The efficient dissolution of cellulose is a long-standing goal in cellulose research and is still of great importance. This article gives a short survey of the relevant literature with respect to historical developments and potential industrial uses of ionic liquids and then proceeds to the latest results in cellulose/ionic liquid chemistry. Cellulose can be dissolved in several ionic liquids and can easily be regenerated by contacting with water. Dissolution and reconstitution experiments, fiber characteristics and molecular mass distribution data are described. The single crystal X-ray structure determination of the cellulose solvent 1-allyl-3-methylimidazolium chloride is presented.
162 references are given.

Keywords: *cellulose, ionic liquids, 1-allyl-3-methylimidazolium chloride, X-ray diffraction*

Introduction

Definition and properties

An ionic liquid (IL) is a liquid that contains only ions. In the broad sense, this term includes all the molten salts, for instance, sodium chloride at temperatures higher than 800°C. Today, however, the term "ionic liquid" is used for the salts whose melting point is relatively low (below 100°C) [2]. In particular, the salts that melt at room temperature are called "room-temperature ionic liquids" (RTILs).
Room temperature ionic liquids consist of bulky and asymmetric organic cations such as 1-alkyl-3-methylimidazolium, 1-alkylpyridinium, 1-methyl-1-alkylpyrrolidinium or ammonium ions. A wide range of anions is employed, from simple halides which inflect high melting points, to inorganic anions such as tetrafluoroborate and hexafluorophosphate and to large organic anions like bis(trifluorosulfonyl)amide, triflate or tosylate (Figure 1). As one example, the melting point of 1-butyl-3-methylimidazolium tetrafluoroborate [BuImMe][BF_4] with an imidazole skeleton is about –80°C, and it is a colorless liquid with high viscosity at room temperature.

The notable characteristics of ionic liquids are their non-measurable vapor pressure, thermal stability, wide liquid range, and solvating properties for diverse kinds of materials. Another important feature of ionic liquids is their designability: miscibility with water or organic solvents can be tuned through sidechain lengths on the cation and choice of anion. Furthermore, they can be functionalised to act as acids, bases or ligands.

Because of their properties, ionic liquids attract great attention in many fields, including organic chemistry, electrochemistry, physical chemistry, and engineering. In addition, their non-volatility results in low impact on the environment and human health, and they are recognised as solvents for "green chemistry."

However, it remains to be seen how "environmentally-friendly" ILs will be once widely used by industry. Research into IL aquatic toxicity has shown them to be as toxic or more so than many current solvents already in use. Balancing between zero Volatile Organic Compounds (VOC) emissions, and avoiding spills into waterways (via waste ponds/streams, etc.) should become a top priority. That said, with the enormous diversity of substituents available to make useful ILs, they ought to be designed with the foresight of having useful physical properties and less toxic chemical properties [3].

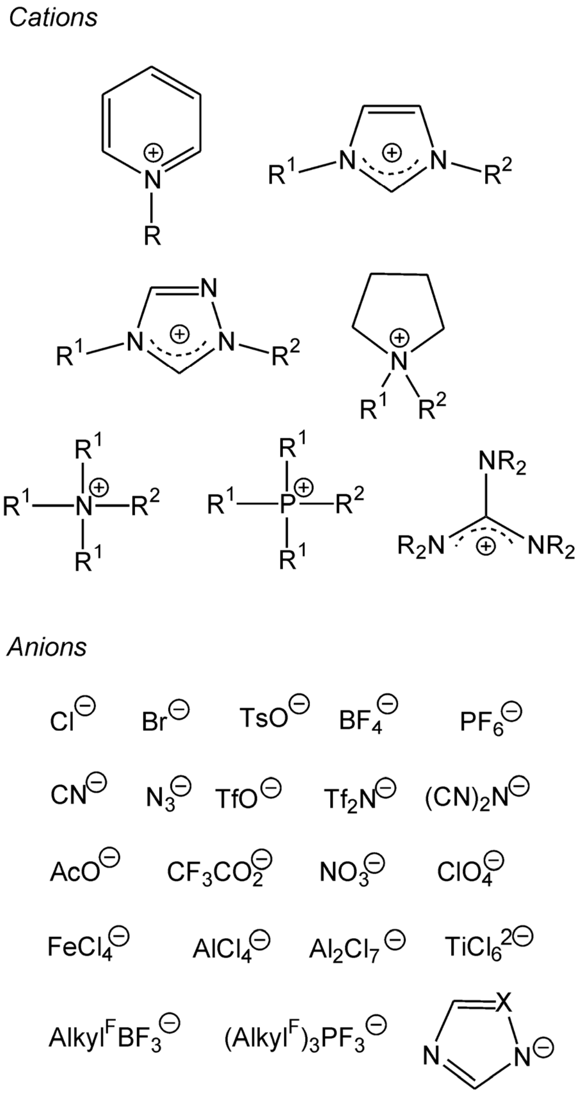

Figure 1. The cation (usually organic) and the anion (usually inorganic) present in ILs [4] are designed so that the resulting salts cannot pack compactly. As a result, ILs do not easily crystallise and remain liquid through a wide range of temperatures [5].

Synthetic concepts for ILs

Principal synthetic concepts for ILs [6] involve quaternisation reactions to generate the cation followed by anion (often halide) metathesis, either by (a) addition of metal salts to precipitate the undesired anion, possibly use of silver salts, (b) addition of strong Brönsted acids to release the unwanted anion as the volatile corresponding acid, (c) use of ion exchange resins, or (d) treatment with Lewis acids to form complex anions such as chloroaluminates. Efficient synthetic procedures for imidazolium salts were described [7, 8]. Often traces of the halide ions or acids remain in the product, either giving rise to liquid eutectic mixtures of otherwise solid salts or leading to unwanted chemical reactivity. Halide-free ILs can be produced by using alkylcarbonates as alkylating reagents and removing the carbonate as gaseous CO_2 or unsoluble metal salt [9, 10].

History

The original family of great-grandfather ILs, *N*-alkylpicolinium halides, was described in 1899 [11] with melting points which classify them as RTILs. Even earlier (1876), some members of this class of salts have been prepared as sirupy liquids by the later Nobel laureate Ramsay [12]. Other great-grandfather ILs, quaternary anilinium salts, were reported at the beginning of the twentieth century [13, 14, 15, 16, 17, 18]. Generally, these early reports are overlooked or ignored. Alkylammonium nitrates were described in 1914 [19]. Several water-unstable chloroaluminates and chloroferrates were discovered in the following years. The systematic utilisation of RTILs was reported by Hurley and Wier in 1951 [20]. In their work, electrodeposition of metals from fused mixtures of ethylpyridinium bromide and metal chlorides was studied. The next decades saw the discovery of low-melting *N*-ethyl-2-ethoxypyridinium tetrafluoroborate [21] and the development of guanidinium chlorides [22] and quaternary imidazolium salts [23, 24, 25, 26], which may be called "grandfather ILs" from today´s point of view. The list of ILs grows daily. Most recently, the 1st International Congress on Ionic Liquids (COIL), held in June 2005 in Salzburg (the City of Salt), Austria, attracted more than 400 participants from 33 countries (Figure 2).

Figure 2. Some of the authors among other participants of the COIL 2005 meeting in Salzburg, Austria.

New developments

In recent years, new guanidinium-based liquid salts [27], countless imidazolium salts, even imidazolium melts with carborane [28] and stannaborane anions [29], pyridinium, and pyrrolidinium salts, or eutectic mixtures [30, 31, 32] were reported. New tetraalkylphosphonium-based ILs with rather high viscosities showed nonlinear optical behaviour [33]. Fluorine-containing cations [34], such as polyfluoroalkyl-1,2,4-triazolium salts [35] possess excellent properties with respect to air-, water-, and thermal stability. Low viscosity ILs, the hydrophilic dicyanamides [36] and the hydrophobic perfluoroalkyltrifluoroborate [10, 37, 38] were investigated. Low-coordinating and non-fluorine containing anions such as bis(oxalato)boranates (BOB) were studied [39]. Properties of imidazolium salts depend on the nature of the anions [40, 41] as well as on the alkyl chain length of 1,3-dialkylimidazolium cations [42, 43]. The physico-chemical properties and reactivities of ILs were reviewed [44, 45]. For analytical applications [46, 47, 48, 49] the nature of both cation and anion is essential. Flammability and thermal stability of trialkylimidazolium salts were found to be more dependent upon the anion than the cation [50]. Recently, energetic ionic liquids such as azido derivatives of 1,2,4-triazolium salts, notably nitrate and perchlorate [51], and other energetic azolium salts with low melting points were described [27, 52, 53, 54]. However, it should be cautioned that reported melting points (Figure 3) are often unreliable due to the hygroscopicity of these materials and the existence of polymorphs [47, 55]. Finally, the vapour pressure of [BuImMe][Tf_2N] was experimentally determined by the Knudsen effusion method [56].

Polarity and solubility

The solubility of ILs in water depends on the nature of the anion, temperature and the length of the alkyl chain on the organic cation. Tetrafluoroborates, chlorides, nitrates, and trifluoroacetates display complete miscibility with water, whereas hexafluorophosphates, triflimides, and other perfluorinated anions impart very low solubilities in water. The hydrophilic/hydrophobic behaviour is important for the solvation properties of ILs as it is necessary to dissolve reactants, but it is also relevant for the recovery of products by solvent extraction.

Empirical solvent polarity scales give insight into solvent-solute interactions. Recently, the solvent parameters α, β, and π^* of several ILs were determined using three solvatochromic dyes [57].

Task-specific ILs

The concept of task-specific ILs (TSILs), which incorporate functional groups designed to impart to them particular properties, stimulated applications extending far beyond those likely for more conventional ILs [58]. One important feature of these liquids is the possibility of tuning their physical and chemical properties by varying the nature of the anion and cation. It is evident that the number of possible combinations is extremely high, and it should be possible to tailor the best IL for any application [44].

The acidity of the C(2)-H in imidazolium cations is well known, and they can be deprotonated to form carbenes [59]. In order to improve the stability against basic ligands, the 2-methylimidazolium cation was introduced.

ILs containing thiol-functionalised imidazolium cations [60] for the modulation of gold surface properties were synthesised. ILs with nitrile-functionalised alkyltrifluoroborate anions [61, 62, 63], zwitterionic liquids [64, 65], and dual-functionalised ILs [61, 66] were reported.

The dicobalthexacarbonyl adduct of 1-allyl-3-propargylimidazolium tetrafluoroborate was the first ionic liquid bearing an organometallic moiety covalently attached to the cation [67]. 1,3-dialkyne-functionalised imidazolium salts were described [68]. The chromium tricarbonyl fragment was introduced onto the imidazolium cation [69]. Imidazolium cations with ferrocenyl appendages were prepared [70]. Metal-containing imidazolium-based ILs were reviewed [71].

ILs containing reducing (cyanoboranate, trichlorogermanate(II)) or oxidising anions (perchlorate, chlorate) open new areas in synthetic chemistry [72].

Different methods to prepare chiral ILs either from chiral starting materials or by asymmetric synthesis and their applications were reviewed [73].

In addition, 1-methyl-3-octylimidazolium tetrafluoroborate was used for enbalming and tissue preservation, and as a fixative for histological purposes [74, 75]. At least, ILs are odorless.

Miscibility

Many ILs are immiscible with either water or organic solvents, so their use in creating biphasic systems has attracted interest, especially for separation purposes. Therefore, novel liquid-liquid partitioning systems (water-ionic liquids) have been considered [76, 77].

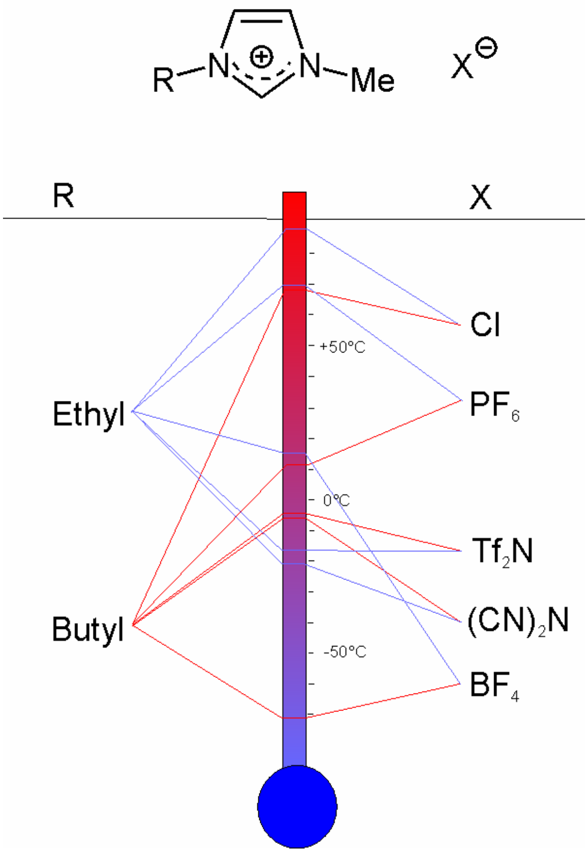

Figure 3. Melting points of selected imidazolium-based ionic liquids

Potential and Drawbacks as Solvents and Reaction Media for Industrial Processes

Industrial aspects of ILs have been reviewed recently [78, 79, 80, 81]. Some of the most intriguing highlights are discussed in the following paragraphs.

Extraction of metal ions

A series of hydrophobic TSILs, designed to extract Hg^{2+} and Cd^{2+} from water, were prepared by appending urea-, thiourea-, and thioether-substituted alkyl groups to imidazoles and combining the resulting cationic species with PF_6^- [82]. ILs were examined as novel media for the extraction of rare earth metal cations such as Eu^{3+}, Ce^{3+} and Y^{3+} [83].

BASIL process

This commercial application (biphasic acid scavenging utilizing ionic liquids) uses *N*-methylimidazole on a multiton scale to scavenge acid that is formed in the process. The reaction results in the formation of the ionic liquid *N*-methylimidazolium chloride, which has a melting point of 75°C. Conventional acid scavengers such as triethylamine produce solids, whereas the ionic liquid separates as a clear liquid phase from the pure product and is recycled.

Desulfurisation

CuCl based ILs exhibit remarkable desulfurisation ability for gasoline [84]. Very promising ILs for deep desulfurisation (down to values of 10 ppm S or even lower) are $[BuImMe][OctSO_4]$ and $[EtImMe][EtSO_4]$, as they are halogen-free and available from relatively cheap starting materials [85, 86]. $[EtImMe][BF_4]$, $[BuImMe][PF_6]$, $[BuImMe][BF_4]$ showed high selectivity for extractive desulfurisation and denitrogenation [87], optionally in the presence of an oxidising agent which oxidises the sulfur compounds to sulfoxides or sulfones during the extraction step. Fuels that can be desulfurised by this method are gasoline, crude petroleum, liquefied petroleum gases, diesel fuel, jet fuel, and distillate fuel oils [88].

Absorption of gases

One of the most exciting and impressive potential industrial applications of ionic liquids is their use for the storage and delivery of gases that are highly toxic, flammable, and/or reactive. The electronics industry uses toxic gases such as phosphine (PH_3), boron trifluoride (BF_3), and arsine (AsH_3) to dope silicon with phosphorus, boron, and arsenic ions. It was realised that chemical complexation could be a superior alternative to physical adsorption and that ionic liquids have properties that are ideally suited for this application [89, 90]. The solubility of carbon dioxide in [BuImMe][PF_6] and [BuImMe][BF_4] was studied [91, 92], and enhanced CO_2 absorption in poly(ionic liquid)s was observed [93]. It was also found that the nature of the anion had the most significant influence on the gas solubilities [94, 95]. The selective and reversible oxygen absorption in an IL was patented [96]. Recently, the solubilities of carbon dioxide, ethane, methane, oxygen, nitrogen, hydrogen, argon, and carbon monoxide were compared [97].

Catalytic reactions in ILs

The key to waste minimisation in chemicals manufacture is the widespread substitution of classical "stoichiometric" syntheses by atom-efficient, catalytic alternatives. In the context of homogeneous catalysis, efficient recycling of the catalyst is a *conditio sine qua non* for economically and environmentally attractive processes. Motivated by one or both of the above issues, much attention has been devoted to homogeneous catalysis in biphasic systems. Similarly, the use of ILs as novel reaction media may offer a convenient solution to both the solvent emission and catalyst recycling problem [4, 98, 99]. Some unidentified mechanism is operating in olefin dimerisation [100].

Nonaqueous biocatalysis [101] and biochemical transformations in ILs [102] were reviewed.

Hydroformylation

Hydroformylation of alkenes has excellent potential as a reaction for use with IL systems allowing continous-flow reactors to be used [103]. Supercritical fluid-ionic liquid biphasic systems were described for the separation of the products from the catalyst [104, 105].

Hydrogenation

Increased rates and effective recycling of the catalyst were observed for the rhodium-catalysed hydrogenation of alkenes in ILs [106, 107]. There has been some speculation that hydrogenation in ILs is due to colloidal rhodium particles [108]. Again, temperature-dependent miscibility and phase-separation add to the opportunities of these processes.

Oxidation

ILs were used for asymmetric epoxidations, oxidation of alcohols to carbonyl compounds, and $PdCl_2$-catalysed oxidation of styrene to acetophenone (Wacker process) [109]. The coordinating ability of the anion was found to affect the kinetics of these oxidation reactions [110]. A mixture of [BuImMe][BF_4] and water was recycled up to eight times in the $PdCl_2$/CuCl-catalysed oxidation of terminal alkenes (with an increase of selectivity in the case of 4-methylstyrene) [111].

Oligomerisation and polymerisation

The high polarity of ILs should make them attractive solvents for ionic polymerisation processes [112]. The methodology is still in its infancy but has great potential for the future [99].

Magnetic ILs

Recently, the IL [BuImMe][$FeCl_4$] was discovered to exhibit an unexpectedly strong magnetic behaviour [113]. This property may lead to novel and unusual applications.

Brönstedt-acidic systems

A new series of Brönsted acid-base ionic liquids were derived from the controlled combination of a monoprotonic acid with an organic base under solvent-free conditions. Bis(trifluoromethane-sulfonyl)amine (Tf_2NH) and imidazole were mixed. The resulting Brönsted acid-base ionic liquid system was investigated as a candidate for a new proton conductor such as a fuel cell electrolyte to operate under anhydrous conditions and at elevated temperature [114].

Zwitterionic ILs containing a sulfonic acid group in a pyridinium cation were successfully employed for catalytic esterification reactions [64].

Electrochemistry

Electrochemical aspects and applications were recently reviewed [115]. ILs have clearly potential as conducting media with large electrochemical windows. For example, reversible electrochemical deposition of magnesium on a silver surface was realised in the IL [BuImMe][BF_4] [116]. The hydrophobic ILs [BuImMe][PF_6] and [Tf_2N] were used in developing a highly efficient anode system for lithium/seawater batteries [117].

Materials science

The unique adaptability and flexibility of ILs provides an attractive alternative for synthetic protocols which are otherwise inaccessible. Thus, exciting new materials such as TiO_2 microspheres, Bi_2S_3 nanorods, or CuCl nanoplatelets with unique and tunable properties have been obtained [118].

Carbohydrates and other biomacromolecules, wood, pulp, and paper

ILs offer promise as solvents for the dissolution of highly polar compounds such as carbohydrates. Over the past few years, carbohydrate chemists have witnessed the use of ILs in a variety of important reactions [5].

There is an increasing willingness to develop new cellulose-based materials due to the fact that cellulose is the earth's most abundant biorenewable macromolecular resource.

The efficient dissolution of cellulose is a long-standing goal in cellulose research and development and is still of great importance. There are various solvents known [119], however, among quaternised nitrogen bases only *N*-methylmorpholine-*N*-oxide monohydrate is applied commercially. The cellulose is processed via direct dissolution to produce fibers (Lyocell process) [120]. Side reactions and byproduct formation in the system NMMO/cellulose have been reviewed [120].

Many solvents have been studied with regard to their application as medium for homogeneous phase chemistry under lab scale conditions. The application of *N,N*-dimethylacetamide/LiCl and dimethylsulfoxide in combination with tetrabutylammonium fluoride trihydrate has broadened the diversity of synthetic paths. In addition, the degree of substitution and the distribution of functional groups may be controlled.

In his pioneering work, Graenacher [121] first suggested in 1934 that molten *N*-ethylpyridinium chloride, in the presence of nitrogen-containing bases, could be used to dissolve cellulose. However, this seems to have been treated as a novelty of little practical value since the molten salt system was, at the time, somewhat exotic and had a relatively high melting point (118°C).

The unconventional dissolution of cellulose in molten lithium perchlorate trihydrate was demonstrated to be efficient for acetylation and carboxymethylation reactions [122].

Cellulose can be dissolved in a number of ILs (so-called green solvents) and easily regenerated by contacting with water or alcohols. This allows a simple, benign system for the processing of cellulose into fibers, monoliths, and films by forming into an aqueous phase. This has potential environmental and cost advantages over current processing methodologies which make use of volatile or hazardous solvents [123].

The dissolution of cellulose in [BuImMe]Cl [124] and the production of cellulose films reconstituted from [BuImMe]Cl [125] looked promising. The ILs used have the ability to dissolve cellulose with a degree of polymerisation (DP) in the range from 290 to 1200 in high concentrations. Using [BuImMe]Cl, no degradation of the polymer was observed. By ^{13}C NMR measurement, it was concluded that this IL is a so-called non-derivatising solvent [126]. However, our results are to the contrary. It is evident, that ^{13}C NMR in not a suitable method to determine molar mass distributions.

"New" and powerful non-derivatising solvents (1-allyl-3-methylimidazolium and 1,3-diallylimidazolium chlorides) for cellulose were described [119, 127], and conductivity and viscosity data were given [128]. Homogeneous acetylation of cellulose in the "new" IL [AllImMe]Cl was reported [129]. However, this IL is not new at all [23, 24].

ILs that dissolve carbohydrates in high concentrations include alkyloxyalkyl-substituted imidazolium dicyanamides [130]. Other imidazolium-based RTILs containing ether and alcohol groups in the side chain [131, 132, 133, 134], even poly(ethyleneglycol)imidazolium salts (grafted system) [135], were described. The oligo-ether units are expected to act as Lewis-basic/hydrogen-accepting functionalities [136].

The suitability of ILs for dissolving and regenerating silk was studied. Thus, [BuImMe] Cl, [Bu(2-Me)ImMe]Cl, and [EtImMe]Cl were found to be able to disrupt the hydrogen bonding network in silk fibroin [137, 138]. Starch was selectively depolymerised by mixing with 1-butyl-3-methylimidazolium chloride. Stirring native barley starch at 100°C gave a product mixture containing monomeric products of depolymerised amylose, but amylopectin remained intact. However, all the starch was converted into monomeric products at 150°C [139]. This is an interesting example of selective degradation of biopolymers. [BuImMe]Cl was also used for the dissolution and regeneration of wool keratin fibers, which can be used to prepare wool/cellulose blended materials directly [140]. Solubilisation and derivatisation of the amino polysaccharide chitin [141] in RTILs clearly has potential for exciting new products [142, 143].

Certain ILs were proposed for wood preservation [144, 145, 146]. Impregnation of paper using ILs as curing agents reportedly decreased strength, improved wettability, and provided resistance to moulds and fungi [147].

Let us take a look at the patent situation: there are of course numerous patents for ILs, e.g. [148, 149], but only a very limited number concerning ILs and cellulose [150, 151, 152, 153, 154, 155]. It is surprising which patents are granted today, taking into account that they involve long-known facts.

Drawbacks

Lack of exhaustive physical parameters such as conductivity, viscosity etc. are a serious drawback for the industrial use of ILs at the moment. The establishment of a comprehensive database was proposed [156], and in 2003, an international effort was launched through the IUPAC to meet this important need.

Among the different generations of ILs, hydrolytically stable yet hydrophobic ILs would allow easiest recovery from biphasic processes (such as spinning cellulose fibers into an aqueous precipitation bath). However, these systems can obviously be never designed to dissolve carbohydrate-based macromolecules, since their solubilisation relies on the competitive replacement of intermolecular hydrogen bridges which is only feasible with hydrophilic solvent systems. Another potential problem with ILs is the possible pathway into the environment through waste water. However, this situation is common with every solvent.

Experimental

Synthesis of 1-allyl-3-butylimidazolium chloride

To 99.5 g of freshly destilled 1-allylimidazole (0.92 mol, 1 equiv.) in a round-bottomed flask equipped with reflux condenser was added an excess of 1-chlorobutane (93.7 g, 1.01 mol, 1.1 equiv.). The reaction mixture was refluxed for 24 h. Excess 1-chlorobutane was removed by means of an oil pump (80°C) yielding 182.7 g of a slightly yellow, viscous liquid (98% of theory).

^{1}H NMR ($CDCl_3$): δ 1.12 (3H, t, J 7.3 Hz), 1.54 (2H, m), 2.10 (2H, m), 4.50 (2H, t, J 7.3 Hz), 5.13 (2H, d, J 6.3 Hz), 5.65 (2H, m), 6.30 ppm (1H, m), 7.91 (1H, m), 8.00 (1H, m), 9.38 (1H, s). ^{13}C NMR ($CDCl_3$): δ 13.3, 19.3, 32.9, 49.5, 51.7, 122.0 (2C), 122.6, 130.1, 137.0 ppm. IR (neat, ATR): 3047, 2957, 2934, 2871, 1644, 1561, 1458, 1424, 1163, 994, 942 cm^{-1}. Mp.: not crystalline down to –50°C, turns into a glass.

Synthesis of 1-allyl-3-butylimidazolium dicyanamide

To a solution of 18.5 g 1-allyl-3-butyl-imidazolium chloride (0.092 mol, 1 equiv.) in 80 ml acetone were added 8.17 g of sodium dicyanamide (0.092 mol, 1 equiv.). The suspension was stirred for 24 h at room temperature, then sodium sulfate was added. The mixture was stirred for additional 20 minutes and then filtered with suction through a G4 frit. The solvent was removed by means of a rotary evaporator and the product finally dried on a vacuum line (oil pump, 70°C, 8 h) yielding 20.7 g of a slightly yellow liquid (97% of theory).

^{1}H NMR (neat, C_6D_6 external locking capillary): δ 1.06 (3H, t, J 7.3 Hz), 1.48 (2H, m), 2.04 (2H, m), 4.44 (2H, t, J 7.3 Hz), 5.07 (2H, d, J 6.3 Hz), 5.59 (2H, m), 6.25 ppm (1H, m), 7.85 (1H, m), 7.94 (1H, m), 9.32 (1H, s). ^{13}C NMR (neat, C_6D_6 external locking capillary): δ 13.7, 19.7, 32.2, 49.9, 52.0, 119.9, 121.7, 122.9, 123.2, 131.5, 136.6 ppm. IR (neat, ATR): 3136, 3093, 2961, 2874, 2225, 2191, 2124, 1561, 1461, 1304, 1160, 993, 944 cm^{-1}.

Synthesis of 1-allyl-3-methylimidazolium dicyanamide

To a solution of 27.9 g 1-allyl-3-methyl-imidazolium chloride (0.175 mol, 1 equiv.) in 80 ml acetone were added 15.6 g of sodium dicyanamide (0.175 mol, 1 equiv.). The mixture was stirred for 24 h at room temperature and then dried with sodium sulfate (2 spatulas). After stirring for additional 20 minutes the mixture was filtered with suction through a G4 frit and the solvent removed by means of a rotary evaporator. After drying the product on a vacuum line (oil pump, 70°C, 8 h), 29.2 g of a reddish liquid were obtained (88% of theory).

^{1}H NMR (neat, C_6D_6 external locking capillary): δ4.21 (3H, s), 5.13 (2H, d, J 6.3 Hz), 5.61 (2H, m), 6.31 (1H, m), 7.88 (2H, m), 9.24 (1H, s) ppm. ^{13}C NMR (neat, C_6D_6 external locking capillary): δ 36.6, 51.9, 119.9, 121.4, 122.9, 124.4, 131.7, 137.2 ppm. IR (neat, ATR): 3136, 3093, 2961, 2874, 2225, 2191, 2124, 1561, 1461, 1304, 1160, 993, 944 cm^{-1}.

Synthesis of 1-allyloxy-3-methylimidazolium dicyanamide

To a solution of 4.3 g 1-allyloxy-3-methylimidazolium iodide (0.016 mol, 1 equiv., prepared from 1-allyloxyimidazole [157]) in 30 ml of distilled water were added 2.8 g of silver dicyanamide (0.016 mol, 1 equiv.). The suspension was stirred at room temperature. A yellow precipitate of silver iodide was formed, and 10 ml of acetone were added. Stirring was continued for 1 h, then the suspension was filtered with suction through a S4 frit. The solvents were removed by means of a rotary evaporator and the product dried on a vacuum line (oil pump, 70°C, 12 h) yielding 2.6 g of a light brown liquid (79% of theory).

^{1}H NMR (DMSO-d_6): δ3.84 (3H, s), 4.91 (2H, d, J 6.6 Hz), 5.30 (2H, m), 6.02 (1H, m), 7.72 (1H, t, J 2.0 Hz), 8.13 (1H, t, J 2.0 Hz), 9.58 (1H, t, J 2.0 Hz) ppm. ^{13}C NMR (DMSO-d_6): δ 36.6, 81.9, 119.1 119.3, 121.6, 124.5, 129.8, 133.5 ppm. IR (neat, ATR): 3120, 3085, 3019, 2228, 2192, 2124, 1572, 1451, 1423, 1307, 1156, 936, 888 cm^{-1}.

Synthesis of 1-allyl-3-propargylimidazolium chloride

To 9.76 g of 1-allylimidazole (0.09 mol, 1 equiv.) were added 8.07 g of propargyl chloride (7.76 ml, 0.11 mol, 1.2 equiv.). While the reaction mixture was stirred for 24 h at room temperature, the colour turned to black. Two spatulas of activated charcoal and 20 ml of CH_2Cl_2 were added. The suspension was stirred for 2 h at room temperature and filtered with suction through a G4 frit with a kieselguhr pad and a silica layer. The frit was washed with acetonitrile (10 ml). The solvents were removed under reduced pressure (oil pump, 50°C) yielding 12.9 g 1-propargyl-3-allylimidazolium chloride as an amber liquid (77% of theory). Heating the compound to 150°C caused decomposition.

^{1}H NMR ($CDCl_3$): δ2.82 (1H, t, J 2.5 Hz), 4.91 (2H, d, J 6.6 Hz), 5.31 (4H, m), 5.88 (1H, m), 7.57 (1H, m), 7.70 (1H, m), 10.22 ppm (1H, s). ^{13}C NMR ($CDCl_3$): δ 39.7, 52.2, 74.5, 78.0, 122.4, 122.5, 122.6, 130.0, 136.8 ppm. IR (neat, ATR): 3129, 3062, 2119, 1557, 1422, 1343, 1154, 994, 945 cm^{-1}.

Dissolution experiments

The IL was melted at 100-105°C, stabilising agent (0.1 % propyl gallate) was added if desired, then cellulose (FEZ 1167, 3%; KZO3 or Solucell 1175, 10% and more) was added and stirred until a clear solution was obtained (30 mbar) as indicated in Tables 1 and 2.

NMR experiments

^{13}C NMR spectroscopy of carbohydrates such as cyclodextrin in ILs is an emerging field of research [158]. A Bruker AC 200 spectrometer was used.

Spinning experiments

Spinning experiments were performed by a dry jet–wet spinning process according to the Lyocell process (use of an air gap; water as spinning bath; 100 µm nozzle).

Gel permeation chromatography (GPC)

Molecular mass distribution of reconstituted cellulose samples was determined by gel permeation chromatography (size exclusion chromatography) using DMA/LiCl as eluent. The method was described in detail earlier [159].

Results and Discussion

Solubility experiments

Solutions of 3% cellulose could be obtained only in chloride-containing ILs (Table 1). The presence of water in the IL was found to decrease the solubility of cellulose [124]. The acidity of the C(2)-H in imidazolium cation-based ILs is presumed to be beneficial for cellulose solvation (hydrogen bonds). Although oxygen-containing side chains [130, 136] were expected to facilitate solvation, cellulose was insoluble in [AllOImMe]Cl. It was also insoluble in dicyanamides and other ILs (Table 2). Solutions of 10% cellulose in [BuImMe]Cl and in [AllImBu]Cl are shown in Figure 4. The solution in [AllImBu]Cl turned irreversibly into a jelly on cooling.

Table 1. Solubility of 3 % cellulose (FEZ 1167) in ILs

Ionic liquid	Solubility
1-Butyl-3-methylimidazolium chloride	+
1-Allyl-3-methylimidazolium chloride	+
1-Allyl-3-butylimidazolium chloride	+
1,3-Diallylimidazolium chloride	+
1-Butyl-2,3-dimethylimidazolium chloride	slow
1-Allyl-3-propargylimidazolium chloride	reacts
1-Butyl-2,3-dimethylimidazolium thiocyanate	–
1-Butyl-3-methylimidazolium saccharinate	–
1-Butyl-3-methylimidazolium tosylate	–
1-Butyl-3-methylimidazolium bisulfate	–
1-Allyl-3-methylimidazolium dicyanamide	–
1-Allyl-3-butylimidazolium dicyanamide	–
1-Allyloxy-3-methylimidazolium dicyanamide	–
1-Allyloxy-3-methylimidazolium chloride	–
Choline chloride : urea = 1 : 2	–

Table 2. Solubility of cellulose in [AllImMe]Cl and [BuImMe]Cl

Solution no.	Ionic liquid	Pulp	Conc. (%)
(1)	[AllImMe]Cl	KZO3 (1085)	12.5
(2)	[AllImMe]Cl	KZO3 (1085)	12 [a]
(3)	[AllImMe]Cl	Solucell 1175	10
(4a)	[BuImMe]Cl	Solucell 1175	11
(4b)	[BuImMe]Cl	Solucell 1175	16 [b]
(4c)	[BuImMe]Cl	Solucell 1175	25 [c]

[a] The pulp was suspended in 50 ml of water, which evaporated during the dissolution process

[b] 5 % pulp added to 11% solution

[c] 9 % pulp added to 16% solution, many undissolved fibers

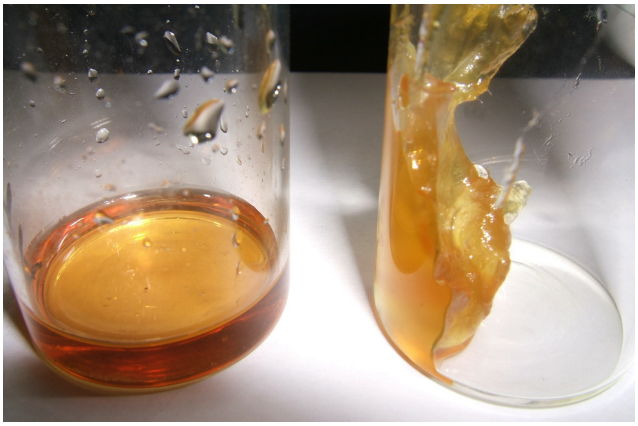

Figure 4. 10 % "solutions" of cellulose in 1-butyl-3-methylimidazolium chloride (left) and in 1-allyl-3-butylimidazolium chloride (right) at room temperature.

NMR results

Although cellulose could not be dissolved in all of the tested dicyanamides, solutions of other carbohydrates were obtained by stirring for 20 minutes at 60°C. The ^{13}C NMR of the disaccharide palatinose (14%) was recorded at 20°C in [AllImBu][$(CN)_2N$] (Figure 5) and found to be identical with published data [160].

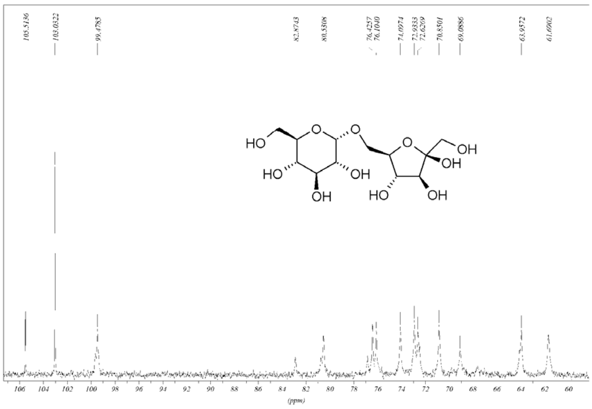

Figure 5. ^{13}C NMR of palatinose in [AllImBu][$N(CN)_2$]

GPC results

In [BuImMe]Cl, excessive degradation of the cellulose was observed in 25% solution at 100°C, but could be prevented by the presence of propyl gallate as stabiliser. In contrast, little degradation occurred when [AllImMe]Cl was used with or without stabiliser. The results are summarised in Table 3. Molecular mass distribution of reconstituted cellulose samples is shown in Figure 6. The second maximum in the curve for [BuImMe]Cl arises from the stepwise addition of the cellulose (cf. Table 2, entry 4b). It is evident that [AllImMe]Cl is a truly non-degradative solvent, whereas pure [BuImMe]Cl cannot be considered a "non-derivatising" solvent [124, 126].

Table 3. GPC results of reconstituted cellulose from IL solutions w/o stabiliser

	Mn (10^3 g/mol)	Mw (10^3 g/mol)	w(DP <50)	w(DP <100)	w(DP >2000)
Starting material (Solucell 1175)					
	67	170	1	10	12
[AllImMe]Cl, KZO3 (1085)					
unstabilised	40	191	5	9	17
[AllImMe]Cl, Solucell 1175					
stabilised	58	149	2	5	9
unstabilised	51	132	2	5	7
[BuImMe]Cl, Solucell 1175					
stabilised	43	94	2	7	2
unstabilised	10	27	34	57	0

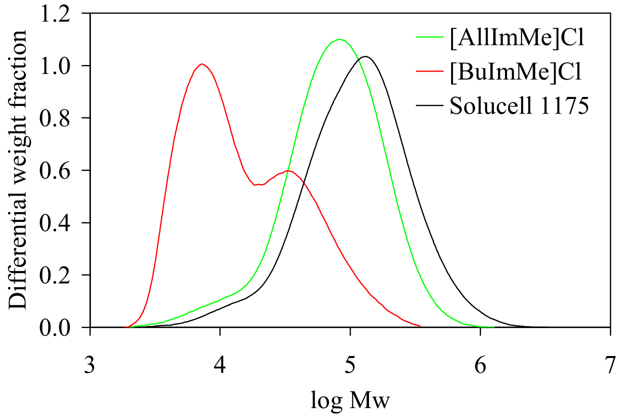

Figure 6. Molecular mass distribution of cellulose (Solucell 1175) recovered from unstabilised solutions in [AllImMe]Cl and [BuImMe]Cl

Fiber data

The fibers obtained from IL solutions exhibit somewhat lower tenacity and elongation values compared with conventional Lyocell fibers. However, we expect to improve these values by optimising the spinning parameters. Weight, tenacity and maximum elongation data of the dry fibers are summarised in Table 4. A typical fiber as prepared from [AllImMe]Cl solution is displayed in Figure 7.

Table 4. Data of fibers spun from [AllImMe]Cl and [BuImMe]Cl solutions

	Yarn count (dtex) [a]	Tenacity (cN/tex)	Elongation (%)
[AllImMe]Cl, 75°C, unstabilised, KZO3 (1085)			
Average	1.3	32.2	8.4
Minimum	1.0	23.3	6.7
Maximum	1.6	37.3	10
VarCoeff	10.6	11.2	11.8
[AllImMe]Cl, 100°C, unstabilised, Solucell 1175			
Average	1.6	26.8	10.8
Minimum	0.7	21.7	7.2
Maximum	2.0	31.1	13.2
VarCoeff	22.8	9.7	17.8
[AllImMe]Cl, 80°C, stabilised, Solucell 1175			
Average	1.3	36.8	11.2
Minimum	1.1	27.6	7.5
Maximum	1.6	43.6	13.7
VarCoeff	9.6	10.9	15.3
[BuImMe]Cl, 100°C, stabilised, Solucell 1175			
Average	1.3	33.1	11.5
Minimum	1.1	20.9	5.3
Maximum	1.6	39.6	14.2
VarCoeff	10.6	12.4	18.7
[BuImMe]Cl, 105°C, stabilised, Solucell 1175			
Average	1.0	37.9	11.3
Minimum	0.8	33.1	8.0
Maximum	1.3	42.9	13.7
VarCoeff	12.3	8.4	12.3

[a] g/10000 m fiber

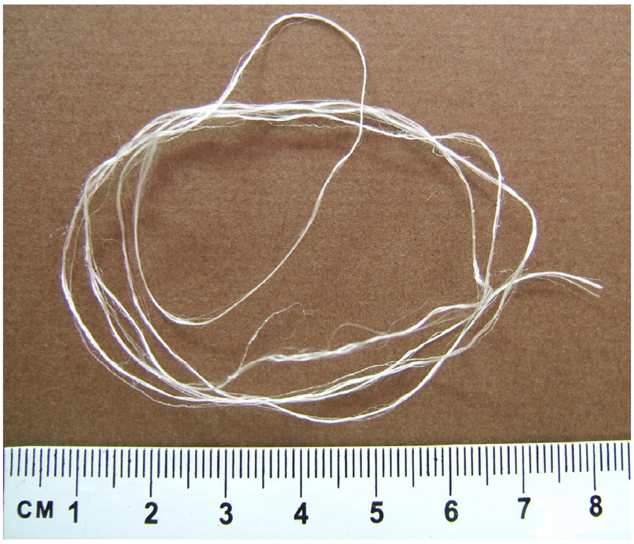

Figure 7. Cellulose fibers obtained from [AllImMe]Cl

X-ray diffraction single-crystal structure

An X-ray crystal structure determination of the grandfather IL 1-allyl-3-methylimidazolium chloride [65039-10-3] (mp.: 17°C [129]; in contrast, 55°C was reported by Sigma-Aldrich-Fluka [161] and confirmed by us by DSC; maybe there are polymorphs, but this compound definitely is very hygroscopic) from commercially available [162] single crystals, was carried out, using Mo K_α radiation and refined on F^2: space group $P2_1/c$, monoclinic, a=7.931, b=12.836, c=16.452 Å, β=96.22°, V=1665.0 Å^3, Z=4, D_{calc}=1.266 g cm^{-3}, μ=0.387 mm^{-1}, T=173 K, 12319 reflections collected, 3535 independent (R_{int}=0.034), 2857 (I>2σ(I)), θ range 2.0-26.9°, R_1(I>2σ(I))=0.0364, wR_2(I>2σ(I))=0.0735, R_1(all =0.0523, wR_2(all)= 0.0789, GOF=1.053. A crystal packing diagram is shown in Figure 8, short C(2)-H$\cdots$Cl distances of 2.58 Å are indicated. In the two independent molecules in the asymmetric unit, the allyl group was found to be tilted out of the ring plane by 59.3 and 89.6°, respectively (Figure 9).

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-286726. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

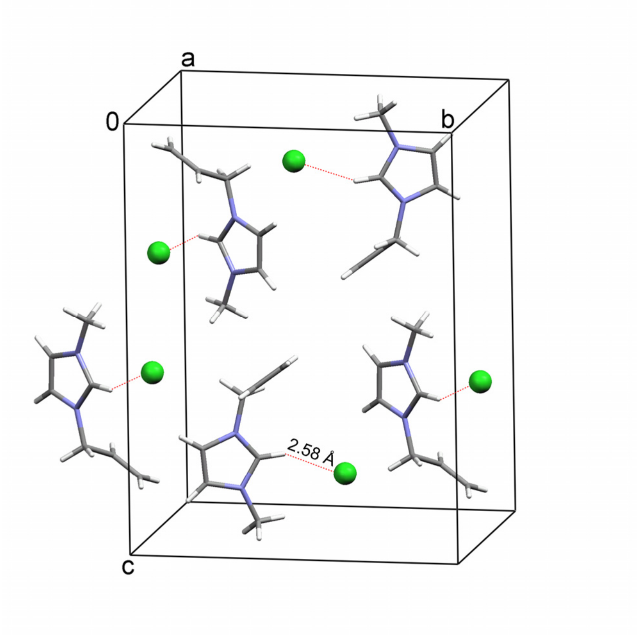

Figure 8. Crystal packing of 1-allyl-3-methylimidazolium chloride showing short C(2)-H···Cl contacts of 2.58 Å

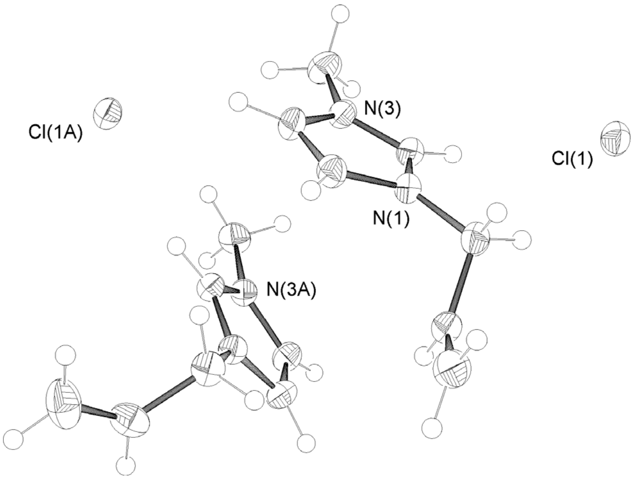

Figure 9. ORTEP plot of 1-allyl-3-methylimidazolium chloride (50% probability ellipsoids) showing the two independent molecules

Conclusions

The opportunity to use ILs as solvents for processing of cellulose was investigated. Over the last ten years, interest and publications involving ILs have expanded exponentially. At this moment, it is really too early to pick favorites in this area. Exciting developments are to be expected, e.g. fibers from molecular composites such as silk/cellulose or wool/cellulose hybrid fibers. The use of chiral ILs for biomacromolecules may also hold promise for interesting developments in the future.

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NEW CELLULOSIC MATERIALS PRODUCED BY THERMOPLASTIC PROCESSING OF SILYLCELLULOSE

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Abstract

The application of melt spinning processes for the production of cellulosic fibres would be a significant sign of progress for economic and environmental reasons. A process for melt spinning of trimethyl-silycellulose (TMSC) was developed. Bis- (trimethyl-)silylcarbamate (BSC) was found to be excellent for the silylation of cellulose due to good swelling and penetration into cellulose. The synthesis could be performed without catalyst and absolutely salt free. For this reason silylcellulose had superior melt processing properties and could be melt spun without any additives at temperatures below 250°C with spinning speeds up to 1000m/min. Pure cellulosic fibres were obtained after hydrolysis of the silyl-groups. Hexamethy-disiloxane formed could be recycled by catalysed insertion of isocyanuric acid which was received by thermal decomposition of urea. The resulting fibres properties were close to tyre cord yarns. All process chemicals were recycled. It was Thought that the process is still on a laboratory scale so that there is potential for launching the pilot plant scale due to the high productivity of the process.

Introduction

The motivation for this work is the serious ecological disadvantages associated with the viscose process. Approx. 90 % of regenerated cellulose fibres are produced by the viscose process, in which sulphurous effluents and exhaust air (e.g. H_2S, CS_2, mercaptanes) inevitably occur. Very low limiting values for basic process chemicals demand expensive downstream cleaning technologies. Alternative processes are based mainly on the use of other types of cellulose derivatives for a wet spinning process or on direct solvents for cellulose.

These alternative routes are faced with general problems of wet spinning processes: solvents, salts and washing baths have to be recycled and the spinning speed is limited. This is significantly reducing the productivity. One important step towards higher productivity would be taken if the wet spinning processes could be replaced by a melt spinning process. Should this attempt be technically feasible, fibres could be produced free of solvents, salts, heavy metals and sulphur. This task was being investigated in a BMBF research project [1]. The process developed [2] and the properties of the new man made cellulosic materials will be presented in this paper.

Process development

It was essential for a successful process development to find a suitable cellulose derivative that could be melt-processed without decomposition. Additionally strict requirements were claimed to potential derivatizing agents: they must be recycable and easy to handle, and must not harm the environment and the workplace. Only very few cellulose derivatives are considered for this purpose. From the family of thermoplastic cellulose derivatives, trimethylsilylcellulose (TMSC) seemed to meet the technical requirements, and was therefore selected as the basic polymer for the process development. The basic reaction of TMSC synthesis is shown in Fig. 1. Three hydroxyl-groups can be silylated per anhydroglucose-unit (AGU). A degree of substitution from 0 to a maximum of three is possible. State-of-the-art TMSC syntheses are unsatisfactory. The syntheses described are performed in homogeneous solution forming high salt contents and are characterized by extreme reaction times, and can therefore not be used for melt processing and technical processes [3-7].

The thermoplastic processing of trimethylsilylcellulose on a laboratory scale is discussed elsewhere [4,8]. The processing temperatures used are over 300 °C, and therefore already in the thermal decomposition range and not suitable for technical applications.

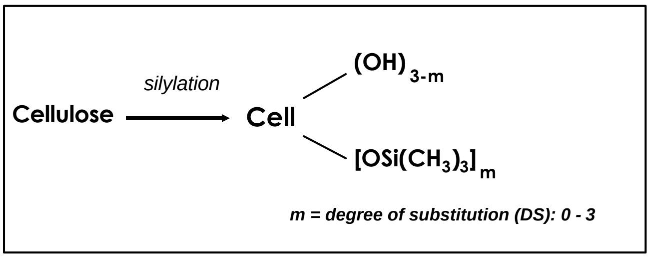

Figure 1. Basic reaction of cellulose silylation

It was a major subject to develop new synthesis strategies to improve the melt processability of the TMSC products and the productivity of the synthesis significantly. Fig. 2 shows a schematic diagram of the TMSC process to be developed and explains the technical conversion:

Bistrimethyl-silylcarbamate (BSC) was used as new silylating agent for cellulose which has proved to be the best choice. The advantages of BSC are described in the next chapter. In a subsequent hydrolysis stage, the silyl-groups are hydrolyzed (regeneration step) to obtain cellulosic fibres. It is important for a successful technical conversion that the hydrolysis product hexamethyldisiloxane (HMDS) can be transformed to the initial silylating agent in a recycling step. All chemicals used for TMSC synthesis are therefore subjected to technically practicable process recycling steps.

The proposed recycling for the silylating agent is illustrated in fig. 2 where isocyanic acid is inserted in HMDS forming bistrimethylsilylcarbamate (BSC), which is used again for cellulose derivatization. The source for isocyanic acid is the thermal decomposition of urea.

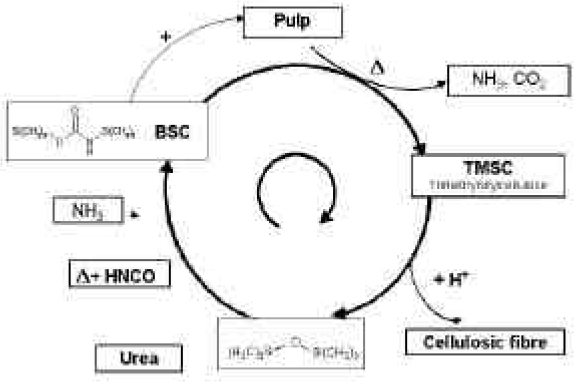

Figure 2. Schematic diagram of salt-free cycle in the production of man made cellulosic fibres from Trimethylsilylcellulose (TMSC)

Results and Discussion

The research project therefore had three major objectives: TMSC-synthesis, fibre production and silylation agent recycling. The economic and ecological technical conversion criteria were the focal point in each case.

During the optimisation of the TMSC synthesis, best product properties with respect to melt processing were obtained by using BSC for silylation. BSC has several advantages compared to other silylating chemicals: it reacts autocatalytically with high yield. The derivatization is completely salt free. In contrast to hexamethylendisilazane (HMDZ), the use of a silylating catalyst is not necessary. BSC itself is good swelling media for cellulose which results in high yields and short reaction times. The good penetration of cellulose with BSC leads to minimized side reaction.

Therefore pure, homogeneous products with excellent thermoplastic properties are obtained by silylation of cellulose with BSC. By using BSC, TMSC synthesis could be performed economically under controlled conditions. On the basis of homogeneous substitution distribution, proved by X-ray structural analysis, which results in very good melt processing, processing temperatures could be reduced to 250-260 °C. This temperature range is below decomposition temperature, making possible the decomposition-free thermoplastic processing of TMSC products for the first time. This is made clear by the TGA-curve in fig. 3, where the onset of decomposition is above 300 °C.

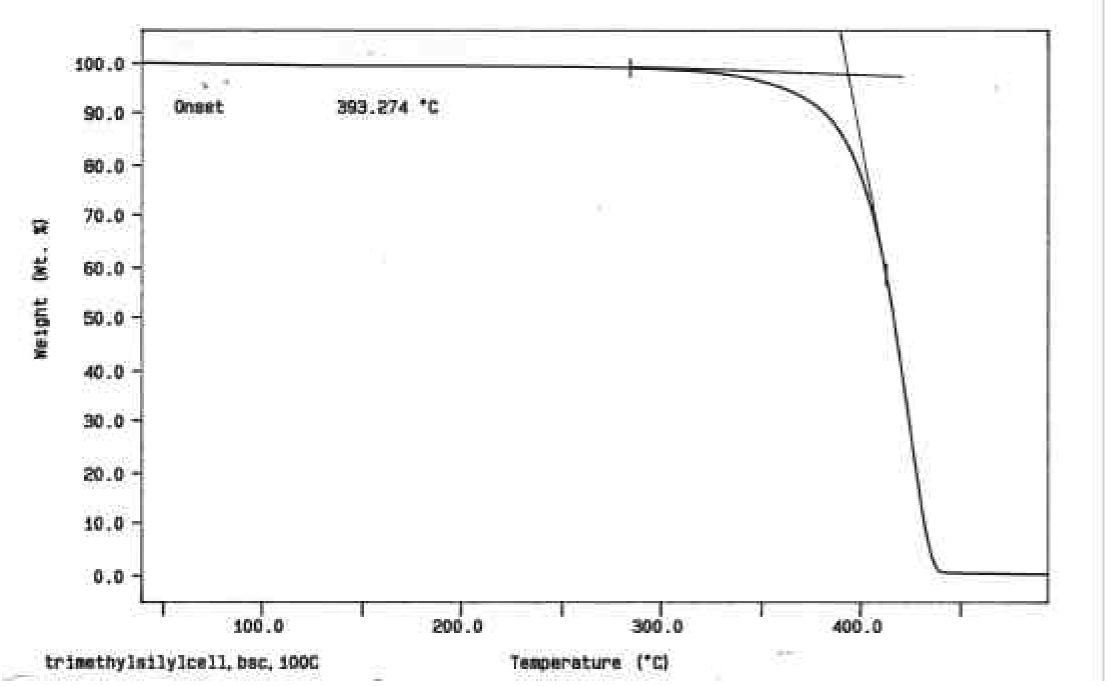

Figure 3. Thermogravimetric analysis of homogenous sub. TMSC (DS = 2.1)

Thermoplastic TMSC based on the optimized synthesis using BSC have a degree of substitution (DS) of about 2.0- 2.2, a degree of polymerization (DP) of about 230-550 and a melting range of 245- 255 °C. These TMSC products have been processed without difficulty on a standard melt spinning plant. The fibres were produced at spinning speed of 250 – 1000 m/min leading to cellulose products with new properties due to polymer orientation. Success has also been achieved in hydrolyzing the silyl-groups completely, meeting an important technical conversion criteria. Hydrolysis of silyl-groups was controlled by infrared measurements. Figure 4 illustrates FTIR-measurement of fibres treated directly after spinning online in a closed godet with 1n HCl during 2min. Under these conditions a temperature of 40°C is sufficient for complete hydrolysis of silyl-groups indicated by reduction of characteristic Si-vibrations.

The fibre characteristics are summarized in table 1. It was surprising that the fibre parameters of hydrolyzed TMSC fibres almost meet technical fibre standards although spinning trials were performed on small scale equipment. The good fibre properties were a result of a fibre structure conversion from amorphous (TMSC fibre) to cellulose II structure (TMSC-hydrolyzed) with a degree of crystallization of about 45 % (figure 5). The gained properties underline that the newly developed TMSC process has great potential for producing a new types of man-made cellulosics mainly for technical applications.

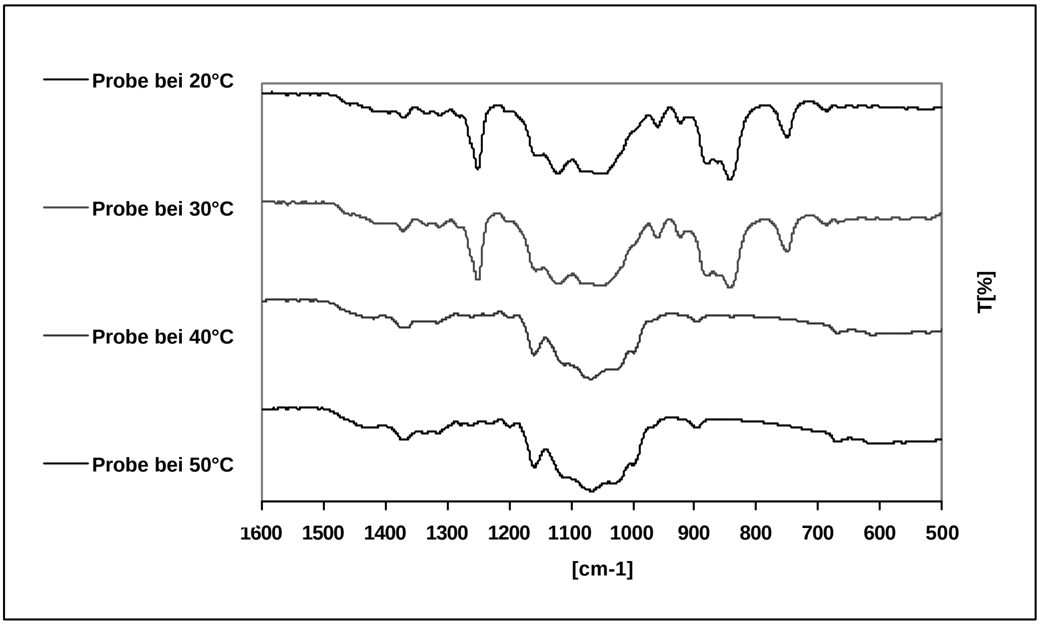

Figure 4. : Control of hydrolysis of silyl-groups by FTIR measurements

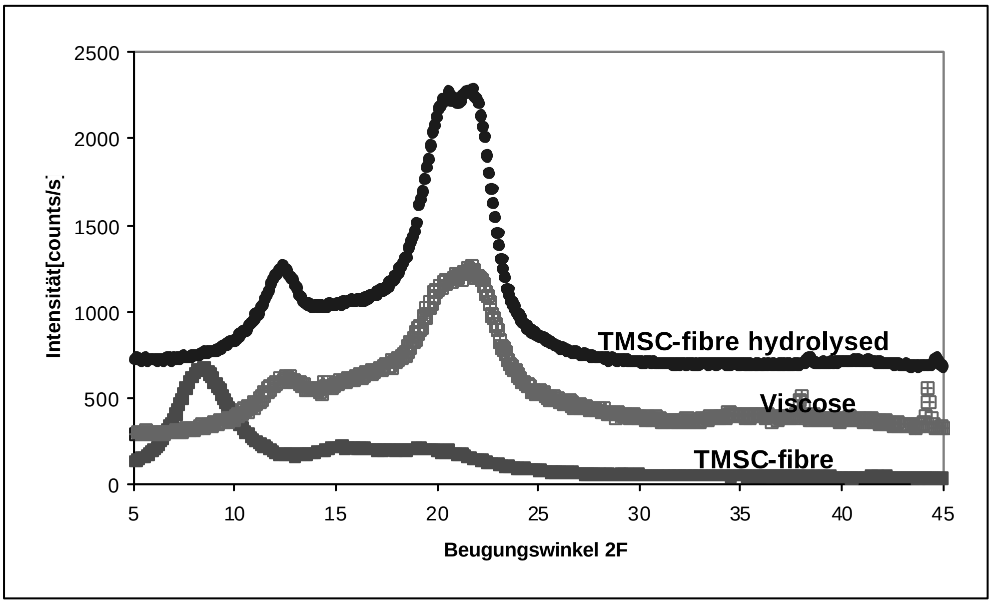

Figure 5. Fibre structure conversion after hydrolysis of silyl-groups

Table 1. Fibre properties

	as spun	as spun	hydrolyzed	hydrolyzed
Spinning speed [m/min]	250	1000	250	1000
Titer [dtex](12 f)	110	145	70	92
Tenacity (dry) [cN/tex]	14,2	16,3	32,5	34,2
Elongation (dry)	4%	4%	5,5%	4,5%
E-modulos (dry) [cN/tex]	581	620	1350	1580
Tenacity (wet) [cN/tex]			31,2	34,5
Elongation (wet)			6,5%	5,2%
E-modulos (wet) [cN/tex]			660	720

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EVIDENCE OF AUTOCATALYTIC REACTIONS IN CELLULOSE/NMMO SOLUTIONS WITH THERMAL AND SPECTROSCOPIC METHODS

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Abstract

The thermal stability of cellulose/*N*-methylmorpholine-*N*-oxide (NMMO) solutions were investigated using UV/VIS spectrometry with a temperature programming cuvette and caloric measurements by means of the Systag calorimeter RADEX (mini-autoclave). Both analytical methods allow to characterise the influences of stabilizers and additives. With the temporal course of the optical density, temperature and pressure thermal runaway reactions with gas evolution and accumulation of chromophoric degradation products were recognized. Kinetic model calculations compared with UV/VIS measurements demonstrate the existence of autocatalytic reactions in cellulose/NMMO solutions released by carboxyl group containing additives or iron contaminations. Varying the heating rate autocatalysis can be proved by dynamic caloric measurements as well.

Keywords Autocatalysis, Calorimetry, Exothermic processes, Lyocell fibres, N-Methylmorpholine-N-oxide, UV/VIS spectrometry, Mini-auto*clave*

Introduction

Manufacture and plastic deformation of polymer solutions occurs under the influence of temperature, mechanical energy and pressure. Solutions of cellulose are obtained by the direct dissolution of the polymer in *N*-methylmorpholine-*N*-oxide monohydrate (NMMO). The ternary mixture of cellulose, NMMO and water represents the plastic mass for the Lyocell process (dry and wet spinning). After extruding through nozzles, this mixture passes the draft zone and is regenerated in an aqueous precipitation bath [1,2]. High amounts of insoluble additives can homogeneously be distributed into the cellulosic fiber by keeping the structure generating new functional properties. For example, adsorbing materials or ion exchange resins can be applied for modification of the fiber [3,4], which can be used, e. g., for lowering the water hardness or for the uptake of heavy metals from process and waste waters.

Although the dissolution of cellulose in NMMO and the fiber spinning are entirely physical processes, chemical alterations appear under industrial conditions involving both discoloration and degradation reactions of NMMO and cellulose. These reactions result in lowering the recovery rate of the solvent and decreased product performance. Time management of the industrial Lyocell process requires temperatures exceeding 85°C to prepare homogeneous cellulose/NMMO solutions within economically acceptable time. The solution becomes coloured at this temperature. Under certain conditions, even exothermicities, so-called thermal runaway reactions may appear, which may end up in deflagrations [5,6].

Chromophore formation is accompanied by both cleavage of the cellulose and degradation of the solvent NMMO. Lukanoff et al. [7] reported about DP loss even at a temperature of 85°C. Increasing the temperature of the solution to approximately 170°C a violent self heating reaching temperatures up to 250°C and a severe gas evolution are observed [8,9]. Mainly, the

thermal instability of NMMO, the content of heavy metals and reactive end groups of cellulose affect the chemistry of the Lyocell process. Due to the energy-rich N-O bond, NMMO is able to enter into numerous reactions. *N*-Methylmorpholine, morpholine, carbon dioxide and formaldehyde are the main degradation products [10,11]. Furthermore, unstable and highly reactive intermediates such as aminiumyl radical [12] and carbonium-iminium cation [13,14] have already been found to occur. Stated by Rosenau et al. [15,16], this carbonium-iminium ion is the main species inducing autocatalytic degradation of NMMO.
The control of the described reactions by an outer process management is limited as in typical polymer solutions. Apparently, sporadic and uncontrollable reactions are influenced by additives, reaction products and process surroundings. Therefore, a stabilization of the system cellulose/NMMO is necessary, especially in the case of modified solutions. Additionally, the small thermal conductivity of the reaction mixture on a large scale plant is a crucial issue, i.e., the reaction heat of chain reactions once started can be eliminated not fast enough. Consequently, only a combination of several chemical inhibitors which affect both NMMO and cellulose accompanied by technical safety measures diminish the risk of exothermicities effectively [17-19].

Further establishment of the Lyocell process and the development of technologies for the production of special fibers proceed parallel to the search for new stabilizers supposing the precise analytical characterization of the thermal degradation of cellulose/NMMO solutions. The present study describes recently established methods, which permit better estimation of the thermal potential.

Materials and Methods

Reagents

Chemicals were obtained from Merck, Darmstadt, Germany and were of the highest purity available. *N*-Methylmorpholine-*N*-oxide (NMMO; BASF, Ludwigshafen, Germany) was used as 50% (v/v) aqueous solution. The cellulose used was a bleached spruce sulfite pulp characterized by the following data: content of α-cellulose = 90.6%, degree of polymerisation (DP) = 495, carboxyl groups = 6.9 µmol/g, carbonyl groups = 48.3 µmol/g, moisture = 7.5%. Caustic soda and propyl gallate were applied as stabilizers. Modification was provided with an acidic cationic exchange resin based on polyacrylic acid (IMAC HP 336, Rohm & Haas, Frankfurt/M., Germany).

Preparation of cellulose solutions

227 g of NMMO and 13.9 g of cellulose were weighed in a laboratory reactor. Stabilized solutions were prepared by addition of 0.06% propyl gallate and 0.04% NaOH with respect to the cellulose content. 25 ppm Fe as powder (10 µm), respectively, 1 and 2% glucuronic acid were added with respect to the cellulose/NMMO solution. Modification was carried out with 12.8 g of an acidic exchange resin and 12.8 g of activated carbon to give 49% modified solutions with respect to the cellulose/NMMO solution. After stirring the mixture for 15 min at room temperature the reactor was connected to a Rotavapor (appr. 30 mbar) and the temperature of the reactor was raised up to 90°C gradually. A solution was obtained after stirring for 240 min, and was immediately subjected to the measurements.

Reaction calorimetry

Fundamental thermal investigations were realized with the Systag calorimeter RADEX (mini-autoclave) [20-22]. Approximately 2 g of the cellulose/NMMO solution were used in the steel vessel (design pressure: 100 bar) equipped with bursting disk and an internal sensor device for temperature determination. Ensuring a defined thermal resistance of the airspace between jacket and vessel, the temperatures of sample and jacket are measured continuously. For dynamic measurements (screening), the vessel was heated with a heating rate of 0.75 K/min from room temperature up to 300°C followed by holding this temperature for 1 h.

UV/VIS spectrometry with temperature programming cuvette

A Shimadzu UV-2401 spectrometer was used for monitoring of temperature and time dependent changes in cellulose solutions by plotting the extinction-time graphs covering a wave length range of 200-600 nm. Figure 1 illustrates the cuvette designed for this purpose [22]. By an electronic controller (P.I.D.) an adjustable temperature can be adjusted between room temperature and 150°C. Reaction kinetics were calculated by means of extinction-time plots recorded with a wave length of 400 nm, a temperature of 120°C and an optical density of 0.35 mm.

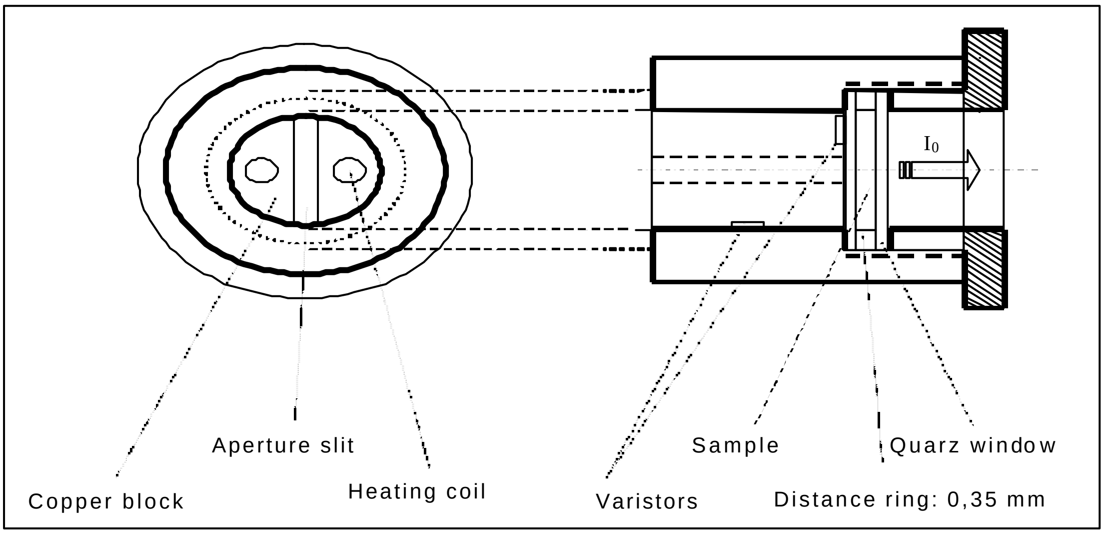


Figure 1. Design of the cuvette for heating of cellulose solutions.

Results and discussion

Spectroscopic investigations

Cellulose/NMMO solutions exposed to temperatures up to 120°C show increased formation of chromophores, which can be identified by time-dependent UV/VIS spectroscopy at about 400 nm (Figure 2). Measuring the optical density temperature- and concentration-time graphs are registered useful for analyzing thermal runaway reactions and to detect the accumulation of dangerous degradation products.

Figure 3 displays extinction-time graphs of non-modified solutions compared to Figure 4 that displays solutions modified with the acidic ion exchange resin (IER). Whereas in the beginning of the measurements the extinction of the unmodified solutions start with amounts less than 0.2, the modified solutions show shifts to extinctions above 2. This behavior is caused by self absorption of the IER. Noise of extinction > 3 is attributed to the low intensity of the transmitted light.

Significant changes of extinction dependent on temperature are obvious in both cases. However, the shape of the curves follow different kinetic laws. It is useful to define three temperature phases in order to compare the extinction-time graphs.

Phase I:

Up to 110°C the slopes (dE/dt) of modified as well as non-modified solutions are virtually linear with only small deviations over the entire period of measuring time. If the induction period is longer than the observation time (400 min) no autocatalysis can be proved. Thus, changes of extinction is to be observed at higher temperatures.

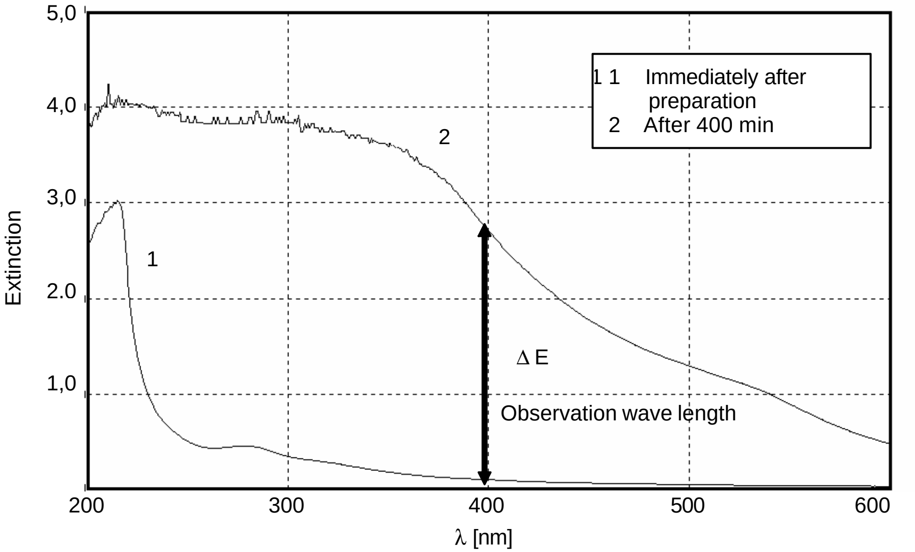


Figure 2. Changes in UV/VIS spektrum of a 9% cellulose/NMMO solution heated at 120°C for 400 min.

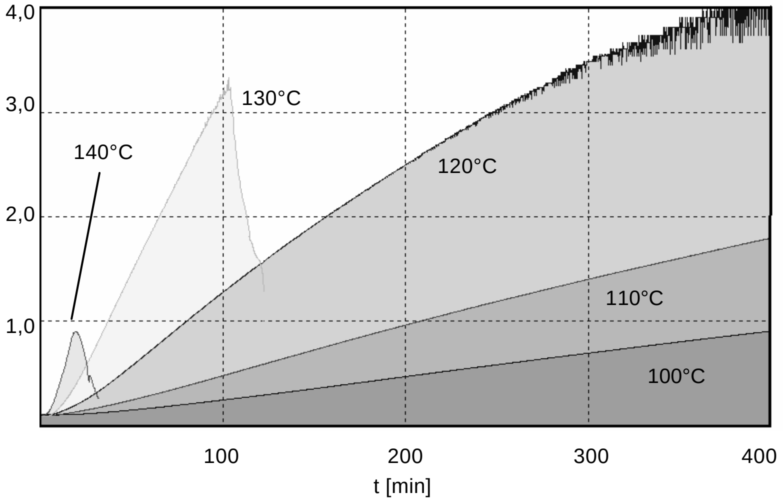


Figure 3. Relationships between heating time of a 9% cellulose/NMMO solution and extinction at different temperatures. Determined at λ 400 nm.

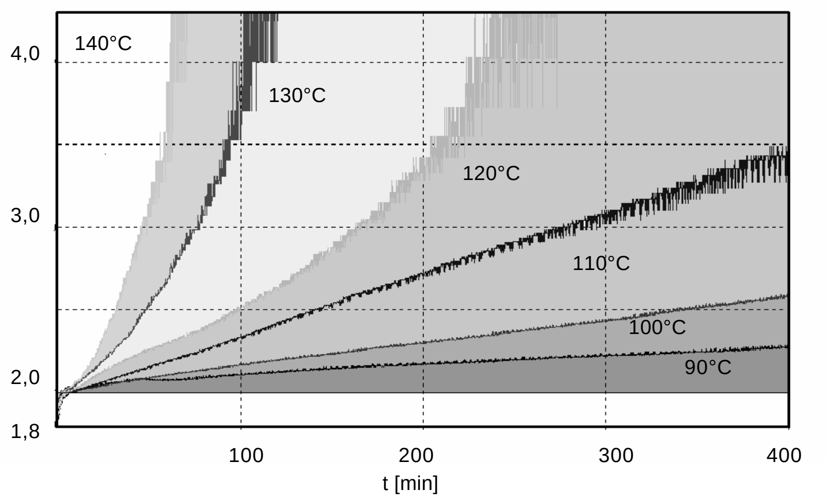


Figure 4. Relationships between heating time of a 9% cellulose/NMMO solution modified with an acidic ion exchange resin and extinction at different temperatures. Determined at λ 400 nm.

Phase II:

At 120°C the modified solutions show strongly curved slopes of extinction compared to the non-modified solutions, that indicate an increased formation of chromophores, or more byproducts. Since cellulose and/or additives are probably able to trap by-products, their concentration in the homogeneous phase remains low. No further reactions are catalysed. The dynamic equilibrium between formation and deformation of catalysts causes the state of uncertainty that could change the direction due to external influences or disruptions.

Phase III
:
When increasing the temperature this state of equilibrium is left. The extinction-time curves of the modified solutions rise exponentially after an induction period. This behavior indicates an autocatalytic reaction mechanism running with a positive feedback, i.e. the reaction product (catalyst) has a positive effect on the reaction. The local amount of catalysts, e. g. carbonium-iminium ion, reaches such a high level that the consumption by water or cellulose cannot compensate its production, the reaction with NMMO will become uncontrollable and will lead to an exothermic event [23]. As obvious from Figure 4 autocatalysis competes with thermal degradations but proceeds at a forced rate. In contrast, the non-modified solutions exhibit a fundamental other behavior. After a merely short increasing the extinction declines erratically caused by segregation processes of the ternary system of NMMO, cellulose and water. Crystallisation of cellulose minimizes the extinction owing to the superior transparency in the measuring cell. Disturbing the solution behavior of the system the formation of catalysts is inhibited. No autocatalysis with the typical induction period appears.

For the evaluation of the stability of cellulose/NMMO solutions the temperature of 120°C and an observation time of 400 min turned out to be favourably.

Both thermally instable substances or inadmissible process conditions and side reactions with autocatalytic character cause exothermicities of cellulose/NMMO. The item *autocatalysis* refers to special term of homogeneous catalysis resulting in the formation of catalyst as reaction product during subsequent reactions. Consequently, this catalyst effects the process of the reaction and accelerates it additionally [24,25]. Proving the existence of autocatalytic reactions in cellulose/NMMO solutions the extinction-time curves of the UV/VIS spectroscopic measurements were confronted with results of kinetic model calculations. In fact, the origin of the investigations lies in a heterogeneous autocatalysis superimposing by thermal degradation of the NMMO with cellulose and the effect of an ion exchange resin as a suspension. With particle sizes < 10 µm, cellulose concentration of 9% and an assumed homogeneous distribution of the starting materials, the description of the concentration-time graphs can be accepted as a quasi-homogeneous autocatalysis.

Based on Lambert-Beer`s law, the rate of reaction v_i of the compound i with the concentration c_i is proportional to the temporal change of extinction:

$$E_i = \varepsilon_i c_i d$$

$$v_i = \pm \frac{1}{\nu_i} \frac{dc_i}{dt} = \pm \frac{1}{\nu_i \varepsilon_i d} \frac{dE_i}{dt}$$

E	Extinction
ε	Extinction coefficient
d	Optical layer thickness
ν	Stoichiometric factor

Table 1 comprises the parameters for kinetic model calculations. Figures 5 and 6 display the concentration-time graphs for an autocatalysis and an autocatalysis superimposed by a thermal degradation.

	Autocatalysis	Thermal degradation
Reaction equation		
	Start $A \xrightarrow{k_0} B$	$A \xrightarrow{k_2} C$
	Autocatalysis $A + B \xrightarrow{k_1} 2B + P$	
Reagents	A: NMMO B: Catalyst P: Chromophoric degradation product	A: NMMO C: Chromophoric degradation product
Concentration	$a_0 = 1$ mol/l $b_0 = 0.001$ mol/l	$a_0 = 0.25$ mol/l $c_0 = 0.33$ mol/l
Rate constant	$k_1 = 0.1\ l \bullet mol^{-1} \bullet min^{-1}$	$k_2 = 0.025\ min^{-1}$
Accounting equation	$x_1 = a_0 - a = b - b_0 = p$	$x_2 = a_0 - a = c - c_0 = q$
Accounting equation of the superimposition	$z = p + q$	
Rate law	$\frac{dx_1}{dt} = k_1 \bullet (a_0 - x_1) \bullet (b_0 + x_1)$	$\frac{dx_2}{dt} = k_2 \bullet (c_0 - x_2)$
Integration of the rate law	$k_1 t = \frac{1}{a_0 + b_0} \ln \frac{a_0 (b_0 + x_1)}{b_0 (a_0 - x_1)}$	$k_2 t = \ln \frac{c_0}{c_0 - x_2}$
Turning point	$\frac{d^2 x_1}{dt^2} = 0 \qquad t_{tp} \frac{1}{a_0 + b_0} \ln \frac{a_0}{b_0}$	

Table 1. Kinetic model calculations for cellulose/NMMO solutions.

The starting concentration of the catalyst b_0 in the beginning of the autocatalysis was chosen to be 0.001 mol/l. This amount is approximately equivalent to the average concentration of formaldehyde, which is formed in cellulose/NMMO solutions. Own investigations of aqueous extracts of cellulose/NMMO solutions without additives by means of HPLC measurements have resulted 10-30 mg formaldehyde per liter solution. Formaldehyde is able to react with morpholine generating the catalyst carbonium-iminium ion as reported [9,14].

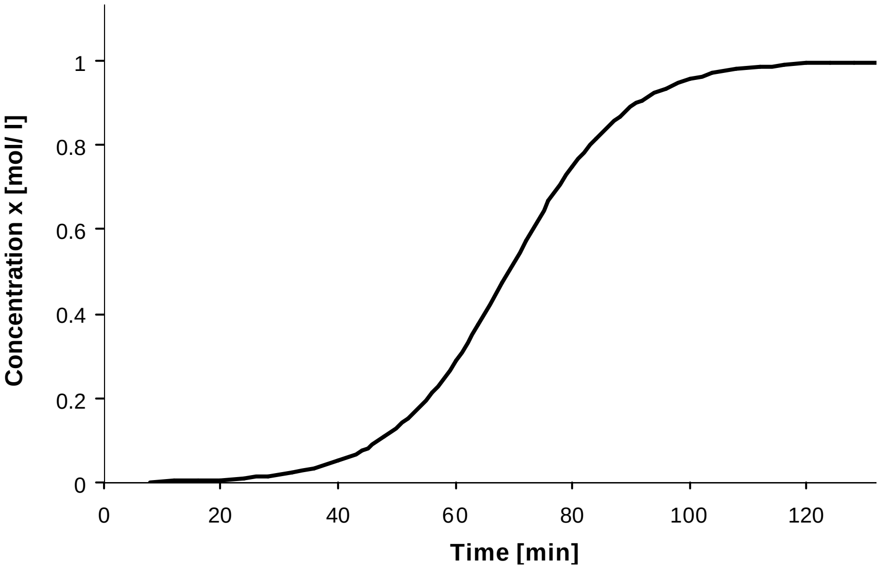


Figure 5. Concentration-time graph of the autocatalysis.

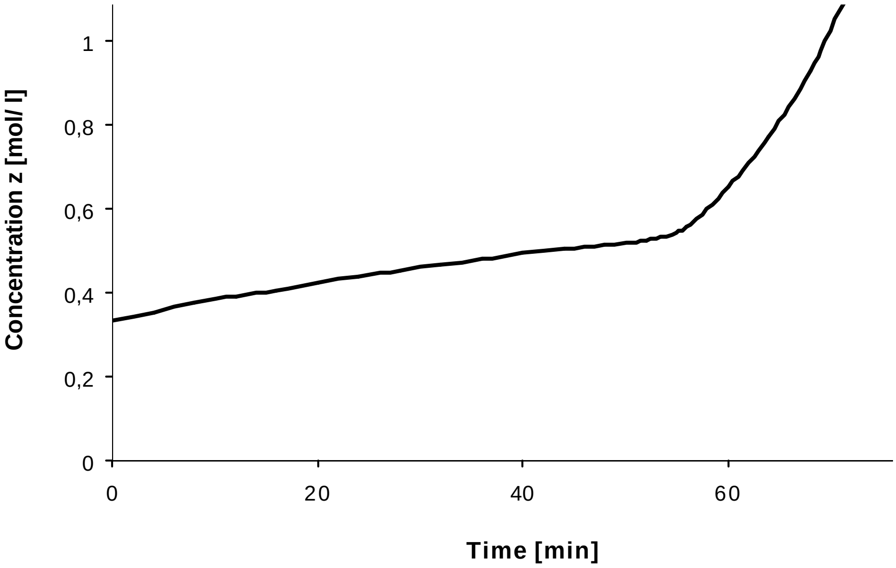
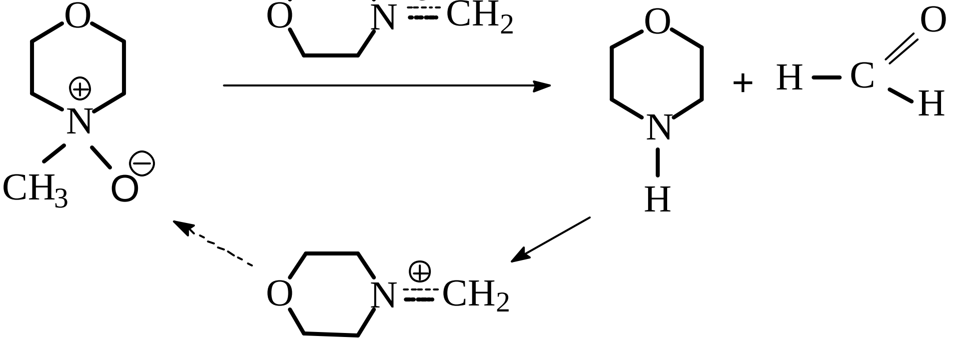


Figure 6. Concentration-time graph of the superimposition of autocatalysis and thermal degradation.



Scheme 1. Autocatalytic degradation of NMMO reported by Rosenau et al. [11].

The concentration of NMMO was defined to be 1 mol/l. Although this amount is less than the usually applied concentration in lab-scale tests (6-7 mol/l), the heterogeneity and the heat-flux behavior of the system were considered. The displayed concentration-time graph of a complex reaction (Figure 6) allows to describe the extinction-time curves of the modified solutions in Figure 4. Autocatalytic course starts to become obvious at 130°C (Phase III) and is completed after 250 min. As expected, the calculated rate constants of the thermal degradation for the unstabilized and stabilized solution are lower than the rate for the modified one (Table 2). The effectiveness of a stabilization is indicated by a lower rate constant. Respectively, the insertion of carboxyl groups by an IER definitely results in autocatalytic reactions [23].

Solution	Rate constant of the thermal degradation k_2 [min^{-1}]
Unstabilized solution	$7.3 \bullet 10^{-3}$
Stabilized solution	$2.9 \bullet 10^{-3}$
Solution, modified with acidic ion exchange resin	$2.5 \bullet 10^{-2}$

Table 2. Calculated rate constants.

To explain the effects of concentration and time more illustratively sugar acids were comparably added into the cellulose/NMMO solutions, since this supplies the understanding of reactions caused by IER [26]. Figure 7 shows the extinction-time graphs of solutions with glucuronic acid and IER.

Whereas the extinction of the solution added with 1% glucuronic acid (graph 1) increases gradually indicating a typical thermal degradation reaction, the solution with 2% glucuronic acid (graph 2) shows an exponentially course even after 35 min. Evidently, the amount of carboxyl groups is high enough that the forming of chromophores proceeds very fast. Compared to these courses extinction of the IER (graph 3) exhibits a slope after an induction period of approximately 100 min. Graphs 2 and 3 show the typical behaviour similar to Figure 4 – the thermal degradation is superimposed by the autocatalysis.

Noteworthy, during that period the course of IER runs below the solution with 1% glucuronic acid indicating the temporary stabilizing behavior of cellulose and IER. Meanwhile the local concentrations of intermediates is enhanced accelerating the reaction rate. IER is a branched polymer embedded in the entanglement structure of the cellulose. The carboxyl groups are sterically hindered and their reaction with NMMO is possibly inhibited. Furthermore, besides their polymeric networks cellulose and IER function as a radical interceptor of intermediates, e g. *N*-(methylene)morpholinium cation. It seemed to be a stabilizing effect depending on time.

Up to the characteristic turning point t_{tp} (Table 1) of the autocatalysis the reaction rate is increasing. The time of t_{tp} for small starting concentrations of the catalyst b_0 is determined by the logarithmic term, i.e. an exponential decrease of b_0 affects longer time periods reaching t_{tp} (linear slope of extinction). Thus, only 25 ppm Fe is sufficient changing the reaction behaviour after an induction period of 250 min perceptibley (Figure 8).

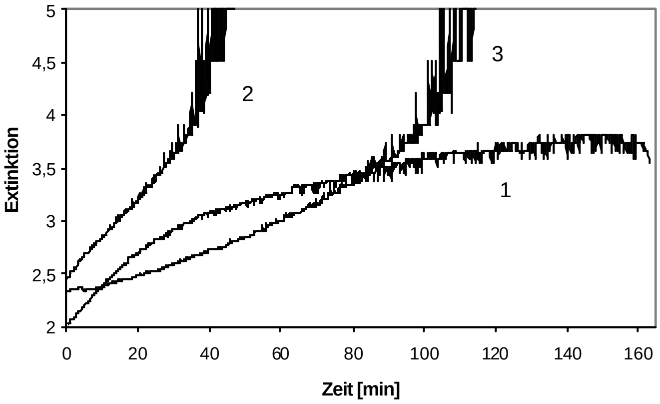


Figure 7. Extinction-time graphs of 9% cellulose/NMMO solutions added with 1% (1), 2% (2) glucuronic acid and modified with an acidic ion exchange resin (3). Determined at λ 400 nm.

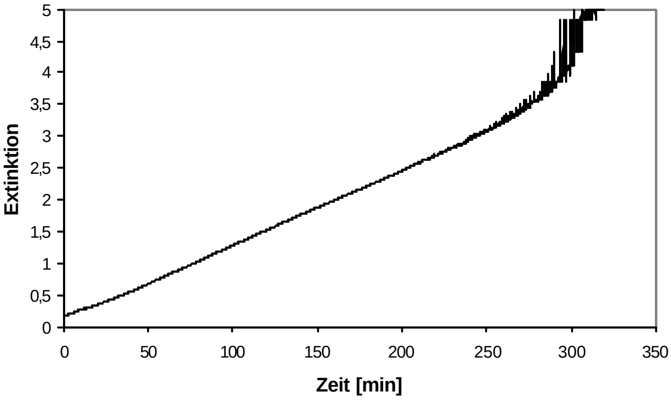


Figure 8. Extinction-time graph of a 9% cellulose/NMMO solution added with 25 ppm Fe. Determined at λ 400 nm.

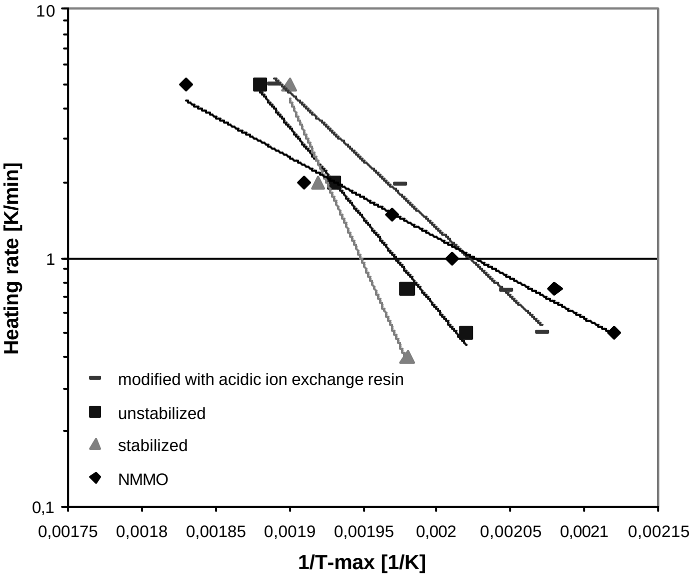


Figure 9. Relationships between heating rate β and reciprocal temperature maximum of 9% cellulose/NMMO solutions and NMMO.

Calorimetric Measurements

Kinetic parameters from dynamic experiments by means of the mini-autoclave provide information about the temperature dependent degradation reactions. Change of the heating rate β leads to a shift of the temperature maximum. Linear relationship is received by plotting the heating rates against the reciprocal temperature maxima [27]. The temperature dependence is illustrated for different cellulose/NMMO solutions and NMMO in Figure 9.

The shift of the temperature peak is influenced by the thermal stability of the substance. Assuming a change of the heating rate by factor 10, temperature shifts lower than 40 K are attributed to reactions with usual kinetics and shifts over 40 K to autocatalytic reactions (40 K rule; [28]). Table 3 contains the peak shifts for the analysed solutions. According to the 40 K rule, autocatalytic reactions are more pronounced in the modified solution and NMMO.

Solution	Peak-shifts [K]
Unstabilized solution	37
Stabilized solution	21
Solution, modified with acidic ion exchange resin	46
NMMO	74

Table 3. Peak-shifts of different cellulose/NMMO solutions and NMMO by changing the heating rates β from 0.5 to 5.0 K/min.

Conclusions

This report describes techniques that characterise the hazard potential of cellulose/NMMO solutions and provide evidence of autocatalytic reactions. By a short-time increasing of temperature a catalyst can be generated in cellulose/NMMO solutions due to an exothermic reaction, a catalytic influence by protons or heavy metals initiating an autocatalytic degradation. Over the induction period of the autocatalysis the temperature increases slowly. An erratic enhancement of the reaction rate appears unless the catalyst reaches a critical concentration and the reaction system moves far away from the equilibrium. As a consequence of this spontaneous temperature increase, exothermic degradation reactions are observed running out of control and accelerating the reaction.

Because of the complexity of the processes in the mixtures, several analytical techniques have to be employed to evaluate the influence of additives or stabilizers. Combination of UV/VIS spectrometry and caloric measurements with the mini-autoclave permit to draw conclusions about the reaction kinetics by means of the temporal course of extinction and respectively temperature. To determine whether a cellulose/NMMO mixture is uncontrollable or remains within harmless limits, combination of both techniques is a useful tool.

Acknowledgements

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OBSERVATIONS ON LYOCELL FIBRE FORMATION

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Abstract

A computer simulation of the lyocell air-gap spinning process has been developed. By combining this with empirical observations and results of fundamental studies, major advances in understanding have been achieved. These have been applied to deliver significant efficiency improvements in commercial Tencel production.

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Abstract

In order to develop a commercially viable lyocell production process, it is essential to maximise spinning stability. This requires a good understanding of the fundamental factors that influence fibre formation. In this paper, the results of studies of those factors will be reviewed. In particular, development of a computer simulation of the interactions within the lyocell air-gap is described. Model predictions are compared with practical measurements. Key findings that have been implemented to improve commercial lyocell production are highlighted.

INTRODUCTION

The basic principles for 'air-gap' spinning of lyocell fibres are well-known. Laboratory scale production (up to a few hundred filaments) is, from a practical standpoint, relatively straightforward. However, the process equipment required is expensive so maximising productivity of the fibre formation step is essential for viable commercial manufacture of Lyocell. For staple fiber, there are typically several million individual filaments per spinning line.

The major industrial players have intensively studied lyocell fibre formation and proposed various design solutions. In this paper, we present a history of spinning productivity development within Tencel. In particular, we will highlight the role played by computer simulations of fibre formation within the air-gap.

Overview

There are obvious trade-offs to consider when optimising a fibre production process, such as:

- Polymer content & flow properties of spinning solution
- Production speed
- 'Unit productivity' (e.g. jet size, filament packing)
- Design simplification (e.g. minimise costs, maintenance)
- Process 'robustness' (ease of operation, resistance to problems/fluctuations)

To enable an optimum solution to be arrived at, a key technical question to answer is:

'Why do filaments break?'

The question is simple, for lyocell the answer is very complex. There are complex interactions between the various parameters during fibre formation. A good fundamental understanding of these is a pre-requisite for successful commercial implementation. In commercial lyocell operation, the air-gap process is particularly intolerant of individual filament breakages. There are many factors that influence filament breakage, some practical/operational, some technical. This paper will focus on developing understanding of the technical factors, examples of which are shown in figure 1. For example, discovery of the significance of a cooling cross-draught was critical to successful scale-up. Understanding the mechanism to enable design optimisation has been a high priority.

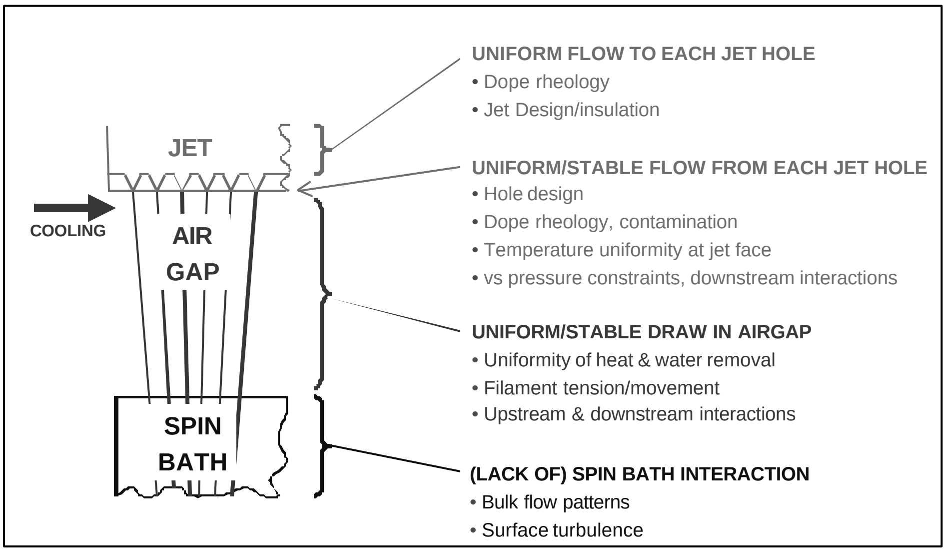


Figure 1. Examples of parameters that influence spinning stability

Tencel has developed a multi-faceted strategy to understand the fundamentals of lyocell fibre formation. Key elements are:

- Empirical pilot scale practical/iterative studies
- In-depth investigations of model systems (often single filament)
- Development of computer simulations

At the core of the programme is the development of a computer model of the air-gap spinning system.

The Air Gap Model

There are three key stages in the development of the air-gap model.

STAGE 1 is to decide what we need the model to predict. Ideally we would like the model to tell us when filaments will not spin. Rather than trying to construct a theoretical model of spinnability, we have used empirical experiments to define the spinnability of a filament in terms of its environmental variables such as the air temperature and line speed.

STAGE 2 is to apply the data on the failure criteria to develop a model of an individual filament that will interact with its environment in an appropriate manner. As will be made clear shortly, we need a model that will predict the exchange of heat, moisture and momentum with its environment. The model must also allow obvious process parameters such as line speed, spinneret hole size, polymer concentration and temperature to be included. As far as possible, model predictions are validated against experiment.

STAGE 3 is to incorporate the single filament model into a model that takes account of larger scale features such as air injection systems, the shape and temperature of the jet bodies etc. This is an area that can be treated by conventional computational fluid dynamics packages (CFD). Again, simulation performance is tested, as far as possible, against practical observation.

The key challenge from a modelling perspective is the combination of the small-scale details of the individual filament model and the larger scale CFD model. Constructing a CFD model at the smallest scale would require much computational effort.

When validated, the aim was to couple the air gap model with simulations of other key process sections (jet design, spin bath liquor flow) and apply predictions from this exercise to optimising overall spinning productivity.

Each of the stages is now considered in more detail

STAGE 1 – What are key spinning failure criteria?

Practical methods of characterising the stability and failure modes of lyocell filaments have been devised. For a single filament we can define a set of independent parameters that characterise the spinning process. We can use these parameters to characterise a surface in many dimensions that divides the "spinning space" into spinning and non-spinning regions. We refer to this as a stability surface. We have found that the filament spinnability is quite insensitive to some of the parameters but highly sensitive to others. We can illustrate the results by fixing all the parameters except two. This leads to the stability surface conveniently being represented by a curve. An example is shown if figure 2.

In this example we spin a single filament through an air gap into which we feed air that has been conditioned. For a given air temperature we increase the absolute humidity until the filament fails. The absolute humidity falls as the air temperature is raised. We have mapped out many such curves for different parameters such as line speeds and jet hole diameter.

A key conclusion from these studies was that if the air gap model can predict the temperature and humidity of the air surrounding the filaments then we could make a decision on the spinnability of the filaments.

STAGE 2 – The single filament model

Given that we recognised the importance of humidity we felt it important to develop a filament model that could adequately describe the transfer of moisture from the nascent filaments to the air. The model was therefore developed from a 2-dimensional model of dry spinning. (Many filament models are 1-dimensional, i.e. a uniform temperature gradient is assumed to exist along the filament. This is not appropriate for moisture transport on time scales of process. The 1-D approximation is good for temperature but not water)

The model solves the transport equations for moisture and temperature in the radial direction (diffusive transport in the axial direction is considered negligible).

$$V\frac{\partial C}{\partial z}=\frac{1}{r}\frac{\partial}{\partial r}\left(rD(C,T)\frac{\partial C}{\partial r}\right)$$

The dope is treated as a Newtonian fluid, with temperature and concentration dependent on viscosity. (We estimated that the thermal effects would dominate any non-linear rheological effects.)

$$r\,C_pV\frac{\partial T}{\partial z}=\frac{1}{r}\frac{\partial}{\partial r}\left(rk(C,T)\frac{\partial T}{\partial r}\right)$$

$$b_{av}=\frac{2p\int_0^R b(C,T)rdr}{p\,R^2}$$

The diffusion coefficients and vapour pressure of the water above dope were determined experimentally. The heat and mass transfer coefficients were those developed by the workers in the dry spinning field. The temperature dependence of the viscosity was determined from in-house rheometry. The model works by estimating the initial tension in the filament and propagating along the filament to determine the final (take up) velocity. This is an iterative process and finishes when the boundary conditions are matched. At each step in the filament direction the transport equations are solved using a finite difference scheme. Output is predicted profiles of, for example, temperature and moisture content through the filament at various conditions.

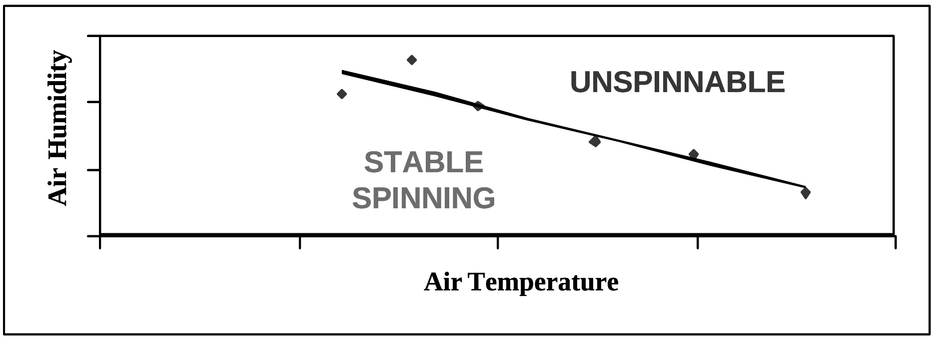


Figure 2. Example of 'response surface' generated via single filament measurements

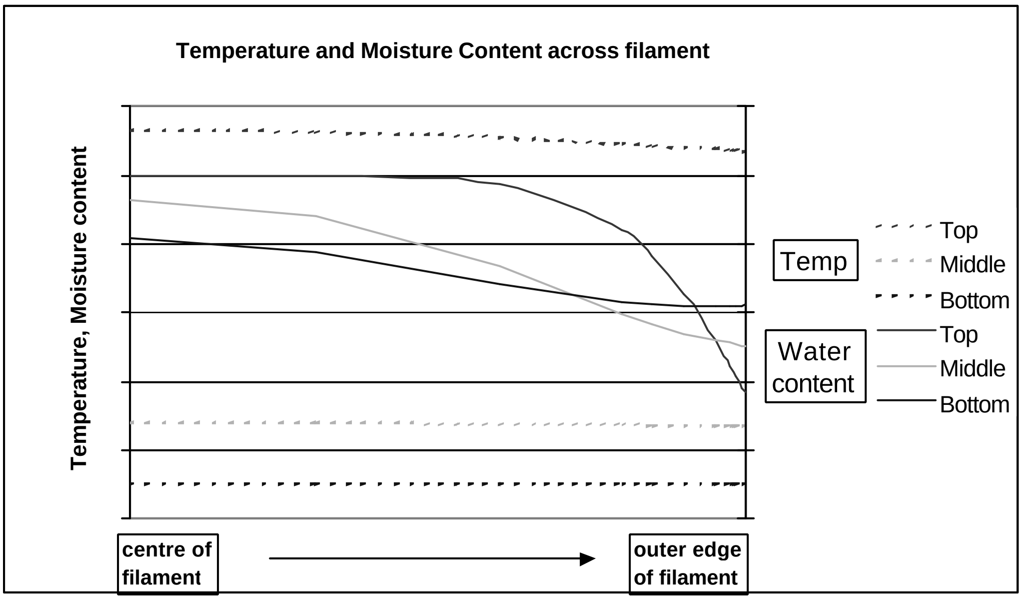


Figure 3. Example of output from single filament model

In figure 3, the x-axis runs from the centre to the edge of the filament. The solid lines show the water concentration in the filament and the dashed lines the temperature. The three curves correspond to different distances from the jet face. The temperature profiles are flat indicating that a 1-D model would have been adequate. The sharper gradients that exist in the water curves demonstrate the need for a 2-D model.

So far as possible, model predictions are tested against practical measurement. We cannot measure moisture/temperature variation within filament directly, so measure the radius of the filament using a high magnification telescope and plotted the results against the model predictions, figure 4.

The agreement is good. We have further tested against IR camera measurements of filament temperature and the agreement is again satisfactory.

STAGE 3 – The CFD model

Several "representative" filaments from stage 2 have been coded into a computational fluid dynamics (CFD) programme. The filaments interact with the air velocity, temperature and humidity of the cell in which they are placed.

The amount of heat, moisture and momentum (fibre drag) exchanged with the filament is added as a source term to the equations that the CFD package solves. The filament calculation sits inside the iterative loop of the CFD program and the combined program iterates until a converged solution is reached. The contribution of each filament is scaled to represent the filament density in the jet. The number of representative filaments is varied to

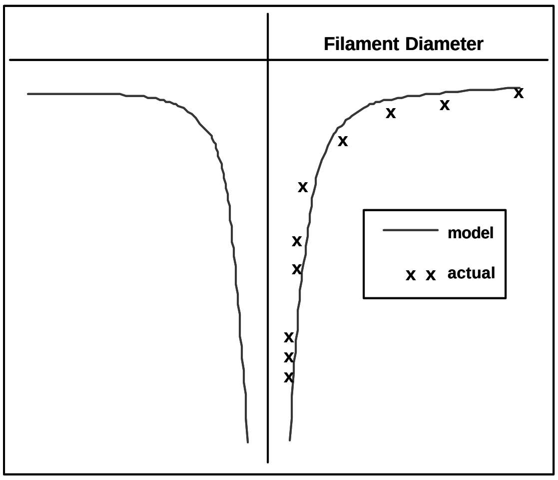
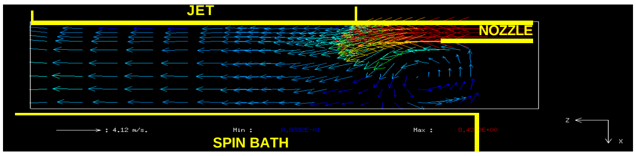
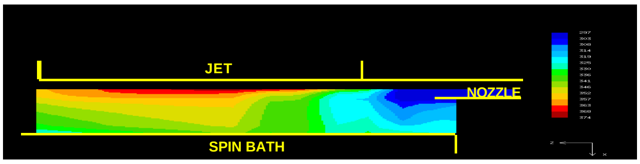


Figure 4. Example of model validation



AIR FLOW



TEMPERATURE DISTRIBUTION

Figure 6. Air flow and temperature predictions, cross-section

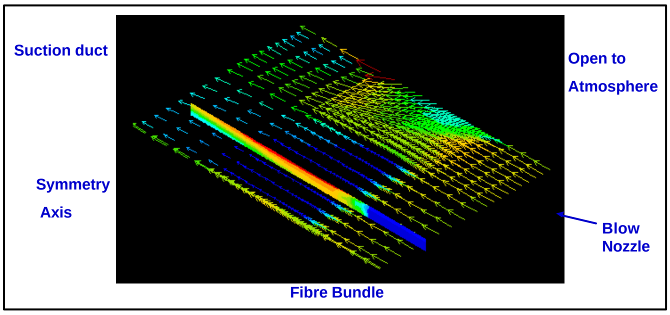


Figure 5. CFD representation of air-gap air flow & temperature distribution

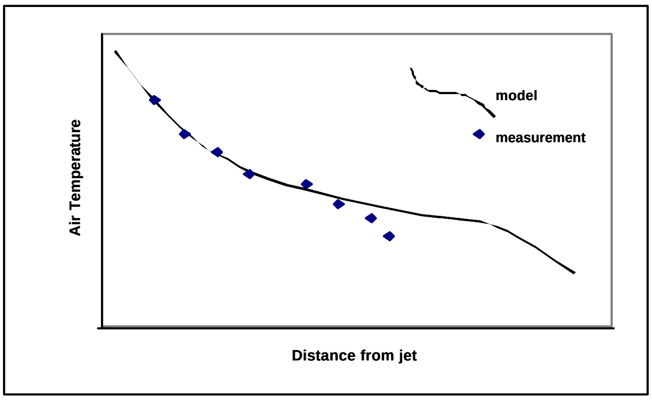


Figure 7. Validation of CFD model of air-gap-air-temperature

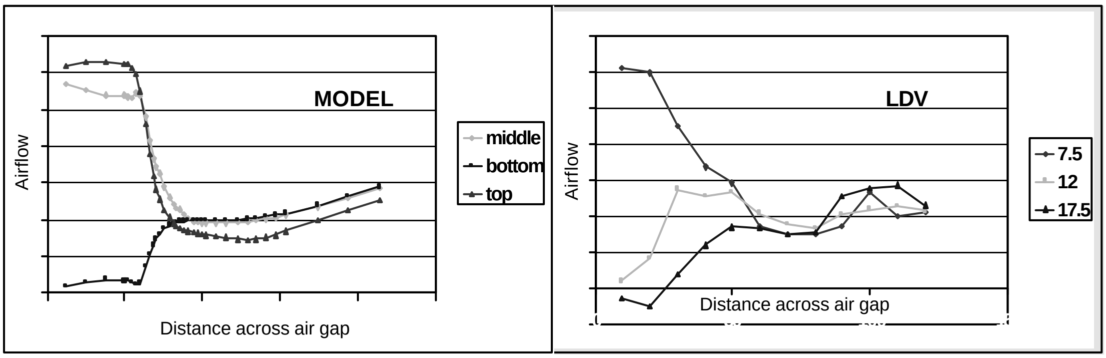


Figure 8. Validation of CFD model. Comparison of predicted and measured air-flow

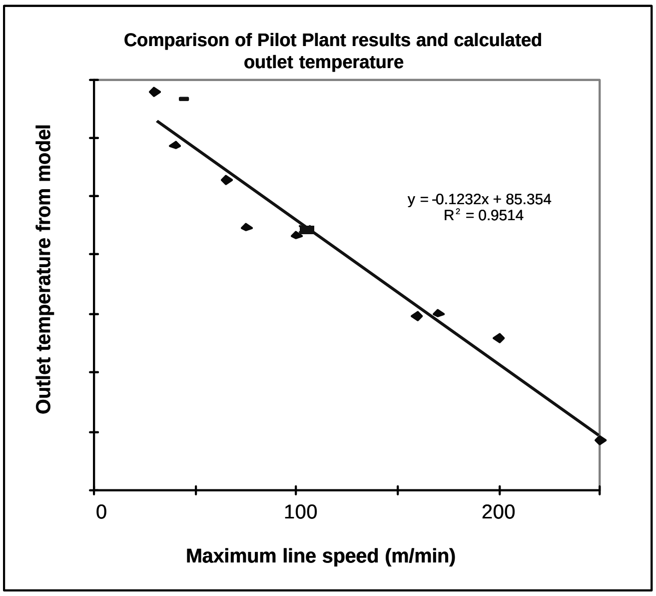


Figure 9. Validation of CFD model. Prediction of spinning failure

ensure that the final solution is independent of the number of representative filaments.

The CFD model of the air gap is three-dimensional. Model output for a typical rectangular jet configuration is shown in figure 5. This represents an air gap with a horizontal blow nozzle located close to the jet face and only partially extending down the air gap depth, a suction nozzle that extends over the entire air gap depth and two jets in the air gap (symmetry implies we only need model one). The outer edge of the assembly is open to atmosphere.

The results are showing the velocity vectors in a horizontal plane and the temperature profile in a vertical plane. Note, for this configuration:

- the way that the air slows on moving through the bundle –due to the fibre drag
- the air coming in from the outside,
- development of the thermal profile within the bundle.

Looking at CFD predictions in cross-section, figure 6. Figure 6 shows the velocity contours in the area of the fibres. Note the way the velocity initially appears faster closer to the jet face but as we move to the suction side of the bundle the profile appears to invert.

The second shows the thermal profile in the bundle. The contour arises because of the combination of heat loss by the filaments, the initial downward flow of the air and the impact of the incoming atmospheric air impinging on the latter part of the jet.

As with the single filament model, so far as possible the CFD predictions have been tested by practical measurement. For example, an array of thermocouples was mounted on a carriage and traversed across a full-size jet assembly with the probe ~2cm away from the filaments. Actual thermal profiles are compared with model predictions. Plotting the expected thermal profile from jet to spin bath at one particular position against the experimental results, figure 7:

In addition to good overall agreement, the measurements confirmed CFD predictions, showing a temperature profile down the air gap, from jet to spin bath. The more detailed data also shows interesting looking “peaks”, located inside the fibre bundles. For this particular trial configuration, many filament failures occurred within these peak temperature zones.

We have further tested the model by using Laser Doppler Velocimetry (LDV) to measure the air velocity within the air gap. The results for air velocities across the air gap at various heights from the jet are shown, figure 8, for both model and experiment. It is worth noting that the inversion of the velocity profile occurs experimentally as well as theoretically.

The validation tests built confidence that the model that could predict air velocities, temperatures and humidity within the air gap with reasonable precision. We can now ask how well the model relates to spinning performance. Various full-scale jet configurations have been tested by evaluating the maximum line speed (before filament failure). The model was used to predict temperature/spinning failure at a given line speed for each configuration. The correlation is good.

Interaction with other process models

The work outlined above has resulted in a robust 'stand-alone' computer model of interactions occurring within the air-gap during formation of lyocell fibre. The value of this model has been further enhanced by coupling with simulations of process interactions directly before and directly after the air-gap, i.e.:

- Dope flow stability & uniformity from spinneret holes
- Spin bath liquor flows, impact on filament deflection in air gap

However, this work is beyond the scope of this paper.

Benefits derived from the Air Gap Model

There have been many benefits to Tencel from the computer simulation programme. At a management level, it has imposed a discipline and focus on the practical studies and prompted important discussions to develop key hypotheses.

In terms of scientific learning, the programme highlighted the significance of air gap humidity and provided an explanation of the flow patterns of the cooling air. The hypothesis regarding the importance of water removal for filament stabilisation (as opposed to a simple thermoplastic cooling mechanism) was first developed from the modelling results.

At a more detailed level, the excellent agreement with practical measurements gave confidence that model could be used as a 'design tool' in optimising the spinning cell, removing need for many costly and time-consuming large-scale practical iterations. 'Weak points' were identified via the model, for example appearance of temperature/humidity peaks and many concepts to remove these weak points could be assessed very easily on the computer.

Conclusions

- Tencel have developed computer simulations which accurately predict temperature, humidity and velocity profiles in the air-gap during lyocell fibre formation.
- The model is based on a combination of single filament and CFD approaches, validated by practical measurements.
- The air-gap model has been central to improving our understanding of the key fundamental parameters which must be controlled to enable viable commercial production of lyocell.
- In particular, maximising efficiency of water removal and uniformity of conditions in air gap
- Many questions concerning formation of lyocell fibres remain unresolved, but current state-of-the-art understanding has allowed successful commercialisation ~120,000 tonnes of lyocell capacity in Europe and USA.
- The robust, high productivity technology gives an excellent platform for the introduction of new product variants.

Lenzinger Berichte, 84 (2005) 110-115

RECENT ADVANCES IN CHEMICALLY TREATED LYOCELL FIBRES

T R Burrow

Tencel Ltd, Derby, UK

Courtaulds worked on the development of Tencel during the 1970's and 80's leading to a commercial launch in 1992. Tencel was the first fully commercial lyocell fibre on the market. It has achieved a strong market position because it offers a unique combination of physical properties and aesthetics that can be produced in fabrics.

Tencel is a special fibre. Because it fibrillates it can be used to create peach touch finishes with a beautiful soft hand. The fabrics have an excellent soft drape. A wide range of applications has been developed starting with soft denim through to shirtings, sheeting and jersey knits.

The Lenzing take over of Tencel means that the capacity for Tencel lyocell production is now 120,000 tonnes per annum.

The unique aesthetics of Tencel fabrics are due to the cellulosic nature of the fibre, the inherent physical properties of the fibre and its ability to fibrillate. Tencel is much stronger than cotton and viscose and has a high wet modulus, which is essential for developing soft but stable fabrics.

Developing the aesthetics of Tencel fabrics requires work to be done to ensure the fabric is stable and to make the fibres fibrillate. Work on the fabric has to be done in a carefully controlled way to ensure that all of the fabric receives the same treatment. This requires special dyeing and finishing equipment which is not always available in a dyehouse.

While the peach touch finish is ideal for some applications it is not suitable for many others. Therefore in order to broaden the market for Tencel we have developed new variants to match the expectations of the market.

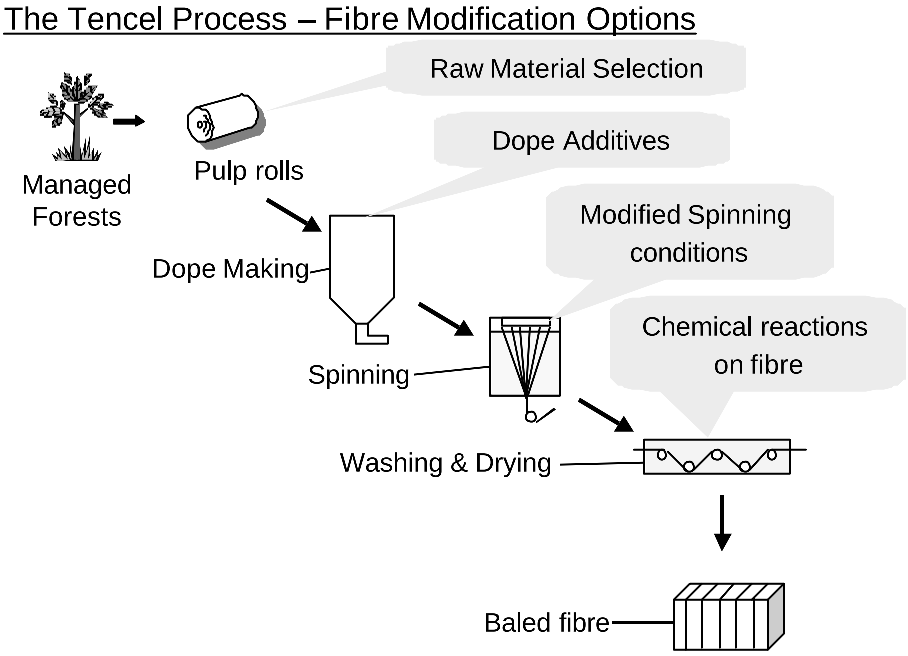
At an earlier Dornbirn conference Peter Hetherington spoke about fibre development from a retailers perspective. He said that customers had an expectation that they would see something new when they walk into a store. They want increased comfort, easier to wear clothing, better fit. Naturally based environmentally responsible products are favoured. And the customer is prepared to buy for specific purposes – clothing for sport, for leisure for travel. Well being is becoming more important and clothing is expected to make a contribution.

Methods of modifying Tencel

The Tencel process is very versatile. The chemical and temperature environments are not extreme. There are a number of opportunities to modify the properties and character of the fibre. New attributes can be added and there has been extensive work on reducing the cost base of downstream processing.

There are four classes of methods of modifying Tencel fibre.

- Raw material selection
- Dope additives
- Modified spinning conditions
- Chemical reactions on fibre



The Tencel Process

The Tencel process uses wood pulp of controlled molecular weight as the raw material. The pulp is shredded and mixed with a solution of N-methyl morpholine-N-oxide (NMMO) in water to form a slurry. Water is evaporated from the slurry in a stirred vacuum vessel at elevated temperature. When the water content drops below a critical level, the cellulose goes into solution to form a "dope".

The dope is extruded through tiny holes under conditions of high shear (high pressure, high viscosity). The stream of dope is immediately immersed in a spinbath containing a dilute solution of NMMO. The individual fibres are gathered together to form a tow – a rope of parallel fibres.

The tow may be washed in its continuous form or it may be cut into staple and washed on a moving wash bed. The fibre (tow or staple) is washed with large quantities of water flowing in the opposite direction to the fibre. It may be bleached.

The wash liquor coming from the process is a dilute solution of amine oxide. This is concentrated by evaporation and reused at the beginning of the process for dope making. Thus the amine oxide is recycled around a closed loop.

Finish is applied to the fibre and it is dried. Staple washed fibre is opened and baled ready for shipment to the processor. Tow is crimped, cut into staple and baled ready for shipment to the processor.

Raw Material Selection

Raw material selection has a minor effect on fibre properties. Different pulps will give fibre with marginally different properties and some pulps will not work in the process. But these differences are not of great enough magnitude to yield a genuinely different product.

Pulp sourcing is of great importance in keeping costs down.

Dope Additives

Dope additives give many options for 'effect' products by adding the effect of the additive to the fibre. A wide range of fibres has been produced on both commercial scale and development scale. Properties imparted include matt, colour, and anti-microbial.

This type of process is generally simple to implement on plant provided that the additive used is compatible with the solvent system and does not contaminate it.

It is not possible to fundamentally change the nature of the fibre (eg fibrillation behaviour) by any of the additive systems tried so far.

Spinning Conditions

From when the lyocell process was first developed there has been considerable effort to modify the properties of the fibre by changing the spinning conditions. In general it has been found that there is a stable range of operating conditions outside of which fibre properties and the economic viability of the process deteriorate.

Obviously altering the spinning conditions is the method used for dimensional changes in the fibre (eg dtex).

Chemical Treatment

Chemical treatment is the only method found so far that gives fundamental changes to fibre properties and its behaviour in fabrics. This has been used by Tencel and Lenzing to produce Tencel A100 and Lenzing Lyocell LF.

Chemical treatment is more complex that the other methods to implement on plant, but the results have justified the effort.

Chemical treatment can be done on line so that the finished fibre needs no further modification or treatment. This creates a unique position for the business. A wide range of potential products can be made. The technology needed has been proven.

A big advantage of on line chemical treatment is that the switch between products can be done very quickly, minimising waste and down time. And because the reactants are introduced downstream of where the amine oxide has been washed out of the fibre, there is little risk of contaminating the solvent system.

However it is necessary to install specialised equipment on the Tencel line to do any chemical treatment. This requires significant capital and the equipment requires space to be available. Once an installation has been made the chemistry employed in any treatment has to fit with the equipment.

On-line treatment is not necessarily the lowest cost process to achieve a particular result. It may be possible to achieve the same by a lower cost fabric treatment.

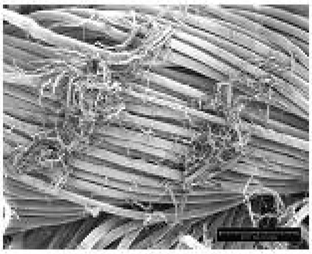
Any chemical reaction on a fibre inevitably affects the properties and behaviour of the fibre. The frictional and tensile properties are particularly affected and hence the processability of the fibre will be altered. This could be an improvement as well as a deterioration depending on the treatment.

On line chemical treatment has been used for a range of products so far and further development is continuing.

Tencel A100

The main development in Tencel has been Tencel A100. This is a non-fibrillating variant of Tencel which was developed to meet identified market needs for a Tencel fibre that did not fibrillate and therefore would be easier to dye and finish, which could be processed on conventional processing equipment and would produce a different aesthetic in fabrics.

TENCEL fibrillation



Standard Tencel fabrics fibrillate when they are subjected to abrasion in the wet state. The outer layers of fibres at the surface of the fabric peel away to give a large number of tiny fibrils. These give Standard Tencel fabrics their peach touch aesthetic.

Fibrillation can be prevented by resin finishing of fabrics made from Tencel. However the fabric is prone to uncontrolled damage unless great care is taken during dyeing if this type of approach is attempted.

The industry wanted a fibre that would not require special care and this is why we developed Tencel A100. Fibrillation is prevented by cross-linking the fibre during manufacture before it is dried. The result is a fibre that processes well and gives a unique set of properties.

Since its launch, Tencel A100 has grown rapidly. The fibre is made at Grimsby. The necessary equipment for on-line treatment was installed during the building of the plant.

The main applications are in jersey fabrics but fibre is selling for knitwear and woven fabrics as well.

In the early phases of the project, fine tuning of the fibre decitex, the line speed, the fibre moisture content and the finish system were needed to give an acceptable yarn quality. Tencel A100 now processes without any problems.

The key selling points are the fabric touch and feel, dyeability & appearance retention and the ease of processing.

The cross-linker used is TAHT (triacrylamido-trihydrotriazine). This is a trifunctional molecule that reacts readily with hydroxyl groups in alkaline conditions at elevated temperature. The molecule has chemistry very similar to reactive dyes.

It can penetrate the amorphous regions of the water swollen cellulose where it reacts with one or more cellulose groups. When it reacts with hydroxyl groups on two cellulose chains it binds them together and prevents them from splitting apart.

Standard Tencel crystallises during manufacture. The crystalline regions are separated by amorphous regions. The whole structure is held together by hydrogen bonds. When the fibre fibrillates it is due to tearing apart the hydrogen bonds in the amorphous regions.

TAHT prevents fibrillation by cross-linking in these amorphous regions.

The Tencel A100 process requires three steps. TAHT is applied as a solution to the washed, but still wet, tow. Alkali is then added to the tow through a dip trough. The tow is then put into an accumulator device for the required reaction time. The accumulator is steam heated. The cured fibre is washed and neutralised and then finished, dried, crimped and cut to staple.

The line used to make Tencel A100 includes application stages for the TAHT and the alkali. An accumulator provides time for the reaction to take place.

The key target for Tencel A100 was to produce a fibre which did not fibrillate. This has been achieved but a number of other benefits have also resulted. Fabrics made from Tencel A100 have the drape and softness of standard Tencel but with a different warm touch. The fibre dyes much more deeply and retains colour exceptionally well.

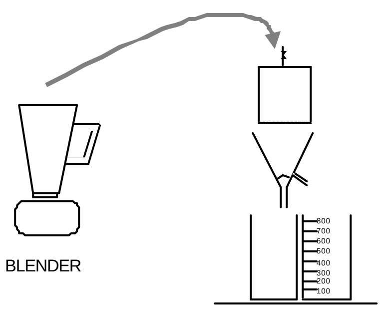
Tencel A100 has the strength and modulus of Tencel. The washing performance is excellent with low levels of shrinkage. Fabrics retain their colour and surface appearance during repeated washing.

Fibrillation Measurement

Fibrillation can be measured using the CSF (Canadian Standard Freeness) test. This was originally developed in the papermaking industry to assess the degree to which a pulp has been refined – split into smaller and smaller fibres. It measures the rate at which water can flow out of a suspension of fibre under controlled conditions.

To test the fibrillation potential of Tencel, fibre is cut to 5mm lengths and put into water in a blender. The blender is run for a period of time during which fibrillation may occur. The longer the blender is run, the more likely it is that the fibre will fibrillate. The suspension is transferred to a vessel with a mesh screen at the base. Water flows through the screen at a rate determined by the resistance to flow provided by the suspended fibre. Below the screen, the water passes into a funnel fitted with an overflow. The higher the rate at which the water flows, the more goes through the

The CSF Test Method



overflow. The greater the amount of water which ends up in the calibrated overflow vessel, the higher the "freeness" or CSF.

Unfibrillated standard Tencel gives a CSF of about 700. After blending for 9 to 11 minutes the CSF would be about 200.

Tencel A100 gives a CSF of 700 initially and after any length of blending up to 36 minutes or more. This demonstrates that the fibre does not fibrillate.

New fibre developments are usually assessed by conducting the CSF test after a range of blending times. Typically the CSF drops rapidly after the fibre has been in the blender for a critical time if the fibre fibrillates.

Tencel A100 does not fibrillate so the CSF remains constant.

Fibre which has been relaxed with sodium hydroxide solution fibrillate more slowly than standard Tencel.

Lenzing Lyocell LF

Lenzing developed their non-fibrillating lyocell fibre – Lenzing Lyocell LF. One of the key targets was to produce a fibre which is free from fomaldehyde. Low levels of formaldehyde can be produced from Tencel A100.

As with Tencel A100, Lenzing Lyocell LF is produced by cross-linking the fibre during manufacture. The cross-linker is chemically different, but operates on the same principle – a trifunctional molecule binds cellulose chains together.

The crosslinker used for Lenzing Lyocell is based on anchor chemistry of reactive dyes. It is colourless, non-toxic and free of formaldehyde.

Crosslinks are formed in the less ordered amorphous regions of the fibre and as a result they strengthen the regions where splitting of the fibre would occur during fibrillation.

The physical properties of the fibre are maintained after crosslinking. Lenzing Lyocell LF has physical properties that are comparable to a good quality cotton.

The fibrillation tendency is greatly reduced, but other properties are as would be expected for a standard lyocell fibre – naturally absorbent, accessible to dyestuffs and the swelling behaviour which is necessary to develop aesthetically attractive fabrics.

Lenzing Lyocell LF is as strong as cotton and much stronger than viscose. It does not fibrillate when fabrics made from it are processed through normal textile dyeing and finishing processes. Fabrics retain a clean surface after processing.

The fibre is particularly good in alkaline processes including mercerisation and causticisation. The bonds formed between the crosslinker and the cellulose are stable to alkaline conditions even at elevated temperatures. Low pH processing may cause the crosslinking to break down.

Tencel A100 and Lenzing Lyocell complement one another in terms of their properties.

The main advantages for Lenzing Lyocell LF are its resistance to stripping, and mercerising, with a sensitivity to pHs lower than 5.

Tencel A300

Tencel A300 is a new lyocell fibre which gives fabrics which do not fibrillate. Cross-linking chemicals are added to the fibre before drying, but they are not cured onto the cellulose.

Instead, the fibre is processed into fabric and then the fabric is cured before it receives any wet treatment. When the resin on the fibres cures, it not only prevents the fibre from fibrillating, but also sets the fabric into the shape it has at the time of curing.

Chemical addition is simple. Chemical selection is more demanding. It is important that the chemicals that are put onto the fabric have an acceptable effect on the processing into yarn and fabric as well as performing as a crosslinker.

Tencel A300 jersey fabrics do not fibrillate. They are resistant to alkaline conditions and have zero formaldehyde. Fabrics do not need to be resinated to give good stability.

A big advantage of the Tencel A300 approach is that the curing conditions for the cross-linker match the heat setting conditions needed for Lycra. Jersey fabrics with Lycra are a key market.

Tencel A300 is a new fibre and is being introduced to the market via selected customers with the knowledge and skills to use it effectively.

Conclusion

The concept of reacting a fibre during production gives the potential for a wide range of products. The Lenzing group now has three non-fibrillating lyocell fibres. Each has its place in the market which complements the positions of the other two. For most process routes and products, one of the three fibres will give the right performance.

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INFLUENCE OF ALKALI-UREA SYSTEM TREATMENT ON LYOCELL FABRICS

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Summary

In continuous dyeing operation, cellulose textiles are treated in alkali mixtures, which, in many cases, contain urea. Urea is well-known to be a potential swelling agent for cellulose. The influence of urea on the properties of CLY fabrics treated in diluted alkali solutions is investigated here.

The influence of low concentration of alkali and urea solutions treatment on Lyocell knitted (CLY-K) and Lyocell woven (CLY-W) fabrics was followed using KOH, NaOH, urea and/or their mixed solutions. The alkali concentrations vary from 0,05 to 0,5 M and urea solution concentration are in the ranges of 10% or 20%. The samples treated with solely solutions and mixed solutions were compared in order to identify the differences inherent to each process. The experimental was carried in pad batch (PB) and pad steam (PS) procedures. The solvent retention (SRV) and water retention values (WRV) analysis were performed to describe the changes in the fabrics structure. The CLY fabrics were dyeing and the K/S values are believed to show differences in shades. K/S results showed changes in the fabric accessibility after alkali/urea treatment compared with the treatments in the solely solutions.

Materials and Methods

The fabrics were supplied by Lenzing AG. The knitted Lyocell fabric (CLY-K) are 100% 1,3 dtex Lyocell, Ring yarn Nm 50/1, B4, knitted fabric, single jersey. The woven Lyocell fabric (CLY-W) is 100% 1,3 dtex/38 nm Lyocell, plain weave construction of 27 ends per 32 picks, 145 g/m^2 , ring yarn Nm 50/1.

Fabric samples of 40x20 cm for CLY-K and 70x30 cm for CLY-W were padded in certain concentrations of solely alkali (KOH and NaOH), solely urea and alkali/urea mixed solutions. The CLY-K fabrics were treated following two procedures: pad batch and pad steam. The CLY-W fabrics were treated following only pad batch procedures. The liquor combinations used for each fabric are described at Table 1.

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SPLITTING TENDENCY OF CELLULOSIC FIBRES

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In alkali solutions, the splitting of lyocell and viscose fibers into their macrofibrils was studied in this work. Ball bearing method, ultrasonic treatment and shear method were tried to analyse splitting of fibers. Viscose fiber show less splitting tendency than lyocell fiber. Various alkali types like LiOH, NaOH, KOH (0.5 M - 12 M) and TMAH, TbuOH (0.25 M – 2.8 M) and their mixtures with urea (0.26 M – 4.26 M) were used as swelling agents. The dependency of swelling time and temperature on splitting was also investigated. It was found that split number of a lyocell fiber ranges up to 44.

Keywords: alkali, fiber, fibrillation, lyocell, swelling, viscose

Introduction

Cellulose is a raw material with a wide variety of end uses in the chemical industry for producing man-made textile fibers. Commercial methods of manufacturing man-made cellulosic fibres include viscose, lyocell, cuprammonium and several alternative processes. Viscose production is based on deriving cellulose with carbon bisulphide [Cook 1984]. Lyocell process includes considerably less production steps and that the tedious production of viscose spinning mass is avoided. Lyocell is the most environment friendly process for producing cellulosic fibres [Kampl et al 1995]. The continuous recycling of the solvent in lyocell process means that the chemical operating costs of the direct dissolution process are low, and the lack of an alkali-ripening step means that the molecular weight of the cellulose forming the final fibre is higher than achieved in carbon disulphide viscose process [Moncreiff RW. 1970]. Different production processes and therefore different production conditions for conventional viscose, modal, and new lyocell fibers cause differences in the structure of the fibers despite the same chemical composition [Fink et al. 1998]. Lyocell differs from other cellulose regenerated fibres by its high crystallinity, high longitudinal orientation of crystallites, high amorphous orientation, low lateral cohesion between fibrils, low extent of clustering, relatively large void (pore) volume [Schurz 1994, Schurz *et al.* 1994, Crawshaw et al 2000 a, b].

Fibrillation of cellulosic fibres seems to be related to the fibrillar structure of the fibre and the degree of crystallinity. Fibres with a lower degree of fibrillar structure (standard viscose, HWM fibre), and fibres with a helical arrangement of the fibrils (cotton) show a less pronounced tendency to fibrillate than fibres where both a marked fibrillar structure can be observed and the fibrils are arranged longitudinally along the fibre axis (polynosic, lyocell) [Nemec 1994]. The fibrillation tendency is directly related to the degree of swelling of lyocell fiber regardless of the alkali type [Zhang et al., part 1]. Fibrillation was inhibited by decrease in fiber swelling [Zhang et al., part 1], decrease in temperature [Zhang et al., part 2], alkali pre-treatment in sodium or potassium hydroxide of 5mol/l due to the fiber reorganization [Zhang et al. 2005] and crosslinking treatments at lower degree of swelling [Zhang et al. part 5, Okubayashi accepted].

In this study, splitting tendency of lyocell fiber into its macrofibrils has been investigated. Different method trials like ball bearing method, ultrasonic and shear test were applied to induce splitting of lyocell fiber. Different concentrations of alkali metal hydroxides and their mixtures with urea were used. The mixture of DMDHEU and $MgCl_2$ is generally used for crosslinking of cellulosic fibres. However in this study DMDHEU and its mixtures with LiCl or $MgCl_2$ were tested on their ability to split lyocell fiber into its macrofibrils.

Experimental

Materials

Lyocell and viscose staple fibers without spin finishing were kindly supplied by Lenzing AG (in Austria) and were used for the experiments. The titer and the length of the fibers were 1.3 dtex and 38 mm, respectively. Analytical grade lithium hydroxide (LiOH,>99%), sodium hydroxide (NaOH, >98%), potassium hydroxide(KOH,>99%),tetramethyl ammonium hydroxide (TMAH, 25%, 2.8 M), tetrabutyl ammonium hydroxide (TbuOH, 40%, 1.5 M), lithium chloride (LiCl), technical grade urea (50g/l, 100 g/l) were purchased from Fluka, magnesium dichloride ($MgCl_2$) used as catalyst was purchased from Merck, 1,3 dimethylol dihydroxyethylenurea (DMDHEU, 75%, Fixapret® CP) used as crosslinker for cellulose fibers was purchased from BASF.

Methods

Ball Bearing Method

This method has been used to induce fibrillation of cellulosic fibres. A mass of fibers (0.5 g) was placed in a metal pot with 50 ml solution and 20 metal ball-bearings (of 0.5 cm diameter and 1 g weight) [Taylor 1991]. The pot was capped and tumbled end-over-end at 42 rpm and at fixed temperatures for 2 h. The fibers were then neutralized with a buffer solution containing 0.01 mol/l acetic acid and 0.01 mol/l sodium acetate (pH 5.0), rinsed with hot water at 50°C and with cold water continuously. After the fibers were dried in an oven at 60°C for 1 h, fibril numbers in fibers were counted on 0.038 mm segments using an optical microscope. Ten fibers from each sample were used to obtain mean values [Zhang et al., part 1].

Inducement and assessment of splitting of cellulosic fibers – Shear Method

For splitting test, one fiber was placed on the microscope slide shown in Figure 1. Alkali solution was dropped on the fiber and fiber was swollen for 1 min. A cover glass was put on to the fiber. The cover glass was pressed onto fiber by putting a weight which had a circle shape at its down side. This weight was placed on the sample resulting in downward weight ranged between 7.4-9.8 N. The area of cover glass (20 mm×20 mm) was used to calculate the downward pressure.

The downward pressure on fiber would be between $\frac{(0.75kg \times 9.8m/s^2)}{4 \times 10^{-4} m^2}) = 18.4kPa$ and $\frac{(1kg \times 9.8m/s^2)}{4 \times 10^{-4} m^2}) = 2.5kPa$.

Then the photos of the fibers were taken by Reichert optical microscope and the split numbers were counted. To evaluate the degree of of splitted fibers, numbers were used. The number 0 means no splitting was observed. 1 means the fiber is unique but some lines were observed on fiber which means splitting is about to start. 2 and higher numbers show how many splits were counted from the fibers. Three fibers were used and their mean value was taken for the average number of split number of a fiber swollen in each type of alkali.

Ultrasonic Treatment

Ultrasonic treatment was determined by sonifier named as Sonorex Digital 10 P, Bandelin. A mass of fibers (0.1 g) was immersed in alkali solutions in glass tubes. Glass tubes were placed in the sonifier and a strong sonic wave (×10%) was radiated onto the fiber for varying duration of times and temperatures. Then, shear method was used to induce splitting so that effect of ultrasonification on splitting tendency of cellulosic fibres was investigated.

Fibre Diameter

Swelling of a fiber in the aqueous medium was determined on the basis of fibre diameter measurements. The diameters of fibers were swollen for 1 min so that the fiber diameter stabilizes and then fibre diameters were measured by Reichert projection microscope. 20 fibers were counted and mean value was taken for each type of alkali swollen in each type of alkali.

Linear density of a fibre used in this study was 0.13 tex. This value means that 1000 m of a fibre weighs 0.13 g. Weight of one fiber is calculated as following:

$$W_{fiber} = (0.13g \times 38mm)/(1000 \times 10^{3}\,mm) = 4.94 \times 10^{-6}\,g$$

If we assume a fibre's cross section as circular, Equation (1) can be used for calculating fibre diameter (d).

$$W_{fiber} = DLp\,(d/2)^{2} \qquad (1)$$

Here, W_{fiber} is the weight of one fiber, D is the density of lyocell, L is the length of the fibre and d is the fibre diameter. Since it is known that lyocell has 38 mm length, and 1.52 g/cm^3 fibre density [Bourban et al 1997], diameter of dry fiber used in this study was calculated as 0.0104353 mm by using Equation (1).

Alkali retention value (ARV)

The fiber samples, 0.5 g in weight, were put into alkali solutions for 2 h at room temperature. The fibers were then centrifuged at 4000×g for 10 min and weighed (W_w). The fibers were washed with hot water at 50°C and cold water, then they were neutralized with the 0.01 M acetate buffer (pH 5) solution, rinsed with hot and cold water again. The fibers were dried in an oven at 105°C for 4 h and the weight was measured (W_d). Solvent retention value in alkali solution (ARV) was calculated by Equation (2).

$$ARV = (W_w - W_d)/\, W_d . D_{alk.} \qquad (2)$$

Here, $D_{alk.}$ is a density of the alkaline solution and it was assumed that D_{alk}. is equal to the density of alkali inside the fiber. The measurement was repeated 4 times for each sample to obtain mean value [Zhang et al 2004, part 1].

Results and Discussion

The fibrillation tendency is directly related to the degree of swelling of lyocell fiber regardless of the alkali type [Zhang et al., part 1]. The shear method applied to induce splitting permits the use of high alkali concentrations compared to the ball bearing method. Conditions of high swelling degree of lyocell and viscose fibers in various alkali solutions were selected from the literature [Zhang et al., part 1].

Figure 1 shows the relation between split number in ball bearing method and ARV of lyocell fiber against concentration of alkali. The highest split number of lyocell fiber was observed when it was swollen in TMAH solution. ARV and split number of lyocell fiber show the same trend for TMAH solution. Above 5 M concentration of alkali solutions, splitting of lyocell fiber wasn't observed. This indicates that splitting is no more directly related to swelling after 5 M concentration of alkali solutions.

Figure 2 and Figure 4 show the relation between fiber diameter and ARV of lyocell and viscose, respectively. Both of them show the swelling degree of fiber so that they show the same trend as it was expected.

Figure 3 shows the relation between split number and ARV of viscose fiber against concentration of alkali. It was found that viscose fiber doesn't have the splitting tendency in alkali solutions. It was also mentioned that viscose fibers didn't fibrillate under the experimental conditions used in Zhang et al., part 1 's work. This may be due to the different fibrillar structure of viscose fibers [Nemec 1994].

Figure 5 shows the split number of lyocell treated with 50 g/l urea and its mixtures with different type of alkali solutions for 1 min and 1 hour at room temperature. Lyocell fiber showed higher splitting when urea-alkali mixtures were used than only using urea. It was shown that split number of lyocell fiber can change by its swelling time with no direct correlation. Time dependency of splitting could also have been observed due to the applied splitting method.

Table 1 shows the split number of lyocell fiber swollen in DMDHEU and LiCl mixture. 1 split of lyocell fiber was observed when 4 M LiCl was used whereas 27 split was observed when mixture of 4.26 M DMDHEU and 0.71 M LiCl was used.

Table 2 shows the split number of lyocell fiber swollen in DMDHEU and $MgCl_2$ mixture. No split was observed when mixture of 4.26 M DMDHEU and 0.71 M $MgCl_2$ was used. On the other hand, when LiCl was used instead of $MgCl_2$, 27 split was observed. 1 split was observed when only $MgCl_2$ was used. It was observed that $MgCl_2$ is more effective than LiCl on splitting of lyocell fiber.

Figure 6 shows the split number of lyocell fiber swollen with 1 M TMAH in ultrasonic and also without using ultrasonic, by only applying shear method. After using ultrasonic, fibers were splitted by applying shear method because it was found that only ultrasonic didn't split lyocell fiber into its fibrils. Temperatures of 40°C, 80°C and different times were used for swelling of fiber in ultrasonification to identify the temperature and time dependence on splitting tendency of lyocell fiber. It was found that, there wasn't a strong correlation between time and split number of lyocell fiber at room temperature without using ultrasonic. Split number slightly increased when temperature increased from 40°C to 80°C in ultrasonic for the same ultrasonic application time (30 min). Split number increased further by the increase of temperature when ultrasonic application time was 90 min. When 40°C or 80°C was used in ultrasonification, there was no significant dependence of time on splitting tendency of lyocell fiber.

Figure 7 shows the split number of urea-alkali mixtures when ultrasonic was used for different temperatures for 1 hour. When the temperature of ultrasonic was changed from 40°C to 80°C, split number increased for TMAH-urea mixture, remained constant for both urea solution and KOH-urea mixture and decreased for TbuOH-urea and NaOH-urea mixtures.

Figure 8 and 9 show the photos of lyocell fiber treated with 0.5 M TbuOH in ball bearing method by using balls and without using balls, respectively. Splitting of lyocell fiber couldn't have been achieved by using ball bearing method since this method applies the friction directly on the fiber so that fibrils are peeled from the surface of fiber which is called as fibrillation.

The maximum split number was observed as 44 when lyocell fiber was swollen at 80°C for 1 h in ultracentrifuge. If we assume that each splitted fibre has the same diameter, d_{fibre}, ≈0.010 mm, the area of a fibre's cross section would be as Equation (3).

$$A_{fibre}=A_{fibril}\times \text{split number} \qquad (3)$$

Fibers and splitted fibrils are assumed to have circle shapes so that equations (4) and (5) are used.

$$A_{fiber} = p\,(d_{fibre}/2)^2 \qquad (4)$$

$$A_{fibril} \times SplitNumber = p\,(d_{fibril}/2)^2 \times 44 \qquad (5)$$

Here, d_{fibril} is the diameter of each splitted fibril and found as 1.5×10^{-3} mm by using equation (2). The diameters of a fiber, macrofibril, microfibril and an elemental fibril was suggested to be 10-30 µm, 0.5-1 µm, 100nm and 5-20 nm, respectively [Schuster et al 2003]. When the diameter of each splitted fibril, 1.5×10^{-3} mm, is compared with this literature, it can be assumed that this study show the achievement of lyocell fiber splitting into its macrofibrils.

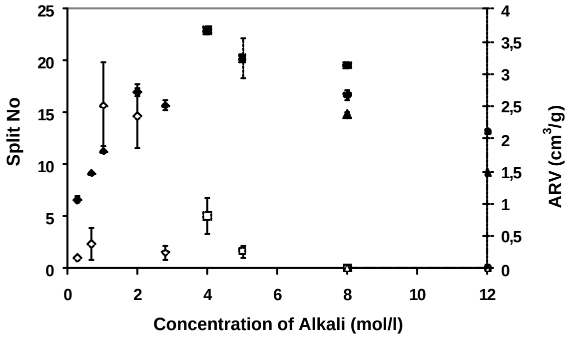

Figure 1. Plots of split number (TMAH ?, LiOH ?, KOH ?, NaOH ?) and ARV (TMAH ?, LiOH ¦ , KOH ? , NaOH ?) of lyocell fiber against concentration of alkali (mol/l)

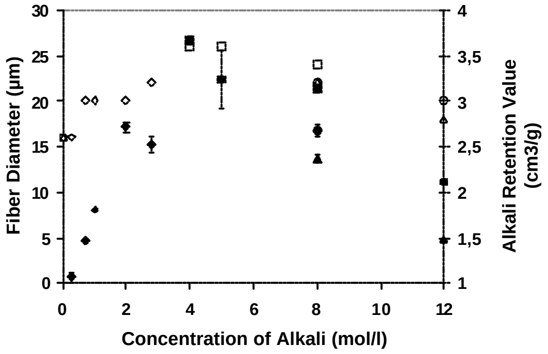

Figure 2. Plots of fiber diameter (µm) (TMAH ?, LiOH ?, KOH ?, NaOH ?) and ARV (cm3/g) (TMAH ?, LiOH ¦ , KOH ? , NaOH ?) of lyocell fiber against concentration of alkali (mol/l)

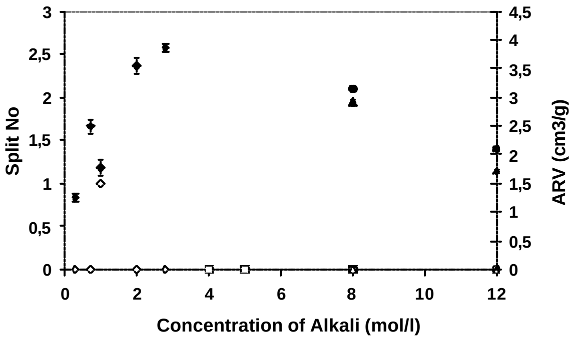

Figure 3. Plots of split number (TMAH ?, LiOH ?, KOH ?, NaOH ?) and ARV (cm3/g) (TMAH ?, LiOH ¦ , KOH ? , NaOH ?) of viscose against concentration of alkali (mol/l)

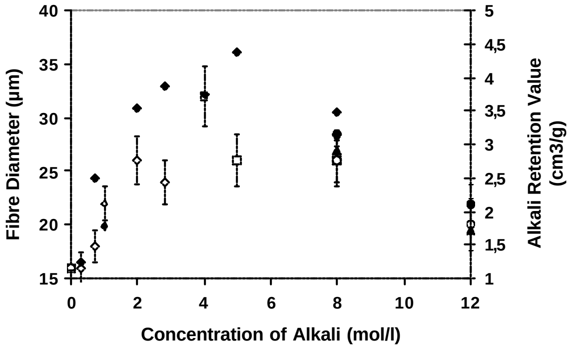

Figure 4. Plots of fibre diameter (µm) (TMAH ?, LiOH ?, KOH ?, NaOH ?) and ARV (cm3/g) (TMAH ?, LiOH ¦ , KOH ? , NaOH ?) of viscose against concentration of alkali (mol/l)

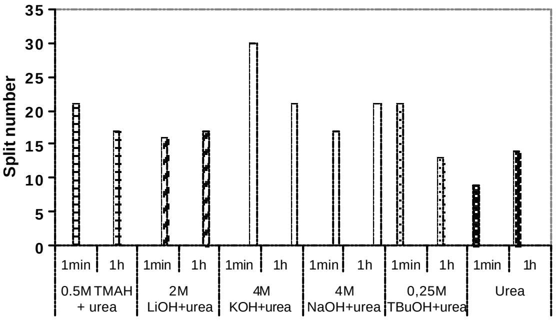

Figure 5. Split number of lyocell fiber treated with different urea-alkali mixtures for different times at room temperature (urea has concentration of 50 g/l)

Table 1. Split number of lyocell fiber treated with DMDHEU and LiCl at room temperature

DMDHEU (conc.)	LiCl (conc.)	Split No
4.26 M	0 M	0
4.26 M	0.71 M	27
0 M	0.71 M	0
4.26 M	4 M	0
0 M	4 M	1

Table 2. Split number of lyocell fiber treated with DMDHEU and $MgCl_2$ at room temperature

DMDHEU (conc.)	$MgCl_2$ (conc.)	Split No
4.26 M	3.15 M	0
0.85 M	0.63 M	11
0.43 M	0.32 M	23
0.26 M	0.19 M	23
0 M	3.15 M	17
0 M	0.63 M	1
0 M	0.32 M	1
0 M	0.19 M	1
4.26 M	0.71 M	0

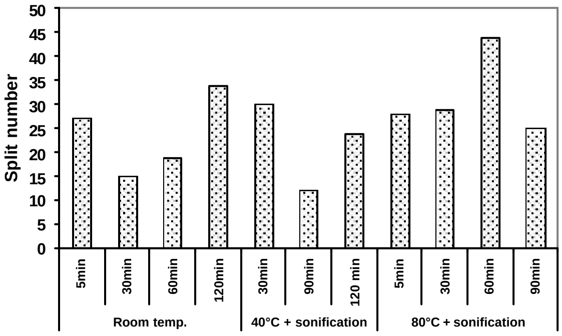

Figure 6. Split number of lyocell fiber treated with 1 M TMAH at room temperature, ultra- sonification at 40°C, ultrasonification at 80°C for different times.

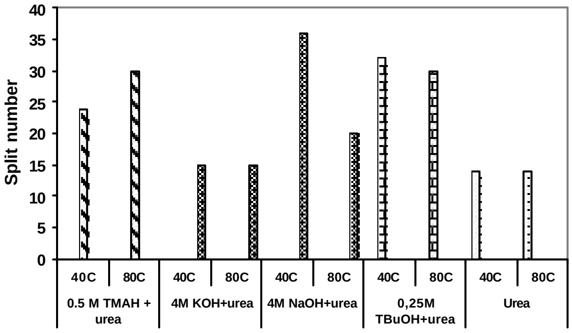

Figure 7. Split number of lyocell treated with different urea-alkali mixtures for different temperatures of the ultrasonification at 1 hour (urea has concentration of 50 g/l)

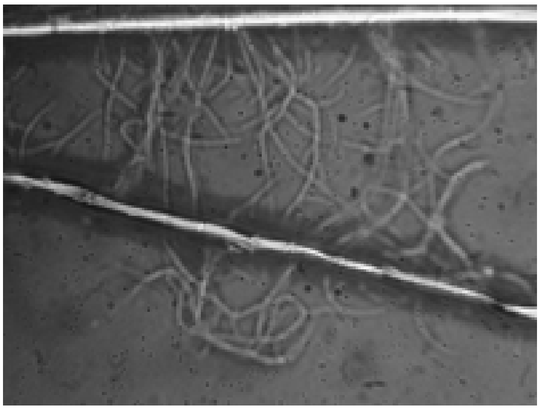

Figure 8. Lyocell fiber treated in 0.5 M TbuOH with ball bearing method by using balls

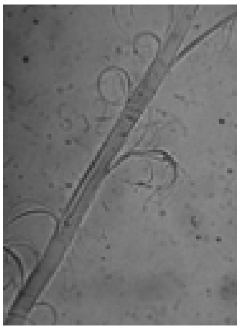

Figure 9. Lyocell fiber treated in 0.5 M TbuOH with ball bearing method without using balls

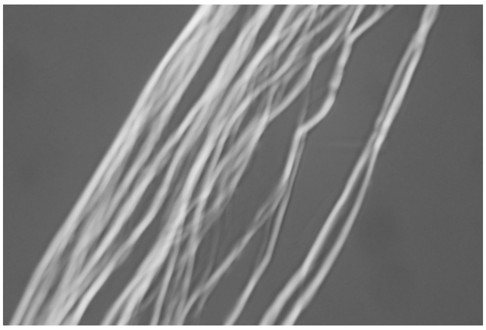

Figure 10. Lyocell fiber treated in 2 M TMAH at room temperature and then splitted by shear method (split number is 15)

Figure 11. Lyocell fiber treated with the mixture of 0.26 M DMDHEU and 0.19 M $MgCl_2$ at room temperature and then splitted by shear method (split number is 2)

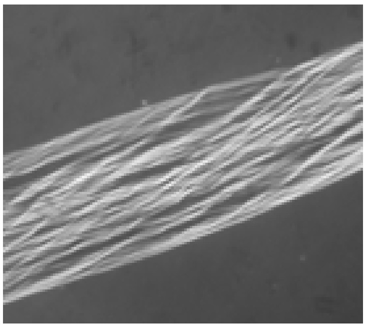

Figure 12. Lyocell fiber treated with 1 M TMAH in ultrasonification at 80°C for 90 min and then splitted by shear method (split number is 24)

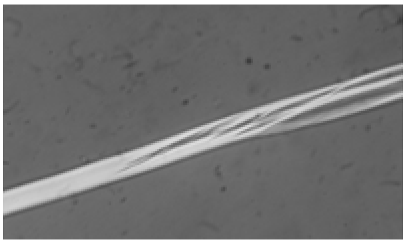

Figure 13. Lyocell fiber treated with 0.7 M TMAH at room temperature and then splitted by shear method (split number is 3)

Conclusions

Different methods were tried to establish a method for splitting of lyocell fiber. Ball bearing method was found too harsch for fiber so that fibrillation occurs instead of splitting. Putting a weight on fiber was found to establish splitting of lyocell fiber which was named as shear method. Neither splitting nor fibrillation occured by using ultrasonic treatment alone. Shear method was applied to fibers and split numbers were evaluated after using ultrasonification. Different time durations and temperatures were investigated for treatment of lyocell fiber in ultrasonification. The effect of ultrasonification was found not to be effective on splitting of lyocell fiber so that it was concluded that it isn't required to induce splitting.

In this work, splitting tendency of lyocell and viscose fibers was investigated. Splitting tendency of lyocell fiber was found to depend on the splitting test conditions like temperature, swelling time, alkali type and alkali concentration. Viscose fiber was found to show much less splitting tendency than lyocell fiber. Since viscose fiber has different fibrillar structure compared to lyocell fiber which has fibrils arranged longitudinally along the fibre axis, fibrillation tendency of viscose was found to be lower than lyocell [Nemec 1994].

Mixtures of DMDHEU with LiCl or $MgCl_2$ are used for crosslinking of cellulosic fibers to retard fibrillation. It was shown that DMDHEU and catalysts can also act as swelling agents so that splitting can be observed for lyocell fiber. $MgCl_2$ was found to be more effective agent in splitting of lyocell fiber than LiCl.

These results indicate new aspects of the interactions between textile chemicals and cellulose fibres.

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THE EUROPEAN POLYSACCHARIDE NETWORK OF EXCELLENCE (EPNOE)

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Introduction

Polysaccharides represent by far the largest group of polymers produced in the world (more than 150 000M tons of polysaccharides per year compared to about 140M tons of synthetic polymers). Fully biodegradable, they are made by Nature. For many reasons, including the fact that their structure is variable (depending on genetics, climate, location on Earth, soil, etc.), their use in highly engineered, functional materials is in its infancy. Nevertheless, and withstanding all difficulties, polysaccharides are the sustainable source of polymeric materials for tomorrow. They offer numerous product development opportunities that are increasingly attractive in light of tightening oil supplies and rising concerns over environmental and biodegradability issues.

The use of renewable raw materials (RRM) such as polysaccharides is one of the targets of the European Union policies with objectives to double the share of renewable energy from 6% in 1997 to 12% in 2010 (COM 1997 599) and to promote biodegradation (European norm EN 13432, directives 2001/77/EC, 2003/30/EC and 2003/96/EC). Several National initiatives have been implemented to boost the study of materials from renewable resources (UK Compostable Packaging Group 2003, German DFG funded cellulose basic research program, Austrian Christian Doppler laboratories).

The same is true for the US efforts where bio-based products have been promoted by means of a pro-active technological policy for several years: President Clinton's Executive Order EO 13134 of 1999, Public Law PL 106-224 for tripling bio-based products by 2010; establishment of a Biomass R&D Initiative, 2002 Farm Bill (H.R 2646/PL. 107-171) that makes the purchasing of biobased products mandatory. A law (second semester of 2005) will ask for the compulsory presence of materials coming from renewable resources in any federal order for any kind of goods.

These are the main reasons why the ***European Commission*** chose to select the topic **polysaccharides** for forming a new ***Network of Excellence.*** This was selected from among thousands of proposals competing for this distinction in all scientific and non-scientific disciplines. The "Network of Excellence"-designation creates a novel type of virtual research organization at the highest level of the 25-member European Union. It is implemented by the European Commission. According to its definition, the purpose of the network is to strengthen excellence in a particular research field by networking resources and expertise and thereby creating critical mass on the global level. A network of excellence is therefore an instrument designed primarily to address the fragmentation of research (in Europe) on a particular topic, whereby the main deliverable will be the restructuring and reshaping of the way research is carried out on that topic. It is thought to be the first step towards the construction of a new European Research Area.

The Polysaccharide Network of Excellence

The **European Polysaccharide Network of Excellence (EPNOE)** is composed of 17 research groups from nine countries, covering the entire range of expertise: all the major polysaccharides (starch, cellulose, hemicelluloses, alginates, chitin) and all necessary disciplines (including chemistry, biology, enzymology, modelling, physics, processing, materials science, simulation, life cycle analysis and economics) are involved. The network will be financed by the European Commission for four years, starting in May 2005. The ***members*** of EPNOE are:

P1: ARMINES-ENSMP-CNRS-Centre de Mise en Forme des Matériaux CEMEF (Higher education, Research), **France**

Role in the project: coordination, chemical physics, thermodynamics, rheology, rheo-optics, modelling. Main general activities: polymer chemical physics, polymer processing, simulation, modelling, rheology and rheo-optics. Areas of expertise: *materials processing, materials rheology, physical characterization, structure-properties relationships, simulation and modelling*.

P2: Department of Chemistry, Christian Doppler Laboratory for Pulp Reactivity, University of Natural Resources and Applied Life Sciences (BOKU), Austria, (Higher Education, Research)**, Austria**

Role in the project: wood organic chemistry. Main general activities: organic chemistry, wood, cellulose pulping and bleaching chemistry, solvent systems. Their areas of expertise: *organic chemistry, oligosaccharide synthesis, lipopolysaccharides, NMR-spectroscopy, immunochemistry, wood chemistry, polysaccharide characterization, analytical chemistry, GPC, NMMO- process chemistry, viscose process, molecular modelling*.

P3: Centre of Excellence for Polysaccharide Research at the University of Jena, (Higher education, Research)**, Germany**

Role in the project: fundamental chemistry of derivatisation Main general activities: Chemical functionalization of polysaccharides. Structure analysis. Structure-properties relationships. Nanostructures. Areas of expertise: *HPLC, GPC, NMR, AFM of polysaccharides and derivatives; chemical modification of polysaccharides, structure-properties relationship*.

P4: Fraunhofer-Institute for Applied Polymer Research, (Research)**, Germany**

Role in the project: structural characterisation, starch applications. Main general activities: Derivatization of cellulose and starch. Chemical modification of starch. Characterisation and testing. Areas of expertise: *molecular properties of polysaccharides (cellulose, hemicelluloses, starch), GPC-MALLS, FFF, HPLC, SLS, viscosimetry, X-ray scattering; polysaccharides processing, materials testing.*

P5: VTT Biotechnology, (Research)**, Finland**

Role in the project: applied enzymology, encapsulation. Main general activities: enzymatic modification of cellulosic fibers, hemicellulose and chitin, starch films and starch encapsulationAreas of expertise: *biotechnology in pulp and paper industry, cellulase, chitinase and hemicellulase enzymology, xyloglucan transferases, discovery of novel xyloglucan-modifying enzymes, AFM, immunomicroscopy*.

P6: Federal Research Centre of Forestry and Forest Products and University of Hamburg, (Research), **Germany**

Role in the project: polysaccharide raw material extraction, hemicelluloses. Taylor-made cellulose production. Main general activities: Enzymology of wood polysaccharides degradation. Enzyme-aided bleaching of primary pulps and enzyme-aided recycling of waste paper. Areas of expertise: *role of extractives in heartwood formation; pulp production and bleaching; characterization of polysaccharides in wood fibers and pulps; investigations on cellulose and hemicellulose derivatives*; *development of chemical and* *biochemical technologies for degradative conversion of wood polysaccharides into chemical feedstocks.*

P7: Abo Akademi University, Laboratory of Forest Products Chemistry, Process Chemistry Group, (Higher education, Research)**, Finland**

Role in the project: Fibre and papermaking chemistry. Mannans, galactans and pectins. Main general activities: pulping, bleaching an refining of wood, recovery of polymeric hemicelluloses from plans, characterisation of lignin. Areas of expertise: *wood and paper chemistry, organic structural chemistry; carbohydrate analysis; spectrometry, chemometrics, surface analysis, applied NMR spectroscopy.*

P8: "Petru Poni" Institute of Macromolecular Chemistry (Research, Higher education), **Romania**

Role in the project: cellulose and hemicelluloses applications. Main general activities: polymer chemistry and physics, polysaccharides, vegetal biomass, pulp and paper technology. Areas of expertise : *radical polymerisation, copolymerisation, functional polymers, polymer solutions, ultrahigh molecular weight polymers; inorganic polymers, ionic polymerisation, chemical transformation of polymers; biosynthesis and biodegradation of wood components, biocomposites; pulp technology, pulp bleaching and biobleaching, package and board manufacture.*

P9: Laboratory for Characterization and Processing of Polymers, University of Maribor (Higher education, Research), **Slovenia**

Role in the project: interfaces chemistry, physics and properties. Main general activities: cellulose fibres, surface chemistry, solid polysaccharides surface properties and surface modification, structure, synthesis of polyfunctional reagents, organic analysis, molecular characterisation, standardised analyses of textile materials, polymer solutions, melts and solids. Areas of expertise: *synthesis, organic analysis, surface and colloid chemistry, structure of fibre forming polymers, recyclable materials testing of textile materials, standardisation; optical sensors, sol-gels and nano technologies.*

P10: A&F, (Higher education, Research), **The Netherlands**

Role in the project: polysaccharide conversion. Main activities dealing with the project: Fundamental and applied research to develop novel industrial applications for renewable resources, e.g. fibre crops, cellulose, starches, and other plant constituents: plant fibre morphology, and fibre cell wall formation, cellulose orientation and structural deformation during extraction and processing, chemical carbohydrate composition in relation to fibre quality, chemical and biotechnological cellulose extraction and modification, lignin chemistry (dyeing bleaching); rheology of thermoplastic starches, particle size distribution, plasticisers and processing aids. Areas of expertise: *molecular interactions of biopolymers and analysis of complex systems; biotechnology and enzymology; pectins and pectinolytic enzymes ; carbohydrate chemistry and biochemistry, lignocellulosic product development.*

P11: Thüringische Institut für Textil- und Kunststoff-Forschung (TITK), (Research), **Germany**

Role in the project: Chemical processing, development of natural polymer applications, molding and shaping. Main general activities: Modification and forming of natural polymers. Chemical recovery of polymer wastes into processable monomers and oligomers. Technology developments. Areas of expertise: *Processing of materials, development of new technologies, materials characterization.*

P12: Institute of Chemical Fibres, (Research)**, Poland**

Role in the project: microbiology, chemistry and applications of chitin, chitosan and alginates. Applications in medecine and agriculture. Main general activities: Biotechnology, microbiology, dynamic biosynthesis of bacterial cellulose. Processing of fibres, films, microspheres, nanostructures. Areas of expertise: *biotechnology, biosynthesis, biodegradation; enzymatic modification of natural polymers; processing of natural and synthetic polymers; natural polymers for medical applications.*

P13: School of Biosciences, Division of Food Sciences, University of Nottingham, (Higher education, Research)**, UK**

Role in the project: Starch processing, applications of polysaccharides in pharmaceutical industry. Main general activities: starch characterisation and processing, materials science of biological molecules in food and pharmaceutical applications. Areas of expertise: *gels, biopolymer mixtures; polysaccharide degradation, Maillard reaction, heat processing of polysaccharides, extrusion; rheology, ultracentrifugation, light scattering, conformations and interactions in dilute solutions, molecular modelling.*

P14: INRA, Centre de Recherches Agro-Alimentaires de Nantes, (Higher education, Research)**, France**

Role in the project: Starch interactions/complexations in multicomponents systems, local order in biomimetic or cell wall architectures. Synergic polysaccharides interactions from dispersions to films. Main general activities : Structures, interactions, and processing of plant polysaccharides from cell walls and organelles to foods and materials. Areas of expertise: *plant cell wall model systems; polysaccharides solid state structures, polysaccharides mixtures; starch interactions; hemicellulose biochemical structure; wood micromechanics; interfaces in foams and emulsions; vibrational microscopy, laser light scattering, solid state NMR.*

P15: Institute of Textile Chemistry and Textile Physics, Christian Doppler Laboratory of Textile and Fibre Chemistry in Cellulosics, University Innsbruck, (Higher education, Research)**, Austria**

Role in the project: Textile applications. Main general activities: textile chemical analysis, physical textile testing, textile processing of cellulose, pre-treatment, dyeing, finishing. Areas of expertise: *electrochemistry, ion-complex; pre-treatment, mercerisation, NMMO-process, waste water; cellulose fibres - pilling, fibrillation, structure modelling.*

P16: University of Utrecht, Department of Science, Technology and Society (STS), (Higher education, Research)**, The Netherlands**

Role in the project: Polysaccharide policy, environmental assessments. Main general activities: Life cycle assessment, Techno-economic analysis, Policy analysis. Areas of expertise: *bio-based materials; energy analysis, material flow analysis and systems analysis.*

P17: University of Graz, Institut of Chemistry, Colloid & Rheology Group (Higher education, Research)**, Austria**

Role in the project: Polymer surface applications, surface and bulk modification and functionalisation. Main general activities: Surface properties and interaction between macroscopic / microscopic solids and components of the liquid phase, structure of polymer materials, surface modifications and functionalisation, sensor systems based on optochemical methods, membranes. Areas of expertise: Surface charge, surface physics of renewable polymer systems, rheology of solutions, optochemical sensing, membrane processes.

Activites of EPNOE

It is the explicit goal of the European Union to organize the scientific communities of its member countries into a cohesive network that integrates the resources and capabilities of the partners and promotes the use of polysaccharides as renewable raw materials for the manufacture of advanced, industrial materials. The ***activity*** of EPNOE will comprise three joint programs of activities dealing with ***integration, research*** and ***knowledge dissemination.***

The joint program on **integration** deals with the following aspects: integration of resources and activities, intellectual and property rights issues, communication, mobility and exchange of personnel, and equality of working conditions.

The joint program on **research** will comprise four main areas:

1. Isolation of polysaccharides as raw materials, structural characterisation and molecular modelling.
2. New principles of enzymatic, chemical and physical conversion of polysaccharides.
3. Combination of different polysaccharides.
4. Advanced materials and products, and new environmentally friendly processing routes for isolated and mixed polysaccharides.

A strong effort for devising a research strategy has been started by the partners, with the organization of brain-storming meetings, evaluation of our collective strength and weakness and an assessment of the equipment of all partners.

Finally, the joint program on **knowledge dissemination** will deal with the collaboration between EPNOE and industry, the establishment of courses and e-learning modules open to academic and industrial scientists, the establishment of a newsletter, an increased visibility of polysaccharide research in the refereed literature, translation of EU national programs and national conferences into English and posting them on the web site of EPNOE, and the adoption of public relation actions targeting citizens and students to promote polysaccharide science.

Several ***administrative bodies*** will be associated with EPNOE, most probably through an independent legal entity. The **Business and Industry Support Group** will be composed of small to large European companies. Its roles are to facilitate the dissemination of knowledge to industry, assistance with start-up ventures, the solicitation of feedback from industry, and the nucleation of academic-industrial collaborations. The **Institutional Support Group** will be composed of professional organizations, scientific societies, and governmental and non-governmental agencies. Its roles are to establish formal links to relevant scientific societies, to help shaping national and European policies, and to support standardization and/or legislation processes. The **Science for Citizens Support Group** will be composed of European scientific journals and press agencies. Its role is to promote the transfer of scientific knowledge towards the citizens of Europe at various levels (scientific journals, general public).

Conclusion

It is a significant challenge to bring together 17 laboratories of different legal status from nine countries with different languages, customs and national laws for the purpose of planning research, education and knowledge dissemination in a collective manner, and this is much more difficult than the classical international scientific collaborations all of us are used to. Nevertheless, we are fully confident that EPNOE will become a major stakeholder in promoting polysaccharide research, developing fundamental knowledge and inventing new applications for polysaccharides.