

Cellulose carbamate: production and applications



Contents

Review:

Cellulose carbamate: production and applications.....4

General	4
History	4
Raw materials.....	5
Pulp.....	5
Applying normal paper pulp	6
Recycled cellulose.....	6
Alternative cellulose sources.....	7
Activation.....	7
Liquid ammonia.....	7
Activation in kneader with NaOH	7
Mechanical absorption of urea.....	8
Enzymatic activation	8
Deep eutectic solvents	9
Urea	9
Formation of cellulose carbamate.....	10
Chemical characterization.....	11
Synthesis routes.....	11
Optimization of the conventional route	12
Applying modified reaction environments.....	13
Alkalization in xylene (CarbaCell).....	13
Alcohol with molten urea.....	13
Applying supercritical carbon dioxide	13
Applying microwaves	13

Deep eutectic solvents.....	14
Solubility with NaOH	14
Solubility	15
Zinc oxane	16
NaOH/Urea as solvent.....	18
NaOH/Thiourea as solvent	18
Freezing	18
Time before spinning	19
Additivition	19
Regeneration	19
Application.....	19
Spinning.....	20
Recovery of alkali.....	20
Fibre	20
Alternative spinning baths	22
Alcohol.....	22
Salt.....	23
Flame retardancy	23
Colouring	24
Film.....	24
Antibacterial materials.....	25
Membranes	26
Foam	26
Chromatography applications.....	27
Economic considerations.....	27
Conclusions.....	27

Copyright © VTT 2019

PUBLISHER:

VTT Technical Research Centre of Finland
P.O. Box 1000
FI-02044 VTT
Finland
Tel. +358 20 722 111

Layout: Innocorp Oy

ISBN 978-951-38-8707-0 (online)
doi: 10.32040/2019.978-951-38-8707-0

Cellulose carbamate: production and applications

Prof. Ali Harlin, D.Sc.

Review:

Cellulose carbamate: production and applications

General

Cellulose is the most abundant polymer on earth. It can be converted into monomers¹, derivatives²⁻³, regenerated materials⁴ and other functional materials⁵. However, cellulose is insoluble in common solvents due to its fibril structure and intramolecular and intermolecular hydrogen bonds.⁶⁻⁷ Several technologies to dissolve cellulose have been developed⁸. Despite being the most commonly applied method, the cellulose xanthate process, also known as viscose (or cellophane), generates several environmentally hazardous chemicals and by-products⁹. Cellulose carbamate is an interesting alternative based on the original work of Hill¹⁰ and Jacobsen¹¹, who showed that the reaction between cellulose and urea gave a derivative that was easily dissolved in dilute sodium hydroxide. Even though there has been extensive development of different solvents since then based on acids, bases, complexing and alternative cellulose reactions¹², cellulose carbamate has fulfilled expectations due to less harmful and inexpensive chemicals, as well as retrofitting ability to existing viscose plants.

History

Attempts to dissolve cellulose, like cotton or the inner bark of mulberry, started in the late 1840s, and has had huge importance for polymer chemistry development as well technical applications of textile fibres and films.¹³
¹⁴ The invention of nitrocellulose led to prod-

ucts like Chardonnet silk¹⁵, Parkesine¹⁶ and Celluloid¹⁷. The first synthetic fibre, Chardonnet silk, was the commercial product name for a regenerated cellulose fibre developed by Count Hilaire de Chardonnet in France in 1884. In 1920, DuPont purchased the rights to the process and sold the fibres under name Fibersilk. Only small amounts of Chardonnet silk were made because the cellulose nitrate mixture and fibres were flammable and explosive.

Already in the 1890s it was discovered that cellulose can be dissolved more safely as xanthate, and the viscous cellulose solution (viscose) could be simply coagulated in ammonium sulphate and then converted back to pure cellulose using dilute sulphuric acid¹⁸. This was later done on an industrial scale in a Mueller spin-bath¹⁹. Despite environmental impacts of by products and volatile odiferous solvents, the viscose process is still the most important method for shaping cellulose.²⁰ Those were, however, problems targeted to be solved.

It has been long known that cellulose and several of its derivatives are dissolving in a aqueous solution consisting caustic soda and urea at room temperature or below. It is also well known it is possible to stabilize ordinary viscose solutions by incorporating therein amide- or imide-containing substances. Several authors have reported on the formation of cellulose carbamate due to a reaction between the OH-groups of cellulose and urea.²¹ Dissolution becomes possible in solvents such as aqueous NaOH by first converting cellulose to cellulose carbamate.

Urea has also been extensively used with alkaline solvents for the direct dissolution of cellulose.²²

An early invention from 1937 by Hill et.al., from company DuPont, comprised the impregnation of cellulose such as wood pulp or cotton linters with a urea provides useful cellulose derivatives which are soluble in dilute aqueous caustic soda.²³ In order to get the urea evenly distributed in the cellulose, one has to impregnate it with an appropriate solution. Solutions of urea in water or alkaline media are proposed in the literature, but they do not give satisfactory results.²⁴

Since then, attempts have been made to improve a major handicap of cellulose carbamate, namely the higher caustic chemical consumption compared to the viscose process. The cellulose carbamate process is advantageous as discovered by the former viscose producer, Kemira Oy Sateri²⁵, in retaining the use of the viscose spinning technology while avoiding the use of hazardous sulphur-containing compounds for derivatization.²⁶ The recent developments of cellulose chemistry have promise for the next development stage of carbamate technologies.

Raw materials

Pulp

Dissolving pulp is the most typical raw material for cellulose carbamates. The activity of dissolving pulp has been discussed based on production method and the raw-material applied. Dissolving pulps are sold according to solubility in sodium hydroxide, the so called S18 or S10 values, as well as impurities content. "Pulp reactivity" is a general term, but it is also a kinetic term and is always related to the end use of such pulps.²⁷ The reactivity of dissolving pulp was experimentally determined in terms of residual cellulose in viscose. The results show that pulps with high acetone extractable fractions, high magnesium contents, low alkali resistance and low viscosity, gave low viscose filter values and low residual cellulose contents. Pulps with low residual cellulose contents also had low carboxyl group contents and low polydispersity. The results indicate that in pulp with high reactivity, the hemicellulose content is low and the cellulose chains are shorter and more soluble in alkali. An explanation of the positive effect from the high extractive con-

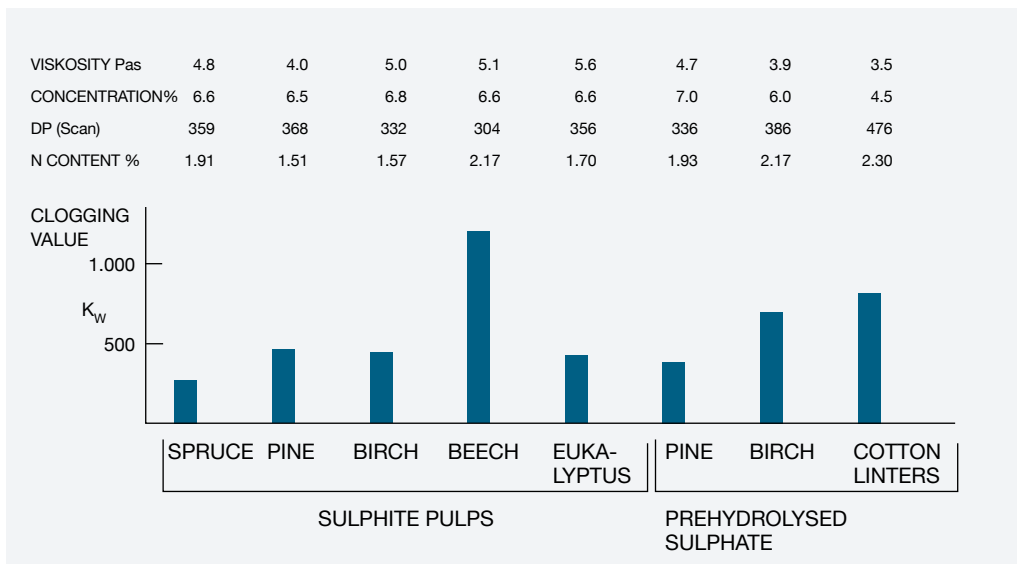


Figure 1: Reactivity of different pulp types.

tent is that the extractives facilitate the diffusion of carbon disulphide.²⁸

Typically, sulphite pulp is assumed to be more active than pre-hydrolysis sulphate-based dissolving pulp.²⁹ It has been defined that softwood-based dissolving pulp is typically more active than hardwood.³⁰ Independent of the choices, the cellulose carbamate process has been successfully applied, even if parameters vary. When comparing different pulp types, especially for the CCA process, it has been observed that sulphite pulps are more active than pre-hydrolysed sulphate pulps and cotton linter. However, for an unknown reason, the sulphite beach pulp was least active³¹ (See figure 1 below).

The concentration of sodium hydroxide in the spinning process is significant in determining the best cost of the process. The need for sodium hydroxide is dependent on the DP. The DP needs to be adjusted.

Never-dried cellulose is considered more active than a dried dissolving pulp, which may have hornificated. One recent invention relates to a method for manufacturing cellulose carbamate comprising the following steps: providing a never-dried pulp, adding urea and mixing said pulp with said urea, mechanically treating said mixture, drying the mixture, and heating the relatively dry mixture, thus providing a cellulose carbamate.³²

Cellulose carbamate has also been produced from microcrystalline cellulose.³³ All-cellulose composites were produced by partial dissolution of two cellulosic sources in a mixture of sodium hydroxide and urea at low temperature. Carbamated microfibrillated cellulose (MFC) was used for thin self-reinforced all-cellulose composites.³⁴

Applying normal paper pulp

There is a method of producing alkali cellulose from “low-cost pulp”. The starting material is first treated with a 10% NaOH solution and subsequently pressed to squeeze out spent liquor containing hemicelluloses. In the

second step the material is treated with an about 16% NaOH solution, and subsequently pressed, thereafter the treated pulp is in the form of alkali cellulose ready for shredding and xanthogenation.³⁵ The same pulp should be useful for carbamation.

Another method was developed for high-hemicellulose fibre raw material, such as for paper pulp³⁶. In this method, the pulp is also treated in two steps with NaOH solutions. In the first treatment step, the concentration of the NaOH solution may be 8 to 25%, preferably 16 to 21%, and in the second treatment step 8 to 25%, preferably 10 to 16%. It is advantageous that in the second step a lower effective sodium hydroxide concentration than in the first step is applied.

Recycled cellulose

Recycled materials are of increasing interest. A method of producing dissolving pulp from a recycled fibrous feedstock has been developed. The method comprises providing a fibrous material comprising cellulose, lignin and hemicellulose, said fibre source further having a lignin content of 0.1 to 7% and an ash content up to 3%; subjecting the fibrous material to an alkaline extraction at a temperature of about 0 to 25 °C., to produce fibres having a reduced content of hemicellulose; subjecting the fibres thus obtained to a bleaching treatment carried out with oxidative chemical reagents in order to reduce the lignin content of the fibres; and recovering the fibres thus obtained. By means of the method, dissolving pulp can be produced from recycled paper and cardboard products.³⁷

Even recently is presented a method for treating cellulose-based raw material especially for manufacture of regenerated cellulose-based products, characterized in that hemicelluloses in the raw material are first dissolved in a raw material-specific alkali solution. The obtained hemicellulose alkali solution is then oxidized for degrading hemicelluloses, and the oxidized alkali solution is re-used in the same process.³⁸

Alternative cellulose sources

However, there are several alternative cellulose sources. Cotton and cotton linter has been applied by several researchers. The same methods are used as with pulp, but the challenge is the activation of cotton having a more compact fibril structure. Recently, a treatment processes to apply textile-based materials as dissolving pulp was developed.³⁹

Chemical modification of cotton cellulose with the aid of supercritical carbon dioxide has been studied. In this method, urea was first impregnated into the cellulose pulp using supercritical carbon dioxide as a solvent and carrier, followed by the esterification of cellulose at a suitable temperature, resulting in cellulose carbamate. The yielded cellulose carbamate is endowed with high nitrogen content and good solubility in alkali. Further, the nitrogen content of modified cellulose can be adjusted by the impregnating pressure, esterification temperature and esterification time.⁴⁰

Bamboo fibres have been utilized in synthesizing the cellulose carbamate with urea. The application required optimization of the concentration of sodium hydroxide solution used for activating, activation time, aging time, urea soaking time, the concentration of urea solution, reaction time and reaction temperatures.⁴¹

Cellulose carbamate (CCAs) was produced also from kenaf core pulp (KCP) using the microwave reactor-assisted method.⁴²

Activation

High accessibility is an essential prerequisite for homogeneous substitution of cellulose material. Cellulose structure can be affected by means of mechanical activation. Grinding enables both activation and inactivation.⁴³ One practical option is the use of a ball-mill.⁴⁴ It has been observed that micro crystalline cellulose MCC can be fully molecularly dissolved in NaOH and that the samples are

stable for up to 2 months at room temperature (22 ± 1 C) at these low concentrations.⁴⁵

The Arbron process applies never-dried bleached pulp which is steam evaporated to medium consistency. Cellulose fibres are first fractured to microparticles at 150–160 °C with 5 bar steam. The reaction takes place in an up-flow reactor in 1 hour where heating is applied with direct steam and reaction conditions are acidic by means of added sulfuric acid.⁴⁶ Under these conditions, also the molar mass adjusts.

The pretreatment of cellulose can be performed with alkali hydroxide⁴⁷ or ammonia⁴⁸, with hot water under pressure⁴⁹ or with enzymes⁵⁰ or by post-treatment of the cellulose carbamate with water or aqueous acid in heat, optionally under pressure⁵¹. This provides, more or less, soluble cellulose carbamates, but their solution characteristics are still in need of improvement.

Liquid ammonia

In the Cellca process, cellulose is treated with liquid ammonia and dissolved urea. Thereafter the ammonia is removed before reactions occur. The proposed benefit of the ammonia is that it enables distribution of the urea throughout the cellulose.⁵² Liquid ammonia opens up and changes the crystal structure of cellulose.⁵³ Liquid ammonia near its boiling point also dissolves enough urea so that one impregnation provides the required amount of urea into the cellulose.

Activation in kneader with NaOH

According to one invention, a process was developed for the preparation of CCA starting from NaOH activated cellulose or pulp under a mechanical kneader. In the process, the urea distribution is improved by means of opening the lamellae crystal structure of the cellulose fibres. The actual process is based on the following steps: a) first, a mixture of activated

cellulose or pulp and urea is produced in a mixing unit with shearing treatment, b) the mixture is dried c) and then reacted at a temperature between 120 and 180 °C to the reaction product, the cellulose carbamate.⁵⁴

weight of the cellulose. The process is based on repeated compression of the mass. The patent proposes certain equipment enabling efficient absorption.⁵⁵

Mechanical absorption of urea

A particularly simplified method for production of CCA is based on the invention of absorbing urea into cellulose in an aqueous solution. A high solid technique/dry technique method for the production of cellulose carbamate has been described. In this technique dry cellulose pulp is mixed with an auxiliary agent and urea under mechanical work at a high consistency and the reaction is thereafter carried out in an oven. The urea amounts needed to reach acceptable dopes is most preferably less than 22% of the

Enzymatic activation

In one study, chemical and enzymatic pre-treatments have been applied to increase the accessibility of cellulose materials. Dissolving pulp has been treated with a mono-component endoglucanase. Fock's method showed a microscale process similar to the viscose process increasing cellulose reactivity. Simultaneously, the viscosity decreased, but at the given viscosity level, the enzymatic pre-treated pulp had a higher reactivity than the pulp subjected to acid hydrolysis. A mono-component endoglucanase can thus be used to increase the reactivity and accessibility of dissolving pulp in the

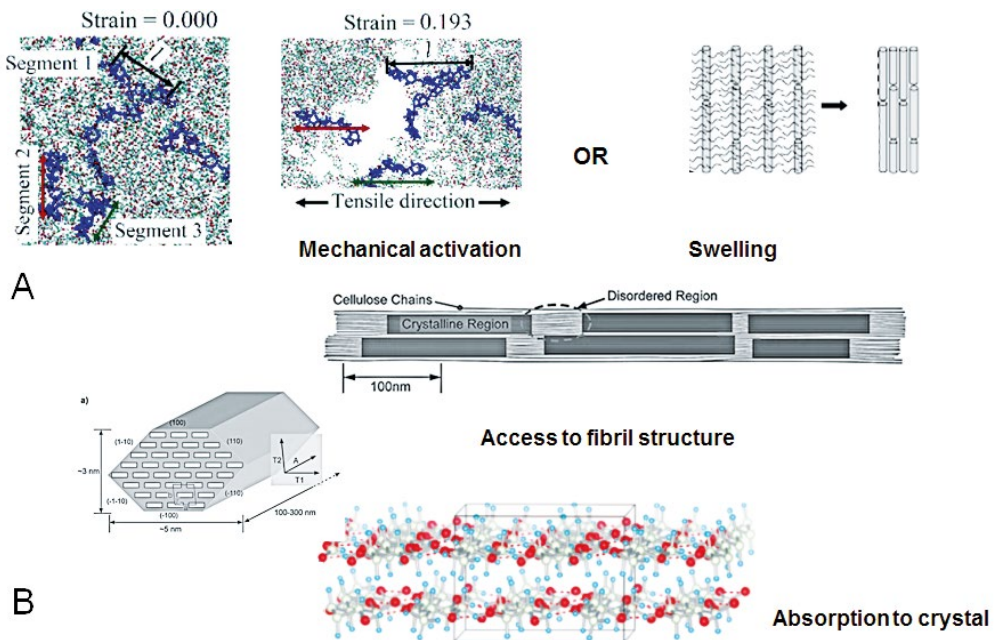


Figure 2: Efficient carbamation require A) cellulose action mechanically⁵⁶ or chemical swelling⁵⁷ and B) sufficient time to complete absorption to the crystal structure of cellulose-I β (side view)⁵⁸

viscose process.⁵⁹ The chemical fibre institute in Lodz has applied the methods of reduced degree of polymerization to form cellulose carbamates.⁶⁰

Deep eutectic solvents

The physicochemical properties of deep eutectic solvents (DES) are comparable to ionic liquids. They are, however, composed of two or three chemicals that consist of a hydrogen bond donor and a hydrogen bond acceptor. These components form a eutectic mixture with a lower melting point than the individual components. Compared to ionic liquids, DESs are generally considered to be easier to prepare, less expensive and less toxic.⁶¹ Choline chloride (ChCl) and urea has been the most popular DES system probably due to the availability of these chemicals and their low melting point (~12 °C).⁶²

Recently, choline chloride/urea (ChCl/urea), a typical DES, has been found to possess various applications in organic synthesis, electrochemistry, and nanomaterial

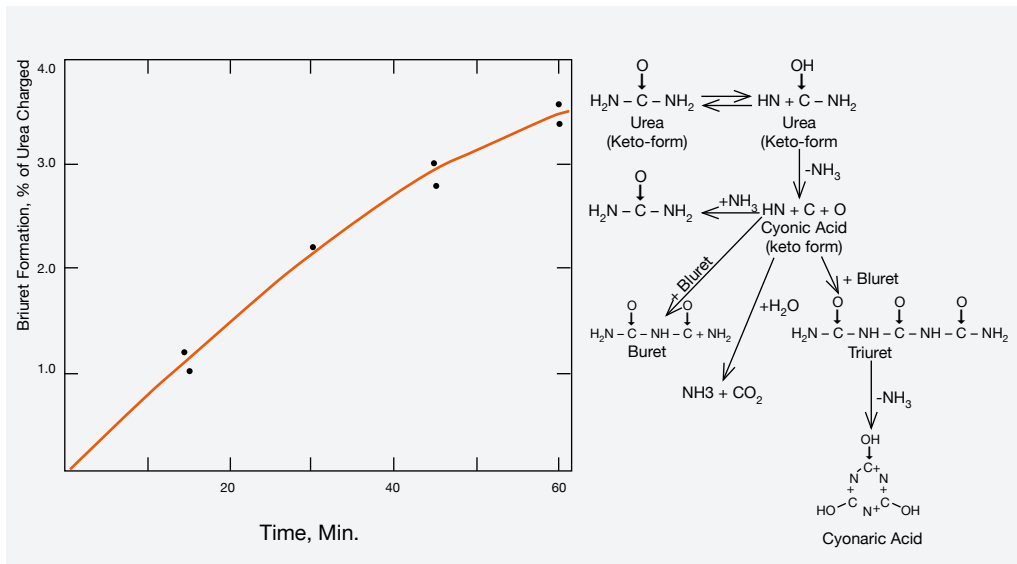
preparation, also enamel to plasticize cellulose and regenerated cellulose⁶³, as well fibre spinning medium⁶⁴ to a pre-treatment prior to nanofibrillation.⁶⁵

It has also been observed that after treatment of Avicel® (cellulose) with a DES comprising betaine monohydrate and urea, there can be a decrease of crystallinity of at least about 10–15% and enabling even urea distribution in the cellulose matrix.⁶⁶

Access of urea in the cellulose structure on a molecular level is essential for the quality of the carbamate formed (see Figure 2 above). There are several methods enabling this to take place, like mechanical activation by means of milling like a ball mill or hammer mill or alternatively by means of chemical swelling like when exposed to alkaline solution.

Urea

Urea is produced on an industrial scale by the exothermic Bosch–Meiser urea process applying liquid ammonia with gaseous car-



Formation of biuret in 140°C (left) and the biuret formation mechanism (right).

bon dioxide. In 2012, worldwide production capacity was approximately 184 million tonnes.⁶⁷

In urea manufacturing, small amounts of biuret form as an impurity as two molecules of urea combine with the loss of a molecule of ammonia. The compound is not useful for fertilizers but is used as a non-protein nitrogen source in ruminant feed⁶⁸, but for carbamation reaction, biuret is inefficient.

Urea serves an important role in the metabolism of nitrogen-containing compounds by animals, and is the main nitrogen-containing substance in the urine of mammals. It is a colourless, odourless solid, highly soluble in water, and practically non-toxic (LD50 is 15 g/kg for rats). Dissolved in water, it is neither acidic nor alkaline. Urea-containing creams are used as topical dermatological products to promote rehydration of the skin. Urea is used as well as a component of animal feed, providing a relatively cheap source of nitrogen to promote growth.

Higher temperatures than 175 °C will lead to formation of cyanuric acid (CYA) by thermal decomposition of urea, with release of ammonia. The conversion commences at approximately⁶⁹



Cyanuric acid crystallizes from water as the dihydrate, which is especially harmful for spinning solutions. Isocyanic acid can be recovered from cyanuric acid only at very high temperatures between 325 and 350 °C, which are unpractical for cellulose reactions. Isocyanic acid is a colourless substance and is volatile and poisonous (LC50 Inhalation 0.49 mg/l, LD50 Dermal >9,400 mg/kg, LD50 oral >10,000mg/kg) with a boiling point of 23.5 °C.

Formation of biuret is risk-related forming cyanic acid. The enol form of urea is formed at 132 °C and cyanic acid is dominant at 150 °C, while at 170 °C and above bi- and triuret are formed, which are yet reactive with cellulose but forming undesired derivatives.⁷⁰

Formation of cellulose carbamate

Cellulose carbamate is a carbamic-acid-ester derivative of cellulose (Figure 3). It is soluble in alkali and, for this reason, has attracted strong interest for fibre regeneration from wood pulp as an alternative to the vis-

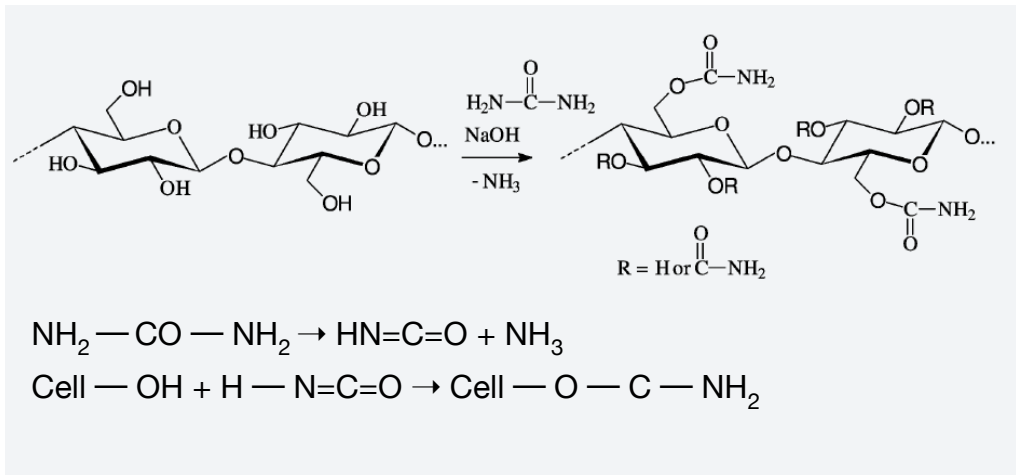


Figure 3: Cellulose carbamate formation reaction.

cose process.⁷¹ The derivative is obtained by heating urea together with cellulose, through reaction with the isocyanic acid produced by decomposition of urea when heated rapidly to above its melting point of 133 °C.⁷²

Typically, the CCA reaction is carried out at temperatures in the range of 135 to 180 °C, as previously shown. This is prior the art. Higher temperatures than 175 °C will lead to formation of cyanuric acid by thermal decomposition of urea, with the release of ammonia.⁷³

Isocyanic acid is a colourless substance, is volatile and poisonous, and hydrolyses to carbon dioxide and ammonia. This is why carbamation needs to be performed in closed vessel and formed off gasses need to be washed to remove especially ammonia.

Chemical characterization

The IR spectrum of CCA showed an obvious new absorption peak at 1714 cm⁻¹ that was attributed to the stretching vibration of the carbonyl (C=O) in urethane groups.⁷⁴ It has been reported that some derivatization procedures led to the transformation of alkalinized cellulose with urea into similar structures as cellulose modifications II and IV.⁷⁵ In this process, CCA displayed the same distinct peaks as native cellulose with 2θ values of 14.8°, 16.3°, and 22.6° corresponding to the (110), (110), and (020) planes of the cellulose I crystalline form. Reference literature suggested that chemical modification did not change the crystalline form of cellulose. Furthermore, the degrees of crystallinity (χ_c) of the native cellulose and CCA were determined to be 72% and 65%, respectively. With the reaction of cellulose and urea, the substitution of the hydroxyl groups might mainly occur in more accessible amorphous regions and on the surface of the elementary crystallites. These conditions led to the reduction of the density of hydrogen bonds and partially destroyed the crystalline structure of cellulose, which was beneficial for the dissolution of CCA. The 13C NMR spectra also verified

the presence of the typical cellulose I crystal form of cellulose and CCA.⁷⁶

Synthesis routes

Several variations are reported on the basic process: pre-treatment or activation of the cellulose with alkali or liquid ammonia⁷⁷, performing the reaction in organic media, e.g. xylene and toluene^{78 79}, supercritical-CO₂ assisted impregnation of the cellulose with urea^{80 81}, subjecting reaction mixtures to microwave heating⁸² or electron beam irradiation⁸³. All are aimed at achieving a homogeneous distribution of the substituent in cellulose pulp, which promotes its dissolution in alkali, and helps achieve the solution properties required for fibre spinning.

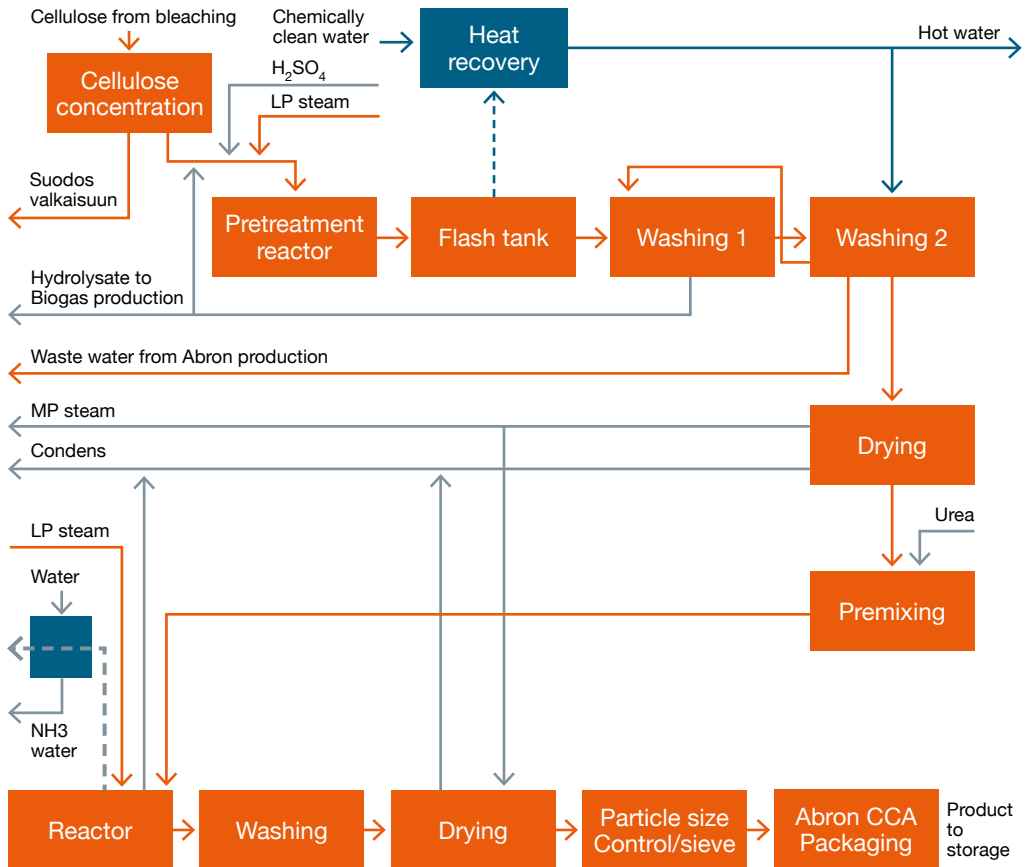
The early method of DuPont consists of essentially steeping, pressing, drying, baking and washing. First cellulose steeping cellulose is made in an excess volume of an aqueous solution of at least 15% urea and 2 to 10% sodium hydroxide, preferably containing a small quantity of a wetting agent such as sodium “Lorol” (the fraction of saturated alcohols obtained by hydrogenation of coconut oil, and consisting mainly of Ca and Cu alcohols) sulfate. Secondly, the impregnated cellulose is pressed until it contains from about 0.75–2.5 parts by weight of the steeping liquor per part of the original dry cellulose. The concentration of the steeping liquor and the press ratio are so adjusted that after pressing from 4 to 8 parts by weight of sodium hydroxide, and from 20 parts of urea per 100 parts of original dry cellulose. Thirdly, the pressed material is dried and baked to the dry product at reaction temperature, preferably at 120–150 °C. Although higher temperatures may be used provided, the time of heating is suitably adjusted) until the product is soluble in dilute aqueous caustic alkali and discontinuing baking before the product becomes insoluble; and finally washing the baked product to improve its colour and to remove unreacted urea and by-products.⁸⁴

Optimization of the conventional route

Cellulose carbamates were successfully prepared from the cellulose/urea mixtures with low content of urea through conventional heating. Urea content in the mixture, reaction temperature and time play important roles in the carbamation of cellulose. The urea content of the mixture was optimized between 3.4 and 4.6 wt % for enhancing the solubility of CCAs and saving the cost of materials. The reaction temperature and time were set at a maximum of 170 °C and 2.0 h to avoid the carbonization and cross-linking of cellulose. CCAs retained the cellulose I crystalline

form and the CI values hardly changed with the incorporation of carbamates. Furthermore, both the reacted cellulose/urea CU mixtures and CCAs prepared under optimized conditions could be well dissolved in NaOH/ZnO solution and the washing process could be abandoned completely. Because of the low consumption of urea and no wastewater discharge, the economic and green process reported here would be particularly beneficial for industrialization.⁸⁵

The more recent production of cellulose carbamate takes place by the introduction of urea in optionally activated pulp and reacting the urea with the pulp at a constant temperature, above the lying at about 132 °C decom-



position temperature of the urea into isocyanic acid and ammonia, either in the dry phase⁸⁶ or in an inert liquid organic reaction medium⁸⁷. While increasing reaction temperature and reaction time increases the degree of substitution of the cellulose, the solubility of the cellulose carbamate produced in aqueous alkali metal hydroxide solution and the stability of the solution is deteriorated at the same time by the action of heat and the prolonged reaction time. In the figure below, a flow chart of the Arbron carbamation process is presented.

Applying modified reaction environments

Alkalinization in xylene (CarbaCell)

It has been shown that, contrary to previous assumptions, a reaction of cellulose with urea at temperatures that are significantly below the decomposition temperature converting urea into ammonia and isocyanic acid. The reaction starts already at 80–90 °C and proceeds even in this temperature range at a satisfactory rate. According to the characteristics of the operational cellulose and the nature and extent of the selected activation process begins the reaction at reaction temperatures ranging from 80–110 °C and the temperature is increased progressively as the reaction rate decreases due to decreasing urea concentration.

Preferably, the reaction is carried out in a plurality of series-connected reactors, wherein the reaction temperature is raised depending on the total number of the reactors from one reactor to the next reactor, in each case 5 to 30 °C. At, for example, *o*-xylene as the inert organic reaction carrier and three reactors, a reaction temperature of about 80 °C for the first reactor recommends about 120 °C for the second reactor and about 140 °C for the third reactor. At five reactors, the respective temperatures are from about 80 °C, 100 °C, 120 °C, 130 °C and finally 140 °C. The temperature intervals between each two adjacent reactors may be the same or different sizes.⁸⁸

Alcohol with molten urea

Even further, one invention relates to a method for producing cellulose carbamate from cellulose and urea applying especially molten urea at a temperature of 135 °C to 160 °C. The process is a reaction of alkali or earth alkali or cellulose esters with degrees of substitution (DS) of 0.1–0.4. Excess liquor is preferably washed with methanol, which can be recycled.⁸⁹

Applying supercritical carbon dioxide

In order to overcome the diffusion barrier in cellulose against urea, also advanced technologies have been applied recently. One example of these is modification cellulose assisted by supercritical carbon dioxide SC-CO₂. CCA was successfully prepared from soft wood pulp at 150 °C and 3,000psi (207 bar) for 6 hours. Compared to conventional methods SC-CO₂ was shown to be more efficient in the modification of wood-derived cellulose. The modified cellulose had a considerable increase in nitrogen content.⁹⁰

Applying microwaves

A method has also been proposed for producing cellulose carbamate by reacting cellulose with urea heating the reaction mixture by electromagnetic radiation of a frequency range between 100 MHz and 100 GHz for 2 minutes to 3 hours to a temperature in the range from 100 °C to 250 °C. This method accomplishes the objective of the invention by a uniform temperature distribution in the reaction mixture during thermal treatment of the cellulose-urea mixture. The method offers the advantage of the reaction temperature being reached in a short time and moreover, the energy distribution in the reaction mixture is almost homogeneous because of the uniform distribution, which is a benefit of nearly dry matter.⁹¹

Cellulose carbamates were synthesized efficiently from the cellulose/urea mixture under solvent- and catalyst-free conditions by microwave irradiation. The method used in this work seems to be convenient for the synthesis of carbamates starting from various sources of cellulose, such as cotton linter, reed, bagasse and wood pulps with different degrees of polymerization is appropriate for the method. Urea content in the mixture, mass of the mixture and pulsed microwave energy has an active influence on the reaction. The urea content in the mixture was optimized between 30 and 40 wt% for saving the cost of materials and recycling urea.⁹²

Deep eutectic solvents

DES appear in the horizon as an attractive and cost-effective option for using ionic solvents in biotransformations. DESs are often produced by gently warming and stirring two (bio-based and cheap) salts (e.g. choline chloride and urea). First, successful uses of DESs in biotransformations were reported recently.⁹³ It may be expected that knowledge accumulated in (second generation) ILs and biotransformations could be turned into real applications by using these DESs, and third generation ILs, in the coming years.⁹⁴

Carbamoylation of various cellulosic materials was systematically studied, using a reactive dissolution approach. Reactions with cellulose or pulp and aromatic isocyanates, were initiated as heterogeneous mixtures in hot pyridine. As the reaction proceeded, homogeneous solutions were obtained. However, attempts to synthesize highly substituted cellulose carbamates, with aliphatic isocyanates in pyridine, failed; homogeneous solutions were not achieved, even after long reaction times. One of the major problems in

the synthesis of cellulose carbamates is the formation of undesired low molecular weight (MW) by-products, along with the main product.⁹⁵

Carbamate conversion was observed when wet pulp was treated with a urea-based DES system; this was found to occur most readily at 120 °C.⁹⁶ The ChCl-urea as a pre-treatment in order to remove hemicelluloses and lignin from corn stover prior to butanol fermentation was shown to be ineffective.⁹⁷ The influence of a cellulose-compatible DES system based on choline chloride and urea on bleached pine pulp fibres was revealed using a systematic approach with complementary research methods. DES treatment carried out for 16 h at 100 °C has been found to have no influence on pulp fibre morphology. In addition, no evidence on the derivatisation of cellulose was observed during the DES treatment. Negligible changes were observed in the xylose, mannose and arabinose content and thus, minor dissolution of some of the hemicelluloses cannot be excluded. Thorough examination by NMR and Raman spectroscopy revealed that the nitrogen residuals originate from tightly bound choline chloride. In addition, Raman spectroscopy data suggest that cationic choline ions are interacting with the anionic groups of cellulose fibres via electrostatic interactions.⁹⁸

Solubility with NaOH

The cellulose carbamate can be dissolved in 8% sodium hydroxide to a strength of 5–10%. The dissolution is best done at temperatures around or below 0 °C. A typical colour of the solution is yellowish. Because the carbamate groups hydrolyse in alkaline media, the solutions should be handled at low

temperatures. At zero, the hydrolysis is slow enough to allow for storage up to several days⁹⁹ (see figure 4 above).

Solubility

The most essential aspect for fibre spinning is the quality of the solution. The quality can be measured by means of the clogging indicator Kw (filtration indicator) which represents the content of insoluble matter in solution. It also indicates the gels formed in the solution. This is a common measurement for the quality of

a solution, and particularly a measure for the clogging tendency of a fibre nozzle. Normally a solution with $K_w < 2000$ is considered good from the perspective of fibre application. Because of this, the process has been improved over the years.¹⁰⁰

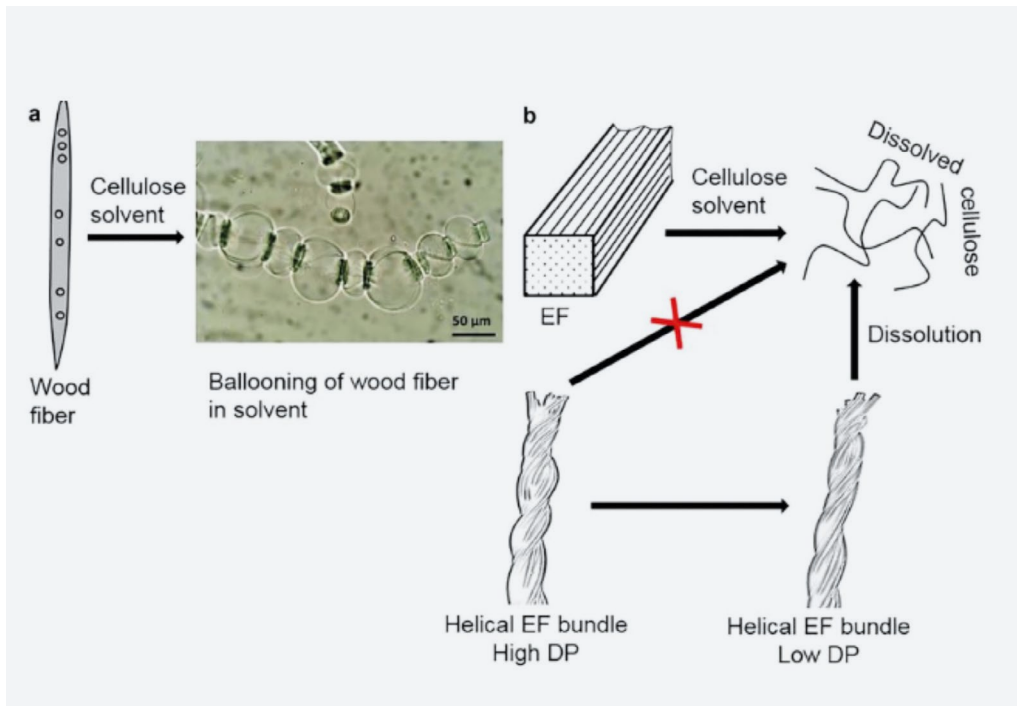


Figure 4: Schematic illustration of cellulose dissolving in alkaline solution¹⁰¹, indicating dissolving starting from amorphous areas and necessity of reduction of the degree of polymerization of DP (high DP is typically higher than 400).

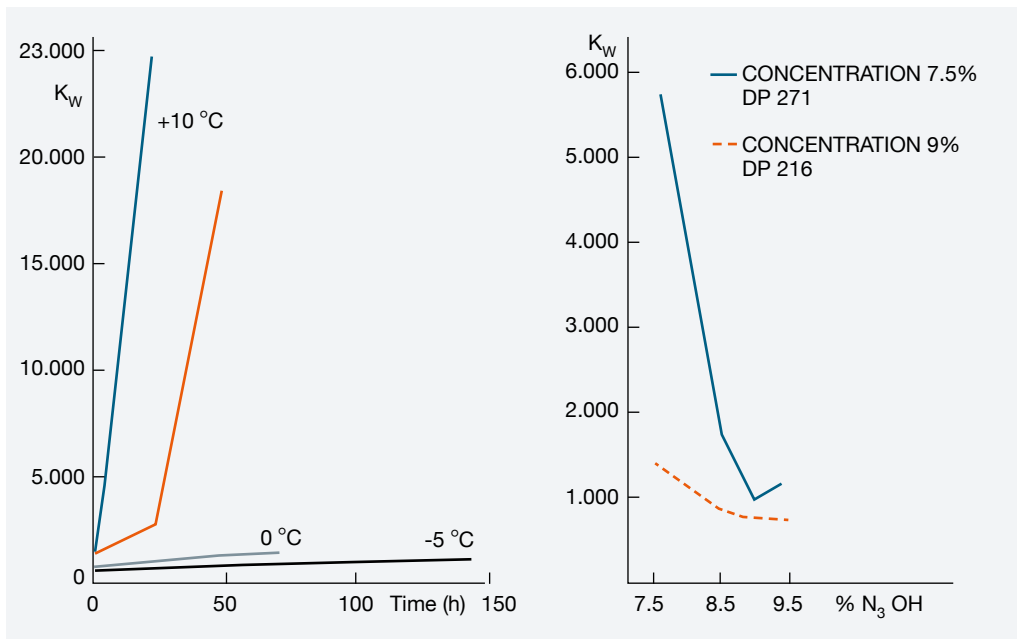


Figure 5: Clocking values of cellulose carbamate solution.

Good solubility and stability are prerequisites for achieving the required quality characteristics of regenerated cellulose products and on the economic performance of the method, which must be characterized by the highest possible levels of cellulose dopes and the least possible use of sodium hydroxide. Solubility depends on the degree of polymerization (DP). Clocking values of cellulose carbamate solution are presented in Figure 5.

Very low DP 200 and below enable very high cellulose concentrations up to 9.5 weight % with a sufficient process of viscosity (ball viscosities $50 \text{ s}^2\text{Cm}/20^\circ\text{C}$), but affected the fibre strength, while a DP higher than 300 limits the concentration below 6 weight % increasing spinning chemical consumption over economically economic thresholds. Optimum DP seems to be at 270–280.

The nitrogen content of CCA has also a profound influence on the solubility of CCA. Solubility increased as the nitrogen content of CCA increased from 0% to 1.57% (DS = 0.19) and then decreased until 4.40% (DS =

0.56). It was thus determined that a high degree of substitution was not necessarily significant for better dissolution, which could be achieved at a CCA nitrogen content between 1 and 2%.

Zinc oxane

The solubility of CCA in the NaOH/ZnO solution initially increased to reach the optimum NaOH concentration range between 7 to 8.5 wt %, followed by decreasing with increasing concentration of NaOH.¹⁰² The solubility of CCA increased significantly even with the addition of 0.4 wt % ZnO to the NaOH solution. CC was completely dissolved in the NaOH solution at more than 2.0 wt % of ZnO content, and thus, the solubility of CC in the NaOH solution could be significantly improved with the addition of a small amount of ZnO (0.4 to 2.0 wt %). However, the CCA solution with high amounts of dissolved ZnO was found unstable. As a result, 7 to 8 wt % NaOH/0.4 to 1.6 wt % ZnO aqueous solution was selected as an optimum solvent for

CCA. The concentration of CCA could be reached to 8 to 9 wt % as the DP of CCA was about 400, which was similar to the levels of the viscose method.

Freezing temperature influences the solubility of cellulose carbamate in both the NaOH and NaOH/ZnO solutions. Only a small fraction of CCA with a low molecular weight is dissolved under temperatures between -5 to 10 °C. The solubility of CCA rapidly increased as the temperature decreased from -5 to -23 °C, saturated at -12 °C or below in both solvents. The results indicated that lower freezing temperature was vital in achieving such an optimum CCA dissolution.¹⁰³

Gelation of cellulose in 8% NaOH solutions with and without ZnO have been studied for various cellulose and ZnO concentrations (4 to 6% and 0 to 1.5%, respectively) in a wide range of temperatures (-5 °C to 50 °C). Gelation times exponentially in-

creased with increasing ZnO concentration and with decreasing cellulose concentration and solution temperature. Gelation times of cellulose-NaOH-water-ZnO systems were found to follow a semi-empirical model correlating these three parameters. It has been suggested that ZnO acts as a water molecular “binder” stabilizing cellulose-NaOH-water solutions.¹⁰⁴

The solubility of zinc oxide in 5% Na₂O solution increases slowly, and then increases faster in 5% to 28% Na₂O solution at 25 °C, in 5% to 29% Na₂O solution at 50 °C, in 5% to 30% Na₂O solution at 75 °C and in 5% to 34% Na₂O solution at 100 °C, respectively.¹⁰⁵ Non-dissolved ZnO particles were observed above 0.8 to 0.9% ZnO in 8% NaOH-water.¹⁰⁶ It has been observed that certain impurities like Ca²⁺ may cause recrystallization of ZnO/NaOH solutions. The influence of zinc and urea are shown in Figure 6.

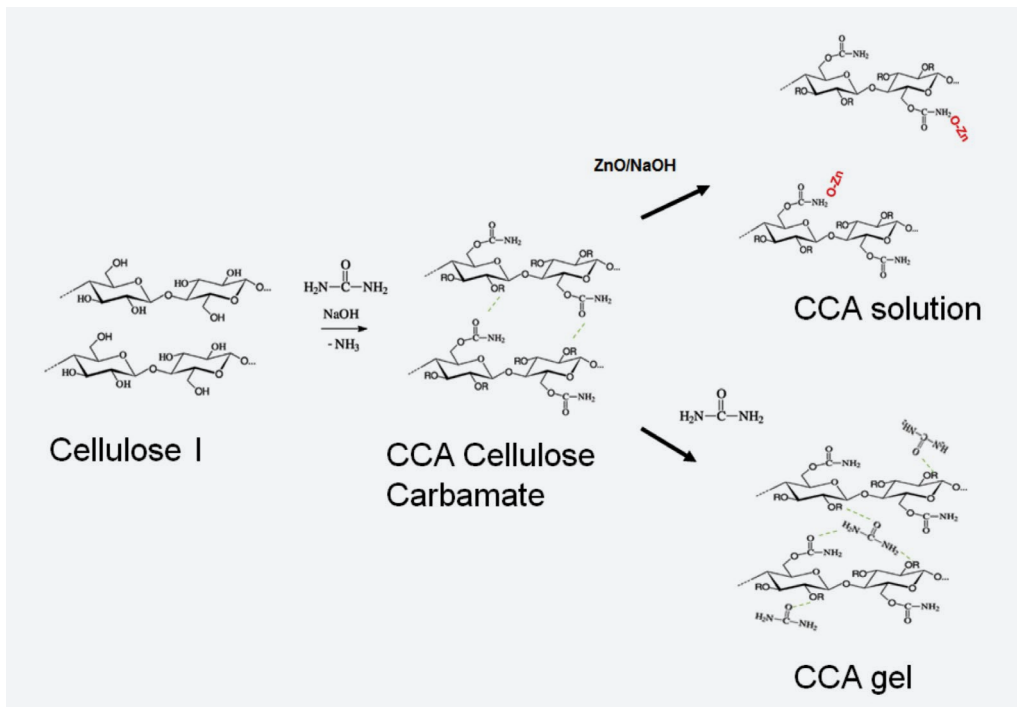


Figure 6: ZnO/NaOH prevent gelation of the cellulose carbamate, while high concentration of urea (e.g. 4wt% or more) may cause and extend gelation.

NaOH/Urea as solvent

Urea can improve the solubility and stability of cellulose in aqueous alkali solution, however its role has not been confirmed. Urea has no strong direct interaction with cellulose or sodium hydroxide, nor does it have much influence on the structural dynamics of water. However, urea may play its role through van der Waals force. It may accumulate on the cellulose hydrophobic region to prevent dissolved cellulose molecules from re-gathering. The driving force for the self-assembly of cellulose and urea molecules might be hydrophobic interaction. In the process of cellulose dissolution, OH⁻ breaks the hydrogen bonds, Na⁺ hydrations stabilize the hydrophilic hydroxyl groups and urea stabilizes the hydrophobic part of cellulose.¹⁰⁷

The experimental results indicated that although the crystallinity of cotton linter almost did not change during the enzymatic pretreatment, the solubility of cellulose in cold NaOH/urea solution increased from 30% for original cotton fibres to 65% for enzymatic treated fibres, which was mainly attributed to the reduction of cellulose's molecular weight by the enzymatic treatment. Moreover, the dissolution time was also greatly shortened by the enzymatic pretreatment. The results suggest that the effect of crystallinity of the cellulose on the cellulose dissolution in NaOH/urea solution is much less than that of molecular weight. It was found that temperature plays a dominant role in cellulose fibre solubility in NaOH/urea solution.¹⁰⁸

NaOH/Thiourea as solvent

Several other publications appeared recently on the dissolution and modification of cellulose in mixtures of an aqueous base with urea and thiourea.^{109 110 111 112}. Zhang and co-workers have shown that cellulose can be dissolved in an aqueous solution of NaOH (7 wt %) / urea (12 wt %). Starting from a pre-cooled mixture at -12 °C, cellulose dissolves within 2 min. The urea hydrates could possi-

bly be self-assembled at the surface of the NaOH hydrogen-bonded cellulose.¹¹³ The solutions are rather unstable and sensitive to temperature, polymer concentration, and storage time^{114 115}. Recent alternatives of interest include the systems LiOH/urea^{116 117} and NaOH/thiourea¹¹⁸. These solvents were extensively studied towards the regeneration of cellulose by fibre spinning and film casting^{119 120 121 122 123}. Again, cellulose materials with a huge surface were accessible via this path showing different aerogel morphologies depending on the processing¹²⁴.

Moreover, it has been shown that cellulose regeneration can be combined with blending processes. Thus, nanoparticle-containing materials were prepared^{125 126}. Besides regeneration of cellulose, the homogeneous chemical modification of cellulose in this medium was intensively investigated. It was demonstrated that these aqueous media are very good solvents for homogeneous etherification reactions of cellulose^{127 128}, which is reasonable because the solvent already contains the base necessary to start the reaction.

Freezing

Cellulose is partly soluble in an aqueous solution of sodium hydroxide in a concentration of about 10 % w/w. The amount of cellulose that is soluble in NaOH/H₂O depends on the degree of polymerization and also mode of crystallinity¹²⁹. Isogai investigated the solubility of cellulose from several sources but never succeeded in preparing cellulose solutions of higher concentrations than 5 %¹³⁰. A method for complete dissolution of cellulose in lye solutions was also patented in 1994¹³¹. For cellulose to dissolve in alkaline aqueous media, it needs to be cooled well below room temperature. Soube et al. completed the phase diagram for the ternary system cellulose/NaOH/H₂O¹³². Taking the amphiphilic properties of cellulose into account, it is not surprising that it has been shown that cellulose in NaOH/H₂O is in fact not completely dissolved but forms aggregates¹³³.

The procedure for dissolving cellulose in aqueous alkali/urea-systems is based on

a freeze-thaw method. The solvent is pre-cooled to below the freezing point of water before cellulose is added and kept cold until complete dissolution of the polymer ¹³⁴.

Recent studies on alkali dissolving has given clear evidence that the pressure seems to have similar effects as freeze-thaw for dissolving. Applying 100bar overpressure in chilled conditions improves dope as much as freezing in a closed vessel (causing some 7000bar in cell wall). High pressure may change the freezing point of aqueous solvents, but the influence on cell wall accessibility is not yet fully understood.

Time before spinning

Cellulose carbamate can be stored for long times in dry ambient conditions without changes in the degree of polymerization or nitrogen content.¹³⁵ However, when contacted with sodium hydroxide the cellulose carbamate starts to disintegrate and lose its solubility. As a result, the formed solution has to be applied within a reasonable time after formation. The observation means the process has to be residence time controlled. Figure 7 expresses the effect of various hydrolytic treatments on alkali solubility of Cellca fibres.

Additivation

Sodium hydroxide solutions with different additives have turned out to dissolve cellulose more efficiently than the binary NaOH/H₂O system itself. Such additives are, for example, poly(ethylene glycol) (PEG) ^{137 138} and urea ¹³⁹ and/or thiourea ^{140 141 142}. The fact that sodium hydroxide, PEG and urea are all environmentally friendly and pose low toxicity towards humans and animals makes these solvent systems interesting for large-scale applications. However, mixed systems always pose high demands on recovery systems, and the amount of additives needed in these systems makes recovery and reuse quite necessary.

Regeneration

Application

Cellulose carbamate applications of fibre, film and sponge structures have been reported. Most favoured are cellulose-based fibres, which are expected to grow both in woven and nonwoven markets.¹⁴³ The viscose process has long been favoured in the regener-

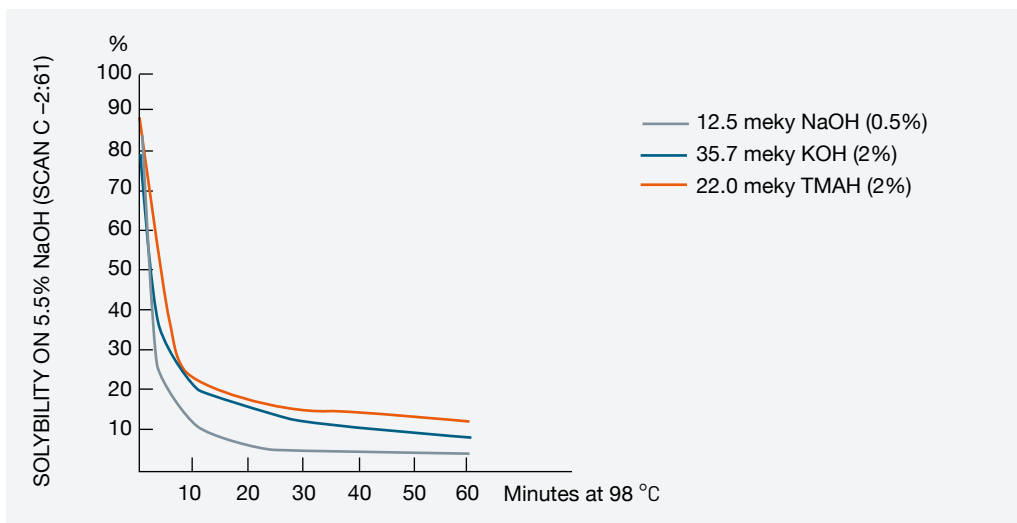


Figure 7: Effect of various hydrolytic treatments on alkali solubility of Cellca fibres ¹³⁶.

ated cellulose industry. In the past decade, global viscose fibre production has shown an average annual growth rate of about 5% with a production output of 3.4 million tons in 2011.¹⁴⁴

The carbamate group also increases reactivity and imparts microbiostaticity to cellulose^{145 146}. That favours use of the derivatized polymer in absorbent products for hygiene and medical applications¹⁴⁷ such as films in food packaging¹⁴⁸, as adsorbents for heavy metals^{149 150}, and in the creation of flame-retardant products¹⁵¹.

Spinning

Fibres can be chemically spun from solutions of cellulose carbamates in many ways, but typically emulating the viscose process. The spinning machine uses Spinnerets with diameters of 40–90 μm . As the solutions do not need “ripening”, spinning can be carried out as soon after dissolving as deaeration permits. The composition of the spinning bath can be almost the same as for viscose spinning. Adding aluminium sulphate to the spinning bath can influence fibre properties to some extent. The CCA spinning process has been recently modelled using non-linear modelling.¹⁵²

Without additives (modifiers) in the carbamate solution or spinning bath, the fibres can be stretched over 100% in hot water (85–95 °C) and maximum tenacity is achieved somewhere between 100% and 120%. In air the stretchability is about 10% less, and the maximum tenacity is also correspondingly lower. Use of additives typical in the spinning of high wet modulus or polynosic fibres did not improve the stretchability or the textile properties.

Apart from sulphuric acid, other coagulation baths have also been tested. Promising results have been achieved with alcohols. The figure 9. shows how the tenacity and elongation of the fibres depend on the

stretching when the spinning bath contains 75 wt.% methanol, 22.5 wt. % water and 2.5 wt. % sodium hydroxide. The stretchability is about the same as in a sulphuric acid bath, but the maximum tenacity is only 2.4 cN/dtex, and elongation is low.

Recovery of alkali

A cyclic process has been proposed for producing an alkali aqueous solution of cellulose carbamate, for precipitating the cellulose carbamate from the alkali solution and for recovering and recycling the remaining chemicals. The process comprises the following steps: (a) an alkali solution of cellulose carbamate is prepared by dissolving cellulose carbamate in an aqueous solution of sodium hydroxide, (b) the solution obtained in step (a) is contacted with a precipitation aqueous solution containing sodium carbonate, whereby the cellulose carbamate is precipitated and can be removed, (c) from the solution in step (b) sodium carbonate is crystallized and is returned to the precipitant solution in step (b), and (d) mother liquor containing sodium hydroxide, obtained, e.g. remaining from step (c) is returned to step (a) for dissolving cellulose carbamate. The crystallizing in step (c) is accomplished in two or several steps by cooling.¹⁵³

Fibre

Textile fibres are the most-researched topic. The highest cellulose carbamate route for producing fibre strengths has been reported with Cellca fibres, which have carbamate removed after treatments. They reached 3.1 cN/dtex strength. Typical values reported for CCA fibres are 2.2 to 2.4 cN/dtex. Respective wet tensile strengths are 1.1 to 1.5 cN/dtex¹⁵⁴ Comparison of cross sections of different regenerated fibres are presented in Figure 8, and mechanical properties in Figure 9.

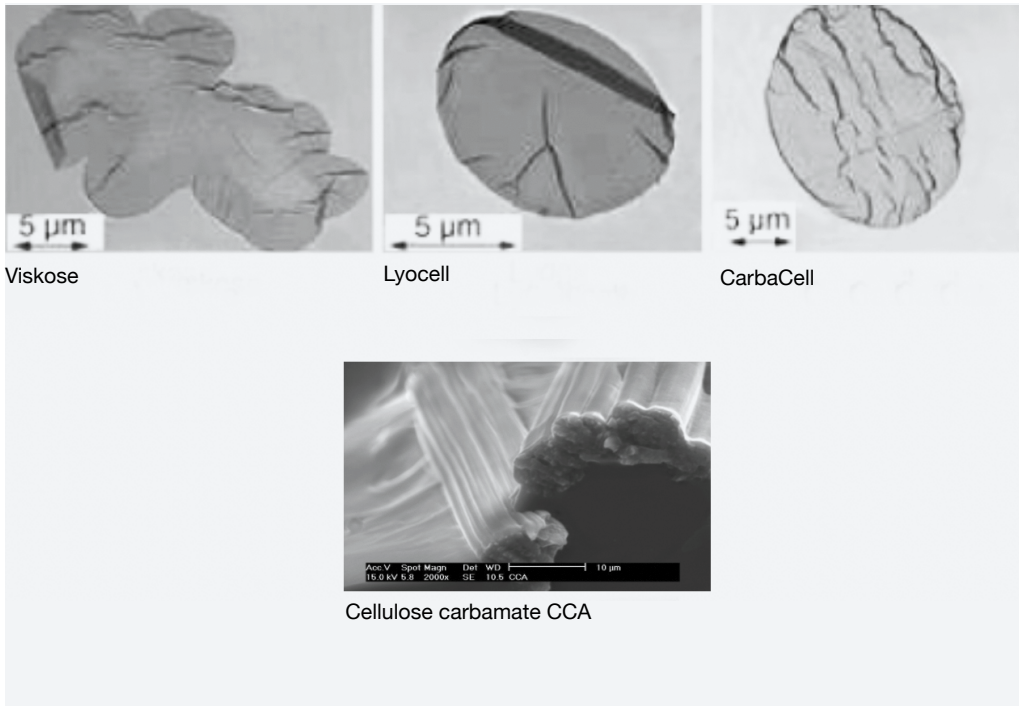
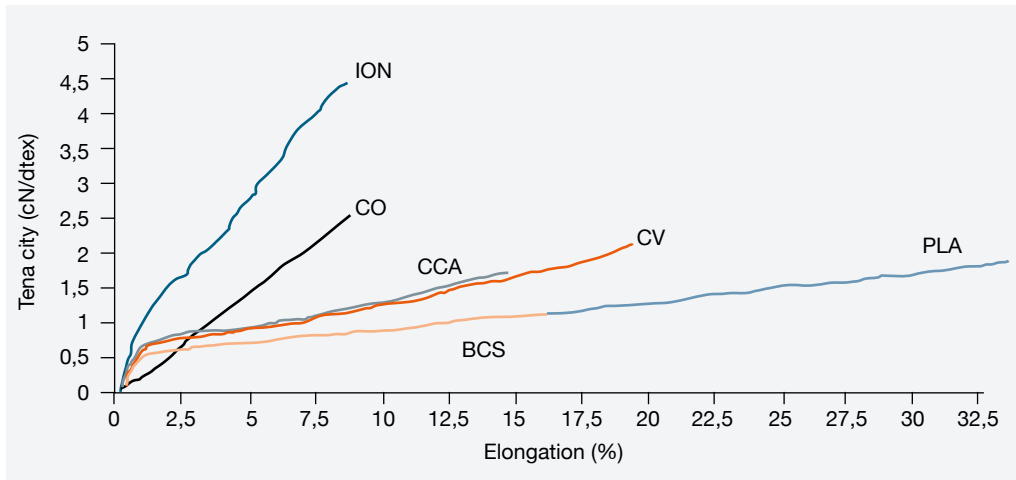


Figure 8: Comparison of cross sections of different regenerated fibres.



Fibre	Young's modulus (cN/dtex)	Tenacity (cN/dtex)	Elongation (%)	Flexibility (nM ⁻¹ m ⁻²)	
CO	1,68 ± 0,48	32,4 ± 17,8	2,54 ± 1,08	8,31 ± 2,61	12,3 ± 5,5
CV	1,80 ± 0,12	42,5 ± 5,16	2,11 ± 0,14	17,4 ± 1,2	29,0 ± 7,6
PLA	1,70 ± 0,23	25,0 ± 10,1	1,90 ± 0,72	33,8 ± 10,7	16,0 ± 5,4
BCS	2,04 ± 0,33	38,3 ± 4,4	1,14 ± 0,18	15,9 ± 3,9	38,2 ± 17,8
CCA	1,71 ± 0,21	48,4 ± 5,3	1,70 ± 0,20	15,9 ± 3,9	29,8 ± 17,6
ION	1,63 ± 0,23	107 ± 13	4,46 ± 0,56	7,25 ± 1,19	20,3 ± 21,9

Figure 9: Comparison of mechanical properties different regenerated fibres. (CO = cotton, CV = viscose, PLA = polylactic acid, BCS = biocelsol direct alkali, CCA = cellulose carbamate, ION = ioncel).

Alternative spinning baths

Apart from sulphuric acid, other coagulation baths have also been tested. They enable alternatives for chemical recovery, like the sodium carboxylic system benefitting pulping chemical recovery. Simultaneously, the coagulation time is increased and different fibre properties are achieved.¹⁵⁵

Alcohol

Positive results have been achieved with alcohols. A typical spinning bath contains 75 weight % of methanol, 22.5 of water and 2.5 of sodium hydroxide. The tenacity and elongation of the fibres depend on the stretching, having the same elongation but lower tenacity of 2.4 versus 3.1 cN/dtex with the same stretching. The higher alcohol contents reduce both tenacity and wet modulus. Figure 10 expresses tenacity and elongation of Cellca fibres coagulated in an acid bath, and in an alcohol bath.

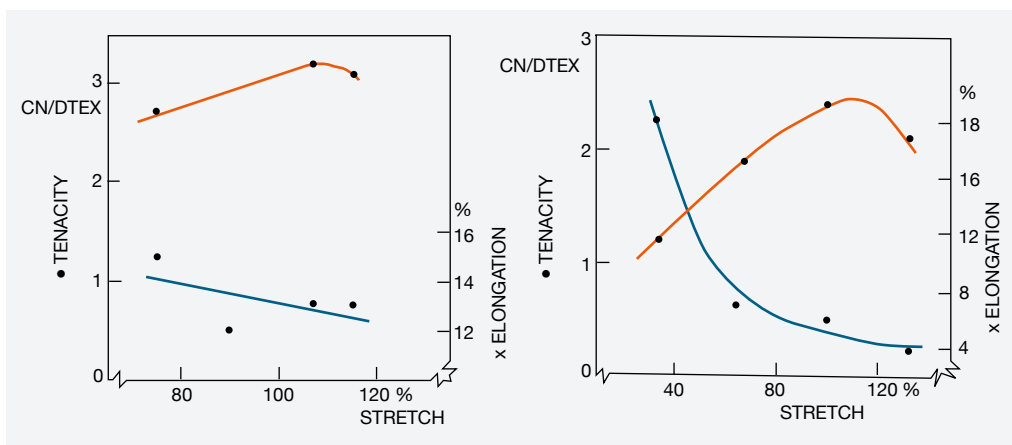


Figure 10: Tenacity and elongation of Cellca fibres coagulated (left) in an acid bath, and (right) in an alcohol bath, as functions of stretch.

Salt

Only a limited number of results is reported on salt solutions in the spinning baths. However, several of the salt systems are providing interesting results. The coagulation mechanism is different, is more diffusion- than reaction based, and means longer immersion times up to 2–3 minutes as well as the pronounced effect of temperature. Achieved tenacities are even lower than with alcohol baths at 1.5–2.1 cN/dtex.

Spinning cellulose carbamate from n-morpholine oxide is also reported. By variation of temperature, dwell time and cellulose concentrations can be adjusted for cellulose carbamates of special DP and DS for solutions having up to 30% of cellulose carbamate in NMMO. The high concentration solutions having, however, a specific rheological behaviour. In the spinning concentrations, up to 21% were applied and tensile strengths up to 6.0 cN/dtex and modulus 250 cN/dtex was achieved. Simultaneously, nitrogen content was reduced from 3% to 0.5%.¹⁵⁶ In comparative research, cellulose carbamate and cellulose were used as raw materials, respectively, and CCA fibres and Lyocell fibres were spun by the dry-jet wet spinning method using N-methylmorpholine-N-oxide (NMMO) as the solvent. The rheological behaviour of

different raw materials/NMMO-H₂O spinning dopes, as well as the structure and properties of the resulting fibres were compared. The results show that both kinds of spinning dopes belong to the typical shear thinning fluids, and the apparent viscosity of CCA spinning dope is lower than that of Lyocell spinning dope under the same conditions, which will be conducive to improving the concentration of CCA spinning dopes. Compared with Lyocell fibres, the crystallinity and orientation of CCA fibres are lower, thus the mechanical properties of CCA fibres are decreased slightly, whereas CCA fibres show better anti-fibrillation properties.¹⁵⁷

Flame retardancy

Flame and glow-proof materials can be produced by phosphorylation of cellulose-based fabrics.

Phosphoric acid (cons.) can be used to phosphorylate cellulose. The reaction is selective to the primary hydroxyl group at the cellulose C6 position. Urea can be used with the phosphoric acid in the process to avoid degreasing of the fabric tensile strength.¹⁵⁸
159 160

The flame retardant cellulose fibres were spun by an eco-friendly process, i.e., add-

ing certain P-N containing flame retardants, 1,2-bis(2-oxo-5,5-dimethyl-1,3,2-dioxaphosphacyclohexy-1-2-imino)ethane (DDPN) and N,N'-bis(5,5-dimethyl-2-phospha-2-thio-1,3-dioxan-2-yl) ethylene diamine (DDPSN) to the carbamate solution, and the mechanical and flame retardant properties of the prepared cellulose fibres were studied. The results show that the dry tenacity is less than that of viscose fibre, but wet tenacity and wet modulus of the polyblend fibres are slightly higher than those of viscose fibres. When the mass fraction of this kind of retardants in the cellulose fibres is larger than 18% and the limiting oxygen index (LOI) of the polyblend flame retardant cellulose fibres is larger than 25%, the fibres meet the flame-retardant requirements.¹⁶¹

Colouring

The partial carbamate reaction of cellulose with urea has been applied to improving dyeing. Some cellulose carbamate derivatives of aromatic amines are favourable to dyeing. The treatments of cellulose with urea are believed to be significant in the sense of improving fibre and cotton cloth, and so a precise curing condition should be considered to determine optimum cellulose carbamate reactions. The conventional curing procedures at elevated temperature had been applied to the cellulose materials, which were pretreated to soak in an aqueous padding solution of urea and dried at 116 °C.¹⁶² Cellulose carbamate filaments show improved dye properties compared to viscose.¹⁶³

Film

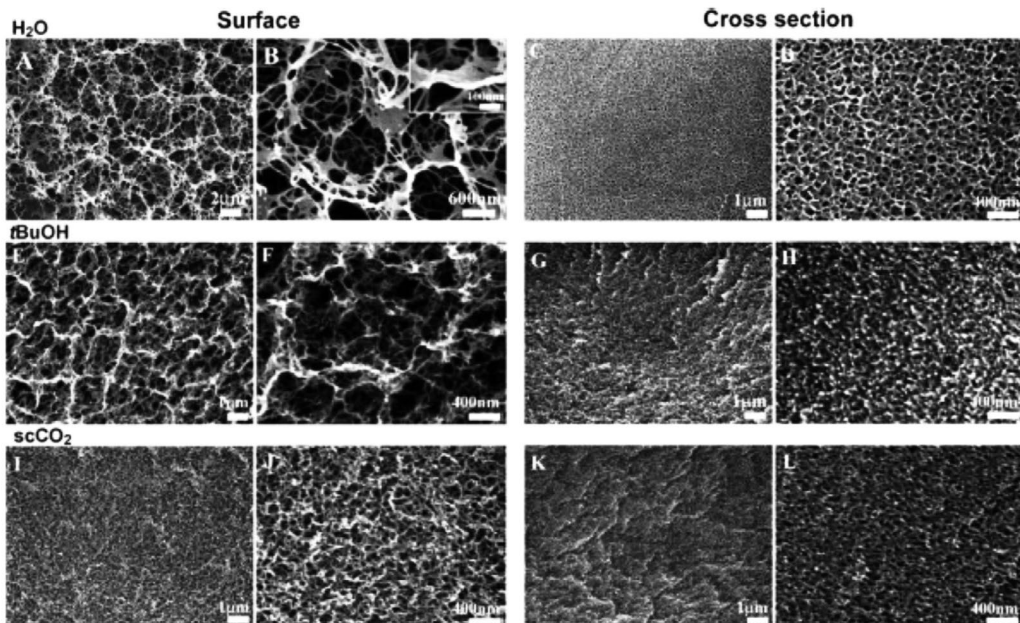
Cellulose carbamate has been applied for films entitled to flexible electronic devices to replace the glass as transparent windows. Flexible, transparent, and very strong cross-linked cellulose films with a thickness of about 10 µm with highly optical transparency have been prepared by cross-linking free cellulose chains with epichlorohydrin (ECH) in its aqueous solution. The film also showed

a low coefficient of thermal expansion (CTE) of about 6.9 ppm/K, which is superior to that of glass. Then the as-prepared cellulose film was combined with a dried foam ultrathin film of reduced graphene oxide to prepare a new, flexible, transparent, very strong, and electrically conductive thin film.¹⁶⁴

Regenerated cellulose membranes with microporous structure were prepared from cellulose carbamate-NaOH/ZnO solutions coagulated with 3 wt% H₂SO₄ solutions at 10°C for 10–15 min. The membranes displayed the cellulose II crystalline form with a relatively low crystallinity index. The nitrogen content of the membranes was in the range of 0.54 to 0.77%. The concentration of coagulant, and coagulation temperature had an obvious influence on the formation of membrane pores, leading to water permeability, but not according to the coagulation time. The apparent pore diameters of the membranes were in the range of 197 to 624, and the water permeability determined by flow rate method varied from 10.93 to 23.66 mL h⁻¹ m⁻² mmHg⁻¹ according to pore size. The films exhibited good tensile strength (120 MPa) and elongation at break (15%).¹⁶⁵

Recently, Yang et al. prepared high-performance flexible films from different cellulose sources in a solvent of alkali and urea.¹⁶⁶ The films showed good gas barrier properties over the entire relative humidity range, and always one order of magnitude lower gas permeability than cellophane films which are prepared via the viscose process. Compared to conventional films from poly(ethylene) and poly(propylene), all cellulose films show increased water vapour permeability, but this is expected due to the intrinsic hydrophilicity of the polysaccharide structure.

Graphene oxide is capable of coordinating on cellulose carbamate. According to dynamic rheology, addition of 2 wt% of graphene oxide prolonged significantly valid spinning time of the cellulose carbamate solution. Microscopy indicated graphene oxide plates were oriented in elongation flow and increased film tensile properties by some 180% and 280% in Young's modulus.¹⁶⁷



SEM images of aerogels prepared from 4 wt% cellulose in aqueous LiOH/urea solution, regenerated with EtOH, and either freeze-dried from H₂O (A–D) or t-BuOH (E–H), or dried from CO₂ (I–L) as indicated. Low-magnification (A,E,I) and high-magnification (B,F,J) images of the surface. Low-magnification (C, G, K) and high-magnification (D, H, L) images of the cross sections of the aerogels. The inset in part (B) shows the SEM image of a tilted sample (from ref. (112) with kind permission from Wiley).

Antibacterial materials

Carbamate cross-linked cellulose films can be prepared in a two-step method using cellulose dissolved in 1-n-butyl-3-methylimidazolium chloride ionic liquid. The new technique involves casting the film from cellulose ionic liquid solution onto a glass surface and application of alkyl/aryl di-isocyanate in dry dimethylsulfoxide solution onto the cellulose – ionic liquid coating on glass and allowing the cross-linking reaction to occur on the pre-formed cellulose coating. The water retention values of the films are shown to decrease with the increase in hydrophobicity of the alkyl/aryl group linker in the carbamate bridges.¹⁶⁸

Cellulose-based ZnO nanocomposite (RCZ) films have been prepared from cellulose carbamate-NaOH/ZnO solutions through one-step coagulation in Na₂SO₄ aqueous solutions. The content of ZnO in RCZ films was obtained in the range of 2.7–15.1 wt %. ZnO nanoparticles with a hexagonal wurtzite structure agglomerated into large particles, which firmly embedded in the cellulose matrix. RCZ films displayed good mechanical properties and high thermal stability. Moreover, the films exhibited excellent UV-blocking properties and antibacterial activities against *Staphylococcus aureus* and *Escherichia coli*. A dramatic reduction in viable bacteria was

observed within 3 h of exposure, while all of the bacteria were killed within 6 h. This work provided a novel and simple pathway for the preparation of regenerated cellulose films with ZnO nanoparticles for application as functional biomaterials.¹⁶⁹

Silver nanoparticles were stabilized on cellulose and cellulose carbamate as a supporting template and their antibacterial activities were studied against *E. coli* and *Staphylococcus*. In the material, a fine grain of silver nanoparticles was dispersed on a micro-cellulose particle with an average size of about 30 nm, so EDS analysis showed the presence of silver metal at more than 80 % atoms and the rest are sodium and magnesium. The antibacterial activity was 4 to 5 mm for *E. coli* and 10 to 25 mm for *Staphylococcus* in the presence of cellulose/ Ag Nps and cellulose carbamate/Ag Nps, respectively.¹⁷⁰

Membranes

Dialysis membranes made from regenerated cellulose are under dispute because of their alleged lack of hemocompatibility. Thus, membranes were introduced made from synthetically modified cellulose, from which hemocompatible membranes can be fabricated by means of chemical surface modifications. For this purpose, a series of cellulose carbamate derivatives were synthesized to profit from the excellent hemocompatibility pattern of the urethane family. A direct dependency between improved hemocompatibility and the degree of substitution (DS) in the cellulose molecule could be found. A degree of substitution below a value of 0.1 led to a nearly complete suppression of complement activation for all cellulose carbamates. In addition, data on cellulose carbamate esters (e.g., cellulose succinate-phenyl-carbamate) show that a simultaneous but balanced substitution with hydrophilic and hydrophobic groups at the surface of the cellulose polymer is a further prerequisite for optimal hemocompatibility.¹⁷¹ The membrane structures are typically formed from advanced

solvents, like NMMO. Also, novel technologies including electro spinning have been reported.¹⁷²

Foam

Because of good fleeciness soft and excellent absorbency sponge is widely used. But the polyurethane foam sponge on the market not only has the disadvantage of raw material shortage and pollution in its preparation but also pollutes the environment after the product is abandoned. With the aim of developing the preparation technology of cellulose sponge that can be naturally degraded, the process of preparing cellulose sponge from cellulose carbamate was studied. Sodium hydroxide solution of cellulose carbamate and a pore-forming agent were kneaded into a sponge mixture and was cooked to regenerate cellulose. The pore-forming agent was dissolved in water leaving voids behind and the cellulose sponge with uniform pore size was obtained. The cellulose sponge had a smooth surface, good flexibility and elasticity with the basic features of polyurethane foam.¹⁷³

Microcrystalline cellulose was modified by crosslinking with toluene diisocyanate under homogeneous phase in the N,N-dimethylacetamide/LiCl solvent system. Modified cellulose films were prepared by the solution casting method and their hydrophobicity, thermal stability, permeability, and degradability were characterized. The hydrophobicity, thermal stability, and mechanical properties of the films were improved by crosslinking according to the comprehensive results.¹⁷⁴

Highly porous regenerated cellulose hydrogels and aerogels were prepared from hydrothermally synthesized cellulose carbamate. Kenaf pulp was used in the experiments. The materials were proposed to be useful for water absorption.¹⁷⁵

Chromatography applications

Cellulose carbamate is used in chiral chromatography, especially with hexane, isopropyl alcohol and ethanol solvents. The CCA column material is well-suited for non-ionic or weakly ionic systems. The benefit is that they operate also in high concentration of water, mobile phase or pure buffers.¹⁷⁶ Modified cellulose tricarbamates are applied also in layer chromatography.¹⁷⁷

Economic considerations

In its original version, the cellulose carbamate process has a handicap over the viscous process in its lower solubility in processable solution. A typical cellulose concentration for CCA is 8 weight % while the viscose process has 9.5 weight %, meaning more usage dissolving and regeneration of chemicals. Also, energy costs are higher due to the need to handle a low-temperature spinning solution.

However, Kemira Oy Sateri showed that with the help of lower raw material costs, the CCA process has been proposed to be competitive with the viscose process.¹⁷⁸ Also, later reports claim that with optimized process conditions it has also been estimated that the CCA process could save some 15–20% compared to that of viscose process¹⁷⁹.

Alkaline consumption in the process can be considered also as an LCA issue. Most essential are the questions on possible use of alternative spinning batch chemistry enabling more efficient chemical recycling as well as energy integration.^{180 181}

Conclusions

In conclusion, cellulose carbamate is a versatile alkaline dissolving cellulose derivatives including various processes and cellulose raw materials. It is especially suited for textile fibres, but also for films, membranes and foams, in addition to several added-value products because of its versatile properties. It avoids utilization of harmful chemicals such as carbon disulphide and has potential to compete with viscose process. Recent process development and detailed understanding of physical chemistry have been shown to provide marked improvements for operation of the cellulose carbamate process. The main improvements are in the dissolution process conditions providing improved solution quality through pre-treatment, forming and handling of the carbamate solution.

References

- 1 Yan, L.; Qi, X. Degradation of cellulose to organic acids in its homogeneous alkaline aqueous solution. *ACS Sustainable Chem. Eng.* 2014, 2, 897–901
- 2 Huang, J. L.; Li, C. J.; Gray, D. G. Cellulose nanocrystals incorporating fluorescent methylcoumarin groups. *ACS Sustainable Chem. Eng.* 2013, 1, 1160–1164.
- 3 Lam, E.; Leung, A. C.; Liu, Y.; Majid, E.; Hrapovic, S.; Male, K. B.; Luong, J. H. Green strategy guided by raman spectroscopy for the synthesis of ammonium carboxylated nanocrystalline cellulose and the recovery of byproducts. *ACS Sustainable Chem. Eng.* 2012, 1, 278–283.
- 4 Rose, M.; Palkovits, R. Cellulose-based sustainable polymers: State of the art and future trends. *Macromol. Rapid Commun.* 2011, 32, 1299–1311.
- 5 Guo, B.; Chen, W.; Yan, L. Preparation of flexible, highly transparent, cross-linked cellulose thin film with high mechanical strength and low coefficient of thermal expansion. *ACS Sustainable Chem. Eng.* 2013, 1, 1474–1479.
- 6 Klemm, D.; Heublein, B.; Fink, H. P.; Bohn, A. Cellulose: Fascinating biopolymer and sustainable raw material. *Angew. Chem., Int. Ed.* 2005, 44, 3358–3393.
- 7 Zhang, H.; Wang, Z. G.; Zhang, Z. N.; Wu, J.; Zhang, J.; He, J. S. Regenerated-cellulose/multiwalled-carbon-nanotube composite fibers with enhanced mechanical properties prepared with the ionic liquid 1-allyl-3-methylimidazolium chloride. *Adv. Mater.* 2007, 19, 698–704.
- 8 Liebert et.al.; Cellulose Solvents: For Analysis, Shaping and Chemical Modification ACS Symposium Series; American Chemical Society, Washington DC 2010
- 9 Rose, M.; Palkovits, R. Cellulose-based sustainable polymers: State of the art and future trends. *Macromol. Rapid Commun.* 2011, 32, 1299–1311.
- 10 Hill, J. W.; Jacobson, R. A. U.S. Patent 2,134,825, 1938.
- 11 Jacobson, R. A. J. Am. Chem. Soc. 1938, 60, 1742.
- 12 A.F.Turback et.al. *Chemtech*, 1980, 10, 5
- 13 F.J. Otto, *Itzehoer Wochenblatt*, 1846, column 1626
- 14 G. Audemars, British Patent 283, 1855
- 15 A.M. Chardonnet, French Patent 165,349 (1884)
- 16 A.Parkes, British Patent 235, 1856
- 17 J:W.Hyatt, U.S:Patent 50, 359, 1865
- 18 C.F.Cross; E.J.Bevan; C.Beadle, Britttish Patent 8,700, 1892
- 19 M.Mueller, Britttish Patent 10,094, 1906
- 20 A.A.Polytov et.al., *Fibre Chem.*, 2000, 32, 3
- 21 Segal L, Eggerton FV (1961) Some aspects of the reaction between urea and cellulose. *Text Res J* 31:460–471
- 22 Cai J, Zhang L (2005) Rapid dissolution of cellulose in LiOH/urea and NaOH/urea aqueous solutions. *Macromol Biosci* 5:539–548. <https://doi.org/10.1002/mabi.200400222>
- 23 US 2134825 A, Hill et.al., DuPont 1937
- 24 Segal, L., F.V. Eggerton: Some Aspects of the Reaction between Urea and Cellulose; *Text.Res.J.*, 31,460 (1961)
- 25 Ekman, K.; Turenen, O. T.; Huttunen, J. I. Finnish Patent 61,033, 1982.
- 26 Fink, H. P.; Ganster, J.; Lehmann, A. Progress in cellulose shaping: 20 years industrial case studies at Fraunhofer IAP. *Cellulose* 2014, 21, 31–51.
- 27 Macromolecular Symposia Volume 280, Issue 1, Version of Record online: 30 JUN 2009
- 28 Cellulose June 2002, Volume 9, Issue 2, pp 159–170
- 29 Lenzinger Berichte, 83 (2004) 79–83
- 30 https://www.fing.edu.uy/iicq/6thicep/. /35_Fernando_Bonfiglio.pdf
- 31 O.T. Turunen et.al., Some Aspects of the Spinning of the Cellulose Carbamate, *Lenzinger Berichte*, heft 59, August 1985
- 32 WO 2015198218 A1, Heidi Saxell, et.al., Stora Enso, 2014
- 33 Cheng Guang-may, *Asian J. Chem*, Vol 13, No1, (2001), 93–98)
- 34 Benoit Duchemin et.al., *Cellulose* (2016) 23:593–609
- 35 US-patent 2,859,210 (Seaman et al.)
- 36 WO 2012/136878 (Carbatec Oy)
- 37 WO 20150225901, Method of producing dissolving pulp, dissolving pulp and use of method, VTT Sari Asikainen, Marjo Määttänen, Ali Harlin, Kyösti Valta, Eino Sivonen, September 16, 2013
- 38 WO2016024047 A1 2016
- 39 PCT/FI2018/050310
- 40 C. Yin et al. / *Carbohydrate Polymers* 67 (2007) 147–154
- 41 Hong, Wei; Li, Qingshan; Di, Youbo; Sun, Jing; Jiao, Tifeng; Xu, Mingshuang; Zhao, Zhou; Xing, Guangzhong, *Journal of Nanoscience and Nanotechnology*, Volume 13, Number 10, October 2013, pp. 6741–6747(7)
- 42 *Carbohydr Polym.* 2014 Jun 15;106:160–5

- 43 Hütterrauch R., Keiner J., Mechanical activation and inactivation of cellulose powders in grinding processes., *Phamazie* 1976, July 31 (7) p. 490
- 44 Yu Zheng, Zongqiang Fu and Min Wu, Effects of Ball Milling Processes on the Microstructure and Rheological properties of Microcrystalline Cellulose as a Sustainable Polymer Additive. *Materials* 2018, July 11(7) p. 1057
- 45 Hagman J. et al., On the dissolution state of cellulose in cold alkali solutions *Cellulose* (2017) 24:2003–2015
- 46 KaiCell Fibers Oy, Biojalostamon YVA-selostus, Pöyry 2018
- 47 EP Patent 0,178,292
- 48 EP Patent 0,057,105
- 49 DD Patent 2 98 789
- 50 PL Patent 159,085
- 51 German Patent 44 43 547
- 52 EP 00057105, Olli Turunen et al., Neste, 1982
- 53 Lewin, M., L.G. Roldan: The Effect of Liquid Ammonia in the Structure and Morphology of Cotton Cellulose; *J.Polym.Sci.*, 36,213 (1971)
- 54 EP1509548A1, Hans-Peter Fink, Fraunhofer IAP, 2005
- 55 WO03064476A1, Kyösti Valta, VTT, 2003
- 56 Hao H, Tam L, Lu Y and Lau D, An atomistic study on the mechanical behaviour of bamboo cell wall constituents, *Composites Part B* 151 (2018) 222-231
- 57 Tekla Tammelin, Eero Kontturi and Monica Österberg, Cellulose—model films and the fundamental approach *Chem. Soc. Rev.*, 2006,35, 1287-1304
- 58 Vinit Sharma, Oakridge National Laboratory, JCP, Nov 2014
- 59 Engström AC1, Ek M, Henriksson G, Improved accessibility and reactivity of dissolving pulp for the viscose process: pretreatment with monocomponent endoglucanase. *Biomacromolecules*. 2006 Jun;7(6):2027-31.
- 60 Cellulose and Cellulose Derivatives: Cellucon '93 Proceedings: Physico-Chemical Aspects and Industrial Applications, J F Kennedy, Glyn O. Phillips, P A Williams, J L Piculell, Elsevier, 30.9.1995
- 61 Abbott AP, Bell TJ, Handa S, Stoddart B (2006) Cationic functionalisation of cellulose using a choline based ionic liquid analogue. *Green Chem* 8:784–786. <https://doi.org/10.1039/B605258D>
- 62 Abbott AP, Capper G, Davies DL et al. (2003) Novel solvent properties of choline chloride/urea mixtures. *Chem Commun* 99:70–71. <https://doi.org/10.1039/b210714g>
- 63 Carbohydr Polym. 2015 Mar 6;117:133-9
- 64 Tenhunen T, Hakalahti M, Kouko J et al. (2016) Method for forming pulp fiber yarns developed by a design driven process. *BioResources* 11:2492–2503. <https://doi.org/10.15376/biores.11.1.2492-2503>
- 65 Sirvio JA, Visanko M, Liimatainen H (2015) Deep eutectic solvent system based on choline chloride-urea as a pretreatment for nanofibrillation of wood cellulose. *Green Chem* 17:3401–3406. <https://doi.org/10.1039/C5GC00398A>
- 66 WO2012145522A3, Georgia tech 2012
- 67 “Market Study Urea”. Ceresana.com. 2012. Retrieved 2013-05-17
- 68 Beef cattle feed, *Encyclopædia Britannica Online*
- 69 Klaus Huthmacher, Dieter Most “Cyanuric Acid and Cyanuric Chloride” *Ullmann’s Encyclopedia of Industrial Chemistry*” 2005, Wiley-VCH, Weinheim. doi 10.1002/14356007.a08 191
- 70 C. E. Redemann, F. C. Riesenfeld, and F. S. La Viola, Formation of Biuret from Urea, *Ind. and Eng. Chem.*, vol. 50, no. 4 ·April 1958
- 71 Kotek R (2007) Regenerated cellulose fibers. In: Lewin M (ed) *Handbook of fiber chemistry*. CRC Press, Boca Raton, pp 668–771
- 72 Klemm D, Philipp B, Heinze T, Heinze U, Wagenknecht W (1998) *Comprehensive cellulose chemistry*, vol. 2: Functionalization of Cellulose. Wiley-VCH Verlag GmbH, Weinheim, pp 161–164
- 73 Klaus Huthmacher, Dieter Most “Cyanuric Acid and Cyanuric Chloride” *Ullmann’s Encyclopedia of Industrial Chemistry*” 2005, Wiley-VCH, Weinheim. doi 10.1002/14356007.a08 191
- 74 Nada, A. A.; Kamel, S.; El-Sakhawy, M. Thermal behaviour and infrared spectroscopy of cellulose carbamates. *Polym. Degrad. Stab.* 2000, 70, 347–355.
- 75 Fink, H. P.; Weigel, P.; Purz, H.; Ganster, J. Structure formation of regenerated cellulose materials from NMMO-solutions. *Prog. Polym. Sci.* 2001, 26, 1473–1524.
- 76 Kamide, K.; Okajima, K.; Kowsaka, K.; Matsui, T. CP/MASS 13C NMR spectra of cellulose solids: An explanation by the intramolecular hydrogen bond concept. *Polym. J.* 1985, 17, 701–706.
- 77 Kotek R (2007) Regenerated cellulose fibers. In: Lewin M (ed) *Handbook of fiber chemistry*. CRC Press, Boca Raton, pp 668–771
- 78 Maimaiti H, Kebier B (2011) Method for preparing cellulose sponge. China Patent 102212211A, vide. *Chem Abstr* 2011:1312576
- 79 Loth F, Schaaf E, Fink HP, Kunze J, Gensrich HJ (2004) Procedure for preparation of cellulose carbamate in an inert organic solvent which is non-miscible with water. Germany Patent 10253672B3

- ⁸⁰ Yin C, Li J, Xu Q, Peng Q, Liu Y, Shen X (2007) Chemical modification of cotton cellulose in supercritical carbon dioxide: synthesis and characterization of cellulose carbamate. *Carbohydr Polym* 67(2):147–154. doi:10.1016/j.carbpol.2006.05.010
- ⁸¹ Yin C, Shen X (2007) Synthesis of cellulose carbamate by supercritical CO₂-assisted impregnation: structure and rheological properties. *Eur Polymer J* 43(5):2111–2116. doi:10.1016/j.eurpolymj.2007.01.041
- ⁸² Guo Y, Zhou J, Song Y, Zhang L (2009) An efficient and environmentally friendly method for the synthesis of cellulose carbamate by microwave heating. *Macromol Rapid Commun* 30(17):1504–1508. doi:10.1002/marc.200900238
- ⁸³ Iller E, Stupin'ska H, Starostka P (2007) Properties of cellulose derivatives produced from radiation—Modified cellulose pulps. *Radiat Phys Chem* 76(7):1189–1194. doi:10.1016/j.radphyschem.2006.12.002
- ⁸⁴ US 2134825 A, Hill et al., DuPont 1937
- ⁸⁵ Fu et al., *ACS Sustainable Chem. Eng.* 2015, 3, 1510–1517
- ⁸⁶ US-Patent 2,134,825, EP-patents 0,057,105, 0,178,292, 0,402,605 A and 0,402,606 A
- ⁸⁷ EP Patent 0,097,685, DE Patent 44 43 547 and 44 17 140 A, US Patent 5,378,827
- ⁸⁸ DE19635473 A1, Gerhard Keunecke, Zimmer Ag, 1996
- ⁸⁹ DE19635707C1, Production of cellulose carbamate from cellulose, Wilhelm Oppermann, DITF Denkendorf, 3.9.1996
- ⁹⁰ Zhang et al. (2013) *BioResources* 8(1), 1398-1408
- ⁹¹ US 2005/0107602 A1, Fritz Loth, Teltow, 2005
- ⁹² Guo et al., *Cellulose* (2010) 17:1115–1125
- ⁹³ Willberg-Keyriläinen, P., Hiltunen J., Ropponen J., Production of cellulose carbamate using urea-based deep eutectic solvents, *Cellulose*; Jan. 2018, vol 25, issue 1. pp. 195-204
- ⁹⁴ *Current Opinion in Chemical Biology*, Volume 15, Issue 2, April 2011, Pages 220–225
- ⁹⁵ Labafzadeh R. S., Kavakka J., Vyavaharkar K., Sievänen K. and Kilpeläinen I. Preparation of cellulose and pulp carbamates through a reactive dissolution approach, *RSC Advances*, 2014, 4, 22434–22441.
- ⁹⁶ Willberg-Keyriläinen P, Hiltunen J, Ropponen J (2017) Production of cellulose carbamate using urea-based deep eutectic solvents. *Cellulose*. <https://doi.org/10.1007/s10570-017-1465-9>
- ⁹⁷ Xu GC, Ding JC, Han RZ et al. (2016) Enhancing cellulose accessibility of corn stover by deep eutectic solvent pretreatment for butanol fermentation. *Bioresour Technol* 203:364–369. <https://doi.org/10.1016/j.biortech.2015.11.002>
- ⁹⁸ Tiia-Maria Tenhunen, Anna E. Lewandowska, Hannes Orelma, Leena-Sisko Johansson, Tommi Virtanen, Ali Harlin, Monika Österberg, Stephen J. Eichhorn, Tekla Tammelin; Understanding the interactions of cellulose fibres and deep eutectic solvent of choline chloride and urea, *Cellulose* 17 Nov 2017
- ⁹⁹ O.T. Turunen et al., Some Aspects of the Spinning of the Cellulose Carbamate, *Lenziger Berichte*, heft 59, August 1985
- ¹⁰⁰ H.Sihtola in *Paperi ja puu* 44 (1962): 5, pp. 295-300
- ¹⁰¹ Carlo Bertinetto Cellulose Elementary Fibrils Assemble into Helical Bundles in S1 Layer of Spruce Tracheid Wall
Biomacromolecules 18(2) · January 2017
- ¹⁰² Kihlman M., et al., Cellulose dissolution in an alkali based solvent: influence of solvents and pretreatments, *J. Braz. Chem.Soc.*, vol 24, no 2 SaoPaulo, 2013
- ¹⁰³ *ACS Sustainable Chem. Eng.* 2014, 2, 2363–2370
- ¹⁰⁴ *Cellulose* (2011) 18:911–920
- ¹⁰⁵ Transactions of Nonferrous Metals Society in China, Volume 22, Issue 6, June 2012, Pages 1513-1516 Vol 22, issue 6, June 2012 Volume 22, Issue 6, June 2012, Pages 1513-1516
- ¹⁰⁶ *Cellulose* (2011) 18:911–920
- ¹⁰⁷ *Cellulose* June 2014, Volume 21, Issue 3, pp 1183–1192
- ¹⁰⁸ *Carbohydrate Polymers*, Volume 72, Issue 1, 3 April 2008, Pages 178–184
- ¹⁰⁹ Zhou, J.; Zhang, L. *Polym. J.* 2000, 32, 866.
- ¹¹⁰ Cai, J.; Zhang, L. *Macromol. Biosci.* 2005, 5, 539.
- ¹¹¹ Cai, J.; Liu, Y.; Zhang, L. *J. Polym. Sci., Part B: Polym. Phys.* 2006, 44, 3093.
- ¹¹² Egal, M.; Budtova, T.; Navard, P. *Cellulose* 2008, 15, 361.
- ¹¹³ Cai, J.; Zhang, L.; Liu, S.; Liu, Y.; Xu, X.; Chen, X.; Chu, B.; Guo, X.; Xu, J.; Cheng, H.; Han, C.C.; Kuga, S. *Macromolecules* 2008, 41, 9345.
- ¹¹⁴ Cai, J.; Zhang, L. *Biomacromolecules* 2006, 7, 183.
- ¹¹⁵ Qi, H. S.; Chang, C. Y.; Zhang, L. *Cellulose* 2008, 15, 779.
- ¹¹⁶ Liu, S. L.; Zhang, L. N. *Cellulose* 2009, 16, 189.
- ¹¹⁷ Cai, J.; Zhang, L.; Chang, C.; Cheng, G.; Chen, X.; Chu, B. *ChemPhysChem* 2007, 8, 1572.

- 118 Ruan, D.; Lue, A.; Zhang, L. *Polymer* 2008, 49, 1027.
- 119 Cai, J.; Zhang, L.; Zhou, J.; Li, H.; Chen, H.; Jin, H. *Macromol. Rapid Commun.* 2004, 25, 558.
- 120 Cai, J.; Zhang, L.; Zhou, J.; Qi, H.; Chen, H.; Kondo, T.; Chen, X.; Chu, B. *Adv. Mater.* 2007, 19, 821.
- 121 Cai, J.; Zhang, L.; Wang, L. *Cellulose* 2007, 14, 205.
- 122 Mao, Y.; Zhou, J.; Cai, J.; Zhang, L. *J. Membr. Sci.* 2006, 279, 246.
- 123 Zhang, L.; Mao, Y.; Zhou, J.; Cai, J. *Ind. Eng. Chem. Res.* 2005, 44, 522.
- 124 Cai, J.; Kimura, S.; Wada, M.; Kuga, S.; Zhang, L. *ChemSusChem* 2008, 1, 149.
- 125 Zhou, J.; Li, R.; Liu, S.; Li, Q.; Zhang, L.; Guan, J. J. *Appl. Polym. Sci.* 2009, 111, 2477.
- 126 Qi, H. S.; Chang, C. Y.; Zhang, L. *Green Chem.* 2009, 11, 177.
- 127 Song, Y.; Sun, Y.; Zhang, X.; Zhou, J.; Zhang, L. *Biomacromolecules* 2008, 9, 2259.
- 128 Song, Y.; Zhou, J.; Zhang, L.; Wu, X. *Carbohydr. Polym.* 2008, 73, 18.
- 129 Kamide, K., Okajima, K., Matsui, T. and Kowsaka, K. (1984). Study on the Solubility of Cellulose in Aqueous Alkali Solution by Deuteration IR and ¹³C NMR. *Polymer Journal*, 16(12): 857-866.
- 130 Isogai, A. and Atalla, R.H. (1998). Dissolution of Cellulose in Aqueous NaOH Solutions. *Cellulose*, 5(4): 309-319.
- 131 Isogai, A., Chiba, J., Atalla, R.H. and Verona, W. *Alkaline Method for Dissolving Cellulose* (1994).
- 132 Sobue, H., Kiessig, H. and Hess, K. (1939). The System: Cellulose-Sodium Hydroxide-Water in Relation to the Temperature. *Zeitschrift für Physikalische Chemie*, B43: 309.
- 133 Roy, C., Budtova, T. and Navard, P. (2003). Rheological Properties and Gelation of Aqueous Cellulose NaOH Solutions. *Biomacromolecules*, 4(2): 259-264.
- 134 Cai, J. and Zhang, L. (2005). Rapid Dissolution of Cellulose in LiOH/Urea and NaOH/Urea Aqueous Solutions. *Macromolecular Bioscience*, 5(6): 539-548.
- 135 Direct Dissolution of Cellulose: Background, Means and Applications. *Intech* 2013.p. 144-178
- 136 Turunen O et al., *Lenziger Berichte* Aug 1985, heft 59, p 111.-117
- 137 Yan, L. and Gao, Z. (2008). Dissolving of Cellulose in PEG/NaOH Aqueous Solution. *Cellulose*, 15(6): 789-796.
- 138 Han, D. and Yan, L. (2010). Preparation of All-Cellulose Composite by Selective Dissolving of Cellulose Surface in PEG/NaOH Aqueous Solution. *Carbohydrate Polymers*, 79(3): 614-619.
- 139 Zhang, L., Ruan, D. and Zhou, J. (2001). Structure and Properties of Regenerated Cellulose Films Prepared from Cotton Linters in NaOH/Urea Aqueous Solution. *Industrial & Engineering Chemistry Research*, 40(25): 5923-5928.
- 140 Zhang, L., Ruan, D. and Gao, S. (2002). Dissolution and Regeneration of Cellulose in NaOH/Thiourea Aqueous Solution. *Journal of Polymer Science Part B: Polymer Physics*, 40(14): 1521-1529.
- 141 Jin, H., Zha, C. and Gu, L. (2007). Direct Dissolution of Cellulose in NaOH/Thiourea/Urea Aqueous Solution. *Carbohydrate Research*, 342(6): 851-858.
- 142 Zhang, S., Li, F.-X., Yu, J.-y. and Hsieh, Y.-L. (2010). Dissolution Behaviour and Solubility of Cellulose in NaOH Complex Solution. *Carbohydrate Polymers*, 81(3): 668-674.
- 143 http://www.ri.se/sites/default/files/files/docs/roadmap_textile_materials_from_cellulose.pdf
- 144 Fiber Industry: Global and China Viscose Fiber Industry Report, 2011–2012. PR Newswire. <http://www.prnewswire.com/newsreleases/global-and-china-viscose-fiber-industry-report-2011-2012-143614006.html>.
- 145 Gaehr F, Hermanutz F (2002) Cellulose carbamate fibrous material suitable for low-salt dyeing and printing, its production and its use. *World Patent* 2002097175A2
- 146 Woodings C (2001) New developments in biodegradable nonwovens. <http://www.technica.net/magazines/emagazines.htm>. Accessed 17 Dec 2012
- 147 Laxen T, Hassi H (2007) Preparation of antimicrobial cellulose material from polysaccharides and its pharmaceutical applications. *World Patent* 2007135245A1
- 148 Bridgeford DJ, Rahman M (1988) Cellulose aminomethanate sausage casings. *European Patent* 0282881A1
- 149 Tajima H, Saito H (1997) Adsorbents containing cellulose carbamate for water treatment. *Japan Patent* 09099238A, vide. *Chem Abstr* 1997:361248
- 150 McNeal I (2010) Adsorption of lanthanides on cellulose carbamate: silica hybrid materials. paper presented at the 41st middle atlantic regional meeting of the American chemical society, Wilmington, DE, United States, vide. *Chem Abstr* 2010:420793
- 151 Cheng B, Ren Y, Kang W (2007) Preparation of flame retardant cellulose fibers using carbamate. *Fangzhi Xuebao* 28:19- 21, vide. *Chem Abstr* 2008:3391
- 152 Abhay Bulsari, Saara Rajala, and Ali Harlin, Non-linear modeling of cellulose carbamate fiber production, *Fiber Journal*, Dec 2018, p.28
- 153 US4639515, by Neste 27. Jan 1987

- ¹⁵⁴ Lenziger Berichte Mai 1984, Heft 57, 38-41
- ¹⁵⁵ O.T. Turunen et.al., Some Aspects of the Spinning of the Cellulose Carbamate, Lenziger Berichte, heft 59, August 1985
- ¹⁵⁶ The European polysaccharide network of excellence (EPNOE): Research Initiatives and Results, Patrick Navard, Springer Science & Business Media, 13.12.2012
- ¹⁵⁷ Gaofenzi Cailliao Kexue Yu Gongcheng Comparison of cellulose carbamate fiber and lyocell fiber using N-methylmorpholine-N-oxide (NMMO) as solvent, Polymeric Materials Science and Engineering 30(11):122-127 · November 2014
- ¹⁵⁸ Reud D, Mazzeno L, Ind. Eng. Chem. 1949, 41(12) 2828-2821
- ¹⁵⁹ Luneva, N., Petrovskaja, L., Ezovitova, T., Russ. J. Appl. Chem, 2007, 80(11) 1923-1927
- ¹⁶⁰ Kaputskii, F.N., Yurkstovich, N.K., Yurkstovich, T.L., Golub, N.V., Kosterova, R.I., Russ. J. Appl. Chem., 2007, 80 (7) 1135-1139
- ¹⁶¹ CHENG B et.al., Tianjin Polytechnic University, China) Preparation of flame retardant cellulose fibers using carbamate, http://en.cnki.com.cn/Article_en/CJFDTOTAL-FZXB200704006.htm
- ¹⁶² Journal of Applied Polymer Science, Vol. 26, 2103-2107 (1981)
- ¹⁶³ Feiya Fu, Quanling Yang, Jinping Zhou, Haoze Hu, Baoquan Jia, and Lina Zhang, Structure and Properties of Regenerated Cellulose Filaments Prepared from Cellulose Carbamate-NaOH/ZnO Aqueous Solution, ACS Sustainable Chem. Eng., 2014, 2 (11), pp 2604-2612
- ¹⁶⁴ Bingqian Guo, Wufeng Chen, and Lifeng Yan, Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, China, ACS Sustainable Chem. Eng., 2013, 1 (11), pp 1474-1479
- ¹⁶⁵ F. Fu, Cellulose (2014) 21:2819-2830
- ¹⁶⁶ Yang, Q., Fukuzumi, H., Saito, T., Isogai, A. and Zhang, L. (2011). Transparent Cellulose Films with High Gas Barrier Properties Fabricated from Aqueous Alkali/Urea Solutions. Biomacromolecules, 12(7): 2766-2771.
- ¹⁶⁷ Lili Yao et.al., Effect of graphene oxide on the solution rheology and the film structure and properties of cellulose carbamate, Carbon 69, April 2014, pp 552-562
- ¹⁶⁸ Anada, S., Carbohydrate Polymers 154 (2016) 8-12
- ¹⁶⁹ F. Fu et.al. ACS Appl. Mater. Interfaces, 2015, 7 (4), pp 2597-2606
- ¹⁷⁰ Hameed Ali Al-Hajjar, et.al...Synthesis and Characterization of Silver Nanoparticle Loaded on Cellulose and Cellulose Carbamate. Journal of Chemical and Pharmaceutical Research, 2017, 9(12):98-103
- ¹⁷¹ Diamantoglou M , Platz J , Vienken J , Cellulose carbamates and derivatives as hemocompatible membrane materials for hemodialysis. Artificial Organs [01 Jan 1999, 23(1):15-22]
- ¹⁷² Haisong Q, in Novel Functional Materials Based on Cellulose pp 25-43, Part of the SpringerBriefs in Applied Sciences and Technology book series
- ¹⁷³ MAMAT Halidan KIBIR Bzuor, School of Chemistry and Chemical Industry Xinjiang University, Preparation of cellulose sponge from cellulose carbamate, CIESC Journal 2012, Vol. 63 Issue (5): 1642-1642
- ¹⁷⁴ Xiayoun Q., et.al., Carbohydrate Polymers 88 (2012) 1272- 1280
- ¹⁷⁵ Sinyee Gan et.al., PLOS One 12(3), e0173743, March 15, 2017
- ¹⁷⁶ Beesley, T.e and Scott, Raymond P.W. Chiral Chromatography, Wiley & Sons
- ¹⁷⁷ Teresa Kowalska, Joseph Sherma, Thin Layer Chromatography in Chiral Separations and Analysis, CRC Press
- ¹⁷⁸ O.T. Turunen et.al., Some Aspects of the Spinning of the Cellulose Carbamate, Lenziger Berichte, heft 59, August 1985
- ¹⁷⁹ ACS Sustainable Chem. Eng. 2014, 2, 2363-2370 Volume 22, Issue 6, June 2012, Pages 1513-1516
- ¹⁸⁰ Cellulose carbamate from a new process, Possibilities and challenges in industrial scale Hans Grundberg, Domsjö Fabriker, COSTFP 1205, presented 08.11.2011
- ¹⁸¹ Leena Katajainen, ProGradu, University of Jyväskylä, 2016

VTT

beyond
the obvious

www.vttresearch.com

