

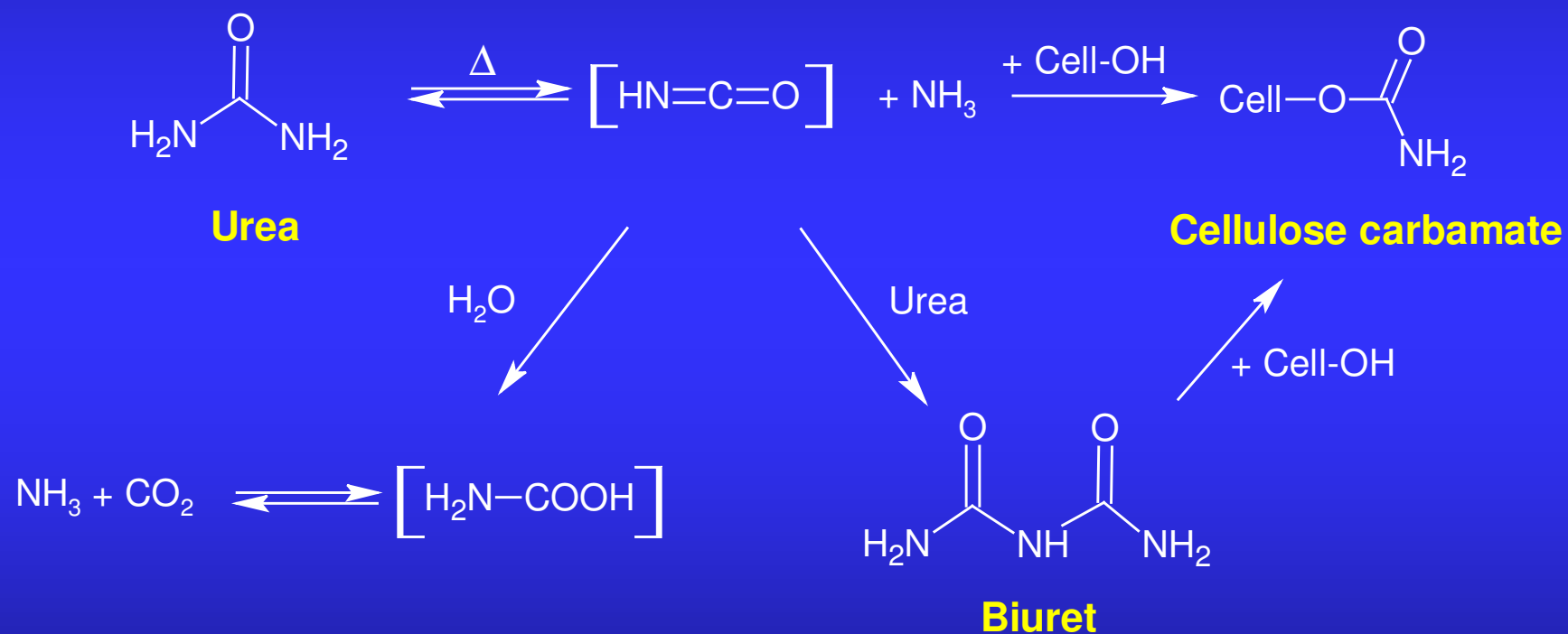
„Allocell“ a New Cellulose Derivative for Applications in Medicine and Hygiene

Franz Effenberger, Frank Hermanutz and Markus Braun

Institute of Textile Chemistry and Chemical Fibers (ITCF),
Denkendorf / Stuttgart (Germany)



Mechanistic Proposals for the Reaction of Activated Cellulose with Urea at Higher Temperature



K. Ekman, V. Eklund, J. Fors, J. I. Huttunen, J. Selin and T. Turunen in *Cellulose: Structure, Modification and Hydrolysis* (Eds. R. A. Young and R. M. Rowell), chapter 7, p131-148, Wiley, New York (1986)

Comparison of some Properties of Intermediates of the Viscose and Cellulose Carbamate Process

Cellulose xanthate:

- prepared in situ from alkaline cellulose and CS_2 as „viscose“ solution, only to handle and hydrolyze using exhaust systems
- xanthate residues have to be removed completely in the spinning process

Cellulose carbamate:

- obtained as an absolutely stable white powder by reacting alkaline cellulose with urea at 135°C
- Hydrolysis in the spinning process can be performed selectively, resulting in cellulose regenerates still partly substituted
- cellulose carbamate solutions can excellently be used for coating textile fabrics

Comparison of some Viscose and Cellulose Carbamate Fiber Properties

Properties

Amorphous /

Crystallinity ratios (%):

Viscose

~ 70 / 30

Cellulose
carbamate:

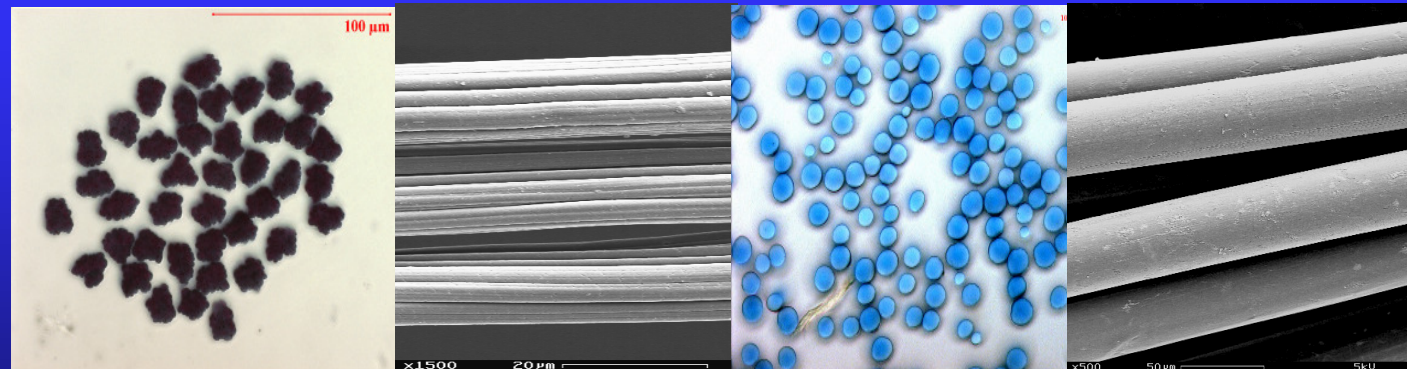
~ 95 / 5

WRV (%):

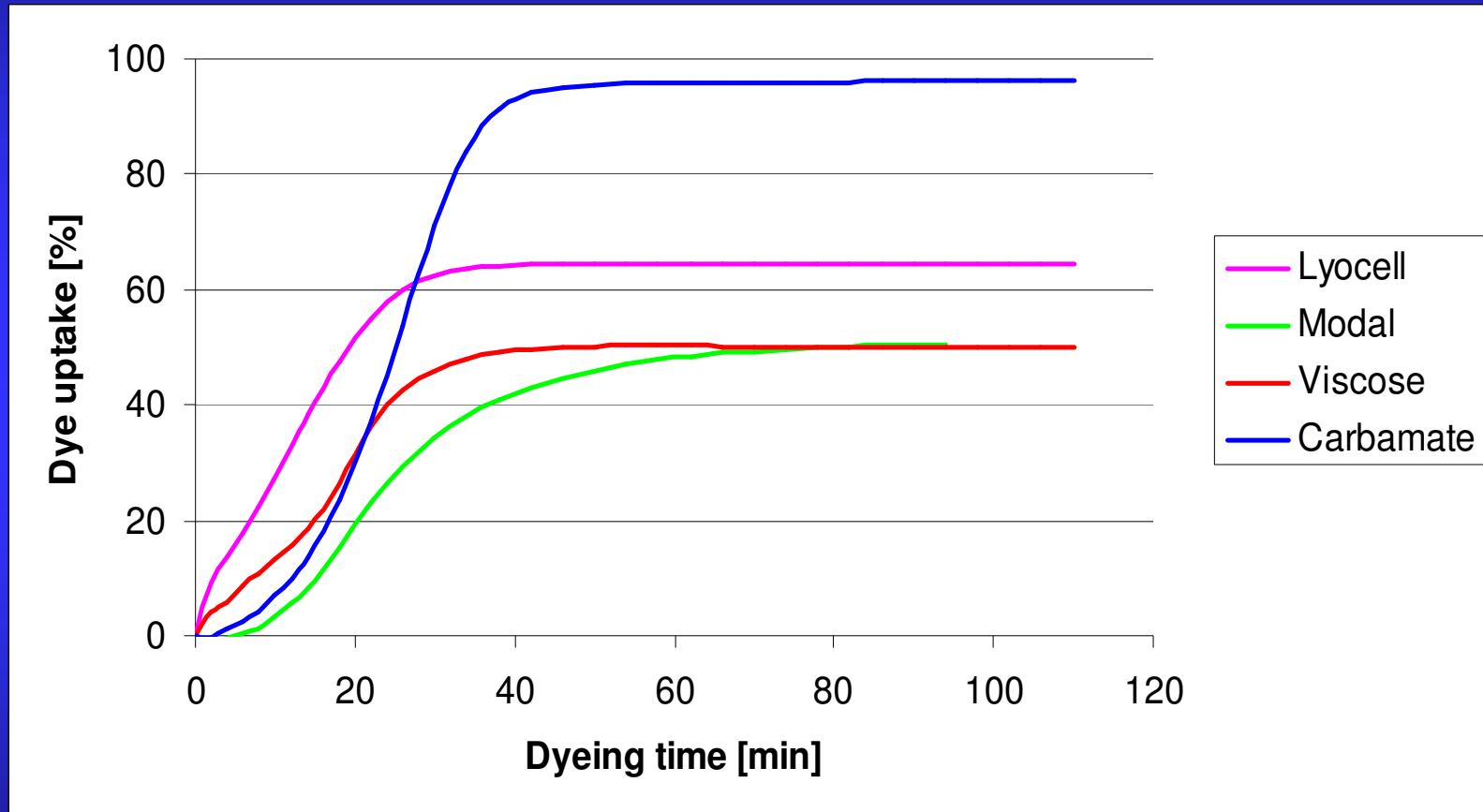
~ 80

~ 150

Morphology:

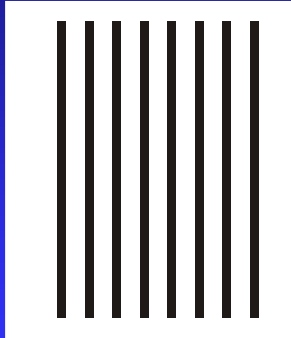


Dye Uptake of Various Cellulose Regenerate Fibers Dyeing with 3% C.I. Direct Blue 71



Swelling and Recrystallization of Man-made Cellulosics

Cellulose I

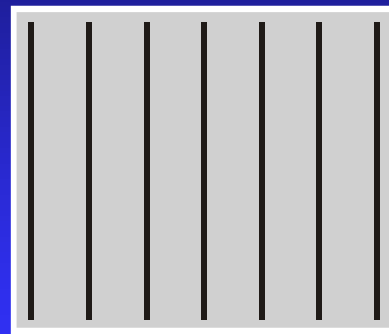


Cellulose-crystallite

Swelling
NaOH/H₂O



Rinsing
Cellulose II

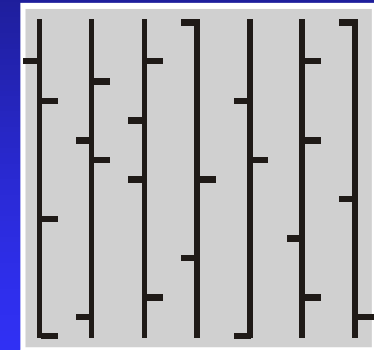


Cellulose-amorphous

Derivatization

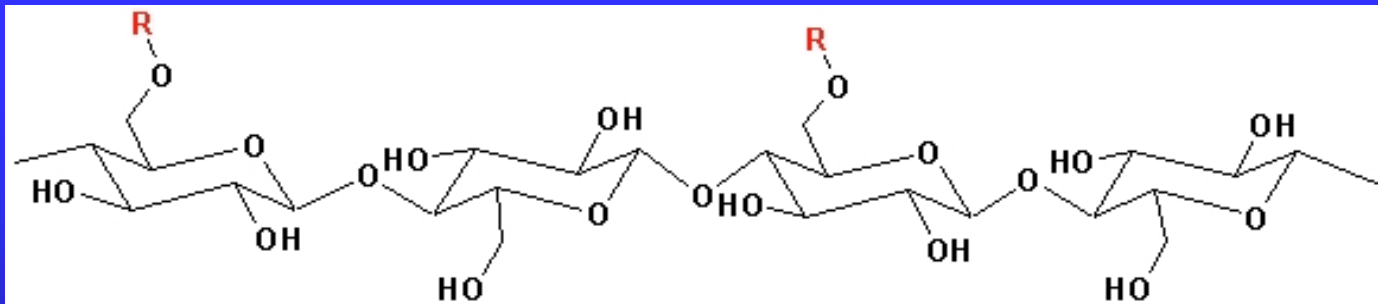
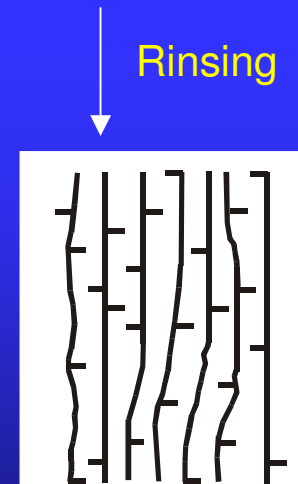


Dederivatization



Cellulose-derivates

Rinsing



DS = 0,5 (average of substitution)

- the typical properties of cellulose remain unchanged with DS values < 0.6

Sorption properties of man-made cellulose fibers are characterized by two parameters, the water retention value (WRV) and the water holding capacity

- **Water retention value (WRV)** is primarily controlled by the super-molecular structure and the internal void system
- **Water holding capacity** is in addition to WRV mainly dependent on surface parameters like fiber crimp, titer, cross section and fiber finish
- The performance of fibers with different profiles regarding WRV and adsorptive capacity is difficult to predict as nonwoven manufacture technology and structural parameters reveal significant influence on nonwoven product properties

**Schmidtbauer, J.; et al.,
Lenzing AG, Technical Textiles 1, 2006, E18 – E22**

Preparation and Stabilization of Nanoscale NaCl-Particles



Netzsch Mini-Zeta,
laboratory scale mill

Grinding conditions:

30 g NaCl / 300 ml Dimethylacetamid

3.5 g Polyvinylpyrrolidone (PVP) as
stabilizer

3000 rpm, 1 hour, r.t.

Diameters of NaCl-Particles

prepared by milling of 30 g NaCl, 1h at 3000 rpm in DMA and variation of the amount of dispergant PVP

PVP [%]	average size [nm]	D16% [nm]	D84% [nm]
47,0	275	269	282
33,4	273	267	281
20,0	275	269	283
14,3	276	270	284
7,3	275	269	282
1,7	297	291	205
0,3	275	269	282

Preparation of Dispersed NaCl in CC / DMA-Solutions

- Initial swelling of CC in methanol (exchanged by DMA)
- Dissolving LiCl in DMA at 60 – 80 °C, followed by addition of the NaCl-dispersion in DMA
- Dissolving of pretreated CC in the NaCl / DMA dispersion at 6 – 8 °C over night

CC: Cellulose carbamate

DMA: N,N-dimethylacetamide

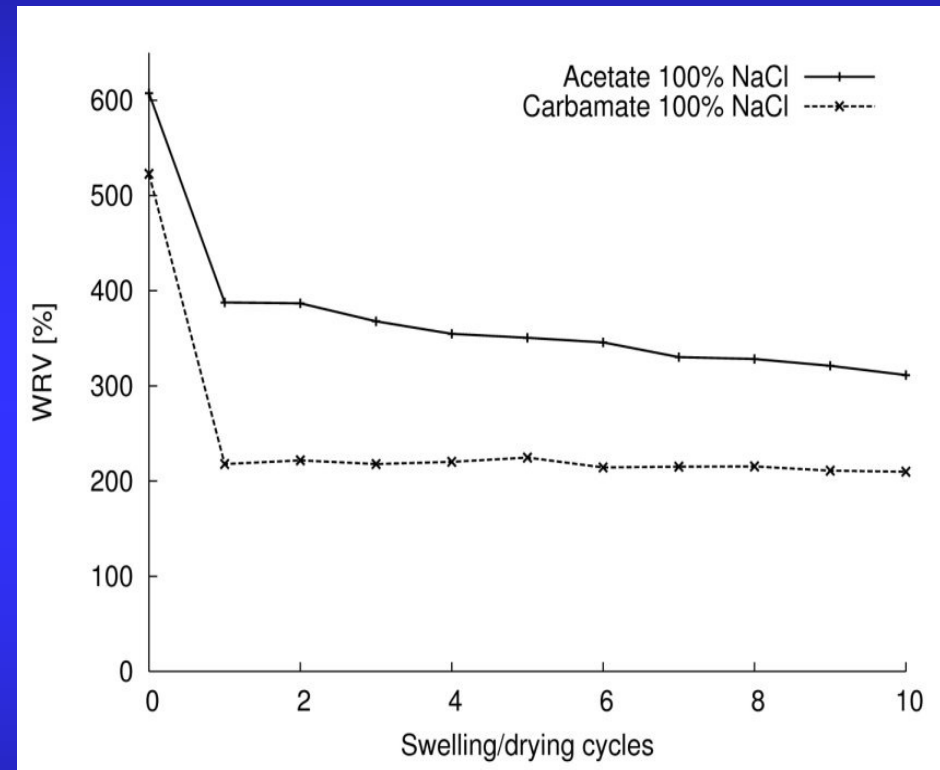
Preparation of Nanoporous Cellose Carbamate Films

- Drying at low temperatures ($\leq 20\text{ }^{\circ}\text{C}$) results in crystallization of NaCl at the surface
- Drying at $105\text{ }^{\circ}\text{C}$: conservation of the particle size, homogeneous distribution in CC-matrix, reduced film quality
- Coagulation in alcohols, especially in isopropanol results in a homogeneous dispersion of the particles in the CC-matrix and a good film quality
- The NaCl particles are removed by water to give nonoporpous CC-films
- The results obtained with CC-films can be applied analogously for the preparation of the nanaporous CC-fibers

Stability of CC-Porosity Depending on Temperature and on Swelling / Drying Cycles

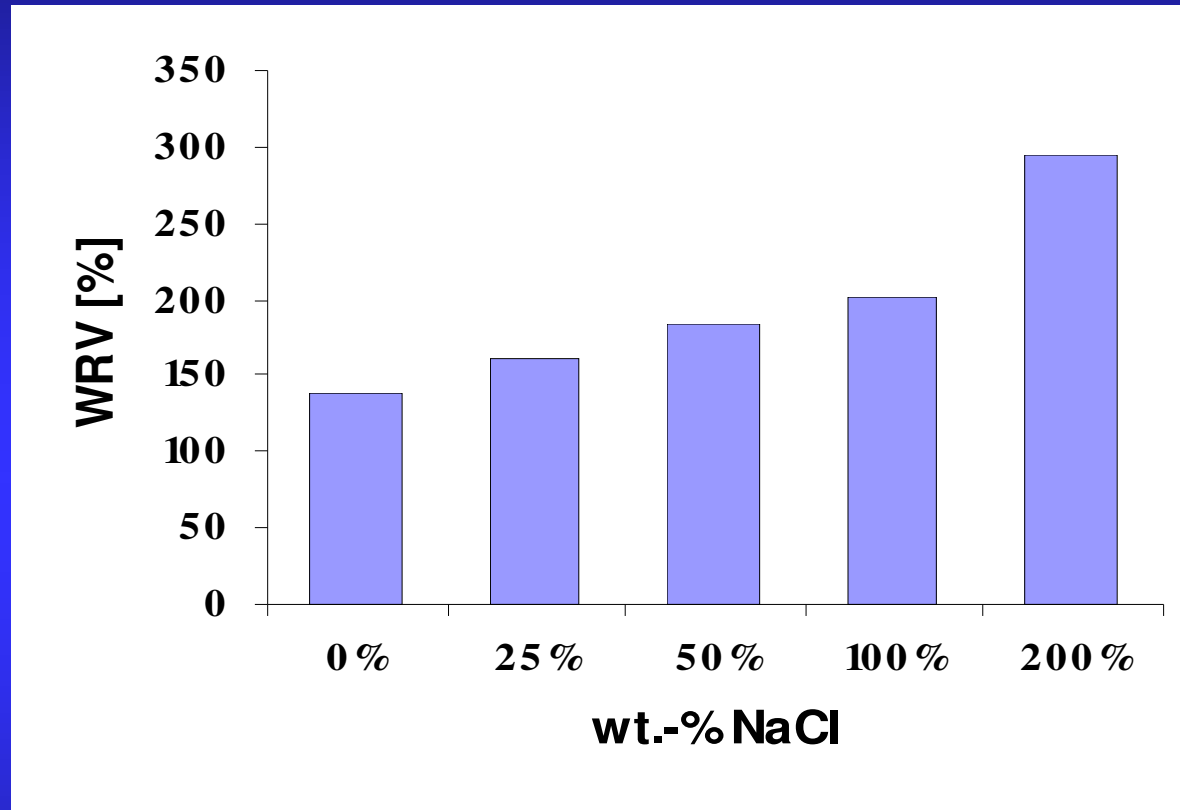
Temperature dependence of WRVs

T	Drying time	WRV (0% NaCl)	WRV (200% NaCl)
20 °C	12 h	138	305
105 °C	12 h	126	305
150 °C	12 h	121	266
200 °C	2 h	122	170



Change of WRV with drying cycles

Water Retention Values (WRV) Depending on NaCl-Particle Concentration



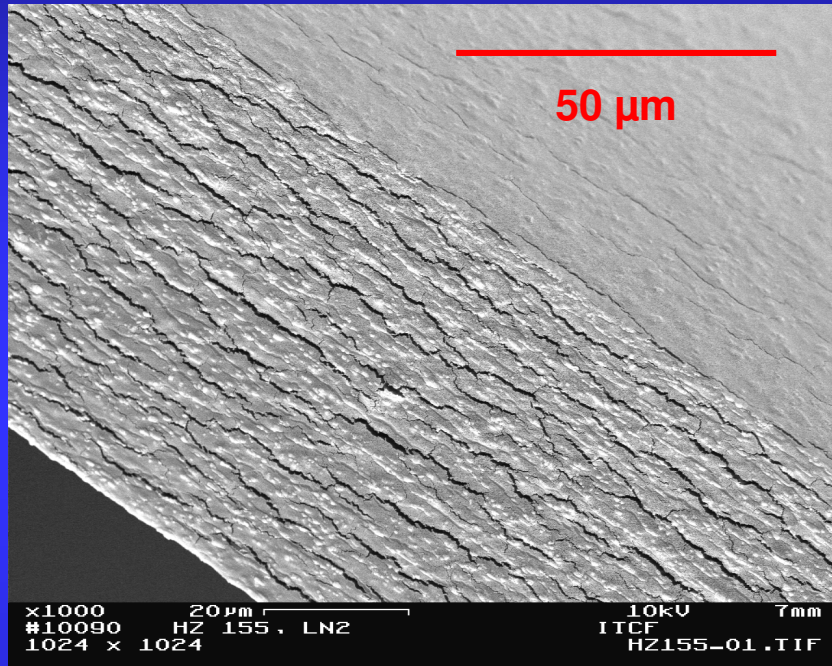
Influence of the particle conc. on WRV-values of CC

WRV and WVP* of CC-Films Depending on NaCl-Concentration and Film Thickness

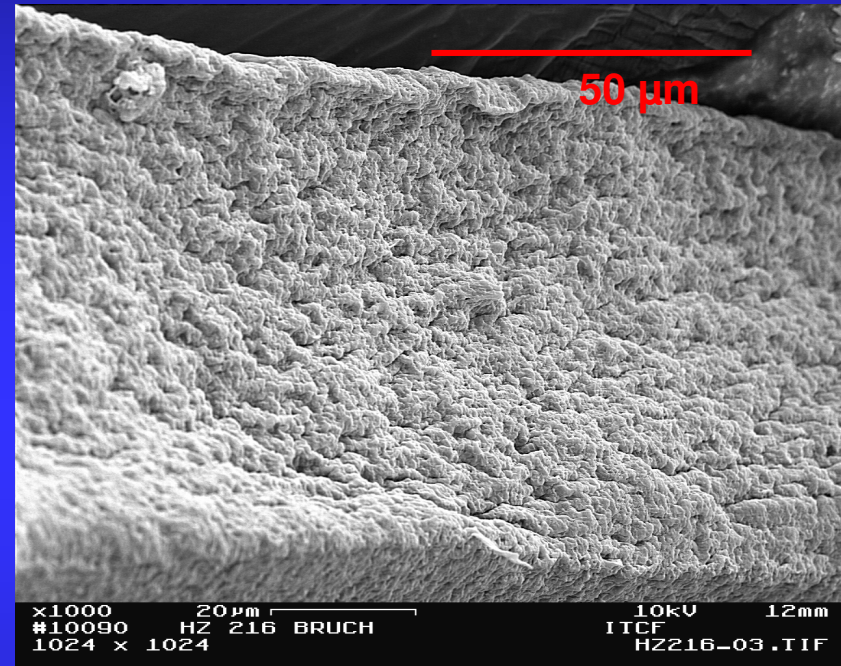
NaCl (%)	0	25	50	100	200
Thickness [μm]	16	13	16	14	21
WRV (%)	138	161	184	202	294
WVP [$\text{g}/\text{m}^2\cdot 24\text{h}$]	2010	2131	2215	2330	2727

*WVP: water vapour permeability [$\text{g}/\text{m}^2\cdot 24\text{h}$]

Air Dried, Isopropanol Coagulated Cellulose Carbamate Films

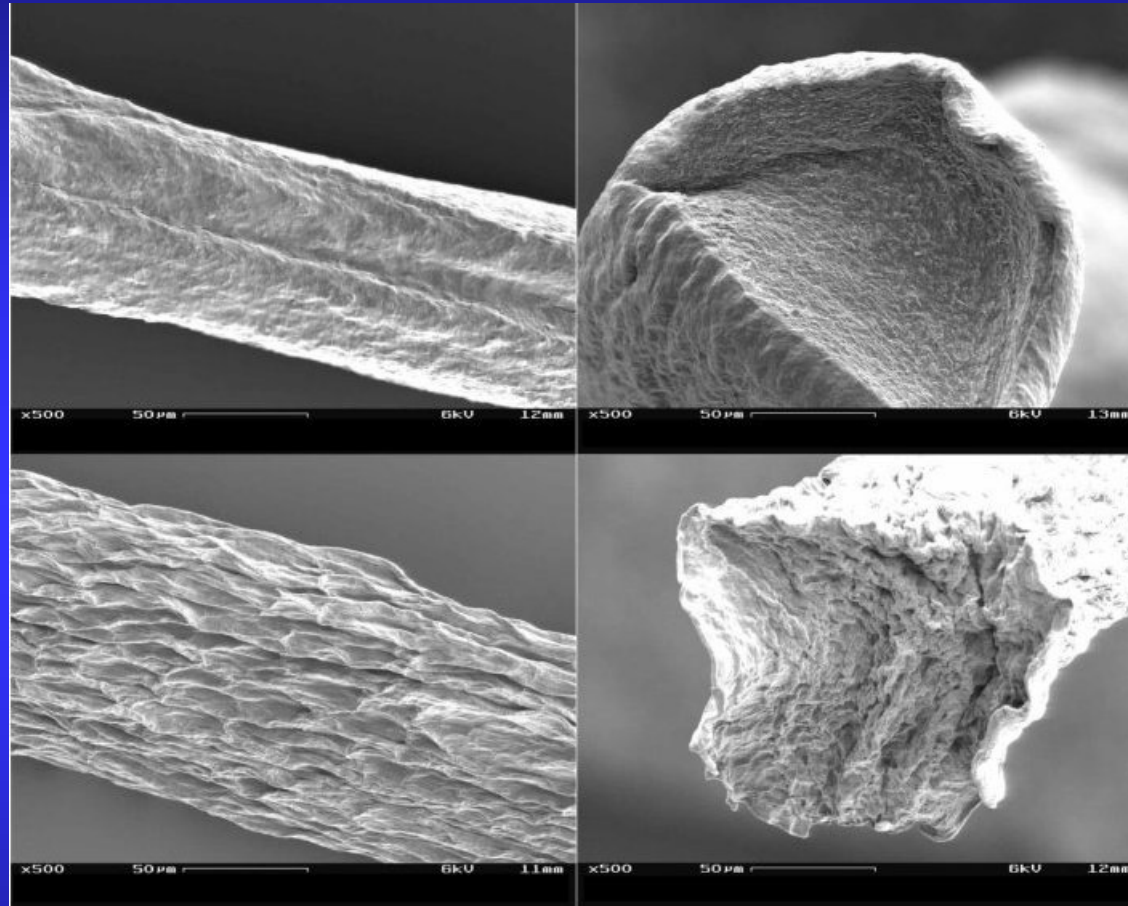


Dried CC-film with 50 wt.-% NaCl



Coagulated in i-propanol and washed CC-film

Cellulose Carbamate Fibers with 100 wt.-% NaCl-Particles, Coagulated in Isopropanol

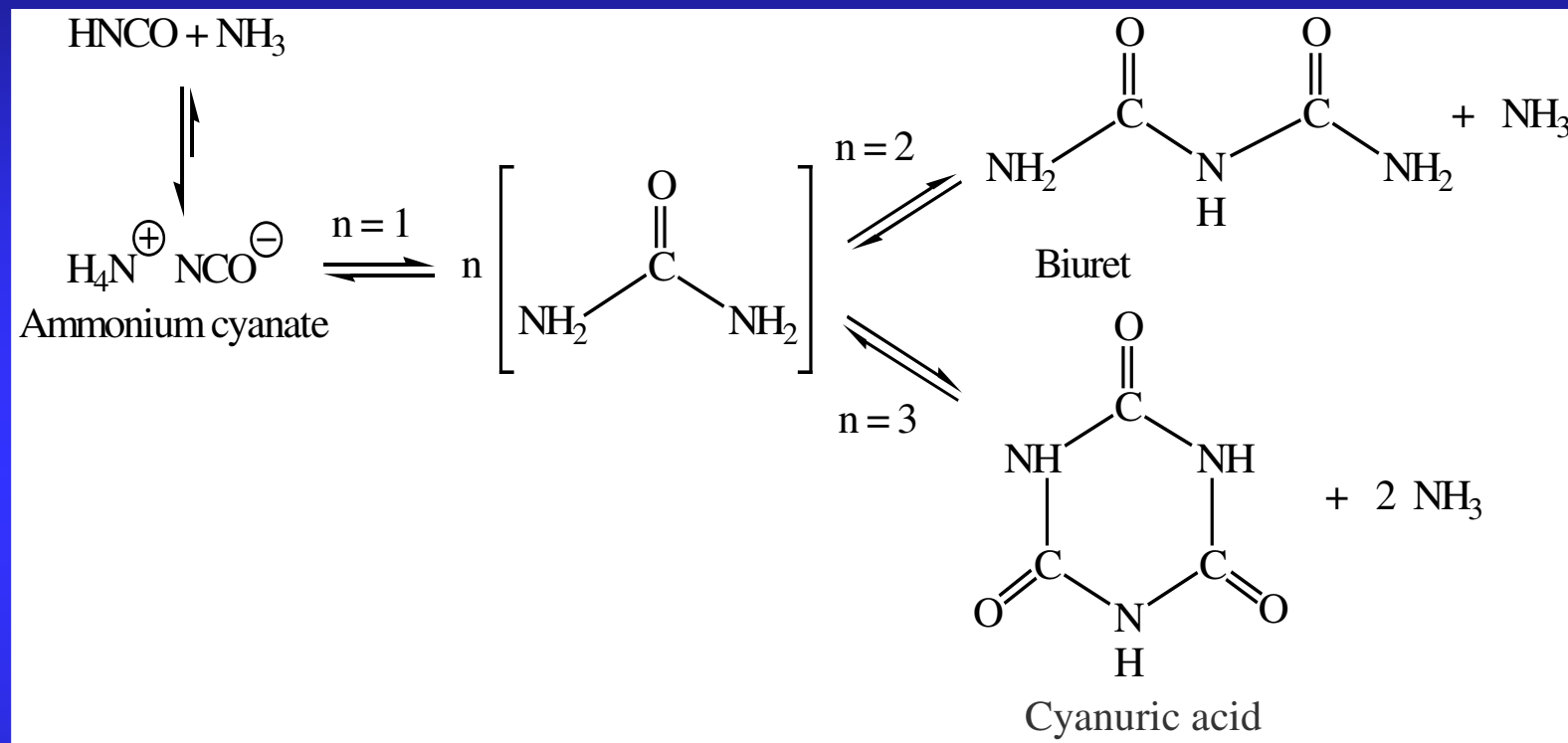


Upper row: longitudinal and cross section of carbamate fibers with 100% NaCl particles
Lower row: longitudinal and cross section after removal of particles with H₂O

Potential Applications of Nanoporous Cellulosics

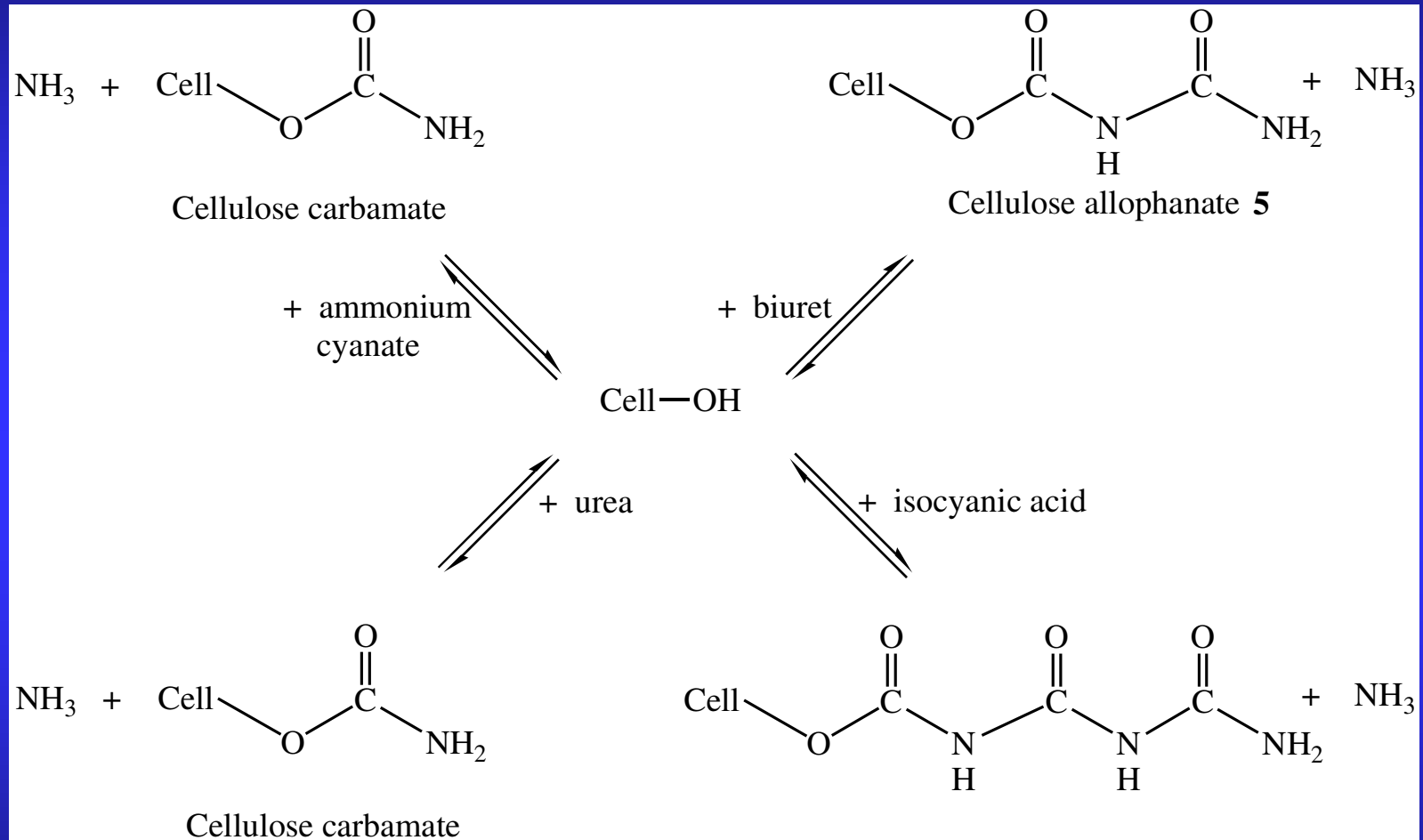
- Regulation of water balance in consumer products (outdoor clothings, functional textiles, home textiles, etc.)
- Utilization of products with a need of high WRVs for medicine and hygiene applications
- Storage of interesting active compounds (drugs, flavours, fragrances, vitamins, ec.)
- Carrier (supporter) for catalysts (enzymes, metal complexes, ec.)
- New coating materials (wall papers, textiles, etc.)

Possible Products Formed by Heating Urea >135°C



K. Ekman, V. Eklund, J. Fors, J. I. Huttunen, J. Selin and T. Turunen in *Cellulose: Structure, Modification and Hydrolysis* (Eds. R. A. Young and R. M. Rowell), chapter 7, p131-148, Wiley, New York (1986)

Possible Pathways of Activated Cellulose with Urea at 135°C



M.A. Braun, K. Bredereck, F. Effenberger, F. Gähr, F. Hermanutz: J. of Appl. Polymer Science, sub. 2009

Summary

- Low substituted cellulose carbamate (DS < 0.5) is to a very high degree ($\geq 95\%$) amorphous and has relatively high water retention values ($\sim 150\%$) in comparison to viscose ($\sim 80\%$) and cotton ($\sim 40\%$)
- The WRV is primarily controlled by the supermolecular structure and the internal void system
- The internal void system of cellulose carbamate can be enhanced considerably by dispersion of NaCl nanoparticles in a solution of CC in DMA, followed by a wash out of NaCl
- Comprehensive structure investigations of CC revealed, that the reaction product of activated cellulose with urea at higher temperature results in the formation of a cellulose allophanate and not a cellulose carbamate
- Nanoporous cellulosics are very interesting materials for various applications