Quality requirements of the dry-wet spinning process – analysis of raw materials, solutions and fibers

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Outline

• Shaping of Cellulose
• Lyocell process
• Aims of analytics
• Monitoring analytics
• Thermostability
From Cellulose to shaped bodies

Non-regular cellulose particles e.g. pulp, short fibres

Cellulose acetate
Cellulose xanthate
Cellulose carbamate
Cellulose silyl ether
Mixed cellulose ethers

Soluble
Fusible

DMAc/LiCl
NMMO • H₂O
BMIMCl

Shaping through regeneration of dissolved cellulose

Thermoplastic shaping

Shaped material
Spinning set-up for manufacturing of fibres

Raw materials
- Cellulose
- Solvent
- Additives

Spinning dope
- Spinning pumps
- Nozzle, ∅ ≈ 70 mm
- Spinning capillaries

Dope storage
- Tank

Spinning

Washing
- Regenerated cellulose filaments

Solvent recovery
- Filament take-up
- Filament
Pilotscale plant of Smart Fiber AG, Rudolstadt – Filament after-treatment, drying and winding.

- Process limits: Dope throughput
  - Take-up velocity
  - Dope viscosity → Deformation force
  - Solvent exchange rate

Restricted processing window
Analytical methods

Raw materials
- Polymers
- Solvent
- Stabilizers
- Additives

Solutions
- Pulp
- Suspension
- Solution
- Melt, Gel

Shaped bodies
- Fibers, Nano-fibers
- Films
- Beads
- Non-wovens

Purity
- Particle size, pH, surface
- Special properties

Solution state
- Spinning behaviour
- Thermostability

Performance
- Special features
## Analytical methods

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Solutions</th>
<th>Fibers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash</td>
<td>Particle size</td>
<td>Textil-physical properties</td>
</tr>
<tr>
<td>Metals</td>
<td>Microscopy</td>
<td>Surface (Elmi, AFM, ZETA-pot.)</td>
</tr>
<tr>
<td>-CO, -COOH</td>
<td>H2O content</td>
<td>X-ray (crystallinity)</td>
</tr>
<tr>
<td>α-Cellulose</td>
<td>DP, molar mass</td>
<td>Porosity</td>
</tr>
<tr>
<td>H2O content</td>
<td>Rheology</td>
<td>Solvent / metals residues</td>
</tr>
<tr>
<td>DP, molar mass</td>
<td>Chromophores (UV/VIS)</td>
<td>Recovery of additive</td>
</tr>
<tr>
<td>Particle size</td>
<td>Thermostability</td>
<td>White degree</td>
</tr>
<tr>
<td>Porosity</td>
<td>pH</td>
<td>Water retention behavior</td>
</tr>
<tr>
<td>Amines</td>
<td>Metals</td>
<td>Adsorption capacity</td>
</tr>
<tr>
<td>pH</td>
<td>Amines</td>
<td>Bioactivity</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>
Raw materials

Solution

Fiber
## Cellulose – Requirements profile

<table>
<thead>
<tr>
<th>Requirement</th>
<th>Requirement Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity (Cuen)</td>
<td>325 – 395 ml/g</td>
</tr>
<tr>
<td>DP (Cuoxam)</td>
<td>480 – 580</td>
</tr>
<tr>
<td>$\alpha$-cellulose</td>
<td>&gt; 90%</td>
</tr>
<tr>
<td>Sum of heavy metals (Fe, Cu, Ni, Cr, Mn, Co)</td>
<td>&lt; 10 ppm</td>
</tr>
<tr>
<td>Sum of alkali/earth alkali metals&lt;br/&gt;NMMO</td>
<td>&lt; 100 ppm</td>
</tr>
<tr>
<td>Soluble content in 20% NMMO</td>
<td>&lt; 0,5%</td>
</tr>
<tr>
<td>COOH groups</td>
<td>&lt; 25 µmol/g</td>
</tr>
<tr>
<td>CO groups</td>
<td>&lt; 35 µmol/g</td>
</tr>
<tr>
<td>White degree</td>
<td>&gt; 90%</td>
</tr>
<tr>
<td>Ash</td>
<td>&lt; 0,5%</td>
</tr>
</tbody>
</table>
Cellulose – Requirements profile

Not to forget:
Origin – cotton, wood
Processing – sulfite, sulfate
Refining - bleaching

\[ \alpha \text{-Cellulose content of various paper and dissolving pulp} \]

<table>
<thead>
<tr>
<th>Type</th>
<th>( \alpha )-Cellulose content, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paper pulps, bleached:</td>
<td></td>
</tr>
<tr>
<td>Spruce, sulfite</td>
<td>89</td>
</tr>
<tr>
<td>Beech, sulfite</td>
<td>89</td>
</tr>
<tr>
<td>Spruce, sulfate</td>
<td>82</td>
</tr>
<tr>
<td>Birch, sulfate</td>
<td>72</td>
</tr>
<tr>
<td>Sulfite dissolving pulps for:</td>
<td></td>
</tr>
<tr>
<td>Regular rayon staple</td>
<td>89 – 91</td>
</tr>
<tr>
<td>High-wet-modulus rayon staple</td>
<td>91 – 93</td>
</tr>
<tr>
<td>Acetate filament yarn</td>
<td>94 – 95</td>
</tr>
<tr>
<td>Sulfate dissolving pulps for:</td>
<td></td>
</tr>
<tr>
<td>Regular rayon staple</td>
<td>93 – 95</td>
</tr>
<tr>
<td>High-wet-modulus rayon staple</td>
<td>95 – 98</td>
</tr>
<tr>
<td>Rayon tire cord (super II – III)</td>
<td>96 – 98</td>
</tr>
<tr>
<td>Acetate filament yarn</td>
<td>98</td>
</tr>
</tbody>
</table>

Hg porosimetry of different charcoals

Extraordinary effect on adsorption capacity but enhanced thermal degradation!

MicroSilver BG™
- porös, 80 – 140 nm

NanoSilver BG™
- kolloidal, 5 – 20 nm

Extraordinary effect on fiber bioactivity but enhanced thermal degradation!

Surface topography on 1 x 1 µm sample size for a cellulose/xanthan fiber from EMIMac (Ra = roughness)

Prof. Dr. Stana-Kleinschek, University of Maribor
Total scan with $\chi$ sections through the reflexes at $2\theta$

Dr. Thomas Schulze, TITK
Target: Dissolution of cellulose

→ Interaction of polymer and solvent is of fundamental importance for understanding and perception of proceeding processes in polymer dissolution
→ structure of regenerates, structural changes of polymer and solvent, dope properties and shaping behaviour should be discussed

<table>
<thead>
<tr>
<th>Cellulose</th>
<th>Solvent</th>
<th>Regenerate Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>cell. xanthate/NaOH</td>
<td>aqueous acids</td>
<td>irregular</td>
</tr>
<tr>
<td>cellulose acetate/acetone</td>
<td>solvent evaporation (water)</td>
<td>irregular/fibrous</td>
</tr>
<tr>
<td>cellulose/Cuoxam</td>
<td>aqueous acids</td>
<td>fibrous</td>
</tr>
<tr>
<td>cellulose/NMMO/H₂O</td>
<td>water</td>
<td>fibrous</td>
</tr>
<tr>
<td>cellulose/ BMIMCl</td>
<td>water</td>
<td>fibrous</td>
</tr>
</tbody>
</table>

→ different fibrous structures of regenerated films regarding to precipitating structures

→ high ordered dissolved state is detectable in viscous NMMO melts containing different amounts of water
→ connected to the distinctive H-bond system existing in solid state
→ at about 62 % NMMO a stable 2,5 hydrate is formed

→ NMMO forms a second stable hydrate, NMMO monohydrate
→ high ordered state won’t be significant changed by the addition of polymers like cellulose but slightly disturbed
→ NMMO monohydrate dissolves cellulose fast macroscopic

$t = 0 \text{ min}$
Fibers dispersed in 60 % NMMO
t = 60 min
After adjustment 80 % NMMO
t = 90 min
After adjustment 80 % NMMO
$t = 120 \text{ min}$

After adjustment 80 % NMMO
Cellulose concentration 12.3 %
Eucalyptus, DP 563
Zero shear viscosity 9910 Pas
Particle volume 1.3 µl/l solution
Max. Particle diameter 18 µm
Colour number 12
Filter amount 31

Particle size criterion:
< 40 µm fiber
< 20 µm filament
Rheometry of cellulose dopes is targeted to …

1. **Determination of the zero shear viscosity**

   rotation mode with controlled shear stress (90 Pa)

2. **Characterisation of the flow behaviour**

   oscillation mode (frequency sweeps between 0.046 and 14.7 Hz) at different temperatures for the calculation of master curves (storage and loss moduli as well as the complex viscosity depending on frequency respectively angular rate, referring to a reference temperature, i.e. 85°C)

   determination of the cross over between storage and loss modulus and the plateau moduli (plateau value of the storage modulus)

   calculation of the weighted relaxation spectra (relaxation time $\lambda_m$, information on the molecular mass distribution of the polymers which are involved in the solution state by rheological methods)
Microscopic images by polarisation light of cellulose solutions in NMMO (16.5%) and EMIMAc (24.9%)

Viscosity measurement of cellulose/EMIMAc solutions at different temperatures at a shearing rate of 0.5 s\(^{-1}\) (Arrhenius plot)
Main actions and degradation reactions in the system cellulose/NMMO

NMMO
lability
oxident

Cellulose
endgroups
sugar acids
radicals

Hydrogen bond system
between cellulose
and NMMO

Contaminations
Iron
Copper

Properties of additives
pH value
-COOH, -NH₂
structure
pore size
particle size
porosity

Temperature
Pressure

Thermal degradation

Oxidation of cellulose, deoxygenation of NMMO

Polonovski type reaction

Radical reaction

40 °C, 1min

0.8×2.0 magnification with microskope SMC 4, Fa. Ascania, heating table Linkam.
104°C, 5 min
112°C, 15 min
116 °C, 20 min
119 °C, 22 min
123 °C, 26 min
126 °C, 28 min
131 °C, 34 min
138 °C, 41 min
141 °C, 44 min
145 °C, 48 min
147 °C, 50 min
149 °C, 52 min
149 °C, 53 min
150 °C, 54 min
150 °C, 54 min
150 °C, 54 min
150 °C, 55 min
150 °C, 60 min
150 °C, 70 min
150 °C, 75 min
150 °C, 80 min
150 °C, 90 min
Accidere ex una scintilla incendia passim
Titus Lucretius Carus (96 – 55 v. Chr.)

'Big fires often arise from a little spark'
Problem of industrial reactors:

Heat development: \( \sim Volume \sim r^3_{\text{Vessel}} \)
Heat release: \( \sim Area \sim r^2_{\text{Vessel}} \)

<table>
<thead>
<tr>
<th>Vessel volume</th>
<th>Cooling time for 1 K</th>
<th>Cooling speed K/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 ml</td>
<td>11 s</td>
<td>5,5</td>
</tr>
<tr>
<td>100 ml</td>
<td>20 s</td>
<td>3</td>
</tr>
<tr>
<td>1000 ml</td>
<td>2 min</td>
<td>0,5</td>
</tr>
<tr>
<td>2,5 m(^3)</td>
<td>21 min</td>
<td>0,047</td>
</tr>
<tr>
<td>25 m(^3)</td>
<td>233 min</td>
<td>0,0043</td>
</tr>
</tbody>
</table>

\[ \Phi = \frac{m_s \cdot c_s + m_g \cdot c_g}{m_s \cdot c_s}, \]
DSC measurements of NMMO and cellulose solutions in NMMO and BMIMCl

Fast screening method, 5 - 20 mg sample mass
Onset-Temperature, reaction enthalpy
Dynamic measurements by means of the mini-autoclave:
Sample mass 2 g, 0.75 K/min, 30 – 300°C
Temperature and pressure!

Onset temperature ($T_{on}$): First thermal activity

Calorimetric measurements

Mini - autoclave
RADEX - Reaction calorimeter
Rapid Detector for Exothermic Processes
Fa. Systag/CH
Calorimetric measurements - mini-autoclave

Comparison of onset - temperatures

- NMNO monohydrate: 163°C
- 11% Cellulose/NMNO: 145°C
- 11% Cellulose/NMNO + NaOH, propyl gallate: 160°C
- 9% Cellulose/NMNO modified with acidic ion exchange resin: 151°C
- 11% Cellulose/NMNO + 50 ppm Fe(III): 146°C
- 11% Cellulose/NMNO + 50 ppm Fe(II): 142°C
- 9% Cellulose/NMNO modified with reactive activated charcoal: 131°C
Calorimetric measurements: SEDEX oven, Fa. Systag/CH

Adiabatic calorimetry: Changes in isoperibolic pressure of cellulose solutions at 110 °C over 96 h.
DEWAR vessel with 300 g sample mass
High Performance Liquid Chromatography (HPLC)

Distillate of cellulose/NMMO solution

High Performance Liquid Chromatography (HPLC)

Comparison of onset temperature ($T_{on}$) and concentration of $N$-methylmorpholine (NMM) in distillates of Lyocell solutions modified with activated charcoal.
Qualitative determination of the volatile compounds in the Cellulose/EMIMAc system (Head-space-GC/MS)
Experimental ESR spectra of NMMO/cellulose solution recorded after 16 min excimer laser ($\lambda = 248$ nm) photolysis at 77 K.

Electron Spin Resonance Spectroscopy

Experimental ESR spectra recorded after 16 min irradiation at 105 K and their simulations

Constructed spectra of pure -NO/ radical and R-NO/′-R′

Suggested pathway
Changes in UV/VIS spectrum of cellulose/NMMO solutions heated at 120°C

Immediately after preparation

After 400 min

\[ \Delta E \]

Observation wave length

Design of the cuvette for heating of cellulose solutions

Extinction-time curves of a cellulose/NMMO solution at different temperatures. Determined at $\lambda$ 400 nm.
Extinction-time curves of a cellulose/NMMO solution modified with an acidic ion exchange resin at different temperatures. Determined at $\lambda\ 400$ nm.
Exothermicity: temperature development exclusively caused by the exothermic reaction accompanied by pressure rise.⇒ sporadically, uncontrollably, autocatalytically running reactions

Determination by calorimetric and spectroscopic methods:
Pressure and temperature rise are overlayed by the pyrolyse

Three steps:
segregation oscillation degradation

Low thermal conductivity Compensation by convection
UV/VIS spectrometry

Extinction-time curves of a cellulose/EMIMAc solution at 120°C, λ 400 nm.
Special designed calorimetric cell.
Changes in isoperibolic pressure of 11% cellulose solution in NMMO at 130°C over 400 min, 3 - 4 g sample mass

Wendler F., Graneß G., Project reports 2008/2010
Adiabatic calorimetry: Changes in isoperibolic pressure of 11% cellulose solution in NMMO at 110°C over 96 h. DEWAR vessel with 300 g sample mass
Adiabatic calorimetry: Changes in isoperibolic pressure of 11% cellulose solution in NMMO at 130°C over 96 h.
DEWAR vessel with 300 g sample mass
Adiabatic calorimetry: Changes in isoperibolic pressure of 11% cellulose solution in NMMO at 130°C over 96 h. DEWAR vessel with 300 g sample mass.
Target:

Dissolution of cellulose

and

to keep the cellulose in solution

under practical conditions:

Time

Temperature
Reasons for dissolution / segregations:

• Solution state
  Networks, gelic behavior

• Morphology
  Crystalline/amorphous regions, surface properties, porosity

• Ionic interactions
  Hydrogen-bond network (NMMO), complexations (LiCl/DMAc, Cuoxam, Cuen, FeTNa)
  Bechtold T., Manian A.P., Oeztürk H.B. et al. 2011. 2nd EPNOE conference, Wageningen, NL

• Amphiphilic character of cellulose
... more practical reasons:

- Time
  
  *Dwell time in reactor, tubes*

- Temperature

- Water content

- Cellulose concentration

- Type of cellulose
  
  *DP, MWD*

- Solvent
  
  *Co-solvent, purity*

- Stabilizers

- Functional additives
  
  *SAP, char coal, carbon black, ceramics, Ag NP*
Conclusions

Monitoring of Lyocell solutions ensures

Choice of appropriate raw materials

Spinning stability

Thermal stability

Requested fiber performance

Recyclability

Process efficiency
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