Methods for Chemical Modification of Nanocellulose

Alistair W. T. King (Docent, Laboratory of Organic Chemistry)

25.04.16 (COST FP1205 Training School, Stockholm, Sweden)
(Towards Sustainable) Methods for Chemical Modification of Nanocellulose

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Motivation to find new products/processes

Ionic Liquids – media for homogeneous processing

Homogeneous vs Traditional Heterogeneous Cellulose Modification

Sustainable Nanocellulose Modification Processes

Nanocellulose & Ionic Liquids (Modification / Analysis)
Finland & Bioeconomy

Finland (5.5 M people, ~75 % forest coverage)

Germany (~ 85 M people)
Fennoscandia – the richest in forest resources in Europe and in the whole world...

Finland
16 m³/person year

Sweden
10

Austria
2

EU average
1.2

e.g. Chile?

Ca. 3-4

Jyri-Pekka Mikkola – Åbo/Umeå
Fibre is the main product, lignin is mostly burnt

(Source: Kvaerner Pulping)

Juha Fiskari - Valmet
A. Stubb (the previous PM):

".. iPhone killed Nokia and the iPad killed the Finnish paper industry.."
Suomussalmi, Kainuu, Finland

Softwood is valued for its fibre-length
Softwood is valued for its fibre-length
Polymeric Feedstock Costs

Why is cellulose not use more extensively?

High purity grade of cellulose

Polymeric Feedstock Cost (€/ton)

- Brazilian Sugar Cane Bagasse: 14
- Bleached SW Kraft Pulp: 139
- Sulphite Dissolving Pulp (Sulicor): 655
- Polypropylene Granules: 810
- Polyethylene Granules: 650
- Polystyrene Granules: 1700
- Raw Argentina Cotton: 1730
- PMMA Sheet: 1450
- Kevlar Yarn: 12400
Why is cellulose not already used similar to petrochemical polymers?

- 1st Semi-Synthetic Polymer - Cellulose II (Textiles, Mercerisation - 1844)
- 1st Synthetic Plastic - Cellulose Nitrate (Parkesine, 1862)
- 1st regenerated cellulose fibre - CuproCellulose (‘Bemberg Silk’, 1897)
- Cellulose Xanthate (viscose/cellophane), CMC, MCC, Cellulose Acetate, etc.

- Cellulose does not have a melting point. Therefore….

  it cannot be melt-processed
Ionic Liquids
CELLULOSE DISSOLUTION: Important bonding interactions

What is an ionic liquid?

‘Ionic Liquids’ are essentially ‘molten salts’ containing one or more organic ions!

Unsolvated ‘Molten Salts’ (m.p.)

- NaCl  801 °C
- [mmim]Cl  125 °C
- [emim]Cl  87 °C
- [emim][NTf₂]  -3 °C
Why are Ionic Liquids Liquid?

Unsolvated ‘Molten Salts’ (m.p.)

- NaCl  801 °C
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Asymmetry, Diffusivity & Ion Size
Bonding Interactions in ILs

van der Waals (weak, short distance …. steric interaction)
H-bonding (strong, short distance…. ~ 2.4 Å)
Other dipolar interactions
Columbic (strong, long distance… up to 10 Å!)

Columbic Force \( \propto \frac{Z^+ Z^-}{r^2} \) (inv. Sq. dist.)

Long distance columbic interaction extends through the crystal or liquid and provides a strong cohesive force

High charge density gives high cohesive energy density (CED) and high hence enthalpy of vapourisation (\( \Delta H_V \))

\[
\partial = \sqrt{CED}
\]

\[
CED = \frac{\Delta H_V - RT}{V m}
\]
Distillable Acid-Base Conjugates

King et al. Angew. Chem., 2011, 50, 6301
[DBNH][OAc]: Suitable rheological properties

m.p. 63 °C

King et al. *Angew. Chem.*, 2011, 50, 6301
Parviainen et al. *ChemSusChem*, 2013, 6, 2161
IONCELL-F Process (ionic liquid-based lyocell process)
Fabrics and garments from IONCELL-F

**SCARF**
Nov. 2013

**DRESS**
Mar. 2014

**MEN’S ACCESSORIES**
Aug. 2014

Almost GPa tenacity Fibres! (~ 0.85 GPa)

Aalto University – Herbert Sixta
Chemical Processing
Homogeneous vs Heterogeneous Chemical Processes

- **Homogeneous (fine chemicals):**
  - Conditions: low temperature to avoid decomposition and vaporisation of components/solvent
  - Selectivity: fine control over reaction selectivity with reactant and catalyst choice
  - Separation: requires purification of components by phase-separation, distillation, chromatography, crystallisation (energy demanding)

- **Heterogeneous (bulk chemicals):**
  - Conditions: wide temperature and pressure ranges
  - Selectivity: poor tuneability giving fixed product quality/specifications
  - Separation: filtration (decantation) or distillation (low number of theoretical plates)
Heterogeneous Processing (Esterification): Cellulose Acetate (CTA)

Fibre surface is pre-activated with $\text{H}_2\text{SO}_4 \rightarrow \text{AcOH soluble Cell-OAc-SO}_4\text{H} \rightarrow \text{Transesterified with Ac}_2\text{O} \rightarrow \text{Insoluble CTA}$

Sassi & Chanzy, *Cellulose 1995*, 2, 111
Heterogeneous Processing (Etherification): Carboxymethyl Cellulose (CMC)

- Cellulose I → Na-Cell I/II
- Alcohols used to aid in penetration of the fibre
- 65-80 % yield, based on ClCH₂COOH with the rest hydrolysed
- Product produced in varying purity grades
- Water soluble dependent on DS
- Non-statistical (block-like) modification

Cellulose Ethers, Ullmann’s Encyclopedia of Industrial Chem.
Homogeneous Processing

- Cellulose can be dissolved to give isotropic mixtures in direct-dissolution solvents:
  - molten salts (alkylpyridinium chlorides)
  - ionic liquids ([DBNH][OAc], [amim]Cl, [emim][OAc])
  - electrolytes (LiCl/DMA, TBAF/DMSO, tetraalkylammonium hydroxides)
  - molecular solvents (H$_2$O-NMMO)

- As cellulose is already in solution (non-crystalline state) modification is **statistical**

- Drawback: polymers are precipitated with co-solvents which gives a major energy penalty when recovering the expensive direct-dissolution solvents
Homogeneous Processing

Friedrich Schiller University of Jena
Center of Excellence for Polysaccharide Research

Distribution of substituents

Repeating unit

Polymer chain

Significant influence on ether properties
New paths for regioselective etherification

Tim Liebert
Nanocellulose Production & Processing
Longitudinal order (crystallinity):
Fringed fibrillar model

Amorphous (Disordered) Regions

Crystalline Regions (Cellulose I)

Fibrillar Bundle

Eero Kontturi – Aalto University
Evidence for the Fringed Fibrillar Model?

Level-off degree of polymerization (LODP)


Eero Kontturi – Aalto University
How to make CNC’s (Cellulose Nanocrystals)

Fringed-Fibrillar Model

crystalline

amorphous

controlled acid hydrolysis

MCC

Tunicate

Cotton

Ramie


Eero Kontturi
How to make NFC’s (Nanofibrillar Celluloses)

- **TEMPO oxidation** followed by mechanical degradation for reduced energy consumption
  - Ultrasound Probe
  - Hydrodynamic cavitation
  - Masuko grinder
  - Microfluidiser
Nanocellulose (1-5 wt %)

The removal of water from these solutions is techno-economically challenging without aggregating the material.

Certain chemical modifications are impossible in presence of water.
Sustainable Surface Modifications
Various Methodologies

- Solvent Redispersion
- Reactive Ball Milling
- Activated intermediates
- Green Fischer Esterification (SolReact)
- Periodate Oxidation (aqueous based, reductive amination)
- Radical Reactions (polymer grafting, poor kinetic control)
- TEMPO Oxidation (C6-OH → COOH, aqueous based)
- Surface Adsorption & The ‘Double-Click’ Method
**Solvent Redispersion**

- HCl or H$_2$SO$_4$ digested, neutralised, filtered and **redispersed** in molecular solvents
- SO$_4$-TW were much easier to redisperse than the HCl-TW due to electrostatic repulsion
- Formic acid allows for formation of formate esters (labile).
- Potential for transesterification in the dispersed state

van den Berg, *Biomacromol.*, **2007**, *8*, 1353
Reactive Ball Milling

- Preparation of dispersed modified nanocelluloses directly from filter paper
- Synergistic action of mechanical treatment and ball milling
- Energy intensive

Activated Intermediates

- **Acid Chlorides & Isocyanates** (moderately expensive, corrosive, water sensitive)

- **Carbodiimides** (rather expensive, severe sensitizers, water sensitive)

- **Click Chemistry** (work in water but very expensive)

(Click Chemistry – Barry Sharpless)
‘Green’ Fischer Esterification (SolReact – Bras group*)

- Acid-catalysed esterification in a water-free melt of organoacids
- $\text{H}_2\text{SO}_4$ digestion of MCC
- Dialysis and pH adjust
- Excess organoacid
- Water evaporation
- Fischer esterification (130°C)
- EtOH dispersion/centrifugation

*Espino-Pérez et al. Biomacromol., 2014, 15, 4551
Periodate Oxidation (in water)

Radical Reactions (not quenched by water)

CNCs →

(i) Ceric Ammonium Nitrate & Nitric Acid
(ii) Methylmethacrylate (MMA)

PMMA-g-CNC’s

{n}

{n}

{n}

(nanostructure maintained!)

TEMPO Oxidation (in water)

- Applied to introduce electrostatic charge during NFC fibrillation
- Considerable energy reduction to produce NFC gels
- Also allows for introduction of COOH groups for further chemical modification

Isogai et al., *Nanoscale*, 2011, 3, 71–85
Surface Adsorption & the ‘Double-Click’ Method

Filpponen et al. Biomacromol., 2012, 13, 736

Still costly but cheap CMC modification may allow for application to a wide range of surfaces!
What about Ionic Liquids?

Neither dissolve cellulose!
IL’s as Additives during Water Removal from CNC’s

(80 °C/Rotary Evap. down to ~ 15 mbar)
CNC’s Regenerated from Ionic Liquid (Still Nano-scaled)

1 – CNC in TEGO P9
2 – CNC in [emim][OTf]

(DMF Added) (Precipitation – Poor Stabilisation)
IL’s as Additives during Water Removal from NFC

(80 °C/Rotary Evap. down to ~ 15 mbar)
NFC Regenerated from Ionic Liquid (Still Nano-scaled)

Some gelation but still suspended

3 – CNF in TEGO P9
4 – CNF in [emim][OTf]

(DMF Added)
Solution-State NMR Analysis of Nanocelluloses

Dissolve cellulose as the DMSO electrolytes!

(DMSO-d6, locking solvent)
Analysis of Nanocelluloses (typical techniques)

- Particle Size: light-scattering, AFM, SEM, TEM
- Charge: zeta potential, titration
- Degree of substitution, Regio- & Chemoselectivity of Modification
  - XPS – X-ray photoelectron spectroscopy (not quantitative, chemoselective)
  - $^{13}\text{C}$ CP-MAS NMR – $^{13}\text{C}$ Cross-Polarisation-Magic Angle Spinning (not quantitative, poor resolution)
  - ATR-IR – Attenuated total reflection IR (not quantitative, chemoselective)
  - Elemental Analysis (.........)
  - Solution-state NMR in ionic liquid electrolytes?
$^1\text{H NMR of MCC (in } [P_{8881}]\text{[OAc]/d6-DMSO)}$
$^1$H NMR of MCC in Electrolyte: Temp. Series (15 - 65 °C)

MCC (microcrystalline cellulose)

DP = ~90

$^1$H NMR of MCC Dissolved in Ionic Liquid Electrolyte

Polymeric AGU C1-\(^1\)H

Terminal Glu C1-\(^1\)H

Anomeric Glu C1-\(^1\)H (reducing end)

Model: PMMA-grafted-CNCs

CNCs (i) Ceric Ammonium Nitrate & Nitric Acid
(ii) Methylmethacrylate (MMA)

PMMA-g-CNC’s

(nanostructure maintained!)

DEPT-Edited HSQC (PMMA-grafted CNCs)
Diffusion-Ordered Spectroscopy (DOSY) Gradient Array

\[ [P_{4444}]OAc \] alpha CH\(_2\) (low MW – fast diffusion)

Cellulose C1 (Polymeric – slow diffusion)

DMSO
DOSY Gradient Array (scaled to maximum peak)

Polymer peaks Increase

Ionic Liquid Peaks Decrease
Diffusion-filtered HSQC & Truncated FID
Conclusions

• Methods for water-free modification of nanocelluloses are in demand. Alternatively we should expand the scope of reactions that work in water.

• By correct choice of ionic liquid you can do ‘high-resolution’ solution-state NMR on nanocelluloses (process optimisation)

• By avoiding dissolution you can stabilise nanocelluloses during drying. This affords the opportunity to do water free chemical modifications
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