Optimising the preparatory step of cellulose nanocrystal production

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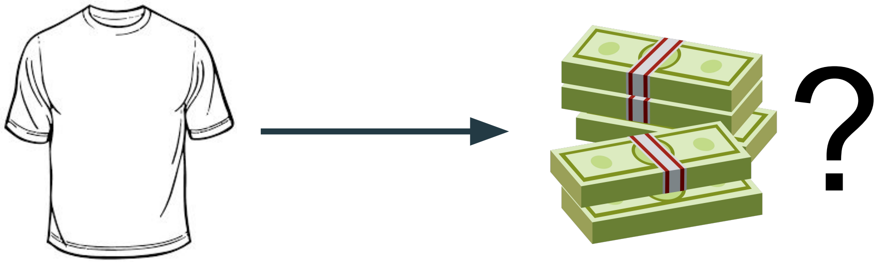
Introduction

- Textile waste is a global problem
  - Europe: 11 kg/person/year
  - 20% is cotton, 65% is polyester
  - Only 1% of all global textile waste is recycled
- EU Strategy for Sustainable and Circular Textiles (2022)
  - Design requirements for textiles
  - Tighter controls on greenwashing
  - Address unintentional release of microplastics through textiles
  - Support to research, innovation, and investments

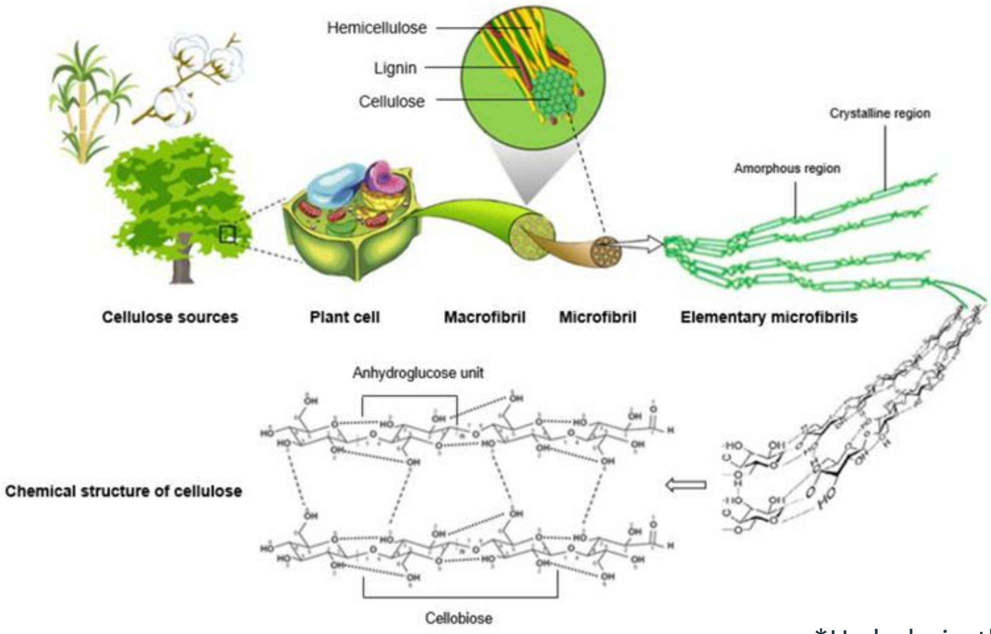
Can an old cotton t-shirt be used as a raw material for valuable products?



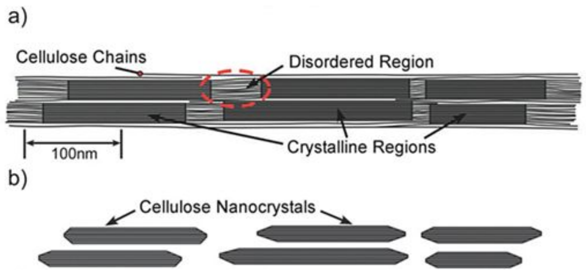
Cellulose

- Cellulose is the most abundant natural polymer on Earth, and it is the main constituent in wood, cotton, and many other plants
- Cellulose is inherently biobased, biodegradable, and compostable. It is also chemically stable, colourless, odourless, non-toxic, and biocompatible
- 140 million metric tonnes of cellulosic pulp is produced annually, mainly from wood. Waste textiles would supply more cellulose.
- Commonly used cellulosic products include paper and cardboard, while novel products include textile fibres, biomedical implants, and microelectronics.
- “The raw material of the future”

Cellulose nanocrystals, CNCs



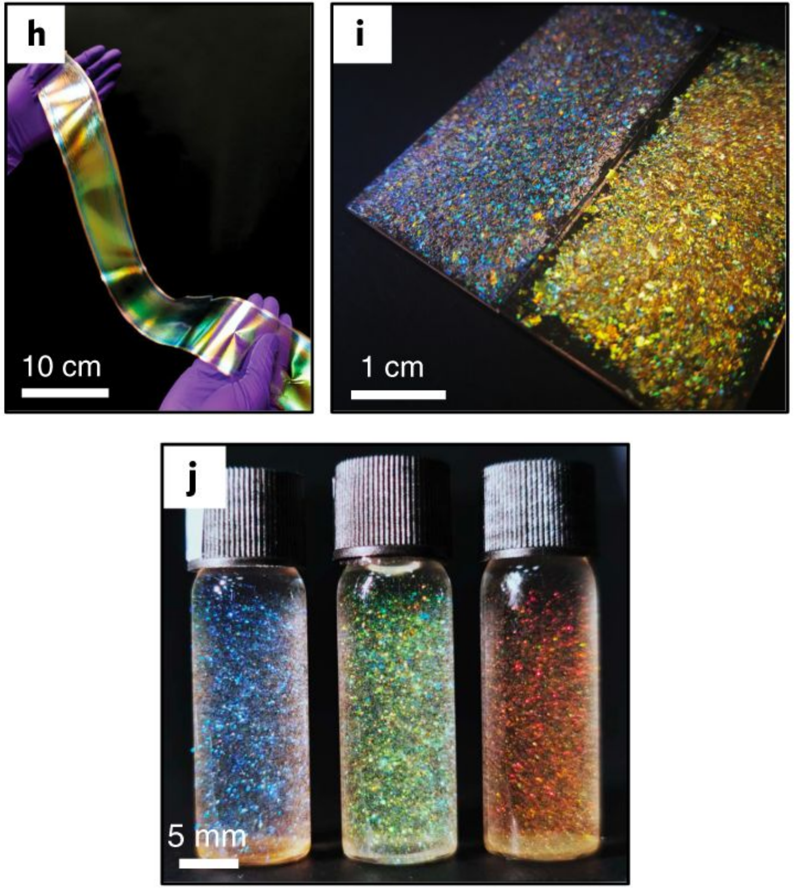
- Cellulose is the main structural component of plant cells, making up most of the cell wall
- Cellulose nanocrystals are crystalline sections of nanofibrils and can be separated by acid hydrolysis*
- The large variety of applications is due to the properties of CNCs: they are hydrophilic, colloidally stable, have a high tensile strength and a large surface area



*Hydrolysis: the breakdown of chemical bonds using water molecules

Applications of CNCs

- Structurally coloured composite films
  - Biodegradable and biobased glitter
- Biomedical applications
  - Medical implants
  - 3d printed artificial blood vessels
  - Antimicrobial membranes
- Bulletproof vests
- Superglue
- Solar cells
- Selective membranes
- Practically anything and everything!



Acid hydrolysis

Old method: aqueous sulphuric acid

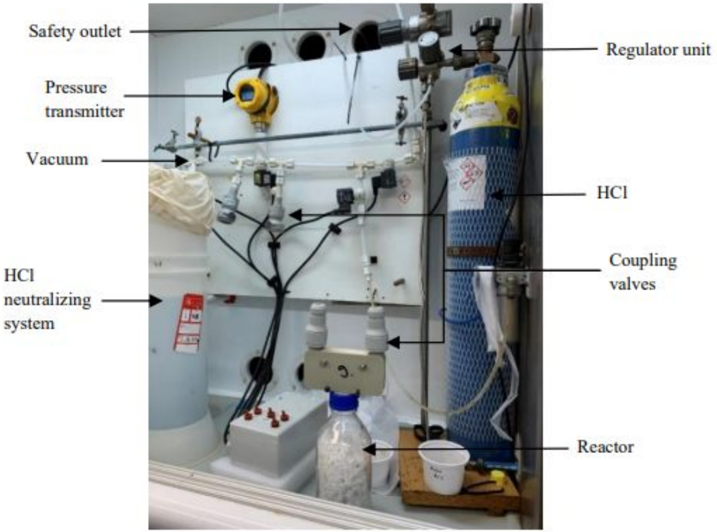
- Effectively degrades cellulose
- High concentration required, >62% but generally >72% is used
- High concentrations make the chemical recovery challenging
- Product must be washed extensively and thoroughly
- High water consumption

New method: gaseous hydrochloric acid

- Developed in Aalto University, 2018
- Gas-phase processing
- Hydrolysed product is easy to separate and purify - the acid is only temporarily adsorbed onto the fibres
- Chemical recycling is relatively simple
- Lower water and chemical consumption

Some things were done for the first time ever in my investigation – waste textiles have never before been used as the starting material for HCl gas hydrolysis, nor has it been combined with an alkaline pre-treatment. I wanted to see if it was possible to make a method that is already great even better.

Experimental setup and method



1. Preparation of the cotton samples
   a. A white, 100% cotton t-shirt was ground by a mill into a fine powder
2. Pre-treatment
   a. Half of the powdered cotton was mixed into a 1M NaOH solution and left to soak for 90 minutes
   b. The sample was washed with excess ion-exchanged water and left to dry
3. HCl gas hydrolysis
   a. The untreated cotton pulp was placed into a glass pressure bottle and HCl gas was added until the pressure inside the bottle reached 1 bar. The pressured bottle was left overnight after which the cotton was washed.
   b. Repeated with the pre-treated sample.
4. Viscometry
   a. Small samples of each condition were mixed with 25 cm^3 of deionized water and 25 cm^3 of a cupriethylenediamine solution.
   b. The solution viscosity was measured with a capillary viscometer
5. Microscope imaging

Example calculation

The Mark-Houwink-Sakurada equation describes the relationship between the intrinsic viscosity and the degree of polymerisation. The values of the constants for the cupriethylenediamine solution used are found in the standard ISO 5351:2004.

Mark-Houwink-Sakurada equation: $\boldsymbol{\eta = Q'DP^a}$
where Q' = 2.28 and a = 0.76 when DP > 950;
and Q' = 0.42 and a = 1 when DP < 950

$$DP = \sqrt[a]{\frac{\eta}{Q'}}$$

1. *M-H-S equation for DP > 950:* $Viscosity = 2.28 \times DP^{0.76} \rightarrow DP = \left(\frac{viscosity}{2.28}\right)^{\frac{1}{0.76}}$
   a. $DP = \left(\frac{470.905}{2.28}\right)^{\frac{1}{0.76}} = 1111.86$
2. *M-H-S equation for DP < 950:* $Viscosity = 0.42 \times DP \rightarrow DP = \frac{viscosity}{0.42}$
   a. $DP = \frac{470.905}{0.42} = 1121.20$
   b. *This value is ignored, as the DP is above 950*

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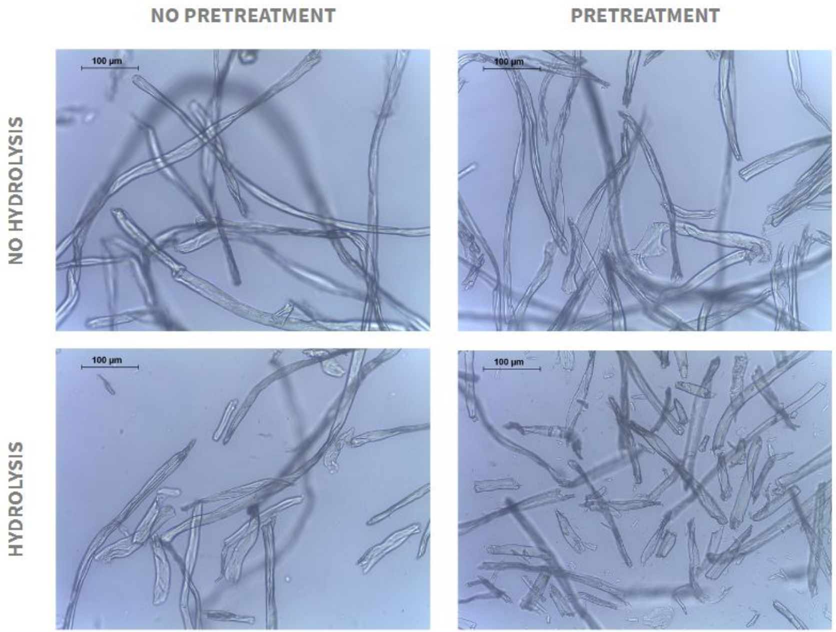
1. η_{ratio} = *Time taken in viscometer × calibration value for CED*
   a. $t = 51.73$
   b. $calibration = 0.1008$
   c. $\eta_{ratio} = 51.73 \times 0.1008 = 5.21$
2. *[η]c values corresponding to* η_{ratio} *from ISO 5351:2004*
   a. $5.21 \rightarrow 2.185$
3. *Viscosity = [η]c × volume of solution ÷ mass of dry pulp (Tab*
   a. *Viscosity = 2.185 × 50 ml ÷ 0.232 = 470.905*

Results



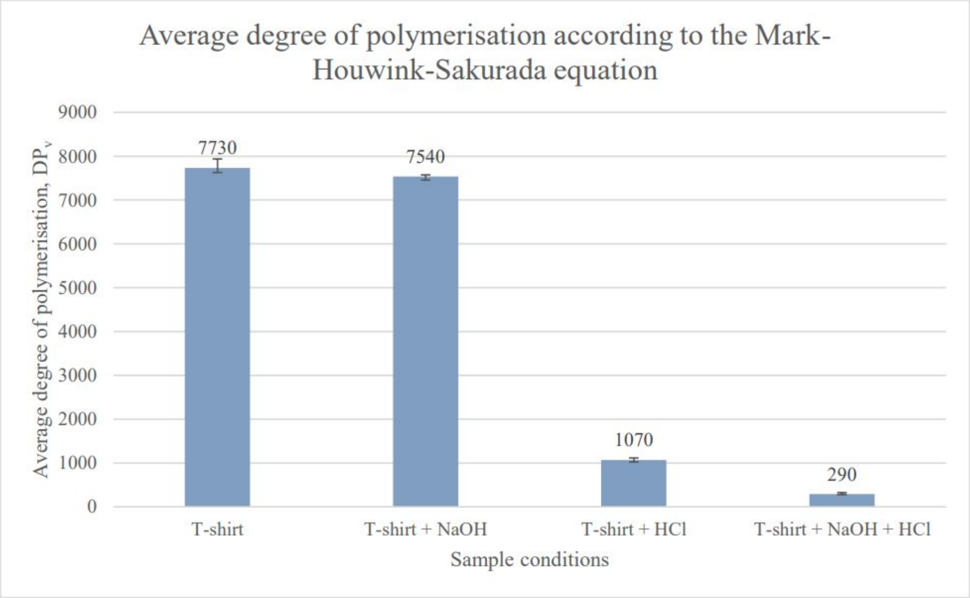
The microscope images show the visible breakdown of the polymers, as the difference between the length of the fibres can be seen.

- Top row: the samples that have not undergone the gas hydrolysis
- Bottom row: the hydrolysed samples
- Left column: samples without the pre-treatment
- Right column: samples with the pre-treatment

From these images, it is clear that the pre-treated and hydrolysed sample (bottom right image) was broken down the most.

The alkaline pre-treatment induces swelling and fibrillation of the cotton fibres, meaning that the HCl treatment was more efficient for the pre-treated fibres.

Results



The degree of polymerisation is a unitless value that represents the length of the cellulose polymer chains.

- The untreated waste cotton has a very high degree of polymerisation
- The alkaline pre-treatment decreased the viscosity (and thus the degree of polymerisation) only slightly
- The acid hydrolysis broke down the cellulose structure
- The impact of the alkaline pre-treatment was remarkable for the acid hydrolysis

Results

Sample	Degree of polymerisation					Standard deviation
	Trial 1	Trial 2	Trial 3	Trial 4	Average	
T-shirt	7640	7628	7716	7938	7730	124.59
T-shirt + NaOH	7561	7561	7572	7454	7537	48.33
T-shirt + HCl	1112	1018	1081	1056	1067	34.26
T-shirt + NaOH + HCl	277	277	282	325	290	20.25

Conclusions:

- Waste cotton can be depolymerised efficiently with the novel HCl hydrolysis method
- The alkaline pre-treatment enhances the hydrolysis substantially
- Further studies are needed to confirm the characteristics of cotton-based cellulose nanocrystals and their applications
- Waste cotton *is* suitable for CNC production

Next steps:

- Detailed analysis of the cellulose nanocrystals produced using waste cotton
- Comparison to the CNCs produced from bacterial and wood cellulose
- Usage of waste-cotton derived CNCs in new applications

Thank you!