

EXTRACTION OF NANOCRYSTALLINE CELLULOSE FROM BAGASSE: AN OVERVIEW

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1. INTRODUCTION

Nanotechnology is the study of the physical (optical and mechanical) and the chemical (melting/ boiling points, reactivity) properties of materials with dimensions ranging between 1-100nm, where unique phenomena enable novel applications. Nanomaterials from cellulose and lignocelluloses play a large role in the nanotechnology field. The development of nanocellulose (both cellulose nanofibers, CNFs and cellulose nanocrystals, CNC) has attracted significant interest in the last few decades due to the unique characteristics they exhibit.

The Young's modulus of nanocellulose with a density for crystalline cellulose of around 1.5–1.6 g cm⁻³ is much higher than the one of glass fibres, around 70 GPa [1] with a density around 2.6 g cm⁻³, which are classically used in composite applications. It is similar to Kevlar (60–125 GPa, density around 1.45 g cm⁻³) [2] and potentially stronger than steel (200–220 GPa, density around 8 g cm⁻³) [3]. Young's modulus, which is the ratio between the Young's modulus and the density, of nanocellulose is around 65 J g⁻¹ for microfibrils and 85 J g⁻¹ for nanocrystals whereas it is around 25 J g⁻¹ for steel [4]. Its tensile strength is about 7500MPa which is greater than that of carbon fiber. Furthermore, cellulose nanoparticles have a strong tendency for self-association because of the omnipresence of interacting surface hydroxyl groups which enables these particles to form load-bearing percolating architectures within the host polymer matrix. Once dehydrated and chemically treated, nanocellulose can form films (which possess remarkable gas barrier properties) and moreover, the low permeability of cellulose can be enhanced by the highly crystalline nature of cellulose nanoparticles and their ability to form a dense percolating network. Provided that strong particle-polymer molecular interactions exist, the smaller particles have a greater [4].

2. SUGGESTED METHODS

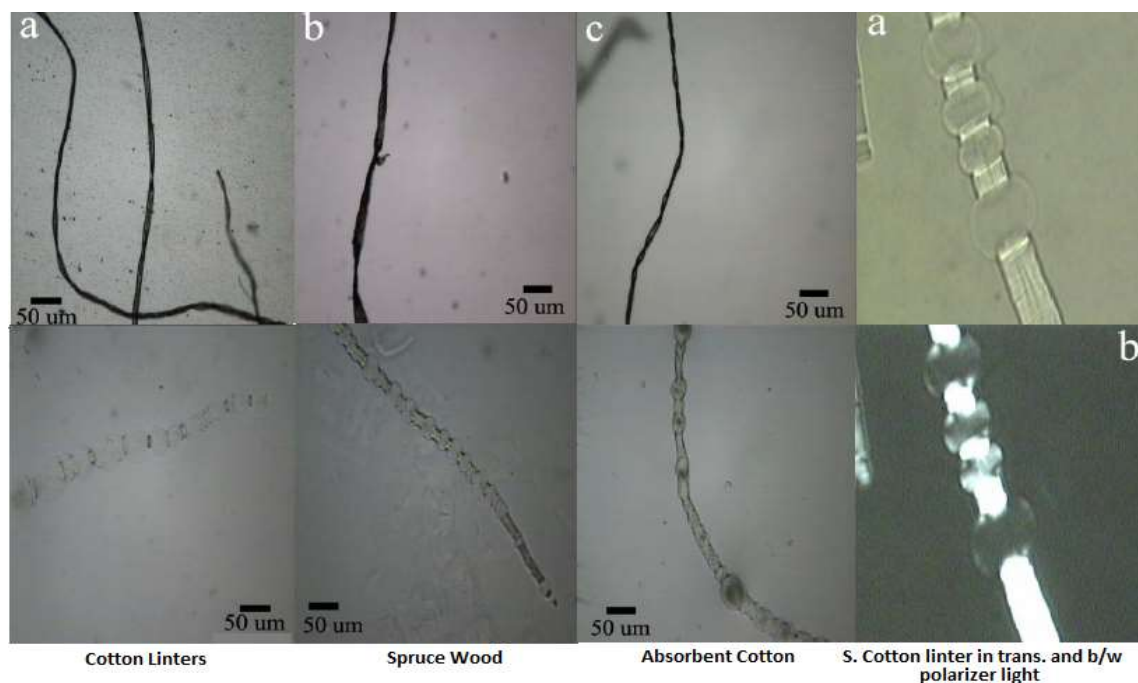
2.1 GENERATION OF NANOCELL.

This section focuses on the generation of nanocellulose from regenerated cellulose fibers (from bagasse). The first suggested method is involves swelling of cellulose with 8%- solution of NaOH [5], whereas the second suggested method relies on the complete dissolution of cellulose in NaOH.

2.1.1 SWELLING OF CELLULOSE

Swelling refers to the increase of volume of material due to absorption of a solvent (common for polymers). Since the focus of this study is cellulose, the preferable solvent for the swelling process is sodium hydroxide. Because cellulose is relatively less soluble in NaOH (relative to other solvents such as NMMO N-Methylmorpholine N-oxide), it is ideal for the swelling process. The swelling of cellulose fibers in NaOH as studied in [5] is a spectacular process with the formation of "balloons". Cellulose fibers from cotton linters, spruce wood and absorbent cotton were chosen in the experiment reviewed in this study. Segregated fibers were taped to a glass plate so as to immobilize them/avoid entanglement and drops of 8%-NaOH solution were placed on the plate in a manner such that the fibers were immersed in the solution. The swelling process was closely monitored using an optical microscope in transmitted light.

"It has been found that the solvents based on NaOH/H₂O do not swell the balloons so much, and they do not make balloons burst (Fig. 1). The balloons reach a certain maximum expansion, smaller than the one of mode 2, and the process stops. The fiber stays like this without dissolving completely. This will be the case for NaOH aqueous solution at -10 °C, similar to NMMO/H₂O at 90 °C, with water contents between 25 and 30%. The swelling mechanism of cellulose fibers in NaOH/H₂O shows that the solvent is not very good.

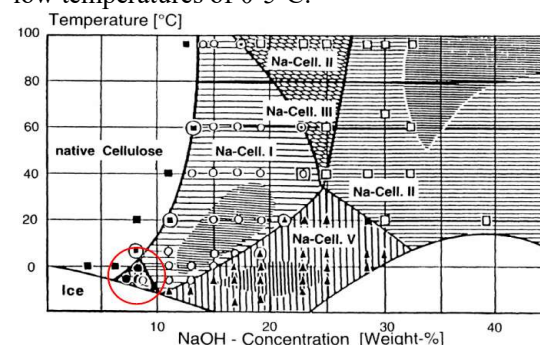


Only cellulose of low DP, like microcrystalline cellulose, can be nearly fully dissolved, with very few insoluble particles present. As soon as cellulose fibers of larger DP that have kept their original structure are put in contact with this solvent, only the cellulose present in the balloons is dissolved. The cellulose solution can be collected when the balloons are mechanically broken during mixing, which is not the case in the type of experiments that are performed here under the microscope. The membrane and the non-swollen sections cannot dissolve, that is, the cellulose fiber is a mixture of dissolved (inside of the balloon) and non-dissolved (non-swollen section and membrane) cellulose parts. It can be deduced from the POM (polarized optical microscope) image of the swollen fiber that the balloons of the fiber were in amorphous state, while the connection areas were still undissolved and in crystalline state. Moreover, at ambient temperature ($>0^{\circ}\text{C}$),

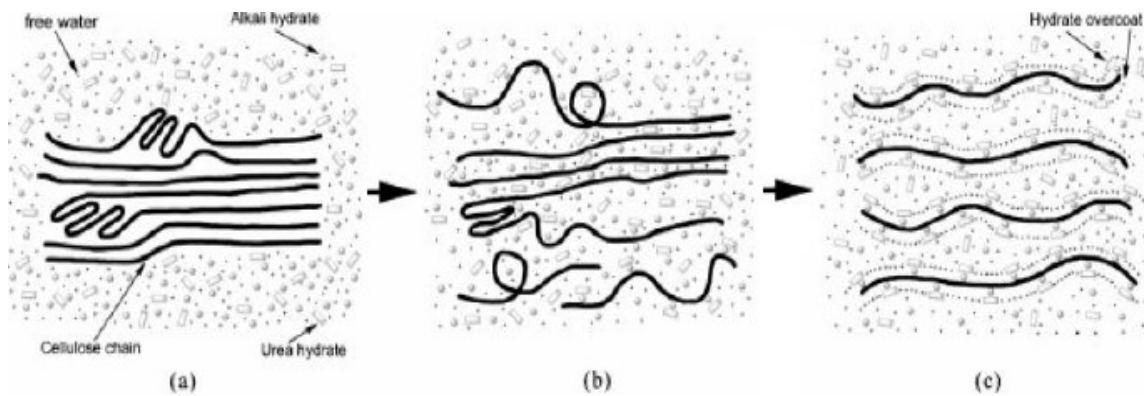
cotton and wood fibers swell homogeneously with no balloon. This seems to indicate that decreasing the temperature below 0°C increases the quality of the solvent. It can be concluded that NaOH on its own does not seem to be the best solvent and it certainly cannot replace powerful organic solvents. It can only partially dissolve celluloses with low DP.”^[5]

2.1.2 SOLUTION OF CELLULOSE

Cellulose is a material that degrades structurally instead of undergoing a phase change. Strong intra- and inter-molecular hydrogen bonds in cellulose prevent its molecules from dissolution in most common solvents. Among a few, NaOH solution can act as a solvent for cellulose of low degree of polymerization (DP) ^[6] at low temperatures and low concentrations. As indicated in the research article [7], NaOH solution can act as a “perfect” solvent for cellulose between the concentration of 8-10% at low temperatures of $0-5^{\circ}\text{C}$.



“NaOH can cause cellulose to swell and in a narrow range of the phase diagram, even can dissolve cellulose. It was found that for low to moderate DP cellulose, the maximal solubility occurs with 8-10% soda solution. Soda hydrates can penetrate the amorphous area of cellulose, then solvate to cellulose and destruct the neighbouring crystalline regions.”



Though NaOH may act as a standalone solvent for cellulose, it has been established that upon the addition of other compounds, the solubility of cellulose in NaOH is increased tremendously. In article [5], The swelling and dissolution treatments were performed with mixtures of sodium hydroxide (NaOH) and water, with or without additives. NaOH–water is a mixture containing 8% (in weight) of NaOH. Two types of mixtures containing additives were prepared with 8% NaOH–water:

– thiourea: mixtures (in w/w) with thiourea as an additive were tested: NaOH (8%), thiourea (6.5%), water (85.5%).

– urea and thiourea: mixtures (in w/w) with thiourea and urea as additives were tested: NaOH (8%), urea (8%), thiourea (6.5%), water (77.5%).

The behaviour of cellulose fibers dissolving in NaOH/thiourea/H₂O is a four step process (mode 2):

- Phase 1: balloon formation
- Phase 2: balloon dissolution
- Phase 3: dissolution of the unswollen sections
- Phase 4: dissolution of the balloon membrane scraps.

This will be the case, for NaOH/thiourea aqueous solution at -10 °C. The zones where the swelling starts increase their size and the fiber has a series of swollen transparent balloons. These balloons grow until they reach a maximum size at which they burst. The balloon will burst when the membrane is not able to sustain the pressure inside the balloon. The whole fiber will then dissolve.

The mechanism of dissolution is schematically depicted in the figure above.

“The mechanism is that NaOH hydrates - urea hydrates - free water - cellulose form a special complex in the solution. NaOH or LiOH destroys inter- and intra- hydrogen bonds between cellulose molecules and urea hydrates function as hydrogen bonding donor and receptor between solvent molecules and prevent the reassociation of cellulose molecules, thus leading to molecular dissolution of cellulose”^[7]

2.2 SEPERATION METHOD.

The suggested method for the extraction of nanocellulose formed in the mentioned methods of generation of nanofibrils and nanocrystals is electrolysis. This method is chosen because of the following reasons:

- Electrolysis of NaOH solution would increase the concentration of the solution as the H₂O molecules are extracted from the solution as Hydrogen and Oxygen at the cathode and the anode respectively.
- A net dipole would develop on the cellulose fibers as they are broken into smaller fibers/crystals (also because the pre-existing hydrogen bonds are broken).
- Collection of nanocellulose shall be easier as the fibrils and crystals would migrate of either of the electrodes depending of their net charge

3. EXPERIMENTAL METHOD

3.1 AIM OF THE EXPERIMENT.

The motive behind this study is to extract nanofibrils and nanocrystals from cellulose. For the purpose of extraction of nanocrystals by the method of swelling cellulose, cotton is used as a source of cellulose. This is so since cotton has a very high degree of polymerization and hence it would not completely dissolve in the NaOH solution. And for the purpose of extraction of nanofibrils of cellulose by dissolution of cellulose, bagasse will be used as a source of cellulose. Cellulose will first be extracted from bagasse by using Soda Pulping and then dissolved in NaOH. This is done so as to ensure that all the cellulose dissolves in NaOH (owing to its low DP)

3.2 EXPERIMENTAL PROTOCOL.

3.2.1 CELLULOSE NANOCRYSTALS

Cotton (considered to be pure cellulose) is used for this procedure owing to its high DP hence allowing fibers only to swell and not dissolve in NaOH.

NaOH solution of (8%, 100ml) is freshly prepared and ~30g of cotton is immersed in it for 24 hours at 0-5°C. The collected swelled cellulose is then washed with distilled water until a neutral pH is obtained. The swelled system is pulverized into a grinder as a wet suspension. This form of mechanical agitation shall break the outer membrane of primary wall to burst and the undissolved crystalline cellulose would be suspended in a slurry of cellulose-NaOH solution system. Upon the application of an electric potential across the solution, the crystals would migrate to either of the electrodes and be collected for analysis.

3.2.2 CELLULOSE NANOFIBERS

The process of extraction is similar to that described above but instead of using a cellulose source of high DP, cellulose of low DP shall be utilized here. For this purpose, cellulose is extracted from finely divided bagasse.

4. REFERENCES

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