Production of regenerated nanocomposite fibers based on cellulose and their use in all-cellulose composites

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Materials Engineering, master's level
2017

Luleå University of Technology
Department of Engineering Sciences and Mathematics
Production of regenerated nanocomposite fibers based on cellulose and their use in all-cellulose composites

A THESIS SUBMITTED TO LULEÅ UNIVERSITY OF TECHNOLOGY AND UNIVERSITY OF OULU FOR THE DEGREE OF MASTER’S IN COMPOSITE MATERIALS

Material science & engineering department

Supervisor:
Prof. Kristiina Oksman

Andrés García Vogel

Luleå, 25.06.17
Acknowledgements

I would like to take this opportunity to thank all the wonderful people that have made the completion of this master thesis possible.

In first place, I would like to express my gratitude to my supervisor Prof. Kristiina Oksman for her generosity, constant advice, encouragement and endless help. I am highly indebted to you and Luleå University of Technology.

Moreover, I express my thanks to all the people in the wood and bionanocomposites, as well as materials department who were always willing to help me.

Last but not the least, I express my heartfelt thanks to my friends and family.

Thank you!

[Signature]
Abstract

Biobased all-cellulose composites (ACCs), in which the matrix and the reinforcement are made out of the same material, have gained a noticeable increased attention in recent years. Their successful application would solve the commonly faced challenges with natural fiber composites regarding their chemical antipathy between the hydrophilic fiber and the usually hydrophobic polymer matrix, while still keeping the advantages of being environmental friendly. Moreover, the use of man-made continuous regenerated cellulose fibers for this purpose could result in unidirectional all-cellulose composites with excellent mechanical properties. In this study, a new processing technique for unidirectional all-cellulose composites, reinforced with continuous regenerated cellulose nanocomposite fibers, has been developed, where the fibers are wound directly after the coagulation bath and then welded together while still being swelled in order to form all-cellulose composite sheets without the need of adding any additional solvent or chemicals. Scanning electron microscopy and tensile testing were used to investigate and compare the microstructure and mechanical properties, of a reference material without nanoreinforced fibers and two variants reinforced with 2 % cellulose nanocrystals (CNCs) and 2 % halloysite nanotubes (HNTs). Analysis revealed that transparent all-cellulose composites with a high compaction degree and minimal warpage during shrinkage, showing high mechanical properties could be made. However, the addition of nanoreinforcements did not lead to any improvements.
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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACC</td>
<td>All-cellulose composite</td>
</tr>
<tr>
<td>BMIMAc</td>
<td>1-Butyl-3-methylimidazolium</td>
</tr>
<tr>
<td>CNC</td>
<td>Cellulose nanocrystal</td>
</tr>
<tr>
<td>CNW</td>
<td>Cellulose nanowhisker</td>
</tr>
<tr>
<td>DP</td>
<td>Degree of polymerization</td>
</tr>
<tr>
<td>FRC</td>
<td>Fiber reinforced composite</td>
</tr>
<tr>
<td>HNT</td>
<td>Halloysite nanotube</td>
</tr>
<tr>
<td>IL</td>
<td>Ionic liquid</td>
</tr>
<tr>
<td>LiCl/DMAC</td>
<td>Lithium chloride N,N-dimethylacetamide</td>
</tr>
<tr>
<td>LTU</td>
<td>Luleå University of Technology</td>
</tr>
<tr>
<td>MCC</td>
<td>Microcrystalline cellulose</td>
</tr>
<tr>
<td>ML</td>
<td>Middle lamella</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium hydroxide</td>
</tr>
<tr>
<td>NMMO</td>
<td>N-methylmorpholine-(N)-oxide</td>
</tr>
<tr>
<td>P</td>
<td>Primary layer</td>
</tr>
<tr>
<td>S</td>
<td>Secondary layer</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SIP</td>
<td>Solvent infusion process</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>VARTM</td>
<td>Vacuum assisted resin transfer moulding</td>
</tr>
</tbody>
</table>
1. Introduction

A composite material is by definition a material consisting of two or more distinctive phases, with the aim of getting the best properties of both materials. Usually there is a harder and stronger discontinuous part, also termed reinforcement, and a continuous part called matrix [1]. The main advantage of fiber reinforced composites (FRCs) is that they offer low density combined with high mechanical properties. No wonder, they have been used in many applications, even in those which require high performance, such as aircraft or automobile industry, and that the market is keeping growing [2]. A good example therefore is the new Airbus A350 XWB, which structural components are made up to 53 % out of composites, resulting in a fuel consumption reduction of 25 % compared to previous models [3].

However, as a result of greater global environmental awareness and running out fossil fuels the demand for “greener” materials with lower environmental impact than traditionally used FRCs has raised in recent years. Consequently, the interest in natural fiber composites (NFCs), also referred to as “biocomposites”, has received a significantly increased attention. Natural fibers, which can be obtained from plant, animal or mineral sources, are from inexpensive nature, environmental friendly and compete well in terms of strength per weight, compared to synthetic fibers [4-6]. Regardless, there is still a lot of work to do in order to be able to compete on an equal footing with most synthetic fibers.

The main challenge with natural fibers is probably to bring out their full potential. Firstly, due to the fact that natural fibers are commonly uneven and short, which means they need to be twisted into yarns to form continuous aligned long fibers. This twisting results in decreased mechanical properties of the yarn compared to the single fiber and makes the impregnation, as well as the compaction of the final composite more challenging [7-8]. This problem could be solved by using regenerated cellulose fibers, man-made cellulosic fibers that can be spun to continuous fibers with uniform dimensions and with properties in the range of common natural fibers.

Secondly, because of the chemically bonding incompatibility between the hydrophilic natural fibers and the usual non-polar polymers, resulting in a bad interface and therefore lower mechanical properties, as a consequence of an inefficient load transfer [9]. Therefore, there has been a new trend towards single polymer composites, to be more precise so called all-cellulose composites, concept which was reported for the first time by Nishino et al. [10], where matrix and reinforcement are made out of the same material, overcoming hereby the bonding incompatibly problem.

In the present study, regenerated cellulose nanocomposite fibers, reinforced with cellulose nanocrystals (CNCs) and halloysite nanotubes (HNTs) will be used as raw materials to prepare all-cellulose composites.
1.1. Background of the project

Within the scope of a project course carried out at LTU from 01.09.2016 till 12.01.17, regenerated cellulose nanocomposite fibers reinforced with cellulose nanocrystals (CNCs) and halloysite nanotubes (HNTs) were successfully manufactured via wet spinning technique. Both nanoreinforcement materials lead to considerable mechanical properties improvements (Table 1.1). Best results were obtained at 2 % reinforcement load. By adding 2 % of CNCs (w/w, in respect to the weight of dissolved cellulose), the stiffness and tensile strength were enhanced by 36 % and 30 %, respectively. In the case of HNTs, elastic modulus could be improved by 57 % and strength by 45 % at 2 % HNT. LiCl/DMAc was used as solvent.

<table>
<thead>
<tr>
<th>Material</th>
<th>Young’s modulus (GPa)</th>
<th>Tensile strength (MPa)</th>
<th>Strain at break (%)</th>
<th>Diameter (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref</td>
<td>11.8 ± 1.0</td>
<td>265 ± 25</td>
<td>11.1 ± 1.7</td>
<td>79 ± 6</td>
</tr>
<tr>
<td>2 CNC</td>
<td>16.0 ± 0.8</td>
<td>345 ± 11</td>
<td>9.3 ± 2.4</td>
<td>61 ± 3</td>
</tr>
<tr>
<td>5 CNC</td>
<td>14.5 ± 1.0</td>
<td>300 ± 08</td>
<td>8.0 ± 1.0</td>
<td>75 ± 6</td>
</tr>
<tr>
<td>10 CNC</td>
<td>9.7 ± 1.4</td>
<td>204 ± 28</td>
<td>8.6 ± 1.6</td>
<td>82 ± 9</td>
</tr>
<tr>
<td>20 CNC</td>
<td>7.5 ± 1.7</td>
<td>161 ± 49</td>
<td>10.3 ± 2.0</td>
<td>93 ± 14</td>
</tr>
<tr>
<td>2 HNT</td>
<td>18.5 ± 2.1</td>
<td>384 ± 33</td>
<td>8.3 ± 1.4</td>
<td>55 ± 3</td>
</tr>
<tr>
<td>5 HNT</td>
<td>18.4 ± 1.5</td>
<td>345 ± 30</td>
<td>7.5 ± 0.8</td>
<td>61 ± 3</td>
</tr>
<tr>
<td>10 HNT</td>
<td>17.8 ± 3.0</td>
<td>364 ± 44</td>
<td>8.2 ± 0.4</td>
<td>66 ± 4</td>
</tr>
<tr>
<td>20 HNT</td>
<td>16.8 ± 1.6</td>
<td>305 ± 33</td>
<td>7.4 ± 0.9</td>
<td>65 ± 4</td>
</tr>
</tbody>
</table>

1.2. Objectives and outline of the project

The aim of the present study is to develop lightweight composites with unidirectional cellulose fibers without a matrix polymer, so called all-cellulose composites with excellent mechanical properties. Cellulose nanocomposite fibers reinforced with CNCs and HNTs, will be prepared by means of wet spinning as shown in the previous project course and used as reinforcement. The concept, processing parameters, as well as mechanical properties and characteristics will be provide.
Original plan:

- Part 1 (Manufacturing): Wet spinning of the fibers at Karlstad University (collaboration)
- Part 2 (Manufacturing): Filament winding of dry preforms at LTC Sport in Finland (collaboration)
- Part 3 (Manufacturing): Compression moulding of the composites sheets at University of Oulu
- Part 4: Study of mechanical properties (tensile testing), as well as morphological structure (SEM) at Luleå University of Technology

Due to time and equipment limitations at Karlstad University, see chapter 4 “Manufacturing Part I (Karlstad University)”, the whole manufacturing part was moved to Luleå University of Technology. However, during the first try outs at Karlstad University a new possible manufacturing method of all-cellulose composites was found where fibers are pressed together right after the solvent removal while still being in a wet state, see chapter 5 “Manufacturing Part II (Luleå University of Technology). Based on these results a new project plan was drawn.

New plan:

- Part 1 (Manufacturing): Wet spinning of the fibers at Luleå University of Technology*.
- Part 3 (Manufacturing): Compression of the all-cellulose composites tapes at Luleå University of Technology**.
- Part 3: Study of mechanical properties (tensile testing), as well as morphological structure (SEM) at Luleå University of Technology

* Carriage for the fibers has to be build and proper spinning parameters have to be found (extrusion and uptake speed)
** Hot press mould for tapes has to be manufactured and proper compression parameters have to be found (pressure, temperature, time)
2. Theoretical background

2.1. Cellulose

Cellulose \textit{(Latin: rich in small cells)} is by far the most abundant and used organic compound on the planet \cite{4,11}. It is the principal constituent and structural component in plants, which main function is to provide them the needed strength, rigidity and mechanical support in order to stand upright and grow. Cellulose is still primary obtained from cotton, which has about 90% cellulose content and wood with 40-50 % cellulose content \cite{11-12}. However, the market of bast fibers, such as hemp, sisal or flax, showing cellulose contents between 70-80 %, has been witnessing a strong grow in recent years \cite{13}. Besides the mentioned sources, cellulose can also be found in several bacterial species, fungi, algae and tunicates \cite{14}. Its application ranges from board, paper and textile over pharmaceutical purposes to fibers and composite materials \cite{13,15-16}.

2.1.1. Cellulose structure

By starting with looking at a molecular level, cellulose reveals itself as a linear syndiotactic polymer composed of repeating D-anhydroglucopyranose units connected to each other by $\beta$-1,4-glycosidic bonds. Depending on the origin of the material the amount of monomeric units, also known as degree of polymerization (DP), will alter between 10 000 and 15 000 \cite{17,18}.

Due to the presence of hydroxyl groups and oxygens in every repeating unit, hydrogen bonds are formed between neighbouring monomers, see Figure 2.1 \cite{19}. This intrachain bonding, which promotes the stabilization of the network and allows a linear configuration of the polymer chain, plays a major role in the physical properties of cellulose \cite{18}. Together with van der Waals bonds the stacking up of several cellulose chains will be enhanced during the natural synthesis process of cellulose, resulting in the creation of elementary fibrils \cite{18}. These elementary fibrils on the other hand will aggregate together, in order to form larger microfibrils \cite{18}. Both, disordered regions (amorphous) and regions with highly ordered structure (crystalline) can be found within these fibrils \cite{19}. The latter, are the main responsible for the good mechanical properties, like high axial stiffness, of cellulose.
Theoretical background

So far only the molecular level of cellulose has been described. However, Figure 2.2 shows the multiscale hierarchical structure of wood. As mentioned before cellulose chains (i) will be attached to each other by van der Waals and hydrogen bonds, and form microfibrils (ii). These microfibrils (5-50 nm in diameter and several microns in length [18]) are again helically wound within the different layers of the cell wall (iv) [20]. The cell wall itself shows a complex composite structure, surrounded by middle lamella (ML) in the exterior, an intercellular region which binds the neighbouring cells together and by lumen, a void space, in the interior [21]. Furthermore, four cell wall layers are distinguished: The primary layer (P) and three secondary layers, S1, S2 and S3. All of these regions are composed by cellulose, hemicellulose and lignin. The primary layer P possesses a random microfibril orientation and is just about 0,1-0,2 µm, making it sometimes really difficult to differentiate it from the middle lamella [21-22]. The first secondary layer S1 is a thin (0,1-0,3 µm) and lignin-rich layer, with arranged microfibril angles at about 50-70° to the long axis of the cell [21-22]. The next layer, S2-layer, is with generally 1-5 µm by far the thickest layer in the cell wall [21]. In addition, it has the highest cellulose content and microfibrils are arranged nearly parallel to the cell axis, with an angle between 10-30° [21]. As a direct consequence, this layer will be of vital importance for the longitudinal mechanical properties of the cell wall. The cell wall is completed with the inner S3 layer. This layer is again a very thin layer, characterized by a high amount of hemicellulose and almost perpendicular (60-90°) arranged microfibrils [21].

2.2. Cellulose dissolution and regeneration

The naturally produced crystalline structure of cellulose is known as cellulose I or native cellulose. Cellulose I can be found in two different polymorphic forms, cellulose I, and cellulose I,, which usually coexist together in a variety of organisms. The proportions of each polymorph depends on the cellulose structure of the different organisms. It is said that cellulose I, is prevailing in bacterial and algae, whereas higher plants, such as trees, cotton etc., contain a bigger amount of cellulose I, [14]. The main difference between these two polymorphs is their
dissimilar hydrogen bonding pattern, respectively the relative displacement of cellulose sheets along lattice planes [14][19].

However, there exist more variations of crystalline cellulose (II, III, IV) (Figure 2.3). All of them have been exhaustively analysed and documented.

As this work focuses on the production of all-cellulose composites based on regenerated cellulose, only a brief insight into cellulose II will be given. Cellulose II, a “man-made” form of cellulose, can be acquired from native cellulose by two kind of processes: regeneration and mercerization. The regeneration process involves the dissolution of cellulose I in a solvent, succeeded by the precipitation in an anti-solvent, such as water, in order to coagulate and arise to cellulose II [14]. Mercerization on the other hand is referred to the swelling of cellulose I in concentrated sodium hydroxide, prior to the removal of the swelling agent, to end up with the final product of cellulose II [14]. It has been reported that cellulose II is energetically more stable than cellulose I, since the anti-parallel chain arrangement of cellulose II is thermodynamically more favourable, than the parallel arrangement of native cellulose [14][24]. Due to this stable structure, Cellulose II is of big industrial interest and relevance, as already demonstrated with cellophane (transparent films), Rayon and Tencel™ (synthetic textile fibers) [18]. Of course, the conversion to another crystalline form brings also some negative consequences with it. As Table 2.1 shows, naturally produced cellulose I is remarkably stiffer than the “man-made” forms. The values in table 2.1 correspond to the results obtained by Nishino et al., who measured the elastic modulus (Ei) of the crystalline regions of cellulose polymorphs in the direction parallel to the chain axis [25].

\[1\] Generally accepted that cellulose IV is just a slightly disordered form of cellulose I [23]
2.2.1. Solvents

Cellulose is not suitable for melt-processing, but it can be dissolved in order to be processed, even though this is rather a challenging and complex process, as cellulose is insoluble in water and in most common solvents [26]. However, still numerous solvents, with high hydrogen bonding capacity, able of breaking the interactions between cellulose molecules, have been found [11]. Some of the most commonly used solvents are N-methylmorpholine-N-oxide (NMMO), lithium chloride/N,N-dimethylacetamide (LiCl/DMAC), ionic liquids (Il’s), and sodium hydroxide (NaOH) aqueous solution [9][11]. From these solvents, NMMO, used for example in the Lyocell process in order to produce regenerated cellulose fibers, is without doubt nowadays industrially the most successful solvent [11].

Within the scope of this project, LiCl/DMAc will be used. LiCl/DMAc is a well-liked solvent in research, because of his efficiency and capacity of dissolving high molecular weight cellulose [9][11]. Besides that, major advantages are that the solutions are colorless and compatible with GPC columns [11]. One of the drawbacks of LiCl/DMAc is that Cellulose has to be “activated” prior to be dissolved in the solvent [9]. This “activation process” usually involves a solvent exchange of the cellulose or distillation of the DMAc/LiCl/cellulose [11]. This step is vital to ensure the interaction of the solvent with the cellulose molecules, as the presence of cellulose bound water needs to be avoid [11]. Due to the fact, that the “activation process” requires extra time and additional solvents, LiCl/DMAc has not made it yet up to an industrial scale [11]. Moreover, the solubility of cellulose increases with bigger LiCl proportions, yet Potthast et al. have reported that the solubility is limited to 8.46 wt% LiCl [9][27].

Table 2.1 E-Modulus for the several polymorphs of crystalline cellulose [25]

<table>
<thead>
<tr>
<th>Crystalline Form</th>
<th>Elastic modulus [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose I</td>
<td>138</td>
</tr>
<tr>
<td>Cellulose II</td>
<td>88</td>
</tr>
<tr>
<td>Cellulose III,</td>
<td>87</td>
</tr>
<tr>
<td>Cellulose III,</td>
<td>58</td>
</tr>
<tr>
<td>Cellulose IV,</td>
<td>75</td>
</tr>
</tbody>
</table>

Figure 2.4 Interaction between DMAc/LiCl and Cellulose [11]
2.3. Natural nanoreinforcements

The interest in natural nanomaterials, one dimension at least between 1-100 nm, has increased in recent years, specially as reinforcing material for bio-composites [4]. Due to their large surface area, the addition of a little amount (1-5 wt%) of nanomaterial is already enough to enhance considerably the mechanical properties of the reinforced material [4]. Among all the alternatives, cellulose nanocrystals (CNC) and halloysite nanotubes (HNT) have been considered for this project.

2.3.1. Cellulose nanocrystals

Cellulose nanocrystals (CNC) or cellulose nanowhiskers (CNW) are rod-shaped particles, that are obtained when native cellulose is subjected to acid hydrolysis, resulting in the removal of the amorphous regions (see Figure 2.5) [18][28]. Sulfuric acid hydrolysis, which results in the formation of negatively charged sulphate ester groups during the process, is probably the most seen CNC isolation method [7].

![Figure 2.5 Crystalline and non-crystalline regions [4]](image)

However, the final acquired CNCs typically own a width between 3-5 nm and a length of 50-500 nm. In addition to this high aspect ratio, CNCs are highly crystalline (54-88 %), which explains their exceptional mechanical properties, as shown in table 2.2 [18][28]. The overall properties and geometrical dimension will strongly depend on the used raw material, as well as on the hydrolysis process conditions [7][18].

<table>
<thead>
<tr>
<th>Material</th>
<th>Tensile strength (GPa)</th>
<th>Young’s modulus (GPa)</th>
<th>Density (g/cm³)</th>
<th>Tensile/ density</th>
<th>Modulus/ density</th>
<th>Thermal exp. coe. (ppm/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNC</td>
<td>7.5</td>
<td>145</td>
<td>1.6</td>
<td>4.7</td>
<td>90.6</td>
<td>3-22</td>
</tr>
<tr>
<td>Glass fiber</td>
<td>4.8</td>
<td>86</td>
<td>2.5</td>
<td>1.9</td>
<td>34.4</td>
<td>13</td>
</tr>
<tr>
<td>Steel wire</td>
<td>4.1</td>
<td>207</td>
<td>7.8</td>
<td>0.5</td>
<td>26.5</td>
<td>15</td>
</tr>
<tr>
<td>Kevlar</td>
<td>3.8</td>
<td>130</td>
<td>1.4</td>
<td>2.7</td>
<td>92.9</td>
<td>-4</td>
</tr>
<tr>
<td>Graphite</td>
<td>21</td>
<td>410</td>
<td>2.2</td>
<td>9.5</td>
<td>186</td>
<td>2-6</td>
</tr>
<tr>
<td>CNT</td>
<td>11-73</td>
<td>270-970</td>
<td>1.0</td>
<td>11-73</td>
<td>270-970</td>
<td>-</td>
</tr>
</tbody>
</table>
2.3.2. Halloysite nanotubes

Recently, halloysite nanotubes (HNTs), a novel 1D natural nanomaterial, has noticed an increased interest as reinforcement for polymers. Halloysite is a dioctahedral 1:1 clay mineral of the kaolin group and can be found in nature in a white stone-like shape, as shown in Figure 2.7 a) [30-31]. The chemical composition of HNTs is Al$_2$Si$_2$O$_5$(OH)$_4$·nH$_2$O, in which n=2 describes the hydrated state (HNTs-10Å) with one layer of water in the interlayer spaces, and n=0 the dehydrated form of halloysite (HNTs-7Å) [30]. The latter structure may be obtained by heating HNTs-10 Å between 30-110°C, leading to the loss of the water molecules between the layers [30-31]. Furthermore, HNTs show a multi-walled tubular structure, where aluminols are mainly situated in the interior of the HNTs, and the siloxanes and a few silanols/aluminols in the exterior and edges respectively (Figure 2.7 b) [30].

![Halloysite nanotubes](image)

*Figure 2.6 The raw halloysite [30] (a); Schematic structure of halloysite nanotubes (HNTs) [32](b)*

A closer look at the properties of this tubular nanoreinforcement reveals a high aspect (ca.10-50), a promising elastic modulus of 140 GPa and low density (2.14-2.59 g/cm$^3$), due to the empty lumen in the core of the material [30]. Further properties are shown in Table 2.3. In addition, HNTs show rather few tube-tube interactions which support uniform dispersion of the material and a relatively hydrophobic behaviour, which enhances a possible hydrogen bond formation between the nanotubes and the polymer matrix [30][33]. By taking into account all the mentioned properties, it gets clear to see why halloysite nanotubes have such a big potential as nanoreinforcement, specially also for cellulose composites.

![Table 2.3 Typical analysis data of HNTs relative to formation of polymer nanocomposites [30]](table)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>Al$_2$Si$_2$O$_5$(OH)$_4$·nH$_2$O</td>
</tr>
<tr>
<td>Length</td>
<td>0.2-2 µm</td>
</tr>
<tr>
<td>Outer diameter</td>
<td>40-70 nm</td>
</tr>
<tr>
<td>Inner diameter</td>
<td>10-40 nm</td>
</tr>
<tr>
<td>Aspect ratio (L/D)</td>
<td>10-50</td>
</tr>
<tr>
<td>Elastic modulus (theoretical value)</td>
<td>140 GPa (230-340 GPa)</td>
</tr>
<tr>
<td>Mean particle size in aqueous solution</td>
<td>143 nm</td>
</tr>
<tr>
<td>Particle size range in aqueous solution</td>
<td>50-400 nm</td>
</tr>
<tr>
<td>BET surface area</td>
<td>22.1-81.6 m$^2$/g</td>
</tr>
<tr>
<td>Pore space</td>
<td>14-46.8%</td>
</tr>
<tr>
<td>Lumen space</td>
<td>11-39%</td>
</tr>
<tr>
<td>Density</td>
<td>2.14-2.59 g/cm$^3$</td>
</tr>
<tr>
<td>Average pore size</td>
<td>79.7-100.2 Å</td>
</tr>
<tr>
<td>Structural water release temperature</td>
<td>400-600 °C</td>
</tr>
</tbody>
</table>
2.4. Cellulose fibers

Two main groups are distinguished among fibers, natural fibers and man-made fibers (Figure 2.7). Natural fibers, can be obtained from plant, animal or mineral sources, being plants the most common choice. Their almost unlimited availability, considering running out fossil fuels, their low environmental impact, also in terms of ease of recycling, their relative inexpensive nature, as well as the fact that they compete well in terms of strength per weight of material have made them a real competing alternative in many applications to most frequently seen synthetic fibers, such as glass, carbon or aramid [5-6]. Their application field ranges from automotive and aerospace, over construction, till sports industries [34].

![Figure 2.7 Fiber classification [5]](image)

When it comes to mechanicals properties (Table 2.4) Flax, Ramie, Hemp and Ramie are amongst the best cellulosic fibers in terms of stiffness and tensile strength performance, comparable to the values of glass fibers for example [34]. Lamentably, the overall mechanical properties of these biocomposites are still far away from those of synthetic fiber reinforced composites. Variations in the chemical composition, given by the geographical location, exact maturity when harvesting, climate in the region, storage, inconsistent dimensions etc. are all factors that can affect the final quality of the natural fibers [5][34][36]. This also explains the big scattering of the mechanical properties values listed in Table 2.4. These drawbacks added to the fact that natural fibers usually need to be twisted into yarns in order to form continuous long fibers, which on the other hand generally results in decreased mechanical properties of the yarn compared to the single natural fiber and makes the impregnation, as well as the compaction of the final composite more challenging, is a big concern regarding their use in composite materials [7-8].
However, there has been an emerging group of fibers which tries to overcome these problems by combining the best of both worlds, natural and man-made fibers. This man-made type of cellulosic fibers are also known as regenerated cellulose fibers. Spinning of regenerated cellulose fibers usually involves first the dissolution of cellulose in some sort of solvent, followed by precipitation in a coagulation medium in order to form continuous fibers. Lyocell, Viscose and Rayon, all produced from wood pulp, are the most known commercially available fibers [5]. The big advantage of regenerated cellulose fibers is that they are long, continuous, with less defects and dimensional variations, and generally easier to process compared to natural fibers. Their mechanical properties (Table 2.5) ranges from Viscose, 9.4 GPa stiffness, till Bocell, a new highly oriented fiber, spun from an anisotropic solution in phosphoric acid, which shows a Young modulus of 44.4 GPa [39-40].

<table>
<thead>
<tr>
<th>Material</th>
<th>Young’s modulus (GPa)</th>
<th>Tensile strength (MPa)</th>
<th>Strain at break (%)</th>
<th>Diameter (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cordenka EHM</td>
<td>32.2 ± 2.2</td>
<td>710 ± 120</td>
<td>3.9 ± 0.7</td>
<td>9.4 ± 0.2</td>
</tr>
<tr>
<td>Cordenka 1840</td>
<td>16.9 ± 1.5</td>
<td>660 ± 80</td>
<td>12.7 ± 1.4</td>
<td>12.9 ± 0.3</td>
</tr>
<tr>
<td>Enkaviscose</td>
<td>9.4 ± 0.5</td>
<td>220 ± 50</td>
<td>17.2 ± 1.3</td>
<td>18.0 ± 0.7</td>
</tr>
<tr>
<td>Cordenka 700</td>
<td>20.0 ± 6.1</td>
<td>660 ± 10</td>
<td>10.7 ± 0.4</td>
<td>13.1 ± 1.3</td>
</tr>
<tr>
<td>Alternative</td>
<td>30.6 ± 0.1</td>
<td>1010 ± 70</td>
<td>4.9 ± 0.3</td>
<td>15.6 ± 1.1</td>
</tr>
<tr>
<td>Cellulose Lyocell</td>
<td>15.2 ± 2.9</td>
<td>540 ± 10</td>
<td>7.0 ± 0.3</td>
<td>12.3 ± 0.9</td>
</tr>
<tr>
<td>LDR Lyocell</td>
<td>15.1 ± 1.5</td>
<td>311 ± 25</td>
<td>27.9 ± 4.5</td>
<td>27.8 ± 0.5</td>
</tr>
<tr>
<td>HDR Lyocell</td>
<td>26.3 ± 1.9</td>
<td>544 ± 35</td>
<td>9.4 ± 1.6</td>
<td>11.7 ± 0.3</td>
</tr>
<tr>
<td>Bocell</td>
<td>44.4 ± 3.0</td>
<td>1201 ± 124</td>
<td>4.3 ± 0.5</td>
<td>12.3 ± 0.5</td>
</tr>
</tbody>
</table>
2.5. Fiber spinning

Forcing a dissolved or melted polymer through a die, in order to create a fiber is also known as fiber spinning. Three main categories are distinguished within fiber spinning: melt spinning, solution spinning and electro spinning.

2.5.1. Melt spinning

Melt spinning is probably the simplest of all spinning techniques, already just because of the fact that there are no issues regarding the involvement of solvents and that a really stable melt of the polymer can be ensured [41]. Anyway, the process is characterized by three main steps: first polymer granulates are melted, then extruded through a die and finally cooled down and solidified in the air or an appropriate liquid [41-42]. A typical melt spun device setup is shown in Figure 2.8.

![Figure 2.8 Melt spinning setup [41]](image_url)

Melt spun-fibers, which can also be produced at high speeds, are generally denser and own lower fluxes than fibers made with solution spinning [42]. Still really thin fibers can be achieved by stretching posterior leaving the die [42].

Overall, melt spinning is the first option for the production of polymers that will not undergo thermal degradation when heating the granulates to the needed temperatures, in order to get a stable melts solution with the required viscosity [43]. Common fibers produced in this way are nylon, polyethylene, polypropylene and polyester [43].
2.5.2. Solution spinning

Solution spinning is one of the oldest man-made fiber production methods, being already introduced at the end of the 19th century [7]. Two techniques are distinguished in this category: wet spinning and dry spinning (Figure 2.9). In both cases viscous polymer is forced through a spinneret, followed by the removal of the solvent, leaving a fiber [44]. The main difference between the two lies on how the solvent is removed. The wet spinning process gets rid of the solvent by coagulation with another liquid in a bath [45]. A well known fiber produced with this method is Viscose. On the other hand, the dry spinning process involves a spinning tower where the solvent is removed by evaporation through the application of heat [46]. The solidification of the fiber is faster in the case of dry spinning. Furthermore, there exist also some variations of the process. One example is dry-jet wet spinning, where an air gap is left between spinneret and bath [7]. Lyocell, a more environmentally friendly man-made cellulose fiber compared to Viscose, is made with this technique [7].

![Solution spinning: (a) Wet spinning and (b) Dry spinning. Adapted from [46]](image)

2.5.3. Electro spinning

Electrospinning, an already very well known process in the nonwoven textile industry, is a method in which electrostatic forces are applied in order to create fine polymer fibers from both natural and synthetic polymers [47-48]. The resulting fibers are said to be in the range between nanometers and a few micrometers, and with a large surface area [48]. Usually, electrospinning is performed at room temperature and atmospheric pressure. The instrument setup consists of three major parts, as shown in Figure 2.10: a high-voltage power supplier (DC), a spinneret (e.g. a plastic syringe) connected to one of the electrodes, as well as a metal collector, which allows the formation of an electrical field due to its opposite polarity [47-48]. As soon as the dissolved polymer solution leaves the tip of the spinneret, it is accelerated towards the collector. On its way the solvent is evaporated in the air, leaving a thin polymer fiber.
It is a quite simple and cost-effective technique, which allows the spinning of a wide range of polymers, while giving the possibility to manipulate the spun fiber composition and produce highly reproducible fiber mats [48].

Table 2.6 shows an overview of the latest results regarding continuous cellulosic fiber spinning. The Table includes data of just cellulose fibers, as well as biopolymers fibers reinforced with nanocellulose. For further information, the reader is referred to the original review work by Oksman et. al [49].
2.6. All-cellulose composites

The idea of almost completely substituting environmentally friendly natural fibers for synthetic fibers is a real ambitious goal. To get there, some challenges, like incompatibility between the hydrophilic fiber reinforcement and the hydrophobic polymer matrix, still have to be overcome, specially on larger industrial scales [26]. This chemically antipathy between the two phases results in low mechanical properties of the composite, mainly due to a weak fiber-matrix bonding, which are not in accordance with the high mechanical performance potential of the single natural fibers [26]. However, one way to solve this problem is to produce all-cellulose composites (ACCs), where the matrix, as well as the reinforcement are made out of the same material [26].

2.6.1. Processing of all-cellulose composites

The first concept of all-cellulose was reported by Nishino et al., who embedded ramie fibers in regenerated cellulose of completely dissolved craft wood pulp [10]. The way Nishino et al. produced their all-cellulose composite is also known as the 2-step method (Figure 2.11 a), which involves the dissolution of cellulose in a solvent, prior to the regeneration together with an undissolved cellulose reinforcement [10][26]. The other common pathway for processing all-cellulose composites is the 1-step method (Figure 2.11 b), in which a solvent is added to a cellulose reinforcement, followed by a partial dissolution of the surface of the cellulosic fibers [26]. The pioneers of the latter method, which is also termed as partial dissolution, surface-selective dissolution and natural fiber welding, where Gindl and Kecks [26][50].
Since then many groups have been working on this exciting topic. Whereas it seems that among solvents, LiCl/DMAc and ionic liquids have been so far the most preferred and used solvents, also in terms of success [51], the choice of cellulose source for reinforcement and matrix has been more open.

Gindl and Keckes were the first ones in proving that all-cellulose composites can be done in a single step [50]. Therefore, they created nanocomposite films by partially dissolving microcrystalline cellulose (MCC) powder (Cellulose I) in LiCl/DMAc. Different proportions of undissolved cellulose I and regenerated cellulose II were tested. Results, showed that transparent films were obtained with enhanced mechanical properties compared to pure regenerated cellulose films. Tensile strength and stiffness could be improved up to 240 MPa (43 %) and 13 GPa (88 %), depending on the exact amount of MCC. Overall crystallinity has been shown to increase with increasing amount of undissolved MCC.

Furthermore, Gindl et al. have been also showing that the use of man-made regenerated cellulose fibers as reinforcement in all-cellulose composites could be a really promising alternative to traditional NFCs and maybe the better choice [51]. All-cellulose composites, using IL as solvent, and epoxy-matrix composites were made out of needle-punched Lyocell and flax fibers nonwoven mats and compared to each other. The obtained Lyocell fibre based ACCs performed excellent in terms of mechanical testing, having properties in the same range as common epoxy based biocomposites, whereas flax based ACCs performed clearly less well. In addition, it was found that the studied all-cellulose composites showed more diffuse thermal softening and a superior thermal degradation resistance, speaking clearly in favour of ACCs and their further investigation.
Even though, both processing methods are possible, the one-step method seems to be more realistic regarding a future industrial up scaling [26]. The main reason here fore is that the overall differential shrinkage, which causes internal residual stresses and dimensional instability, and is still a big problem when manufacturing ACCs, is usually lower for one-step method made ACCs than for ACCs produced via the two-step-method. Huber et al. have been really active in this matter trying to manufacture thicker ACCs (t > 0,5 mm), closer to real life applications, with commonly known industrial manufacturing methods, such as compression moulding or vacuum infusion [52-53].

Compression moulded composites were made by hand-impregnating dried man-made regenerated cellulose Cordenka Rayon fiber textile and linen flax fiber textile with BMIMAc, an ionic liquid [52]. In a subsequent step, four layers were stacked alternating warp- and weft direction respectively and compressed under heat (110°C) with a hot press (1,5 and 2,5 MPa) for a total of 80 min, creating a matrix phase by the partial dissolution of the fibers and the following solvent exchange. The resulting all-cellulose composites turned out to have an average thickness of 1,66 mm (flax laminate) and 1,98 mm (Cordenka laminate) and be fully consolidated with the addition of pressure. Rayon based all-cellulose composites show less voids and more consistency compare to linen based ACCs, leading to a stronger composite (70 MPa vs. 46 MPa ultimate strength). Even though, the laminates were overall dimensional stable, small inter- and intra-laminar voids, formed during the drying process, were observed. Huber et al. concluded that regenerated cellulose fibers would be generally the better choice when solvent-processing, due to less variations in the shape of the fibers and more homogenous dissolution, resulting in a stronger composite with an improved fiber-matrix interface.

In the solvent infusion process (SIP), a slightly variation of the known vacuum-assisted resin transfer moulding (VARTM), Cordenka preform textile layers were first infused, hence impregnated with BMIMAc and then with water in order to weld the fibers together [53]. In between, during the dissolution time, a pressure of 0,2 MPa at 95 °C for a total of 60 min was applied for consolidation of the laminates. The obtained composites were dimensionally stable, no dimensional shrinkage or warpage was observed, and with high volume fractions (>70%). The final thickness of the composites depends on the time and the amount of applied pressure during the manufacturing process. Promising mechanical properties with an ultimate strength of 91 MPa and a stiffness of 4,1 GPa were achieved for the best laminate, as a result of an improved fiber-matrix interface. This improved bonding is believed to be caused by the increased pressure during dissolution, as well as a controlled and uniformed partial dissolution of the fibers possible with the solvent infusion process.

2.6.2. Mechanical properties of all-cellulose composites

An overall evaluation of the mechanical properties given by all-cellulose composites is very difficult, as they depend on many factors such as origin of the cellulose, reinforcement type or processing conditions [26]. Anyway, a general overview and further comparison to other biocomposites was delivered by Huber et al. [9]. As shown in Figure 2.12 a higher Young´s modulus have been reported for several isotropic all-cellulose composites in comparison with conventional biocomposites [9]. One possible reason could be the high mechanical properties of the regenerated cellulose matrix [9][26]. For unidirectional all-cellulose composites, the stiffness values are similar to the ones of biocomposites [9]. This results on the other hand
could be attributed to the solvent interacting with the fibers in the all-cellulose composite and therefore lowering their modulus, or to the modulus of the biocomposites being determined by the fibers stiffness, leaving the interfacial strength of fibre and matrix in the background [9]. In terms of tensile strength, all-cellulose composite show much better results than traditional biocomposites (Figure 2.12).

Table 2.7 shows an overview of recent development in all-cellulose composites and their mechanical properties. For an extensive review about the different processing techniques and their possible effect on the final mechanical properties of the all-cellulose composites the reader is referred to the original work by Huber et al. [9]
### Theoretical Background

Table 2.7 Overview of recent developments in all-cellulose composites and their mechanical properties. Reproduced from Huber et al. [9]

<table>
<thead>
<tr>
<th>No.</th>
<th>Cellulose source for matrix</th>
<th>Cellulose source for reinforcement</th>
<th>Solvent</th>
<th>Fibre volume fraction in %</th>
<th>Tensile strength → (MPa)</th>
<th>Tensile strength ⊤ (MPa)</th>
<th>Young's modulus ⊤ (GPa)</th>
<th>Strain to failure → (%)</th>
<th>Strain to failure ⊤ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cotton linter pulps</td>
<td>Cellulose whiskers (ISO)</td>
<td>NaOH/urea</td>
<td>10</td>
<td>124</td>
<td>5.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Cotton linter pulps</td>
<td>Cellulose whiskers (ISO)</td>
<td>NaOH/urea</td>
<td>20</td>
<td>117</td>
<td>5.9</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>3</td>
<td>Cellulose powder</td>
<td>Hemp fibre (ISO)</td>
<td>NMNO</td>
<td>40</td>
<td>28.9</td>
<td>1.8</td>
<td>20.8</td>
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<td>4</td>
<td>Wood pulp</td>
<td>Ramie fibre (UD)</td>
<td>LiCl/DMAC</td>
<td>80</td>
<td>480</td>
<td>12</td>
<td>4</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Ramie fibre</td>
<td>Ramie fibre (UD)</td>
<td>LiCl/DMAC</td>
<td>85</td>
<td>410</td>
<td>25</td>
<td>4.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Filter paper</td>
<td>Rice husks (ISO)</td>
<td>Ionic liquid (BmimCl)</td>
<td>40</td>
<td>57.5</td>
<td>1.74</td>
<td>5.67</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Filter paper</td>
<td>Rice husks (ISO)</td>
<td>Ionic liquid (BmimCl)</td>
<td>60</td>
<td>56</td>
<td>2.92</td>
<td>2.76</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>Cellulose source for matrix and reinforcement</th>
<th>Reinforcement type</th>
<th>Solvent</th>
<th>Fibre volume fraction in %</th>
<th>Tensile strength → (MPa)</th>
<th>Tensile strength ⊤ (MPa)</th>
<th>Young's modulus ⊤ (GPa)</th>
<th>Strain to failure → (%)</th>
<th>Strain to failure ⊤ (%)</th>
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</thead>
<tbody>
<tr>
<td>8</td>
<td>MCC</td>
<td>(ISO)</td>
<td>LiCl/DMAC</td>
<td>242.8</td>
<td>13.1</td>
<td>8.6</td>
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<td>Beech pulp</td>
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<td>154</td>
<td>12.2</td>
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<td>Filter paper</td>
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<td>LiCl/DMAC</td>
<td>211</td>
<td>8.2</td>
<td>3.8</td>
<td></td>
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<tr>
<td>11</td>
<td>Ramie fibre</td>
<td>(UD)</td>
<td>LiCl/DMAC</td>
<td>85</td>
<td>480</td>
<td>29</td>
<td>26</td>
<td>3.7</td>
<td>4.5</td>
</tr>
<tr>
<td>12</td>
<td>LDR-Lyocell fibre</td>
<td>(UD)</td>
<td>LiCl/DMAC</td>
<td>72</td>
<td>250</td>
<td>9</td>
<td>24</td>
<td></td>
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<tr>
<td>13</td>
<td>HDR-Lyocell fibre</td>
<td>(UD)</td>
<td>LiCl/DMAC</td>
<td>73</td>
<td>350</td>
<td>12</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Bocell fibre</td>
<td>(UD)</td>
<td>LiCl/DMAC</td>
<td>88</td>
<td>910</td>
<td>23</td>
<td>8.2</td>
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<td></td>
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<tr>
<td>15</td>
<td>MCC</td>
<td>(ISO)</td>
<td>LiCl/DMAC</td>
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<td>16</td>
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<td>LiCl/DMAC</td>
<td>105.7</td>
<td>6.9</td>
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<td>LiCl/DMAC</td>
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<td>(ISO)</td>
<td>Ionic liquid (BmimCl)</td>
<td>91.8</td>
<td>5.75</td>
<td>3.76</td>
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<tr>
<td>19</td>
<td>Filter paper</td>
<td>(ISO)</td>
<td>Ionic liquid (BmimCl)</td>
<td>124</td>
<td>10.8</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>Cellulose source for matrix</th>
<th>Cellulose source for reinforcement</th>
<th>Solvent</th>
<th>Additional processing step</th>
<th>Fibre volume fraction (%)</th>
<th>Tensile strength ⊤ (MPa)</th>
<th>Tensile strength → (MPa)</th>
<th>Young's modulus ⊤ (GPa)</th>
<th>Strain to failure → (%)</th>
<th>Strain to failure ⊤ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>Wood pulp</td>
<td>Ramie fibre (UD)</td>
<td>LiCl/DMAC</td>
<td>Immerse in water, acetone, DMAC</td>
<td>80</td>
<td>400</td>
<td>17</td>
<td>25</td>
<td>3</td>
<td>21</td>
</tr>
<tr>
<td>21</td>
<td>MCC</td>
<td>Ramie fibre (UD)</td>
<td>LiCl/DMAC</td>
<td>Wet drawing to align cellulose fibrils</td>
<td>85</td>
<td>428</td>
<td>95</td>
<td>33.5</td>
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<td>22</td>
<td>Ramie fibre</td>
<td>Ramie fibre (UD)</td>
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<td>Mercerization</td>
<td>85</td>
<td>540</td>
<td>25</td>
<td>4.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All-cellulose composites prepared with further fibre or composite processing

Included are the types of cellulose source, reinforcement, solvent and fibre fraction used. Both tensile properties parallel (↑) and transverse (→) to the fibre direction are given where available.

3. Materials and methods

3.1. Materials

Dissolving pulp, obtained from Domsjö Fabriker AB (Örnsköldsvik, Sweden), was used as base material. Freeze-dried cellulose nanocrystals (2012-FPL-CNC-043), hydrolyzed from cellulose pulp, were kindly provided by USDA Forest Products Laboratory (Madison, USA). Halloysite nanotubes (HNTs) were purchased from Sigma Aldrich. Furthermore, N,N-dimethylacetamide (DMAc), as well as lithium chloride (LiCl) were acquired from Sigma Aldrich. In addition, distilled water (H₂O) and methanol (CH₃OH) were used during the experimental section.

3.2. Preparation of the spinning solutions

Prior dissolving the cellulose pulp an activation process was needed, in order to avoid cellulose bond water and weaken the polymer chain into a relaxed conformation [11][54]. Without this pre-treatment the interaction between the solvent and the cellulose molecules can not be ensured. In this case the activation process required a sequence of solvent exchanges. At the beginning cellulose was placed and hold under water for 1 h, followed by the removal of water via vacuum filtration. In a subsequent step a solvent exchange with methanol for another 1 h took place to get rid of the left water. After vacuum filtration, a last solvent exchange with DMAc for 1 h was done. Once again the cellulose was filtrated and then dried at 70°C.

3.2.1. Cellulose dopes

First, cellulose reference dopes without any added nanoreinforcement were prepared (Figure 3.1). Therefore, DMAc was heated up to 105°C under light magnetic stirring and hold for 10 min to ensure that any remaining water was evaporated. Next, DMAc was cooled down to 80°C and LiCl was added under constant magnetic stirring until completely dissolved. The proportions in this case were 8 g LiCl per 92 g of DMAc. Once dissolved, activated cellulose was added to the solution at room temperature and subjected to magnetic stirring during at least 12 h, in order to form a 2 % cellulose spinning dope. In a last step, the new solution was filtered via vacuum through a 80 µm mesh to get rid of undissolved parts and foreign matter.

![Figure 3.1 Scheme of the preparation of reference Cellulose dopes](image)
3.2.2. Cellulose/CNC dopes

To prepare 2 % CNC dopes (w/w, in respect to the weight of dissolved cellulose), first an excess amount of CNC was added to DMAc under constant magnetic stirring, in this case 2.5 g to 500 g, and then stirred for at least 6 hours (Figure 3.2). In order to improve dispersion and distribution of the nanoreinforcements in the cellulose, next the mixture was subjected to a light sonication bath for 1 h, stirred for another 30 min and then hold for 2 min in a stronger sonicator (Cycle: 0.5; Amplitude: 50). After sonication, the mixture was centrifuged for 1 min at 2000 rpm, in order to get rid of the bigger particles. This last centrifugation step was repeated as many times as needed till achieving a concentration at least 0.15 % or smaller. The new CNC concentration was determined via thermogravimetric analysis (TGA). Based on that new concentration, the additional needed DMAc amount for the final dope was calculated and added. The following steps involved the heating of the mixture to 105°C, before adding LiCl at 80°C and the activated cellulose at room temperature, as shown for pure cellulose dopes. Finally, the 2% CNC Cellulose/CNC dopes were passed through the 80 µm filter.

![Figure 3.2 Scheme of the preparation of Cellulose/CNC dopes](image)

3.2.3. Cellulose/HNT dopes

Spinning dopes with HNT as reinforcement were prepared in the same way as the Cellulose/CNC dopes, with the exception that in this case an Ultra-Turrax® T25 was used, instead of a normal magnetic stirrer, to mix the HNTs and DMAc (Figure 3.3). In addition, only the stronger sonicator was applied. Thereby, the mixture was first stirred for 1.5 h, then cooled down for 10 min, before being stirred for another hour. Next, the mixture was sonicated twice for 10 min. In between, it was held at the stirrer for 30 min. In order to obtain the final wished HNT concentration several centrifugation steps at 2000-7000 rpm were needed.

![Figure 3.3 Scheme of the preparation of Cellulose/HNT dopes](image)
3.3. Measurement and characterization

3.3.1. Thermogravimetric analysis (TGA)

To measure the concentration after the centrifugation step when preparing the spinning dopes, a TA Instruments TGA Q 500 model was used. The selected method for the thermal stability measurements consisted of an initial temperature of 40°C, then a ramp with a heating rate of 10°C/min till reaching 250°C, followed by an isothermal at 250°C for 2 min.

3.3.2. Scanning electron microscopy (SEM)

A JEOL JCM-6000 NeoScope scanning electron microscope (SEM) was used for studying the morphological structure and fracture behaviour of the all-cellulose composites.

3.3.3. Tensile testing

A universal tensile testing machine SHIMADZU AG-X with a 5 kN load cell was used to predict the mechanical properties of the all-cellulose composites. The tests were run at a constant cross-head speed of 2 mm/min. The thickness and width of the all-cellulose tapes were measured by optical microscopy at 3 points for each sample. 5 samples were performed per each fiber configuration (Cellulose, Cellulose/CNC and Cellulose/HNT). Samples manufactured at Karlstad University had a gauge length of 40 mm, a thickness of 0.75 mm ± 0.09 (Ref); 0.76 mm ± 0.06 (HNT) and a width of 3.16 mm ± 0.45 (Ref); 2.17 mm ± 0.28, respectively. The samples made at LTU on the other hand, had a gauge of 30 mm, a thickness of 0.78 mm ± 0.09 (Ref); 0.77 mm ± 0.07 (CNC); 0.84 mm ± 0.08 (HNT) and a width of 6.05 mm ± 0.34 (Ref); 5.76 mm ± 0.12 (CNC); 6.45 mm ± 0.23 (HNT), respectively. Furthermore, glass fiber reinforced tabs were used to protect the material from damage and reduce local stress concentrations. Before carrying out the tests, all samples were stored in a conditioning chamber at 23°C and 50% RH for at least 48 hours. The measured average temperature and relative humidity during the tests were 21,3°C and 19,4 % respectively. Load and displacement were recorded until specimen failure. Average values, as well as standard deviations were reported.
4. Manufacturing Part I (Karlstad University)

4.1. Introduction

According to the original plan, see 1.2 Objectives and outline of the project, the idea was to first manufacture enough nanocomposite fibers by means of wet-spinning at Karlstad University, in order to be wounded together and compression moulded in a subsequent step (Figure 4.1). In this last compression moulding step, fibers would be partially dissolved (one-step method) and then welded together to form the final all-cellulose composites. Due to some unexpected problems and limitations with the equipment at Karlstad University, which will be mentioned later in this section, a new processing route was developed to manufacture all-cellulose composites, see chapter 5. Manufacturing Part II (Luleå University of Technology).

![Image: Regenerated cellulose nanocomposite fibers → Partial dissolution → Compression moulding]

*Figure 4.1 Production of all-cellulose composites based on regenerated cellulose nanocomposite fibers*

4.2. Wet spinning

To spin the nanocomposite fibers an Aditya Birla Science and Technology Company Limited wet-spinning machine was used. This machine which was mainly designed for its use in the viscose process, consists of a pump, a 250 ml piston, a spin bath, a spinneret, a stretching unit and a take-up drum (Figure 4.2). The spinning dope is fed from the piston through a connecting tube to the spinneret, which is placed at the end of a J-tube out of glass. The spinneret has a total of 40 holes with a diameter of 80 µm respectively. Between the end of the J-tube and the spinneret a 45 µm filter mesh ensures that remaining dope can be pressed through the spinneret. After leaving the spinneret the multifilament fiber is carried by the stretching unit, three identical rolls which rotate at the same speed. Finally, a bigger take-up drum collects all the spun fibers. The speed of the pump, stretching unit and take-up drum can be set individually on the respective monitoring panels.
4.3. Results and Discussion

4.3.1. Processing of the ACCs

First a series of try-outs had to be performed in order to make the spinning machine work properly. These try-outs are listed in Table 4.1. Once the process was relatively under control the next step consisted in finding appropriate speeds for the pump and the drums. It was found that at a pump rate of 2.09 ml/min, a stretching speed of 6.1 m/min and a take-up speed of 9.7 m/min the process was stable. These parameters would be therefore used for the rest of the trials. However, some of the problems faced during the try-outs, such as blocking of some spinneret holes after a while, not enough solvent exchange and drying time, etc., couldn’t be solved. Regardless it was decided to continue with the processing.

The multifilament fibers (Figure 4.3 a)) were first collected with the take-up drum (Figure 4.3 b)) and then placed for 24 h in water to ensure that all the solvent was properly washed out. During the spinning process the fibers were guided manually along the take-up drum, due to a missing transverse carriage of the machine. Next the roll was dried for another 24 h at 60°C. During this drying process a stiffer core was placed inside the fibers roll to avoid their radial shrinkage. The final obtained sample can be seen in Figure 4.3 c). It can be observed that the fibers stuck to each other and agglomerated more in some parts of the roll than in other, forming already unexpected an all-cellulose composite for itself.

![Figure 4.2 Schematic view spinning machine at Karlstad University](#)

![Figure 4.3 Processing Karlstad University: a) Multifilament fibers, b) Take-up drum with still swelled fibers, c) Final all-cellulose composite sample](#)
<table>
<thead>
<tr>
<th>Try-out</th>
<th>Test</th>
<th>Problem</th>
<th>Solution</th>
</tr>
</thead>
</table>
| 1       | 2% Cell. dope => Dope is not coming out of the spinneret | • Leakage on one end of the silicon tube coming from the piston | • Sealing with some duck tape  
• Dilute dope till 1% Cellulose |
| 2       | 1% Cell. dope => Dope is not coming out of the spinneret | • Leakage on the other side of the tube  
• Machine wasn’t properly assembled as given => Missing of all tightening rings | • Installing of tightening rings  
• New try out with bigger nozzle => Syringe tip => Single fiber |
| 3       | 1% Cell. dope => Dope is coming out of the spinneret => Wet-spinning machine is working properly | • Seems that original coagulation bath is to small for this fiber thickness => Not enough time for a proper solvent exchange | • Longer coagulation bath  
• Switch back to original spinneret |
| 4       | 1% Cell. dope => Dope is coming out | • Fiber filaments seem to be to weak => Multifilament fiber breaks just a few seconds after being rolled up  
• Blocking of some spinneret holes after a while  
• Coagulation time still not enough | • Switch back to original 2% Cell. dopes |
| 5       | 2% Cell. dope => Multifilament fibers could be successfully wound up with the first spinning drum | • Blocking of some spinneret holes after a while  
• Coagulation time still not enough  
• Fibers are partially stuck to each other, as well as to the drum after being dried => Really hard to unwind them as one continuous multifilament fiber  
• Drying time not enough | |
The fact that a composite was formed without the need of partially dissolving the fibers could result in a new interesting processing route for all-cellulose composites where the swelled fibers are wound directly after the water bath, and then welded together by means of compression moulding. This would mean that unidirectional fiber composite sheets could be made without using any additional chemicals.

Therefore, a preliminary evaluation of the manufactured composites was carried out. The bigger strips of the rolls (Figure 4.3 c)) were cut in order to be analysed via scanning electron microscopy (SEM) and tested on their longitudinal mechanical properties.

### 4.3.2. Microstructure

Scanning electron micrographs of the composites cross-sectional view (Figure 4.4) reveal that, specially for the reference and HNT composites a good compaction degree and therefore a good adhesion could be achieved for the majority of the area. However, still some voids and cracks can be seen. In the case of the CNC composite the amount of voids is bigger. One possible reason could be that the amount of material used to process the CNC composite was less than the one used for the other two composites, due to some lost of materials while spinning the fibers.

![Figure 4.4 Scanning electron micrographs of the cross-section of the all-cellulose composites manufactured at Karlstad University](image)

### 4.3.3. Mechanical properties

The results of the tensile test for the ACCs are shown in Table 4.2. No results for the CNC composites are given as there were not enough samples, respectively their dimensions were to inconsistently in order to get some reliable tensile testing data. Therefore, only the results for reference and HNT composites are listed. The results are considerable lower compared to their single fibers, see Table 1.1, but still promising and in the range of some other published papers about ACCs (Table 2.7). Furthermore, the elastic modulus of the ACCs reinforced with HNT nanocomposite fibers was increased by 22% and the strength by 26% compared to the
reference without any nanoreinforcement. The strain, on the other hand, is similar to the reference. These average mechanical properties are probably related to the fact that there has been not a proper stretching, either compaction of the fibers composite during the manufacturing process.

<table>
<thead>
<tr>
<th>Material</th>
<th>Young’s modulus (GPa)</th>
<th>Tensile strength (MPa)</th>
<th>Strain at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref</td>
<td>4.7 ± 0.5</td>
<td>100.1 ± 16.9</td>
<td>11.3 ± 2.3</td>
</tr>
<tr>
<td>HNT (2 %)</td>
<td>5.6 ± 0.5</td>
<td>126.2 ± 0.75</td>
<td>11.4 ± 0.6</td>
</tr>
</tbody>
</table>

4.4. Conclusions

Even though, some limitations given by the equipment, as well as problems faced during the spinning process, could not be solved, some preliminary all-cellulose composites could be made. The scanning electron micrographs and the tensile test results showed that good compaction, respectively mechanical properties in the average range of prior published work were achieved, in spite of the fact that there was not a proper stretching, either compaction of the fibers composite during the manufacturing process.

Following equipment limitations or problems could not be overcome in the given period time:

- No automated transverse carriage
- Blocking of some spinneret holes after a while => Piston and J-tube need to be completely unassembled in order to be cleaned
- Not enough time in the water bath for a proper solvent exchange
- Not enough drying time before reaching the take-up drum => Fibers will partially stick to each other
- O-ring sealant of the pump and spinneret will decompose after a while because of the LiCl/DMAc
- Tube connecting pump to J-tube of the pump will decompose after a while because of the LiCl/DMAc

However, due to the promising fact that unidirectional all-cellulose composite sheets could be made with a new processing route without using any additional chemicals, by wounding the swelled fibers directly after the water bath, and then welding them together by means of compression moulding, it was decided to continue with this manufacturing method. Further testing would be performed at Luleå University of Technology, because of the previous mentioned equipment, as well as time limitations.
5. Manufacturing Part II (Luleå University of Technology)

5.1. Introduction

After the promising results obtained at Karlstad University, see chapter 4. Manufacturing Part I (Karlstad University), it was decided to slightly change the initial manufacturing plan and try to make all-cellulose composites with a new processing method. This new processing method would basically consist in winding the swelled fibers directly after the water bath, and then welding them together by means of compression moulding. However, in order to be able to spin the fibers first a solution had to be found to some of the faced problems with the spinning machine at Karlstad University, like finding proper equipment compatible with the solvent or an automated transverse carriage.

5.2. Wet spinning

A simple set-up was used, in order to spin the fibers and overcome mentioned challenges. The set-up consisted of a pump, a 30mm syringe with a fine nozzle, a long water bath, a self-made automated carriage and a collecting drum, see Figure 5.1. As soon as the solution starts to flow the tip of the jet is immersed in the water ($T_{\text{water}} = \text{room temperature}$) and the fibers are carried along the water bath and moving carriage till reaching the take-up drum. The distance between the carriage and take-up drum, as well as the speed of the carriage, are set in such a way that the misalignment of the fibers on the mandrel is as small as possible. Due to some limitations of the automated carriage, like the minimum speed of the engine, the fibers were recollected in batches of 2 cm respectively in order to decrease even more the misalignment of the final unidirectional composite, see Figure 5.2. Before starting the experiment, the spinning dopes are degassed in the oven for a few hours at 35°C till no air bubbles are visible. The speed of the pump, as well as the speed of the take-up drum can be set individually.

![Figure 5.1 Schematic view of the wet-spinning set-up](image1)

![Figure 5.2 Spacing in the recollecting process for a minimum misalignment](image2)
5.3. Results and Discussion

5.3.1. Processing of the ACCs

First appropriate spinning parameters had to be determined. At a pump rate of 70 ml/hr and a take-up speed of 11 m/min the process was found to be stable. These parameters would be used for the whole manufacturing. Figure 5.3 shows the final processing route in order to make the all-cellulose composites. Fibers were spun out of 400 ml dopes. Once the fibers were recollected successfully with the take-up they were placed in water for 24 h to ensure that all the solvent was properly washed out. Next the roll was cut in order to get a flat fiber sheet, which was then folded transversally to the longitudinal direction of the fibers. In a subsequently step the swelled fiber sheet was stretched and further aligned with the help of a tensile test machine. The stretching ratio hereby was about 1,12. After this stretching step the sheet was folded one more time, in this case in longitudinal direction, to increase its thickness. Finally, the sheet was consolidated in a hot press using a proper mould and vacuum dried at 60°C for a few hours to get rid of all the left moisture. During the consolidation process, first a cold pressing at room temperature and under an initially light pressure which would be increased till 2,1 MPa for 24h was needed to remove the biggest part of the swelled water, then the final pressure of 3,1 MPa at 60°C was applied for another 24 h. The used hot press was not automated, therefore the pressure had to be reset after a while as the pressure would drop. A total of four times the pressure was reset during the respective 24 h. The used aluminium mould can be seen in Figure 5.4. A PET film ensures that the all-cellulose composites have an even surface and don not stick to the mould. Previously carried out try-outs are listed in Table 5.1.

Figure 5.3 All-cellulose composites manufacturing process

Figure 5.4 Hot press mould schematic
<table>
<thead>
<tr>
<th>Try-out</th>
<th>Processing route</th>
<th>Mould</th>
<th>Results for 200 ml dopes</th>
</tr>
</thead>
</table>
| 1       | Wound fibers → Solvent removal → Cutting → Stretching + Drying | -     | • Stretching + drying on tensile test machine  
          |                  |       | • No extra pressure  
          |                  |       | • Bad alignment  
          |                  |       | • Really thin composite |
| 2       | Wound fibers → Solvent removal → Cutting → Folding → Stretching + Drying | -     | • Once folded after cutting  
          |                  |       | • Stretching + drying on tensile test machine  
          |                  |       | • Slightly less misalignment  
          |                  |       | • Thicker composite |
| 3       | Wound fibers → Cutting → Compaction → Solvent removal → Vacuum drying (80 °C) | -     | • Remaining solvent was not removed during compaction  
          |                  |       | • Mould for pressing  
          |                  |       | • Bad alignment => No stretching  
          |                  |       | • High shrinkage |
| 4       | Wound fibers → Solvent removal → Cutting → Folding → Alignment + Stretching → Hot press (80 °C) | -     | • Hot press  
          |                  |       | • Mould for pressing  
          |                  |       | • Too much pressure/ Not optimal mould choice => Fibers will squeeze out under pressure |
| 5       | Wound fibers → Solvent removal → Cutting → Alignment + Stretching → Folding → Cold press → Hot press (80 °C) → Vacuum drying (60 °C) | -     | • Folding before/after stretching  
          |                  |       | • Cold and hot pressing  
          |                  |       | • Mould for pressing  
          |                  |       | • Aligned fibers  
          |                  |       | • Thicker composite |

Table 5.1 Try-out all-cellulose composite manufacturing.
5.3.2. Optical properties

A first visual evaluation of the all-cellulose composites shows a better optical transparency for the reference and the CNC reinforced material (Figure 5.5). Whereas in this both cases the word Cellulose on the underlying paper can be read without any problems, in the case of the HNT reinforced sample it is really hard. Transparency is usually an indicator for good bonding as less light is scattered at their interfaces [55-56]. For the HNT reinforced all-cellulose composite the translucency could be also caused by the halloysite nanotubes nature, meaning that there has not to be a bad interface just because it is not transparent to visible light.

Furthermore, no big warping was observed during regeneration, specially when using more material, 400 ml final test compared to the 200 ml of the try-outs. Less voids are formed due to shrinkage, as a result of the drying process, with increasing material amount.

5.3.3. Microstructure

Scanning electron micrographs from all composite variants are given in Figure 5.6. SEM cross-sectional views reveal that generally a good compaction degree and therefore a good fiber/matrix interface was obtained. The bonding is so extensive that the shape of individual fibers becomes indistinguishable. Nerveless, minimal voids and indicators for future delamination can be seen. SEM surface views show that only a minimal misalignment of the unidirectional all-cellulose composites can be observed.

5.3.4. Mechanical properties

Tensile test results for the all-cellulose composites are shown in Table 5.2. Stiffness values could be almost doubled in comparison with the numbers obtained at Karlstad University, however results are still considerable lower to the ones of to their single fibers, see Table 1.1. Moreover, no improvements were obtained with CNCs and HNTs nanoreinforced all-cellulose composites. Several factors could have contributed to the decreased mechanical properties:

- Not enough stretching of the fibers, hence therefore also no further orientation of the nanoreinforcements
- No longitudinal tension during compaction and drying process
- Fibers shape were indistinguishable in SEM pictures => To much pressure during compaction process may have caused fibre damage
- Interface too strong enabling crack propagation [34]

Overall, the mechanical properties of the all-cellulose composites are still promising and in the range of some other published work, see Table 2.7.
Table 5.2 Mechanical properties all-cellulose composites Luleå University of Technology

<table>
<thead>
<tr>
<th>Material</th>
<th>Young’s modulus (GPa)</th>
<th>Tensile strength (MPa)</th>
<th>Strain at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref</td>
<td>8.4 ± 1.4</td>
<td>125 ± 16</td>
<td>5.8 ± 2.6</td>
</tr>
<tr>
<td>CNC (2 %)</td>
<td>8.4 ± 0.9</td>
<td>125 ± 14</td>
<td>5.0 ± 1.6</td>
</tr>
<tr>
<td>HNT (2 %)</td>
<td>7.4 ± 0.8</td>
<td>117 ± 10</td>
<td>6.3 ± 2.5</td>
</tr>
</tbody>
</table>

Figure 5.6 Scanning electron micrographs of the cross-section of the all-cellulose composites manufactured at Luleå University of Technology.
5.3.5. Fracture behaviour

Scanning electron images of the fracture surfaces of the all-cellulose composites are shown in Figure 5.7. The fractures surfaces reveal delamination and separation of fibre bundles. This effect seems to be more extensive for HNT reinforced all-cellulose composites, indicating a poorer adhesion or compaction and therefore maybe the lower overall mechanical properties.

![Fracture behaviour images](image)

*Figure 5.7 Scanning electron micrographs of the fracture surfaces*
5.4. Conclusions

Using a really simple equipment, a pump, a syringe, a self-made automated carriage and a take-up drum, and without any special optimization of the manufacturing conditions and parameters (spinneret geometry, distance water bath - moving carriage - take-up drum, spinning speeds, compression time and pressure etc.) all-cellulose composites with mechanical properties in the range of previously published work could be successfully manufactured. Thereby, a new processing route for manufacturing all-cellulose composites was developed, where the fibers are wound directly after the water bath and then welded together while still being swelled in order to form unidirectional fiber composite sheets without the need of adding any additional solvent or chemicals. Moreover, this technique showed that “thick” (t > 0,5 mm) ACCs can be easily manufactured by just adjusting the amount of spinning material. The obtained all-cellulose composites were transparent to visible light, at least in the case of the reference material and the CNC reinforced samples, indicating a good fibre/matrix bonding and only minimal warpage and void content could be observed. This warpage and void formation, caused due to shrinkage during the draying process, decreases with the right quantity of spinning material, as well as applied pressure during consolidation. However, no improvements in the mechanical properties were observed for CNC and HNT nanoreinforced all-cellulose composites compared to a reference material.
6. Future work

- Optimization of stretching and drawing conditions
  - Introducing more drums in the spinning process
  - Improve the stretching of the fibers by better clamping
  - Stretching of the tapes right after the cold pressing step, while is still in a wet state
to a preferred orientation of the nanoreinforcement in the direction of stretching
  as shown by Gindl et al. and Pullawan et al. [57-58]

- Optimization of the spinning speeds

- Reduce the speed of the carriage for an even better fiber alignment

- Optimization of time in hot press as well as the applied pressure

- Make a mould already in the final sample size to avoid the need of cutting and
  therefore introducing additional cracks

- Try drying the tapes at room temperature without pressure till almost all the water is
  being removed then hot press

- With Cellulose I fibers it is clear that a good interface and therefore to much
  dissolving of the reinforcement leads to a reduction of the overall mechanical
  properties. In this case it is not completely clear and it should be studied if the
  conservation of the shape of the fibers can affect the final properties if the
  composites.

- Try different dopes viscosities

- Development of a machine that enables stretching and pressing at the same time

- Go back to partially dissolving the fibers using the same spinning equipment
7. References


[47] Bhardwaj N, Kundu SC. Electrospinning: A fascinating fiber fabrication technique. Biotechnology Advances. 2010;28(3):325–347.


