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**BNC Textile: bacterial nanocellulose as a
new and sustainable material for textile
yarn**

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STATEMENT OF INTEGRITY

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RESUMO

Neste trabalho, são discutidas tecnologias de produção de fios para aplicações têxteis tendo a celulose como base. São referidas tendências recentes que visam poupar o ambiente de exploração massiva, como o uso de nanocelulose bacteriana, procurando também responder às necessidades crescentes por fibras alternativas obtidas por processos sustentáveis. A avaliação do ciclo de vida de vários métodos de produção de fibras de celulose foi também abordada.

O objetivo deste trabalho foi a produção de fios a partir de fibras alternativas às existentes no mercado utilizando a nanocelulose bacteriana como matéria-prima. A nanocelulose bacteriana possui características como elevada resistência mecânica, capacidade de retenção de água, estabilidade dimensional, cristalinidade, biocompatibilidade e biodegradabilidade, o que permite explorar a sua utilização em várias áreas como biomédica, cosmética, alimentar, têxtil e papel. Além disso, a sua produção tem um impacto ambiental menor onde não ocorre a destruição de florestas e a sua produção é feita em apenas algumas semanas, um tempo bastante inferior comparativamente ao análogo vegetal que demora meses ou anos.

Foram produzidos filamentos utilizando diferentes concentrações de nanocelulose bacteriana e dois sistemas de dissolução diferentes: o método de dissolução em fase sólida e o método tradicional de produção de Liocel. Pelo primeiro método foi possível obter filamentos com módulo de Young de $20,8 \pm 5,4$ GPa, resistência à tração de $1201,9 \pm 149,2$ MPa e alongamento de $11,5 \pm 0,1$ %. Pelo segundo, foi obtido um módulo de Young de $35,0 \pm 17,2$ GPa, resistência à tração de $1100,0 \pm 480,0$ MPa e alongamento de $6,8 \pm 4,0$ %. De forma a respeitar os critérios de produção de filamentos pelo processo Liocel, foi realizado, posteriormente, um estudo de despolimerização da nanocelulose bacteriana. O grau de polimerização da nanocelulose bacteriana foi reduzido do seu valor original (cerca de 2000) para 602-531, que normalmente é considerado adequado para o processo de Liocel.

Métodos alternativos de produção de filamentos sem a dissolução da nanocelulose bacteriana foram também testados – dry-spinning e wet-drawing, obtendo-se resultados semelhantes em ambos os métodos, com um módulo de Young de $5,4 \pm 2,2$ GPa e $7,9 \pm 3,4$ GPa, resistência à tração de $194,6 \pm 53,2$ MPa e $220,2 \pm 98,4$ MPa, e alongamento de $9,1 \pm 6,3$ % e $14,3 \pm 1,8$ %, respetivamente.

São necessários mais estudos de forma a perceber se a despolimerização da nanocelulose bacteriana é realmente necessária para o processo de Liocel. A produção de fibras sem solventes também requer um estudo mais aprofundado, sendo estas as formas mais sustentáveis de produção de fibras têxteis.

PALAVRAS-CHAVE

Nanocelulose bacteriana, fibra, têxtil, sustentabilidade, celulose, despolimerização, Liocel, fibras sem solvente

ABSTRACT

In this work, the technologies for the production of cellulose-based textiles, their surface modification and the recent trends aiming at sparing the forest from massive exploitation are discussed. The life cycle assessment of several cellulose fibre production methods is also addressed.

The objective of this work was the production of cellulose filaments using an alternative source of cellulose – bacterial nanocellulose – as raw material. Bacterial nanocellulose has impressive characteristics such as high mechanical strength, water-holding capacity, dimensional stability, crystallinity, biocompatibility and biodegradability, allowing to explore its use in several areas, namely in the biomedical, cosmetic, food, textile and paper areas. Besides that, its production has less impact on the environment as no forests are destroyed and its production is faster.

Filaments were produced using different BNC concentrations and two different dissolving systems: the solid-phase dissolution method and the traditional Lyocell production method. From the first method it was possible to obtain filaments with Young's modulus of $20,8 \pm 5,4$ GPa, tensile strength of $1201,9 \pm 149,2$ MPa and elongation of $11,5 \pm 0,1$ %. Through the second was obtained Youngs' modulus of $35,0 \pm 17,2$ GPa, tensile strength of $1100,0 \pm 480,0$ MPa and elongation of $6,8 \pm 4,0$ %. In order to meet Lyocell's production criteria, the degree of polymerization of bacterial nanocellulose was lowered from its original value (around 2000) to 602-531, which is normally considered suitable for the Lyocell process. Although it has been possible to achieve the depolymerization of BNC in a simple way using a chemical treatment, it would be preferable to process the original cellulose, without depolymerization.

Alternative methods of filament production without dissolution were also tested – dry spinning and wet-drawing. Similar results were obtained for both methods with a Young's modulus of $5,4 \pm 2,2$ GPa and $7,9 \pm 3,4$ GPa, tensile strength of $194,6 \pm 53,2$ MPa and $220,2 \pm 98,4$ MPa, and elongation of $9,1 \pm 6,3$ % and $14,3 \pm 1,8$ %, respectively.

Further study on this subject is needed to understand if BNC depolymerization is really needed on a pilot or commercial scale for the Lyocell process. Fibres without solvents also need to be further studied as they are the more sustainable ways of fibre production and there is a growing need for these types of fibres on market.

KEYWORDS

Bacterial nanocellulose, fibre, textile, sustainability, cellulose, depolymerization, lyocell, fibres without solvents

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LIST OF ABBREVIATIONS

BNC – Bacterial nanocellulose

BOD – Biological oxygen demand

CED – Cupriethylenediamine

CNC – Cellulose nanocrystal

CNF – Cellulose nanofibre

COD – Chemical oxygen demand

DP – Degree of polymerization

IL – Ionic liquid

LCA – Life cycle assessment

NC – Nanocellulose

NMMO – N-methylmorpholine-N-oxide

RCF – Regenerated cellulosic fibres

SDGs – Sustainable development goals

TEMPO – 2,2,6,6-tetra-methylpiperidyl-1-oxyl

1. INTRODUCTION

Humankind practices such as the excessive use of non-renewable sources of energy and raw materials, and the unlimited generation of waste in the vast majority of industrial processes, have wide impact on the environment sustainability (Akinsemolu, 2018). Such is the case with the escalating demand for textile products. The demand for textile fibres reached 75.5 million tons in 2010 and is predicted to rise to 133.5 million tons by 2030 (at a growth rate of 3.1 %/year) (Eichinger, 2012; Haemmerle, 2011; Hummel *et al.*, 2015). From the production of raw materials, to spinning, weaving fabrics and dyeing, substantial amounts of water and chemicals are required, including nutrients and pesticides for growing raw materials such as cotton. Downhill, consumers' use also bare a significant environmental footprint from the consumption of water, energy and chemicals from washing, drying and ironing (Sajn, 2019). In 2015, the United Nations set up an agenda aiming to achieve 17 Sustainable Development Goals (SDGs) by 2030, proposing several solutions to improve the economic and social development and providing the essentials to everyone without overwhelming nature (a concept understood as sustainability) (United Nations, 2015). The United Nations Alliance for Sustainable Fashion emerged to ensure the achievement of the SDGs in the fashion industry, throughout the product value chain (United Nations, 2020).

There is an emerging environmental awareness and social concern regarding the environmental impact of the textile industry, highlighting the growing need for developing green and sustainable approaches throughout this industry's supply chain. Uphill, due to population growth and the rise in consumption of textile fibres, new sustainable raw materials and processes must be found. As a unique biopolymer in terms of its structure and properties, cellulose is the most important and available renewable resource for textiles. The physical and chemical modification reactions yielding fibres are of high commercial importance today. Recently developed technologies allow the production of filaments with the strongest tensile performance without dissolution or any other harmful and complex chemical processes. Fibres without solvents are thus on the verge of commercialization.

1.1 Textile fibres

1.1.1 Overview

Fibres are the starting point for all textile products that serve the everyday needs of society. Fibres of short length, called staple fibres, as is the case of most natural fibres, range between 3 and 20 cm in length. A filament is a fibre of indefinite length, being silk the only naturally produced. Most regenerated and synthetic fibres are produced as filaments. Different methods of drawing, spinning and twisting, depending on the fibre type, are used to form a continuous strand of yarn (Sinclair, 2015). The textile is then produced. Conventional textiles are designed, developed, or used for the common decorative, or aesthetic applications. Technical textile products can be grouped into various categories, depending on their application, such as industrial, medical, packaging, sports, automotive, construction, aerospace, geo-textiles, agro-textiles, protective clothing. Each segment has a large variety of products made from diversified fibres/raw materials using divergent manufacturing techniques and equipment (Keller & Giddings, 2020; Rasheed, 2020).

Textiles were produced domestically until the XVII century, mostly from vegetable sources using cotton, hemp and flax but also from animal sources as wool and silk. Then, during the industrial revolution, the production process was mechanized, allowing totally new and faster methods of manufacturing (Texcoms, 2019). The fibres produced until the end of the XIX century were all natural (figure 1). During the 1900s, the production of man-made fibres began, more specifically regenerated cellulose fibres by the Viscose method. The synthetic fibres appeared in the textile market only by late 1930s, made from chemically synthesized polymers (Murthy, 2016; Sinclair, 2015).

Natural fibres, including animal (protein) and vegetable ones, make up almost 40 % of the textile fibres produced annually in the world. Vegetable fibre (cellulose) is extracted from plants (Yu, 2014). The most abundant natural polymer on earth is cellulose, representing about 30-40 % of all terrestrial biomass, with a biosynthesis of 10^{11} tons annually (Akhlaghi *et al.*, 2020; Kafy *et al.*, 2017; Levi *et al.*, 2016). Being biodegradable, renewable, biocompatible and affordable polymer, cellulose has several other uses such as in paper, food additive, excipient, coatings, diapers, textiles and composites (Kim *et al.*, 2019). While generally synthesized by plants, it is also produced by some bacteria, fungi and algae. In plants, cellulose is the main structural component of the primary cell wall (Brigham, 2018).

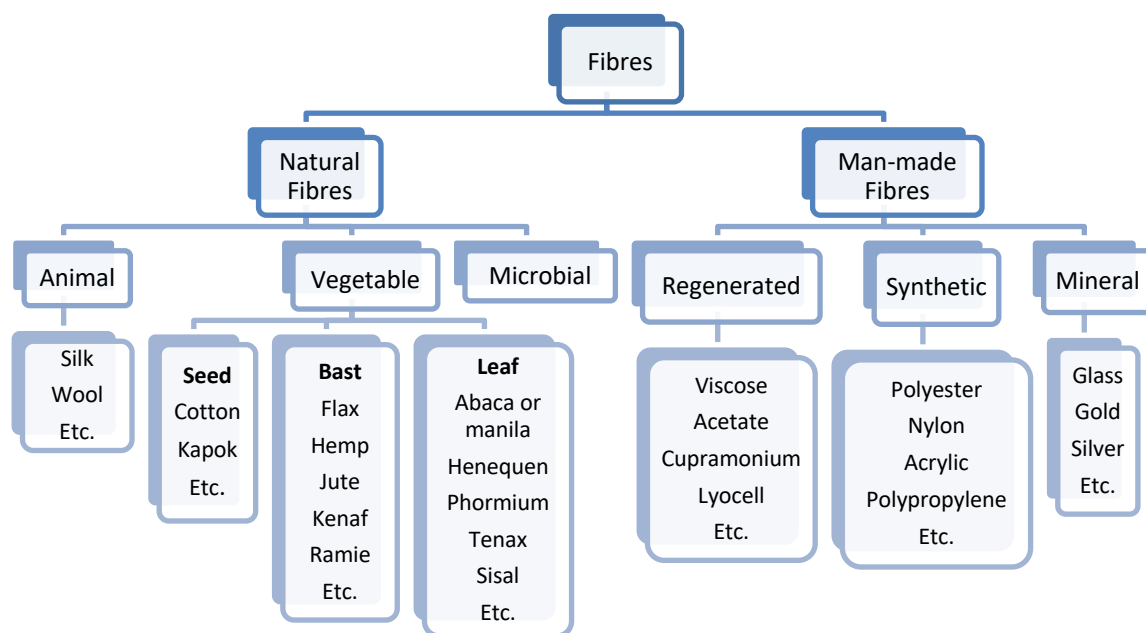


Figure 1. Classification of main natural and man-made fibres (adapted from (Murthy, 2016; Sinclair, 2015)).

Cotton is the most popular natural fibre, accounting for around 90 % of all natural fibres. Cotton is one of the most important natural textile fibre crop, both from the agricultural and manufacturing sectors' perspective. It is the biggest source of clothing as well as being used to produce apparel, home furnishings, and industrial products (Yu, 2014). The use of cellulosic fibres is expected to grow from the current level of 3.7 kg per capita to 5.4 kg by 2030 (Haemmerle, 2011). Cotton fibre contains approximately 90 % of cellulose, dried hemp has 40-50 % and wood 40-55 %, commonly found combined with other substances as lignin and hemicelluloses (Ansell & Mwaikambo, 2009; Wang *et al.*, 2019). In addition to cotton, the most commonly used natural vegetable fibres include flax, ramie, jute, kenaf, and sisal. Cultivation with cotton hybrids will expand and so, the harvest yield from 800 (2010) to 925 kg/ha (2030) will increase its production capacity. However, it will not compensate for the disappearance of arable land and growing demand. It is estimated that only 3.1 kg of cotton per capita will be available in 2030 (Haemmerle, 2011). This so-called cellulose gap offers new opportunities for man-made cellulosic fibres. The gradual replacement of cotton by pulp-based fibres is also necessary from an ecological perspective. Nowadays, new natural fibres, especially vegetable fibre sources, are being exploited, for example, kapok, pineapple, and apocynum (Yu, 2014).

Synthetic fibres have dominated the market since mid 1990s, overtaking cotton. These are made from organic synthetic high-molecular mass compounds and are produced

synthetically from petroleum-based raw materials. They represented up to 63 % of the global fibre production in 2019. The most used synthetic fibre was polyester, with a market share of around 52 % of total global fibre production. Cotton was second, with 23 % (Textile Exchanges, 2020). Currently, fibres have a cost of 1,17 €/kg for cotton, 1,31 €/kg for Viscose and 0,86 €/kg for polyester (Emerging Textiles, 2020).

1.1.2 Novel sources of cellulose and nanocelluloses

In recent years, several nanocelluloses (NC), from microbial and plant sources, have been textured as a source of textile fibres. The interest in NCs is essentially focused on taking advantage of their higher crystallinity, since they promote great mechanical resistance (Nunes, 2014). NC is not a single material type but rather a family of materials with very different features, mostly due to different sources and preparation methods (Clemons, 2016).

1.1.2.1 Bacterial nanocellulose

An alternative to wood/plant cellulose is bacterial nanocellulose (BNC) (Figure 2), a homopolysaccharide extruded by Gram-negative species of the genera *Komagataeibacter*, *Acetobacter*, *Rhizobium*, *Agrobacterium*, *Pseudomonas*, *Salmonella*, *Alcaligenes* and *Sarcina*, the only Gram-positive bacterial genus (Jonas & Farah, 1998; F. Dourado et al., 2016). Different bacteria produce cellulose with distinct morphology, structure, properties and yields (Wang et al., 2019). To obtain high yields of BNC, it is necessary to use the highest cellulose producer species, such as *Komagataebacter xylinus* (Dourado et al., 2016).



Figure 2. BNC membrane before (A) and after (B) purification.

The BNC biosynthesis was first observed in kombucha, a fermented beverage produced by a symbiotic colony of bacteria and yeast, where a cellulose film is formed on the culture media-air interface. It was first reported in 1886 by A. J. Brown, who identified a film with a structure chemically equivalent to that of plant cellulose (Brown, 1886). BNC consists of < 100

nm ribbon-shaped fibrils, composed of 7-8 nm wide elementary nanofibrils aggregated randomly into bundles, without lignin or hemicellulose (Gorgieva & Trček, 2019).

BNC has the same chemical structure as that of plant cellulose. Linear homopolymer of glucose monomers are linked by β -(1 $\rightarrow$ 4) glycosidic linkage with the chemical formula $(C_6H_{10}O_5)_n$. Nevertheless, it has different macromolecular structure and properties (Ullah *et al.*, 2019). The polymerization degrees are within 2000 to 6000 for BNC and 13 000 to 14 000 for plant cellulose, decreasing during pulping and purification. The unbranched chains of cellulose are held together through strong intra- and intermolecular hydrogen bonds to form the elementary fibres and the supramolecular structure (Choi & Shin, 2020; Fang *et al.*, 2020). This structure possesses exclusive properties such as high mechanical strength, water-holding capacity, dimensional stability, crystallinity, biocompatibility and biodegradability (Picheth *et al.*, 2017). Given these features, numerous applications of BNC have been studied: in the biomedical field as a wound dressing, for tissue regeneration/substitution and drug delivery systems; in the textile and paper industries for fibre composites and coatings; in the food and cosmetic industries as an emulsifier and viscosifier (Anton-Sales *et al.*, 2020; Amorim *et al.*, 2020; Klemm *et al.*, 2005; Chawla *et al.*, 2009; Müller *et al.*, 2013; Nimeskern *et al.*, 2013; Lee *et al.*, 2014; Shi *et al.*, 2014; Rajwade *et al.*, 2015). The main application is still as a food product known as *nata de coco*, mostly produced and consumed in Asian countries (Dourado *et al.*, 2016).

BNC can be produced through static or agitated cultures (Wang *et al.*, 2019), most studies being carried out using the former (Zywicka *et al.*, 2015). In this method, BNC is produced in containers filled with nutrients and incubated for defined periods, at around 30 °C and pH of 5.0. The efficiency of BNC production in stationary cultures is strongly connected with the air-liquid surface area (given that *Komagataebacter* strains are mandatory aerobes), where it is produced as a hydrogel sheet containing around 99 % of water (Wang *et al.*, 2019).

To achieve industrial scale production, major exploited alternative fermentation technologies, using specific fermentation media and overproducing mutant strains include agitated and air-lift bioreactors, membrane reactors and horizontal bioreactors. The idea behind is that the agitated/shaking culture facilitates the oxygen delivery to bacteria during cultivation (Wang *et al.*, 2019). Under agitation and aeration conditions, fibrous suspension, or pellets can be obtained. This, however, limits BNC applications, allows cellulose-negative mutants to dominate the population of growing cells (which in turn limits the cellulose yield) and requires

high agitation power (due to the viscous character of the suspensions) (Czaja *et al.*, 2004; Huang *et al.*, 2014; Wang *et al.*, 2019; Rodrigues *et al.*, 2019).

The textile fibres production amounts to 105,6 million tons per year, worldwide (Garside, 2019). The current BNC global production is far below this magnitude and confined to small scale production units (Phisalaphong *et al.*, 2016; Dourado *et al.*, 2016; Piadozo, 2016). Its potential as a sustainable alternative for the textile industry has never been assessed (Choi & Shin, 2020).

1.1.2.2 Plant Nanocellulose

Cellulose is a hydrogen bond cross-linked biopolymer. The hydroxyl groups on one cellulose chain bond with the other to develop rigid and stable molecules, giving the plant stiffness and strength. The hydrogen bonding between cellulose chains makes it insoluble in common organic solvents and water (Thomas *et al.*, 2020). Fibrils are formed by joining cellulose molecules together. These fibrils agglomerate into bundles, which the plant uses to construct its cell wall combined with hemicelluloses and lignin (figure 3) (Lundahl, 2018). The morphology of the cellulose fibrils morphology demonstrates a mesh-like structure (Thomas *et al.*, 2020).

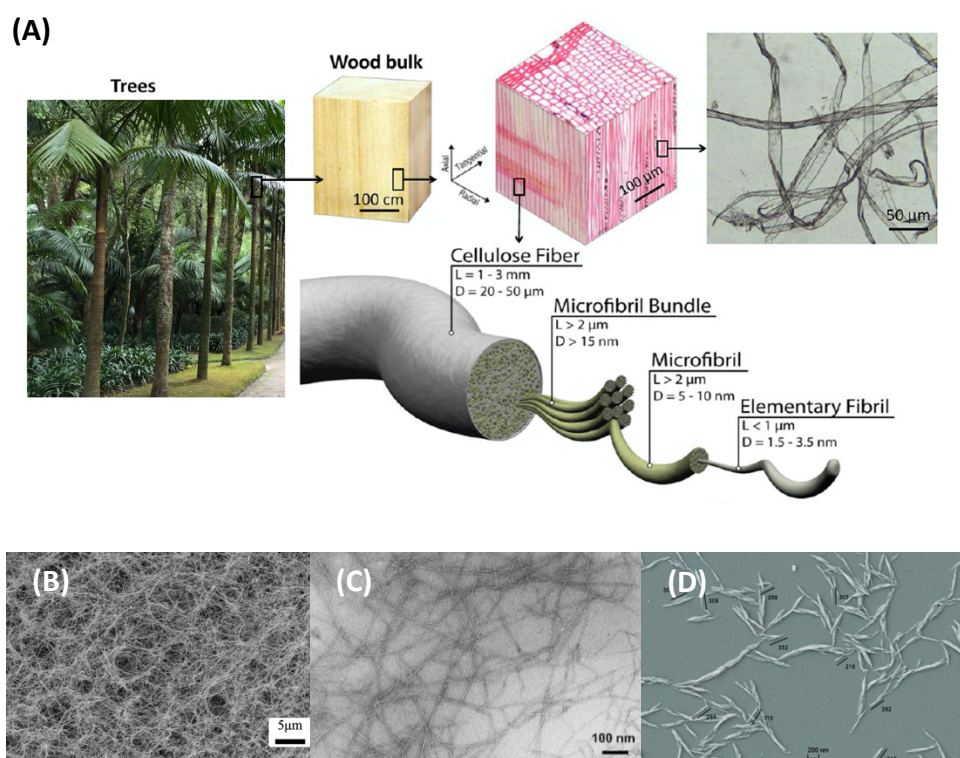


Figure 3. (A) Hierarchical structure of wood fibres: Reprinted (adapted) with permission from (Zhu et al., 2013). Copyright (2013) American Chemical Society. Comparison microscopic image of; (B) bacterial nanocellulose (Li et al., 2017): Published by The Royal

Society of Chemistry, (C) nanofibrillated cellulose: Reprinted (adapted) with permission from (Saito et al., 2007). Copyright (2007) American Chemical Society and, (D) nanocrystalline cellulose (Anžlovar et al., 2018).

NC can be produced by top-down approaches, i.e. the deconstruction of fibres by chemical, enzymatic or mechanical methods in case of plant NC, or by bottom-up routes for BNC (Charreau *et al.*, 2020). Plant NC is typically divided into two main categories: cellulose nanofibres (CNFs) and cellulose nanocrystals (CNCs) (Amorim *et al.*, 2020). The final chemical and physical properties of NC depend directly on the source and preparation conditions of the cellulose (Kargarzadeh *et al.*, 2017). NCs have properties such as high strength and stiffness, low density, biodegradability, high surface area, and low thermal expansion, which led to much research and innovation during the last two decades. Both CNC and CNF have applications as composite materials, paper and board industry, adsorbent products, food and beverages, paints and coatings, adhesives, packaging, oil and gas, electronics, and medical, pharmaceutical and cosmetic product (Charreau *et al.*, 2020).

Different raw materials can be used to obtain NCs such as coconut husk fibre, mengkuang leaves (*Pandanus tectorius*), cotton, *Agave tequilana*, barley wastes, tomato peels, garlic straw residues, forest residues, corncob residue, *Gigantochloa scortechinni* bamboo culms, industrial waste cotton, cassava root bagasse and peelings, sugar palm fibres (*Arenga pinnata*), corn straw and sago seed shells (Ventura-Cruz & Tecante, 2019). The raw material must be pre-treated to remove lignin and hemicellulose by milling, pulping and bleaching. CNCs, also called cellulose whiskers, nanowhiskers, or nanorods, are produced by transverse cleavage of cellulose by acid hydrolysis, using strong acids such as sulfuric and hydrochloric acids (Clemons, 2016), where, under controlled conditions of temperature, agitation and time, amorphous cellulose microfibrils are preferentially cleaved, whereas crystalline regions, which have a higher resistance to acids, are maintained (Charreau *et al.*, 2020). CNC have a nanosized distribution: a diameter of 4-55 nm and 90-400 nm in length (Zinge & Kandasubramanian, 2020). After acid hydrolysis, CNC recovery operations include washing, filtration/centrifugation and dialysis, to remove the remaining acid (Charreau *et al.*, 2020). Due to CNC higher crystalline structure, it has less flexibility than CNF (Zinge & Kandasubramanian, 2020). Recently, CNC have been used as reinforcing components of polymeric matrices, and in the synthesis of polymers with liquid crystalline behaviour for

electronic applications. Currently, CNC is produced in commercial quantities of 2-260 ton/year (Charreau *et al.*, 2020).

CNFs, also called cellulose nanofibrils or nanofibrillated cellulose, are obtained by mechanical disintegration (Amorim *et al.*, 2020). CNF are cellulose structures of high aspect ratio containing crystalline and amorphous regions which form entangled networks. Although CNF isolation is associated with mechanical destructuring methods (pressure, cavitation, shear and impact forces), the high energy consumption needed has led to the integration of pre-treatments to facilitate further fibrillation (Charreau *et al.*, 2020). A common pre-treatment uses a 2,2,6,6-tetramethylpiperidine-1-oxy radical (TEMPO) catalyst to mediate the oxidation of native celluloses, that reduces the energy required to fibrillate (Clemons, 2016). The product obtained is a translucent firm gel. CNF can be applied in absorbent products, reinforcement of composite materials, rheology modifying agents and, especially, papermaking products such as paperboard, tissue-making, deodorant sheets and other cosmetics sheets. CNF is produced in commercial quantities of 24–560 ton/year (Charreau *et al.*, 2020).

1.2 Technologies for the production of Cellulose Textile Fibres

1.2.1 Regenerated cellulosic fibres

Regenerated cellulosic fibres (RCF) are obtained by derivatizing or dissolving cellulose from wood pulp or plant fibres. As the length of wood pulp fibres is too short for textile use, they have to be processed by means of a continuous spinning associated with a regenerating technology (Navard, 2013). In these processes, the structure of the starting cellulose is modified by adding a solvent, which forms an intermediate compound such as sodium or acetate derivatives. Then these intermediate compounds are processed and dissolved, followed by the regeneration of the cellulose fibre (Woodings, 2001). The improvement of cellulose dissolution is a prevailing goal. Cellulose structures undergo several transformations depending on the kind of solvent and treatment conditions. Presently, the most used industrial methods for dissolving cellulose pulp are the Viscose, Cuprammonium, Acetate and Lyocell methods. Cellulose solvents can be divided into two groups: non-derivatizing – comprises systems that dissolve the polymer by intermolecular interactions; derivatizing – relates to all the solvents where the dissolution process is combined with the formation of unstable ether, ester or acetal derivatives. Both groups include aqueous and non-aqueous solvents (Heinze & Koschella, 2005).

Regenerated cellulose was the first man-made fibre applied in the textile and apparel industry, in the early days of its development, during the 1850s. These fibres have a smooth

and lustrous appearance much like silk (although chemically different), and the outstanding water absorption ability of cotton. In 1924 the generic name Rayon was adopted by the U.S. Department of Commerce and various industrial associations to label RCF that include Viscose, Acetate, Lyocell, Modal and Cupro (Chen, 2015; Textile Exchanges, 2020).

With an annual production volume of around 7.1 million tons in 2019, the global production volume of RCF has more than double since 1990. RCF have a market share of about 6.4 % of the total fibre production volume and is expected to increase in the coming years. Viscose is the most important RCF with a market share of around 79 % of all RCF and a production volume of around 5.63 million tons in 2019. Acetate has a market share of around 13 % of all RCF with a production of approximately 0.95 million tons in 2019 but it is mainly used for non-textile applications. Lyocell was the third most used RCF after Viscose and Acetate in 2019. It had a market share of around 4.3 % and a production volume of 0.3 million tons, being this fibre expected to grow faster than the others RCF. Using a production process quite similar to that of Viscose, Modal fibres had a market share of around 2.8 % of the total RCF market in 2019 with a production of around 0.2 million tons. Cupro has a market share of less than 1 % of the total RCF market. There is only one supplier of Cupro, producing around 17,000 tons in 2019 (Textile Exchanges, 2020).

RCF are being used in the most diverse materials, from sportswear to health care textiles, alone or combined with other natural or synthetic fibres, due to their characteristic properties such as tensile strength and smoothness (Karthik & Rathinamoorthy, 2017).

1.2.1.1 Viscose Rayon

The Viscose process is the world's most widely used method for producing RCF. The first patent on the Viscose process was granted to Cross and Bevan in 1893. Over the past 100 years, this process underwent many alterations, although the basic chemistry is still the same, which allowed Viscose to become one of the most widely used regenerated fibres (Wilkes, 2001; Thakur *et al.*, 2017).

The process, shown in figures 4 and 5, consists in dissolving the pulp in NaOH and, after steeping for a specified period of time, shredding and ageing. The viscosity of the pulp depends on the ageing time. The aged pulp is then treated with carbon disulphide (CS₂) to form the orange-colored cellulose xanthate. Lastly, this derivative is dissolved in NaOH with a lower concentration, the starting stage of Viscose formation (Shaikh *et al.*, 2012). The polymer is finally precipitated in acid, for simultaneous neutralization and regeneration of the cellulose in a wet-spinning step. Then, several steps of washing and drawing yield a regenerated fibre of

pure cellulose (Olsson & Westman, 2013; Chen, 2015). Currently, carbon disulphide can be reused up to 70 %, and the remaining 30 % is converted into sulfuric acid (H_2SO_4), which is also recycled (Rana *et al.*, 2014).

Despite being made from wood, the fibre production by Viscose process is known to cause significant environmental problems due to the high usage of chemicals, such as sodium hydroxide, producing sodium sulphate as a by-product. The life cycle of the Viscose process encompasses other impacts, associated to how reagents are produced and recycled, as well as the consumption of energy, the use of fossil fuel and deforestation (Shen *et al.*, 2010).

Recently, the company Nanollose announced the development of a Viscose making process using BNC. This method transforms BNC into Nullarbor™ Tree-Free Viscose fibres using technology which is compatible with existing industry processing and manufacturing equipment (Nanollose, 2020; Jinzarli *et al.*, 2019).

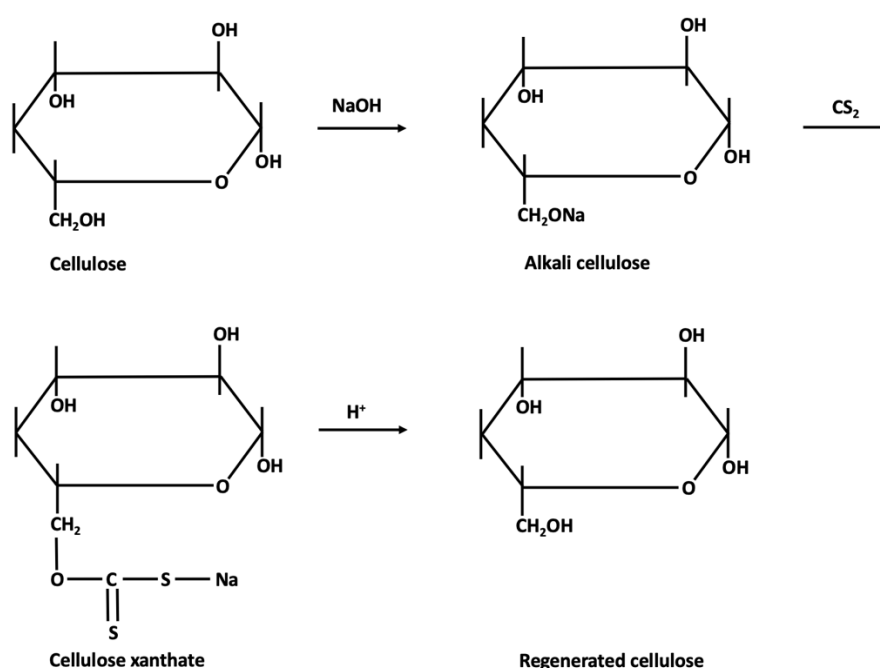


Figure 4. Mechanism of Viscose fibre production (addapted from (McKeen, 2017; Rodgers & Waddell, 2013)).

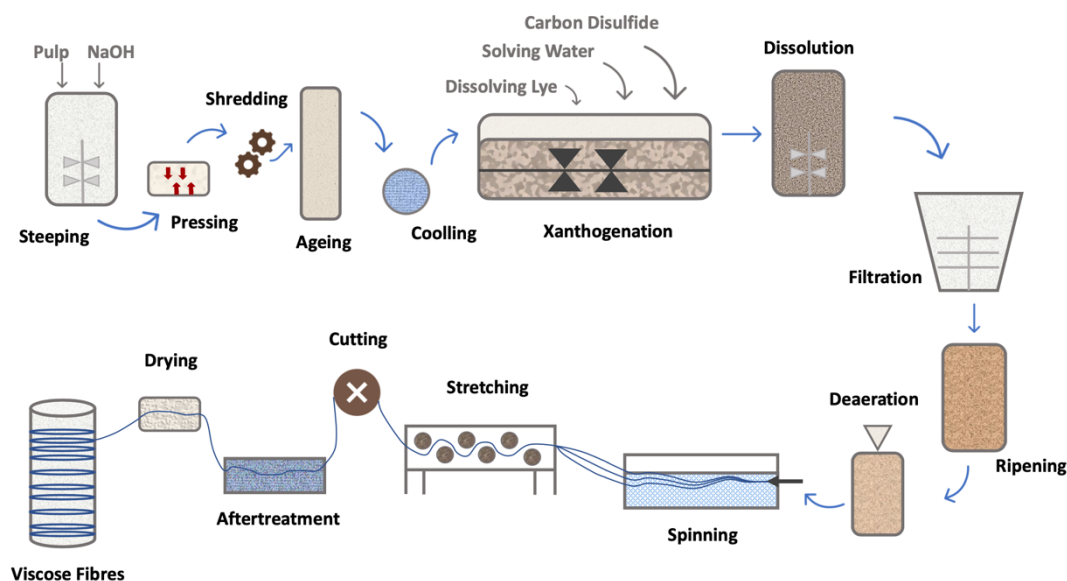


Figure 5. Schematics of Viscose fibre production (adapated from (Alagirusamy & Das, 2015; Sayyed et al., 2019)).

1.2.1.2 Lyocell Rayon

The direct dissolution of cellulose (without derivatization) has been the object of research for many years. This process may also simplify the production of regenerated cellulose by omitting several steps (Olsson & Westman, 2013; Perepelkin, 2007). The technology of direct dissolution of cellulose is a simpler process, reducing the use of chemicals by ten times in comparison to the Viscose process. Also, a direct solvent is easier to recycle, since no byproducts are formed, resulting in a more environmentally friendly process (Olsson & Westman, 2013). However, the Lyocell production costs are higher than the Viscose, due to the high cost of solvent and the use of high temperatures for cellulose dissolution (Alam & Christopher, 2017).

1.2.1.2.1 History of Lyocell

Lyocell is the first successful technology of generation of cellulosic fibres by direct dissolution, resulting in fibres with exceptional properties, making it a serious competitor to the Viscose process, since it is more environmentally friendly (White, 2001; Peng *et al.*, 2017). Lyocell fibre has higher tenacity (especially wet tenacity), higher modulus, lower shrinkage, better thermal stability, higher crystallinity, and greater degree of orientation, than Viscose (Edgar & Zhang, 2020). The Lyocell fibre market is set to grow from 760 million € in 2016 to over 1.35 billion € by 2024 (Pulidindi & Chakraborty, 2016).

A patent describing the basic process of dissolving cellulose by using NMMO solvent was filed by Clarence C. McCorsley in 1981 (McCorsley, 1981). In 1992, in Mobile Alabama, U.S.A., the company Courtauds, achieved the full commercial production of this new regenerated fibre with the trade name TENCEL® (Chen, 2015). Lenzing, an Austrian company, started the production of Lyocell fibre in 1990 with their first pilot plant. The full-scale production plant came into operation in 1997 and the fibre was called Lenzing Lyocell®. In 2004, Lenzing purchased the TENCEL® Group (Perepelkin, 2007). Today, Lenzing is the world's largest Lyocell fibre manufacturer (Rana *et al.*, 2014). Other companies have emerged with their brand names for fibres obtained using this technology, such as Alceru (TITK Rudolstadt), Newell (Akzo Nobel), Acelon (Greencell) and Excel (Grasim) (Sayyed *et al.*, 2019).

1.2.1.2.2 The solvent and the phase diagram

N-methylmorpholine-N-oxide, commonly known as NMMO, is the most used of all non-derivatizing cellulose solvents, due to its ability to directly dissolve high concentrations of cellulose, while preserving the chemical properties of the polymer. The possibility of recycling up to 99,7 % of the solvent, makes the process economically viable and more environmentally friendly (White, 2001; Olsson & Westman, 2013).

NMMO is completely soluble in water and extremely hygroscopic. The high polarity of the N-O bond also results in a pronounced ability to form hydrogen bonds. There are three types of NMMO: anhydrous NMMO, monohydrate NMMO (NMMO·H₂O) with 13.3 % (w/w) H₂O, and disesquihydrate NMMO (NMMO·2.5H₂O) with 28 % (w/w) H₂O (Wikandari *et al.*, 2016). NMMO's oxygen can form two hydrogen bonds with hydroxyl groups from water or cellulose (figure 6), the competition between water and cellulose for these hydrogen bonds, being the central feature of this dissolution process (Maia *et al.*, 1981).

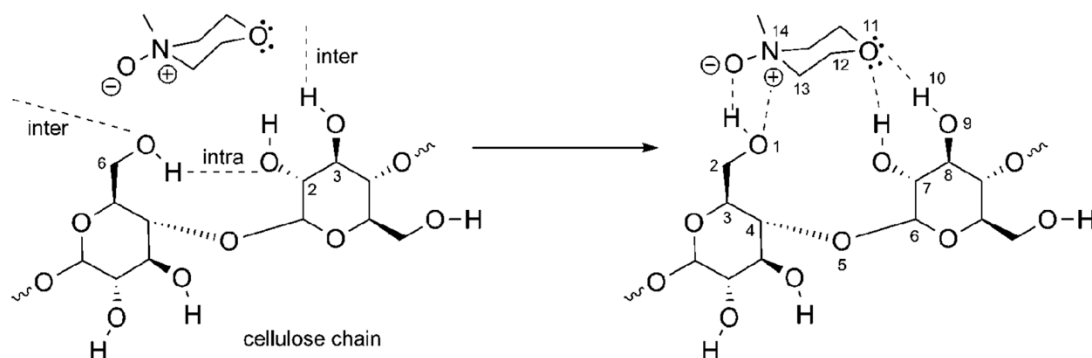


Figure 6. N-methylmorpholine-N-oxide – cellulose dissolution mechanism: Reprinted with permission from (Pinkert *et al.*, 2010). Copyright (2010) American Chemical Society.

Since NMMO is thermally unstable, the dissolution of cellulose in NMMO at elevated temperatures is performed under well-controlled conditions. NMMO degrades at temperatures higher than 120 °C. Due to its reactivity, stabilizers must be added at the beginning of the dissolution process, most commonly propyl gallate (Rosenau *et al.*, 2002).

The degradation of NMMO and subsequent side reactions may include N-methylmorpholine, morpholine and formaldehyde (Olsson & Westman, 2013). Some reactions are induced by transition metal ions such as iron and copper and that's why these must not be used in this process (Klemm *et al.*, 2005). Mechanical energy facilitates the rupture of cellulose-cellulose intermolecular bonds, favoring the interaction with NMMO. Furthermore, the apparent viscosity decreases with shear stress due to cellulose alignment, as expected in non-Newtonian polymer solutions. Viscosity is also dependent on cellulose concentration and degree of polymerization (Olsson & Westman, 2013).

The NMMO – water – cellulose phase diagram (figure 7), shows the relative amounts of H₂O and NMMO required for cellulose dissolution to occur. NMMO – water mixtures are direct solvents for cellulose in its monohydrate state. With a higher amount of water, cellulose will not dissolve, since a competition for NMMO takes place between cellulose and water, the interaction with the latter being favored. Thus, NMMO only links with cellulose when there is shortage of water molecules (Biganska & Navard, 2003). The process (described in more detail in the next section) starts with using a high water content, to induce the swelling of the cellulose fibres. An homogeneous pulp is produced containing, e.g, 35 % of H₂O, 9 % cellulose and 56 % NMMO (point C in figure 7). Then, the excess of water is removed under vacuum (point B). After further water removal, dissolution occurs at point A with a 14 % cellulose, 10 % H₂O and 76 % NMMO (Golova *et al.*, 2010).

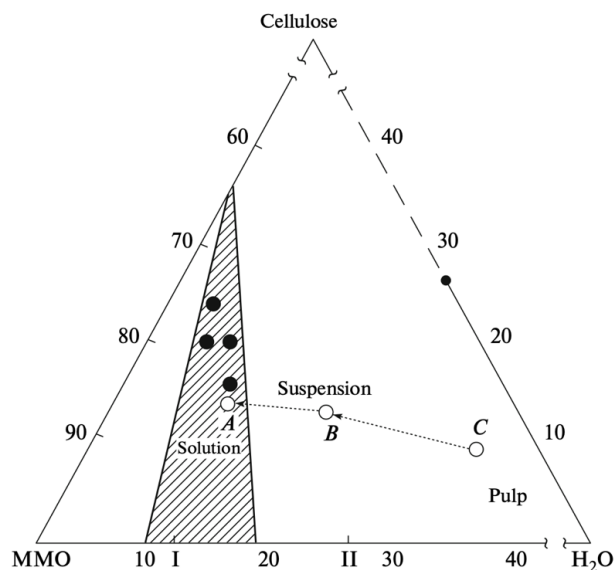


Figure 7. Schematic phase diagram of the cellulose–MMO–H₂O system: (line CBA) variation in the composition of the system during cellulose dissolution via the traditional MMO process; (closed circles) composition of the system during cellulose dissolution via the solid-phase MMO process; (I) MMO monohydrate and (II) MMO 2.5-hydrate (Golova et al., 2013).

1.2.1.2.3 Dissolution process

The first industrial system used to dissolve cellulose with NMMO (figure 8), involved the initial cellulose swelling. A cellulose pulp must first be milled into small particles to improve the surface contact area with NMMO. Then it is mixed with NMMO containing 20-30 % of water (Zhang *et al.*, 2018). The amount of pulp fed to the mixer has to be quantified, to control the cellulose content. Mixing is done at 70-90 °C, with high-speed refiners, to further break down the pulp, improving the solvent wetting. The resulting swollen pulp is then heated to 90-120 °C, under vacuum, to remove excess water, yielding a clear dark amber-colored solution, to a final cellulose concentration within 10 to 18 % (m/m) (White, 2001). The use of low pressure reduces the temperature required for water evaporation, so the NMMO does not undergo exothermic degradation (White, 2001). After dissolution, impurities such as undissolved pulp fibres are filtered. The mixture is then extruded and spun through an air gap into a spin bath with a polar liquid, like water or alcohol. These coagulation agents are miscible with NMMO, removing it from the cellulose solution (Biganska & Navard, 2011). This process is called dry-jet wet-spinning and consist of thousands of small holes through which the solution is extruded into fibres (White, 2001). Various other technologies are used in fibre spinning dope such as kettle-type dissolution, twin-screw extruder dissolution, vacuum mixed propulsive

dissolution and vacuum membrane propulsive dissolution technology. The first one is intermittent, while the others are continuous. Currently, the most used technology in industrial production is continuous vacuum film propulsive dissolution technology (X. Jiang et al., 2020).

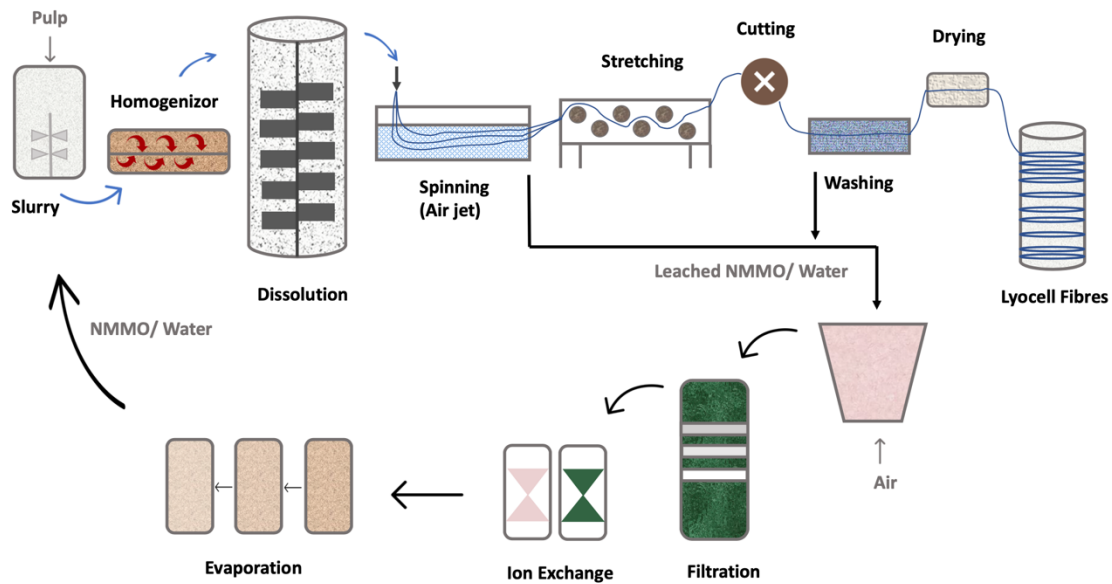


Figure 8. NMMO based lyocell process (addapted from (X. Jiang et al., 2020; Sayyed et al., 2019)).

To facilitate the cellulose dissolution process, various pre-treatment methods have been researched such as enzyme treatment, to enhance reactivity, microwave heating process to reduce crystallinity, mechanical blending technique, enzymatic peeling treatment, ball or vibration milling, steam explosion and electron beam irradiation. However, industrially, most of these are technically and economically non-viable (Sayyed *et al.*, 2020). Pre-swelling at temperatures from 30 °C to 75 °C lowers the pulp's crystallinity and forms a homogeneous solution with lower time and power consumption during the dissolution process. This makes Lyocell process more energy-efficient and sustainable (Sayyed *et al.*, 2020).

The degree of polymerization (DP) of cellulose pulp affects the mechanical strength of Lyocell fibre. The higher DP, the superior the mechanical strength; yet, an excessively high DP may result in a poorer solubility and an increase in the viscosity of spinning dope. The balance between DP and the solubility of dissolving pulp has a substantial impact on the spinning process and the mechanical properties of fibre (X. Jiang et al., 2020). Due to the difference in the degree of polymerization between BNC and plant cellulose, the use of the same concentration may yield different results, given the large difference in viscosity. For example,

a 6 % (m/m) solution of BNC (DP 2000) has a viscosity 10^3 Pa.s, which in the case of wood cellulose (DP of 600) is achieved only at 18 % (m/m) (Makarov *et al.*, 2019).

BNC Lyocell fibres have been produced by Gao *et al.* (2011). In their work, water was added to NMMO at 13.3 % m/m and the mixture was heated at 90 °C for 30 min. Then BNC powder was added (7 % m/m) and the mixture was heated at 80 °C for 12 h. The solution was extruded and BNC filaments were formed. The regenerated BNC fibres had a cellulose II crystalline structure, lower degree of crystallinity, smaller crystalline sizes, and better thermal stability than native BNC. This regenerated BNC fibres had a tensile strength of 0,5-1,5 cN/dtex and extension at break of 3-8 % (Gao *et al.*, 2011).

A different process for Lyocell fibre production, using the NMMO – water – cellulose solid-phase system at a concentration of cellulose under 25 % (m/m), was developed at the All-Russian Scientific-Research Institute of Polymer Fibres (Golova *et al.*, 1992; Golova, 1996). The method uses high-melting hydrate forms of NMMO, which better dissolves cellulose, substantially accelerating the process. The process starts with a solid-phase activation of cellulose by NMMO with a water content of 8 % (m/m) or less. Cellulose dissolution proceeds under triaxial compression, shearing, and forced plastic flow. Under the conditions of all-hydrostatic compression and shear, the mechanochemical activation of cellulose by NMMO occurs via formation of H- complexes. Then, under temperature (105 °C) and shear rate, the cellulose dissolves into a highly homogeneous and concentrated solution (Golova *et al.*, 2013). This method has been successfully used with BNC fibres with a DP of ~1500 and a solid-phase activation of BNC and NMMO (water < 10 %); the mixture was heated at 120 °C until a fluid solution was obtained (Makarov *et al.*, 2019). The authors claim that the (mechanochemical) activation is mandatory for a homogeneous solutions to be obtained, as no swelling occurs. Concentrations of up to 8 % of BNC were used, 6 % being optimal. The fibres were spun by dry-jet wet-spinning into a water coagulation bath. The mechanical properties of the obtained fibres are shown in table 1, along with other synthetic, natural and regenerated (man-made) cellulosic and organic synthetic fibres. The mechanical properties of Lyocell produced with BNC are similar with data for Viscose and Lyocell fibres (Makarov *et al.*, 2019; Makarov *et al.*, 2020).

Nonetheless, the Lyocell process has some limitations related to NMMO's intrinsic properties. The N-O moiety blocks the implementation of redox-active agents, whereas the cyclic ether structure is susceptible to thermal runaway reactions, requiring stabilizers. The side reactions and considerable byproduct formation can cause the degradation of cellulose, a

temporary or permanent discoloration of the resulting fibres, a decreased product performance, a pronounced decomposition of NMMO, increased consumption of stabilizers. So, alternative direct solvents for cellulose dissolution would be highly attractive for environmental and economic reasons (Hummel *et al.*, 2015; Rosenau *et al.*, 2001).

Table 1. Mechanical properties of different fibres

	d (µm)	Young's Modulus (GPa)	Tensile Strength (MPa)	Elongation (%)	References
BNC Lyocell	10,3-15,4	8,6-10,1	420-495	5,5-6,5	(Makarov <i>et al.</i> , 2019)
Ioncel	-	30	700-800	-	(Sashina, 2019)
Lyocell	9	22-31	472-624	6,8-13,7	(Gindl <i>et al.</i> , 2008; Manian <i>et al.</i> , 2018)
Viscose	10,5	9,3-11,6	220-340	8-23,5	(Gindl <i>et al.</i> , 2008; Manian <i>et al.</i> , 2018)
Cotton	10-27	8	600	7	(Bunsell, 2018)
Wool	15-40	2	170	35	(Bunsell, 2018)
Flax	15-20	65	650	1-3	(Bunsell, 2018)
Silk	12	8	400	25	(Bunsell, 2018)
Hemp	45	50	500	1-2	(Bunsell, 2018)
Jute	69	35	350	2.5	(Bunsell, 2018)
Polyamide 66 (Nylon 66)	20	< 5	1000	20	(Bunsell, 2018)
Polyester (PET)	15	15	800	15	(Bunsell, 2018)
Kevlar 49	12	135	3000	4,5	(Bunsell, 2018)

1.2.1.3 Cellulose Acetate

Although not so widely used, another method of producing fibres is available whereby cellulose acetate is obtained. Cellulose acetate is the acetate ester of cellulose. It was produced first at commercial scale by Celanese in 1923 (Sayyed *et al.*, 2019) by reacting a cellulose pulp with acetic anhydride, to form acetate flakes (figure 9). Then, these flakes are dissolved in a solvent and filtered to obtain the spinning cellulose dope solution (Ertas & Uyar, 2017). The cellulose dissolution with acetic acid and acetic anhydride is done with sulfuric acid, in a controlled manner to remove the sulfate and a sufficient number of acetate groups, to yield a product with desired properties. The cellulose dope solution is then extruded through a spinneret and the yarns are produced by solvent evaporation. This process for producing acetate fibre is known as the dry-spinning method (Sayyed *et al.*, 2019), and is mainly used to produce cigarette filters but also for drug delivery and nanofibres. These cellulose acetate fibres have limited use in the textile industry due to their poor strength, poor abrasion resistance and poor thermal retention (Watabe *et al.*, 2018).

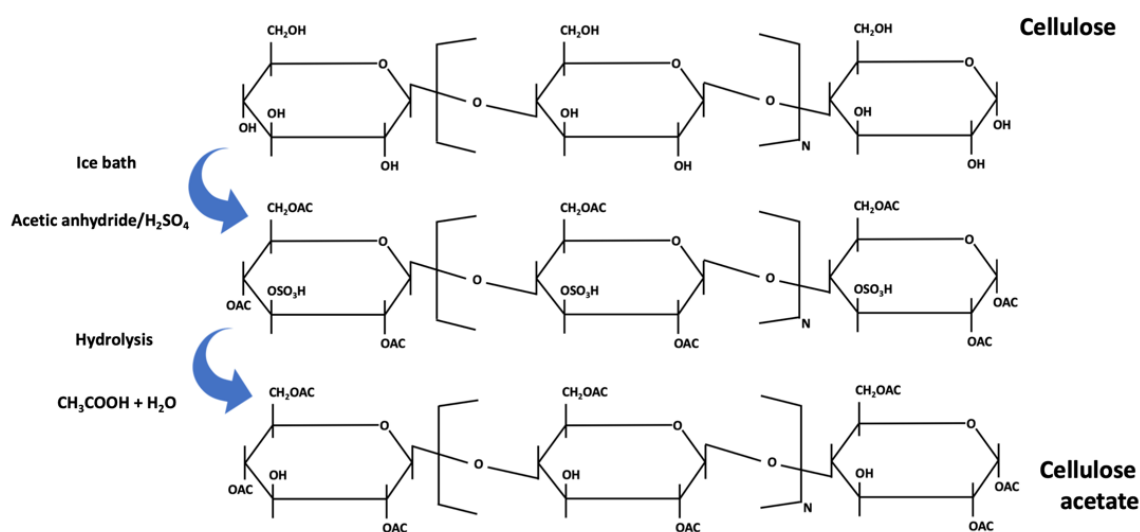


Figure 9. Mechanism of the cellulose acetate preparation (adapted from (Sayyed *et al.*, 2019; Silva *et al.*, 2017)).

1.2.1.4 Ionic Liquids

Research on the use of Ionic Liquids (ILs) for the direct dissolution of cellulose, first used in 2002, has shown promising results. Although this technology is not yet ready for industrial production, the use of ILs is expected to succeed in the future (Isik *et al.*, 2014; J.

Zhang *et al.*, 2017; Hummel *et al.*, 2015; Swatloski *et al.*, 2002). The IL process comes under the Lyocell technology since the cellulose solution is spun according to the NMMO-based Lyocell method, in a dry-jet wet-spinning process where the liquid filament first passes through an air gap and coagulate in a bath where the regenerated cellulosic fibres are formed (Sayyed *et al.*, 2019).

ILs are liquids made-up of cations and anions, thus they can be designated as salts in the liquid state (Singh & Savoy, 2020). Overall, the dissolution process of cellulose in ILs is still not fully clarified (Hermanutz *et al.*, 2019). The ILs ability to dissolve cellulose is due to small hydrogen bond accepting anions that can compete with the hydrogen bonding between the cellulose chains and cations that help increase the solubility (Andersson, 2018). ILs dissolves cellulose with no prior derivatization in concentrations of up to 300 g/L and offer a potentially more environmentally friendly alternative to traditional processes. (Hina *et al.*, 2015; Wanasekara *et al.*, 2016). These solvents are thermostable up to 300 °C with a melting point up to 100 °C. ILs practically do not have vapor pressure, and therefore do not pollute the atmosphere (Sashina, 2019). Due to their wide range of properties, they have been increasingly used in various fields of study such as biochemistry, engineering, physics, etc. as a green solvent. The properties of ILs can be modified depending on their application by altering the combination of cations and anions (Singh & Savoy, 2020).

ILs are usually composed of imidazolium, pyridinium, or organic ammonium cations and anions such as chloride, bromide, or more complex structures such as hexafluorophosphate, trifluoromethyl sulfonate, bis(trifluoro-methylsulfonyl)imide and methylimidazolium chloride ([Amim]Cl) (Sayyed *et al.*, 2019). ILs have been investigated either to dissolve or to create appropriate media for the functionalization of cellulose. For cellulose solubility, the counter anions with halide, such as the imidazolium type, have the best performance. One disadvantage with ILs with halide anions is their relatively high viscosities, which brings processing difficulties during dissolution (Isik *et al.*, 2014). These ILs demonstrate good dissolution characteristics, and it is possible to prepare cellulose dopes in concentration ranges that exhibit good spinnability (Sayyed *et al.*, 2019). For industrial use, any IL selected for cellulose dissolution and processing has to match specific criteria for an economic process development: the IL should be easy to produce, recyclable in high amount (> 99.5 %), possess the lowest possible toxicity, should have literally no vapor pressure, a low melting point, a low propensity to side reactions and degeneration, have high dissolution capability for different pulp sources (Hermanutz *et al.*, 2019; Andersson, 2018). To obtain concentrated cellulose solutions suitable

for spinning, the researchers have tried to use ILs based on imidazolium, pyridinium and ammonium cations (Sashina, 2019). Currently, nearly thousand ionic liquids are described in the literature (Meksi & Moussa, 2017; Wang *et al.*, 2019; Yang *et al.*, 2020; Zhang *et al.*, 2019).

A new class of next-generation of regenerated cellulose fibres named Ioncell have recently been developed utilizing a novel IL solvent 1,5 - diazabicyclo [4.3.0]non-5-enium acetate ([DBNH] [OAc]) (Michud *et al.*, 2016). Ioncell fibres have been shown to exhibit better mechanical properties than all previously known ones, namely, their tensile strength reaches 0,7-0,8 GPa and elastic modulus of 30 GPa (Sashina, 2019; Wanasekara *et al.*, 2016). Several garments have been produced and commercial production is expected by 2025 (Ioncell, 2020).

1.2.2 Filaments without solvents

RCF have beneficial characteristics from both synthetic and natural fibres: they have uniform morphological, mechanical, and physical properties, as synthetic fibres. On the other hand, they bear biodegradability, CO₂ neutrality, and low density of natural fibres. However, their mechanical properties are lower than those of CNF (Hooshmand *et al.*, 2015). To preserve the characteristics of CNF, several studies have been made to elaborate a system of filament production without solvents. Spinning CNF requires lower energy use and no harmful chemicals are used (Lundahl *et al.*, 2017). Instead of dissolution, CNF are dispersed in water and spun into air or recyclable organic solvents. This method was first reported in 2011 and has since then been developed towards increased scalability and improvement of the fibres' mechanical properties (Iwamoto *et al.*, 2011; Lundahl, 2018).

A single cellulose crystallite has a Young's modulus of up to 160 GPa and tensile strength of 6-7 GPa, exceeding those of carbon and Kevlar fibre, in its longitudinal direction, but only 8-57 GPa in its transverse direction (Wang *et al.*, 2017). So the mechanical performance of cellulose can be maximized in structures where the crystallites are well oriented. This can be achieved by spinning, which involve both orientation of the structural units and their entanglement into a filament (Lundahl, 2018). Wet and dry-spinning have so far been applied on CNF at laboratory scale, using a syringe pump, extruder, capillary rheometer or 3D printer (Lundahl, 2018).

In the production of filaments, 2,2,6,6-tetra-methylpiperidiny-1-oxyl (TEMPO) oxidized CNF is used (Iwamoto *et al.*, 2011) and extruded through a spinneret in a wet or dry-spinning process (figure 10). In wet-spinning, a coagulation bath with acetone, water, ethanol or CaCl₂ solution is used. The characteristics for the coagulants are miscibility with water,

moderate polarity and hydrogen bonding ability (Iwamoto *et al.*, 2011; Walther *et al.*, 2011; Kim *et al.*, 2019). The coagulant bath rapidly induces the formation of “a skin” on the surface of the CNF extrudate, stabilizing it against interfibre aggregation, to allow the formation of distinct macrofibres (Walther *et al.*, 2011). In dry-spinning, the dope is forced through the spinneret and the solvent removed by evaporation (Clemons, 2016). Regardless of the spinning method, a high molecular alignment is induced by drawing the fibre immediately after the spinneret. This high induced molecular alignment is key to the high stiffness and strength of the fibres (Clemons, 2016).

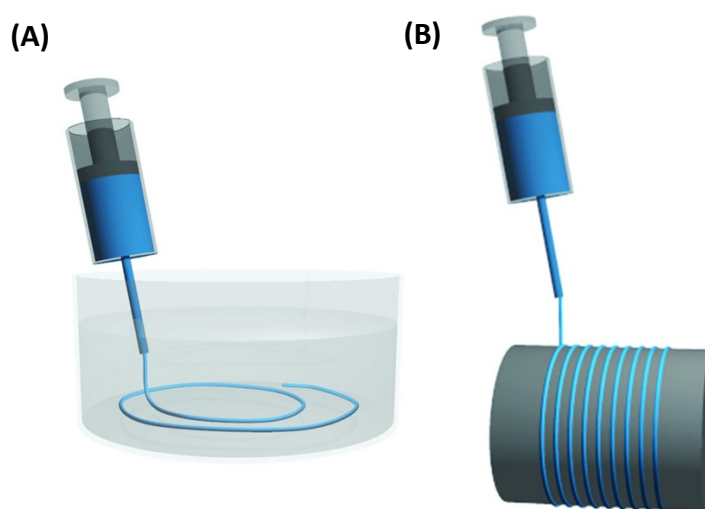


Figure 10. Schematic illustrations of simplified systems for (A) wet-spinning and (B) dry-spinning. Reprinted (adapted) with permission from (Lundahl, 2018). Copyright (2018) American Chemical Society.

Several parameters such as spinning speed, inner diameter and length of needle and drying temperature, influence the alignment of CNF and hydrogen bond formation between CFNs (Kim *et al.*, 2019). In the first report of CNF filament production through a wet-spinning process, the influence of spinning rates (from 0,1 to 100 m/min) were studied. The highest speed rate resulted in filaments with better mechanical properties (Iwamoto *et al.*, 2011). By using post drawing, more efficient alignment of the nanofibrils is achieved resulting in further improvement of the mechanical properties of the fibres (Walther *et al.*, 2011). A controlled wet-stretching procedure is used to induce high fibres orientation, improving their Young's Modulus from 8,2 to 33,7 GPa (Torres-Rendon *et al.*, 2014). Various concentrations of CNF were tested, from 1 % to 12 %, being the higher ones processed through dry-spinning and the lowers by wet-spinning (Hooshmand *et al.*, 2015; Iwamoto *et al.*, 2011; Kim *et al.*, 2019). In a study using a wet-spinning system 2 % (m/m) CNF was considered the ideal solids content for

attaining a high CNF alignment and filament strength, specifically, a Young Modulus of 37,5 GPa and Tensile Strength of 543,1 MPa (Kim *et al.*, 2019). The mechanical properties of CNF filaments produced through the various processes are summarized in table 2.

Table 2. Mechanical properties of different cellulose nanofibre filaments

Spinning	Young's Modulus (GPa)	Tensile Strength (MPa)	Elongation (%)	Reference
Wet-spinning	23,6	321	2,2	(Iwamoto <i>et al.</i> , 2011)
	22,5	275	-	(Walther <i>et al.</i> , 2011)
	33,7	289	1,6	(Torres-Rendon <i>et al.</i> , 2014)
	28,9	369,6	-	(Geng <i>et al.</i> , 2017)
	23,9	383,3	6,6	(Kafy <i>et al.</i> , 2017)
	37,5	543,1	3,7	(Kim <i>et al.</i> , 2019)
Dry-spinning	12,6	222	3,6	(Hooshmand <i>et al.</i> , 2015)
	6,5	100	-	(Ghasemi <i>et al.</i> , 2017)
Flow focusing	86	1570	-	(Mittal <i>et al.</i> , 2018)
BNC wet-spinning	16,4	248,6	3,8	(Yao <i>et al.</i> , 2017)
BNC stretching	65,7	826	2,5	(S. Wang <i>et al.</i> , 2017)

Flow focusing is another method for CNF filaments production, resulting in fibres with the strongest tensile performance, as compared to other methods (table 2). The fibres are obtained by aligning a CNF suspension in a double flow focusing channel involving coagulation with acid, as shown in figure 11 (Mittal *et al.*, 2018). The obtained filament has a Young's modulus of 86 GPa and tensile strength of 1570 MPa, exceeding the mechanical properties of

known natural or synthetic fibres (Mittal *et al.*, 2018). The specific strength of this CNF fibres also exceeds that of metals, alloys, and glass fibres.

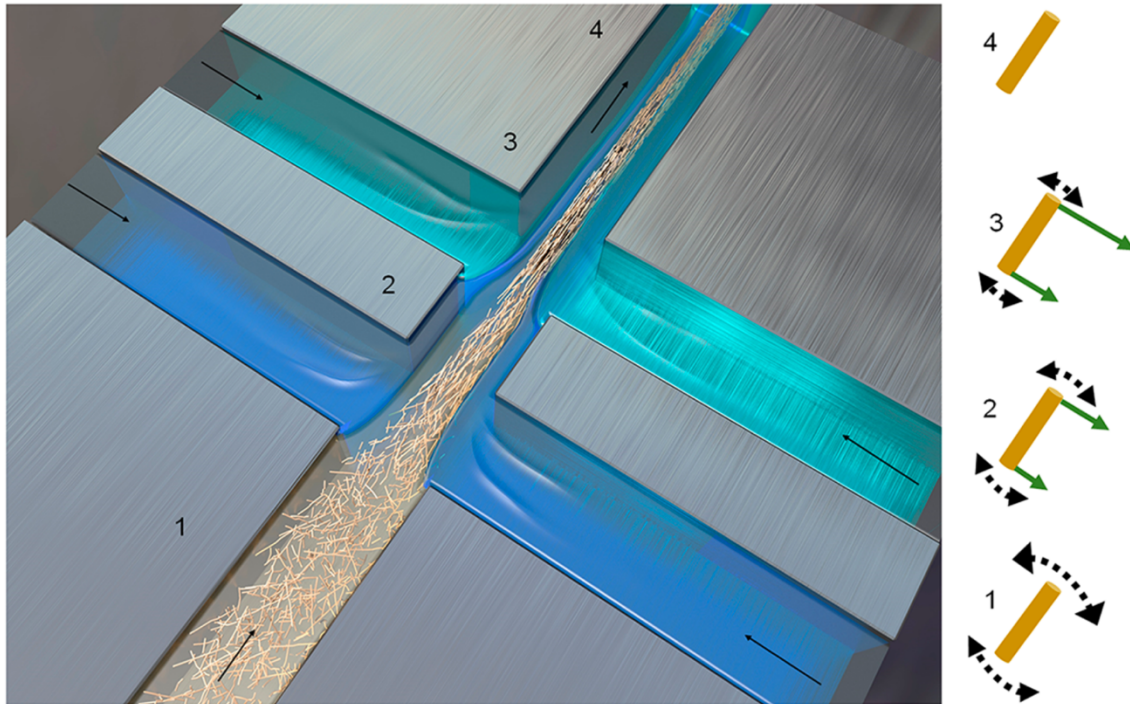


Figure 11. Schematic of double flow-focusing channel used for CNF assembly (Mittal *et al.*, 2018).

To our knowledge, the first and only company, to produce fibres without solvents, cellulose dissolution or any other harmful and complex chemical processes, is Spinnova Ltd (Finland). The raw material is pulp from FSC certified wood. After mechanical pulping, the finely ground pulp mass flows through a unique nozzle, where the fibres and fibrils rotate and align with the flow, creating a strong, elastic fibre network. The fibre is then spun and dried, suitable for spinning into yarn and then knitting or weaving into fabric (Salmela *et al.*, 2016). The future goal is the recycling of the fibres for several times, minimizing the use of virgin materials. Spinnova fibre is now (2020) close to commercialization. The technology has been scaled up from a small pilot scale to an industrial pilot scale (Spinnova, 2020).

Filaments based on aligned BNC nanofibres were prepared by wet-spinning and drawing procedures (Yao *et al.*, 2017). The obtained macrofibres exhibited Young's modulus of 16,4 GPa and tensile strength of 248,6 MPa under optimum process conditions (BNC 5.4 wt %; spinning rate 18,9 m/min), in which nanofibres displayed a high degree of alignment. The nanofibre suspension was prepared by TEMPO oxidation and then spun into an acetone coagulation bath (Yao *et al.*, 2017). BNC Filaments without TEMPO oxidation were also

produced. A super-strong and super-stiff cellulose macrofibres was obtained from aligned ultralong BNC nanofibres via a facile and scalable wet-drawing and wet-twisting method (Wang *et al.*, 2017). The macrofibres showed perfect integrity and well aligned structure, with a tensile strength of 826 MPa and Young's modulus of 65,7 GPa. BNC membranes were cut with a width of 7 mm and were wet-draw, becoming longer and thinner. From these, BNC macrofibres with diameters of around 300 μm were fabricated by wet-twisting and subsequently drying at 90 °C for 12 h (Wang *et al.*, 2017).

1.3 Sustainability and Life Cycle Assessment

The rapid population growth and careless consumption of natural resources are causing serious global problems, such as air and water pollution and global warming. Fossil fuels exceeds 50 % of the world's total energy sources and based on present water consumption, water resources are likely to decrease by 30 % in 2050 (Kazan *et al.*, 2020). In the last few decades, the environmental problems caused by humankind are reaching dangerous levels, being the search and adoption of more environmentally sustainable processes a mandatory paradigm change.

In this regard, environmental impact assessment gains a significant importance to evaluate the environmental effects of industrial activities. Life cycle assessment (LCA) can be used to analyse a product, process or activity repercussions on the environment (Van Der Velden *et al.*, 2014). "Cradle to gate" LCA studies take in account the raw materials and fuels used, as well all the processes involved until the product is delivered at the factory gate for further processing; "cradle to grave" involves, in addition to the later, post-manufacturing processes until the product (garment) end of life (Dibdiakova & Timmermann, 2014).

The global textile supply chain is complex, involving many different stages (figure 12). It is widely recognized that the textile industry is a major contributor to the environmental pollution and resource consumption. Among all, this industry is placed at fifth place in terms of the release of chemical oxygen demand (COD), implying high amounts of wastewater production and chemical consumption (Zhang *et al.*, 2018; Roos *et al.*, 2018). Along COD, textile wastewaters may include materials with a high biological oxygen demand (BOD), total suspended solids, oil and grease, sulfides, sulfates, phosphates, chromium, copper, and/or the salts of other heavy metals. The majority of the chemical used in textile production occurs during wet processing (dyeing, washing, printing, and fabric finishing). Textile dyeing and finishing mills use as much as 200 tons of water for every metric ton of textiles produced. The

textile industry is a major energy-consuming industry with low efficiency in energy utilization. A large quantity of non-renewable energy sources is consumed in the form of electricity, not so much in the process of textile production (15-20 %) but mostly in subsequent laundering processes during consumer use (75-80 %) (Choudhury, 2014).

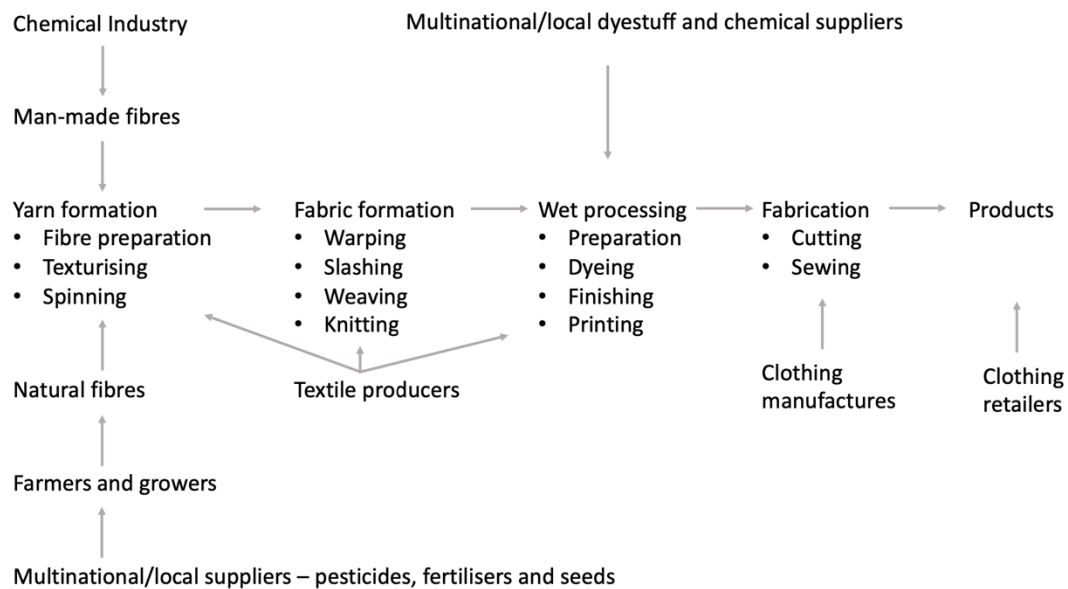


Figure 12. The business involved in the textile and clothing supply chain (adapted from (Choudhury, 2014)).

Although the entire process of textile production generates hazardous wastes, in this review we focus only on raw materials and fibres production. A cradle-to-gate life cycle assessment study, shown in table 3, makes possible to evaluate the environmental impact of different fibre production processes (Dibdiakova & Timmermann, 2014). It is important to mention that, for a true comparative LCA, the same framework must be used for all stages of the life-cycle of a commercial product, process, or service (this means using the same criteria for a life cycle inventory of the required resources (energy and materials) across the value chain and determining the corresponding emissions to the environment). Data here collected was obtained from different sources and therefore a direct comparison of the impact categories is not straightforward.

Table 3. LCA cradle-to-gate of different impact categories per 1000 kg of fibre (functional unit) produced under different methods

Impact Category	Cotton Fibre	Tencel (lyocell)	Viscose Austria	Viscose Asia	Polyester
Water Use (m ³)	5730 ¹	263 ²	445 ²	319 ³	125 ³
Energy Demand (GJ)	55 ¹	65 ³	70 ³	106 ³	96 ³
Global Warming (kg CO ₂ -Equiv.)	2000 ¹	50 ³	-250 ³	3800 ³	4100 ³
Acidification (kg SO ₂ -Equiv.)	41 ¹	13 ³	14 ³	45 ³	21 ³
Eutrophication (kg phosphate-Equiv.)	22 ¹	1,9 ³	1,2 ³	2,3 ³	1,2 ³
Ozone Depletion (x10 ⁻³ kg CFC11 Equiv.)	0,2 ¹	0,07 ³	0,03 ³	0,28 ³	0,07 ³
Land Use (ha/year)	1,07 ¹	0,22 ³	0,69 ²	0,35 ³	0 ⁴

¹(Cotton Incorporated, 2012) ²(Taylor, 2010) ³(Shen & Patel, 2010) ⁴(Dibdiakova & Timmermann, 2014)

Polyester, the most widely used synthetic fibre, has a lower water consumption than the other cellulose fibres, but has the highest impact on global warming from CO₂ emissions and also a high demand on energy (Zambrano *et al.*, 2019). Cotton is the most used natural raw material in textile industry (Kazan *et al.*, 2020). Nutrients and pesticides are used in raw material production to increase quantity and product quality and so, they pollute the groundwater and surface water. Up to 25 % of global pesticide usage in agriculture corresponds to cotton production (Kazan *et al.*, 2020). Although cotton has the advantage of being biodegradable, it has a significant water consumption, with an average global water footprint of 5730 m³/ton in crops production and required water for processing (Cotton Incorporated, 2012). Some of the negative aspects of cotton production can be overcome by growing organic crops but it still has many negative environmental aspects compared to other fibres (Textile Exchanges, 2014; La Rosa & Grammatikos, 2019).

Regarding the processing stage, the Viscose process has different environmental impacts depending on where it is produced (Shen *et al.*, 2010). The problems with these fibres are the chemicals used in the regeneration process and the need for large plantation areas for wood production.

Currently, the most environmentally friendly fibres on the market are produced by the Lyocell process (Shen *et al.*, 2010). The solvent used is non-toxic and recyclable being the main challenge the sustainable sourcing of cellulose. Tencel, made of cellulose from eucalyptus, which grows quickly and requires no irrigation or pesticides, is the best option on the market regarding its environmental impact. BNC may be the solution to Lyocell flaws as it can be produced anywhere without forest destruction. An attributional LCA was applied to a projected production of BNC, by static culture, following a cradle-to-gate approach which includes the extraction of natural resources and their transformation, the production of BNC, the utilities, the energy and equipment used, as well as the treatment and disposal of the waste produced by the BNC process chain. The results showed that water was the main resource used, most of which being returned back to fresh water after treatment. The BNC manufacture facility itself contributed little extent to the consumption of resources and environmental impact of the global life cycle. The materials production (Background System) were responsible for most of natural resources used (water), and the emissions released to the environment, in this case emitted to fresh water (Forte *et al.*, 2019).

2. SPECIFIC GOALS

The main goal of this work was the development of BNC based filaments for the textile industry, as a more sustainable alternative to those currently marketed. BNC fibres must meet the mechanical properties requirements such as those currently established in order to be technically competitive.

The focus of this work was on the use of the Lyocell process, which is the most sustainable spinning process commercially available, for the production of BNC filaments. In this process, the targeted DP using plant cellulose is around 600 (Kosan et al., 2020), thus a significant decrease of the BNC DP may be necessary (as observed below, the DP of BNC is around 2259). On the other hand, although plant cellulose depolymerization is considered essential for Lyocell production, it may not be needed for BNC Lyocell. This would be highly desirable, as it would avoid the use of alkaline solutions required for depolymerization.

To achieve this goal, the research work herein described was performed in three phases:

- Test the conditions for the production of filaments with solvents, without BNC depolymerization, by the solid-phase process and the traditional Lyocell method;
- Define the experimental conditions for the BNC depolymerization;
- Perform exploratory testing of filament production without solvents, by dry-spinning and wet-drawing.

3. MATERIALS AND METHODS

3.1 Materials

Bacterial nanocellulose (HTK CO., LTD, Vietnam); 4-Methylmorpholine N-Oxide Monohydrate 50 % (NMMO-50 %) (Ravago Chemicals) supplied by CeNTI; 4-Methylmorpholine N-Oxide Monohydrate 97 % (NMMO-97 %) (Kayi Chemical Co., Ltd.); Propyl gallate (Enzymatic); Calcofluor White stain (Sigma); Ethylenediamine Copper (II) Hydroxide (Fisher); Sodium hydroxide (Fisher); Dialysis membrane 10 kDa (Orange scientific); Glycerol (Fisher bio reagents); Ethanol (Fisher); Carboxymethylcellulose sodium salt, high viscosity (Acros organics);

3.2 Methods

3.2.1 Production and characterization of the BNC dope

3.2.1.1 BNC dissolution

For the BNC dissolution, the process based on the Lyocell method was used. Two approaches were tested: the NMMO-water-cellulose solid-phase system, based on RF Patent No. 1645308, and the basic Lyocell process used by most Lyocell producers, which is divided into two stages, swelling and dissolution.

In the NMMO-water-cellulose solid-phase system, a mixture of dry BNC (up to 4 % m/v), water (10 % m/v), propyl gallate (0,5 % in relation to BNC m/v) and NMMO-97 % (powder form), added up to 100 % of the final mixture, was prepared. Several samples of 20 mL (total volume) were made differing in BNC final concentration (1, 2, 2.5, 3, 3.5 and 4 % m/v). The total water concentration was fixed at 10 % (m/v), accounting already with the water present in BNC and NMMO. The amount of NMMO used was adjusted according to the BNC concentration. All components were mixed with pestle and mortar to promote mixing of BNC and NMMO. Then, the mixture was placed in an oil bath at 110 °C with agitation, until a translucent amber-colored solution was formed.

In the second approach the swelling step was performed by adding NMMO (50 % m/v in water) and the antioxidant propyl gallate (0.5 % m/v in relation to BNC) to the never-dry BNC (3, 4, 5 and 6 % m/v in relation to NMMO-50 %) and mechanically stirring until a homogeneous suspension was obtained. Afterwards, the mixture was left at rest for at least 30 min at room temperature. The dissolution step was performed in a vacuum rotary evaporator

(Buchi's Rotational evaporator R-20) under the action of a vacuum pump (Buchi's Vacuum controller V-850). The process temperature was 120 °C and the initial pressure 300 mbar. The pressure was gradually reduced to the minimum value achieved by the vacuum pump used, ~ 45 mbar, as the water was evaporated during swelling. The dissolution of BNC was observed when the mixture became a translucent amber-colored solution, characteristic of the so called dope.

In both approaches, the dissolution process can take several hours, being longer for higher BNC concentrations.

3.2.1.2 Dope viscosity – rotational rheometer

The viscosity profiles of the dope samples were obtained with a controlled stress rheometer (DHR-1, TA instruments) with TRIOS Software (TA Instruments) at 80 °C using a cone and plate geometry. Flow tests were performed at increasing shear rates (0.00001 to 1000 s⁻¹). Shear rate versus viscosity graphs were drawn in semi-log scale to better visualize the different rheological profiles at low shear rates. Prior to the rheological analysis, the dope was heated (using a hairdryer) to allow pouring it over the rheometer's plate.

3.2.2 Production of BNC filaments

3.2.2.1 Syringe spinning

BNC filaments were first produced using a syringe for spinning dope solutions with different concentrations (1, 2, 2.5, 3, 3.5 and 4 %), using different needle diameters (900, 800 and 600 µm). The extrusion was made into a water bath at room temperature with an air gap of 20 cm shown in figure 30 in annexes. The filaments were then washed for a few hours and air dried.

3.2.2.2 Dry-jet wet-spinning

The dry-jet wet-spinning equipment (Dienes), located at CeNTI facilities, is represented in figure 13. The dope, obtained as described in section 3.2.1.1 (at 3 % and 5 % BNC) was placed in the 500 mL container (1), which is wrapped with a heating blanket, set at the necessary temperature, 80 °C, for processing. The dope was spun through the spinneret (30 holes, 500 µm diameter), which is located at the end of the dope container shown in figure 31 in annexes. The air gap was of 10 cm and the water bath was at room temperature. Pressure was applied with compressed air, in the direction of the solution passing through the spinneret holes, forming the filaments. After the air gap, the filaments entered the coagulation water bath (2) and then they

were dragged through the wash baths (3), the drawing rollers (4) and finally collected in a roll (5).

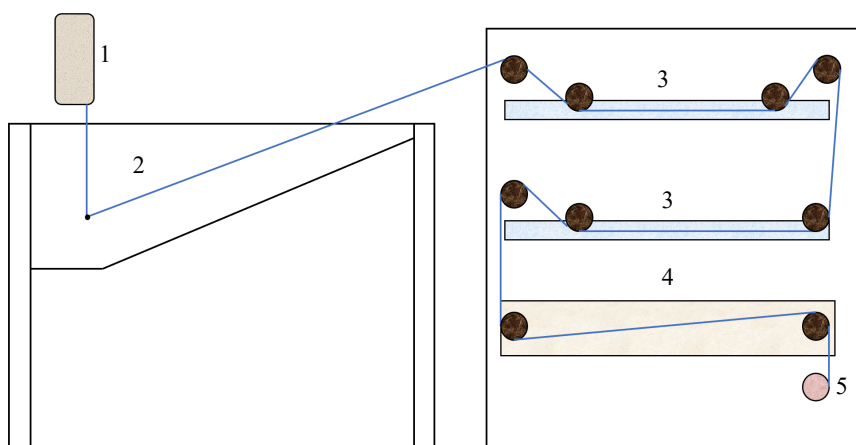


Figure 13. Scheme of the dry-jet wet-spinning equipment located in the CeNTI facilities.

3.2.3 BNC depolymerization and degree of polymerization measurements

3.2.3.1 BNC depolymerization: mechanical treatment

Mechanical treatment was used to lower the degree polymerization (DP) of BNC, by using two approaches: (i) wet defibrillation, where wet BNC membranes (0.1-0.5 % solids) were disintegrated in a blender (Moulinex, high speed blender) for different periods of time (1, 5, 10 and 30 min) at 27000 rpm for 5 minutes followed by a cooling time of 1h. Afterwards, BNC suspensions were stored at 4 °C until use; and (ii) dry grinding, where BNC membranes were previously defibrillated as in the method (i) and then dried at 37 °C for 48 to 72 h and grounded in a High Power Herb Grain Grinder Cereal Mill Powder Grinding Machine Flour 600G for 30 min, allowing the equipment to cool for 15 min for every 30 seconds of grinding. BNC powder was formed and sieved (Retsch) into different particle sizes (< 38 μm , < 63 μm , < 125 μm , < 500 μm and > 500 μm). Ground samples were stored in a desiccator at room temperature until use.

To observe the morphology and size of the BNC bundles obtained by wet defibrillation (i), a drop of each BNC sample was placed on glass slides, stained with 10 $\mu\text{g/mL}$ Calcofluor White stain (Sigma) for 1 min (protected from light), coverslipped and visualized with an optical fluorescence microscope (Olympus BX51) with a DAPI filter (Excitation wavelength: 365-370 nm; Emission wavelength: 421 nm).

3.2.3.2 BNC depolymerization: chemical treatment

BNC depolymerization was also achieved through chemical treatment, using NaOH. This pretreatment is currently used in the Viscose method, which consists of two steps: (i) the mercerization of the cellulose, whereby never-dry BNC suspension (10 % solids) is treated with NaOH and (ii) an aging process, whereby the mercerized BNC is concentrated and left in contact with air for further depolymerization. Firstly, the mercerization step was studied without aging, to optimize the NaOH concentration, as evaluated by determining the concentration of NaOH that allowed the lowest DP (3.2.3.3). NaOH solutions with concentrations of 4.5, 5, 6 and 7 M were prepared and then added to BNC (0.5 % final concentration). The suspensions were placed in a water bath at 50 °C and stirred for 120 min. After mercerization optimization, two new BNC samples, also at 0.5 % final concentration in the mixture, were mercerized with 5 M NaOH and then filtered using a vacuum pump to retrieve most of the NaOH solution. The obtained filtration cakes were then aged by placing them in a water bath at 50 °C and leaving them in contact with air, for 240 min and 360 min, respectively. Afterwards, both samples were dialyzed (dialysis membrane with 10 kDa cut-off) until neutral pH (6.0-6.5).

3.2.3.3 Viscosity and degree of polymerization measurement

BNC viscosity was measured according to ES ISO 5351:2012 “Pulp – Determination of limiting viscosity number in cupriethylenediamine (CED) solution”. BNC was lyophilized at -100 °C and pressure of 0,043 mbar for 3 days (Labogene, coolsafe 100-9 Pro) in the chemical method, for the mechanical method was used the dry BNC obtained. The mass concentration to be measured was firstly optimized as shown in table 4. Since the approximate value of the limiting viscosity of the sample was unknown, a solution of mass concentration between 125 mg/50 mL and 150 mg/50 mL was tentatively used. When the limiting viscosity number obtained was not within the range specified by table 4 for that mass concentration, it was adjusted accordingly.

The chosen amount of BNC was weighed (Mettler Toledo) with an accuracy of $\pm 0,5$ mg. Then, 5,0 mL of distilled water were added and the mixture stirred for 5 minutes; then a total of 5,0 mL of CED solution (1.0 M in H₂O) was gradually added (1,0 mL each time, followed by stirring for 1 min), for better dissolution of the BNC. As oxygen has a degrading effect on cellulose in CED solution, it must be covered to avoid contact between air and the solution. Complete dissolution took less than 30 min. Afterwards, the sample was placed in a

capillary-tube viscometer (Rheotek Ubbelohde) placed in a water bath at 25 °C. Then, the efflux time that the solution took to pass between the first and the second meniscus was measured.

Table 4. Example of the mass concentration ρ to be used, as a function of the targeted limiting viscosity number $[\eta]$.

Limiting viscosity number $[\eta]$ mL/g	Sample quantity mg/50 mL	Mass concentration ρ mg/mL
< 650	250	5
651 to 850	200	4
851 to 1100	150	3
1101 to 1400	120	2,4

The viscosity ratio η_{ratio} was calculated using equation 1, where t is the efflux time of the test solution in seconds and h is the viscometer constant (0,132) in reciprocal seconds. The η_{ratio} was then used to determine the $[\eta] \times \rho$ values using table 12 in the annexes. Then, with the value of mass concentration, the viscosity was calculated.

$$\eta_{ratio} = \frac{\eta}{\eta_0} = h \times t \quad \text{Equation 1}$$

The degree of polymerization (DP) was calculated through Marl-Houwink equation (equation 2). To calculate the DP of BNC without depolymerization, the values of the parameters k (0,0001645) and α (1,9705) were calculated from Tsouko et al. (2015) . For the depolymerized samples, the plant cellulose constants were used: for BNC with a DP < 950, $k = 0,42$ and $\alpha = 1$; for DP > 950, $k = 2,28$ and $\alpha = 0,76$ (Henriksson et al., 2008).

$$[\eta] = k \times DP^\alpha \quad \text{Equation 2}$$

3.2.4 Dry-spinning

Spinning without BNC dissolution was attempted. BNC (3, 5 and 10 %) aqueous suspensions that were disintegrated in a blender (Moulinex, high speed blender) for 30 min and spun into a filament using a Capillary Rheometer (Malvern Rosand RH2000) at CeNTI facilities. The filament was extruded and then dried at ambient temperature in extension. Also,

tests using 3 % BNC + 1 % glycerol and 3 % BNC + 1 % CMC were performed, being the glycerol and the CMC joined in the blender during the 30 min disintegration.

3.2.5 Wet-drawing

The production of BNC filaments using a BNC membrane, without disintegration, was attempted. A BNC membrane was cut into a rectangular shape of size 7 mm × 70 mm then twisted and wet-drawn using a TA.HD plus Texture Analyser machine at a crosshead speed of 1 mm/min until the strain of the sample reached 10 %, 20 %, and 30 %, respectively, shown in figure 32 in annexes. The wet-drawn samples were twisted even more immediately after drawing to reduce water evaporation and then dried at 90 °C for 24 h under tension. BNC macrofibres without wet-drawing (0 %) were prepared using the same method. Samples with glycerol and CMC were also produced by immersing the BNC membranes for 24 h, before wet-drawing process.

3.2.6 Mechanical properties of the BNC filaments

The mechanical properties of the produced filaments were evaluated using the TA.HD plus Texture Analyser machine with a load range of 5 kg. The fibre diameter was measured and the values were used for the calculation of the mechanical properties.

3.2.7 Scanning electron microscope

The powdered BNC and the filament samples were characterized using a desktop scanning electron microscope (SEM) (Phenom-World BV, Netherlands)). All results were acquired using the ProSuite software. The samples were added to aluminium pin stubs with electrically conductive carbon adhesive tape (PELCO Tabs™). Samples were coated with 2 nm of Au (20 Angstrom) for improved conductivity. The aluminum pin stub was then placed inside a Phenom Standard Sample Holder (SH). The analysis was conducted at 5 kV with intensity image.

3.2.8 Statistical Analysis

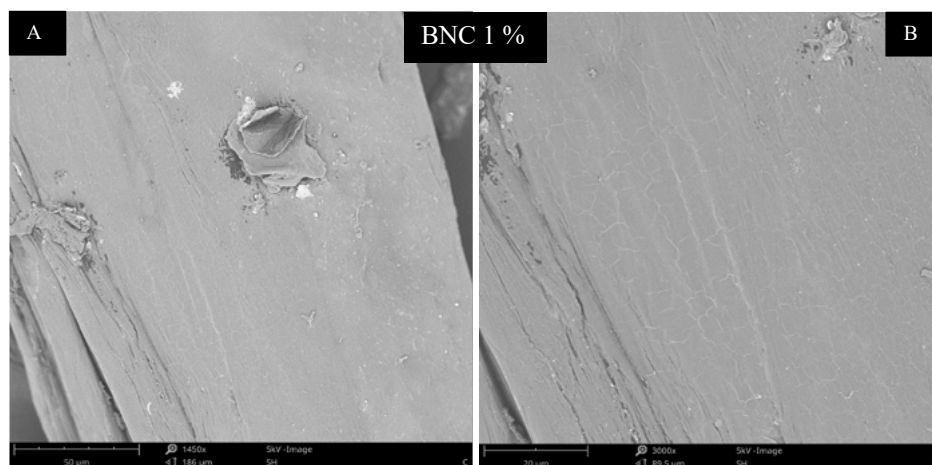
Statistical analysis were supported with Prism version 8.4.3 (GraphPad Software, La Jolla California USA). Using one-way ANOVA and Turkey's post-hoc analysis for pairwise comparison of more than two different means. Two-tailed unpaired Student's t-test was used for comparison of the means between the two samples. Mean differences were considered statistically non-significant (ns) when *p* value was above 0.05.

4. RESULTS AND DISCUSSION

The Lyocell process has been studied for many years and several parameters used in its production are widely accepted (Regau & Vocklabruck, 2013). One of the main parameters for Lyocell is the cellulose pulp DP that should be adjusted to level of 550 to 650 (Kosan et al., 2020). BNC has a much higher DP, around 2259 (table 7), hence its depolymerisation may be necessary. Thus in this work the conditions required for the depolymerisation of BNC were investigated. On the other hand, it has been hypothesised that the native BNC may be suitable for the Lyocell process. Thus, several operational conditions were tested aiming at verifying this possibility and whether it may allow the production of filaments with good properties for textile applications.

4.1 BNC solid-phase dissolution and syringe spinning

BNC Lyocell fibres have already been produced through the solid-phase dissolution process (Makarov et al., 2019). A replication of this process was attempted through a simple and manual process, using a syringe device. In this method there is no water evaporation; the NMMO, water and BNC amounts stay constant throughout the process. BNC-NMMO solutions with BNC 1-2.5 % were successfully dissolved; however, for higher BNC concentrations (3-4 %), lumps were visible in the dope, an indicator of undissolved particles. This problem could be overcome with longer dissolution times. However, this may also lead to higher NMMO degradation, even using the antioxidant propyl gallate. Even without complete dissolution it was possible to form filaments using a syringe. Filaments formed from BNC at 1, 2 and 2.5 % BNC were observed by SEM (figure 14).



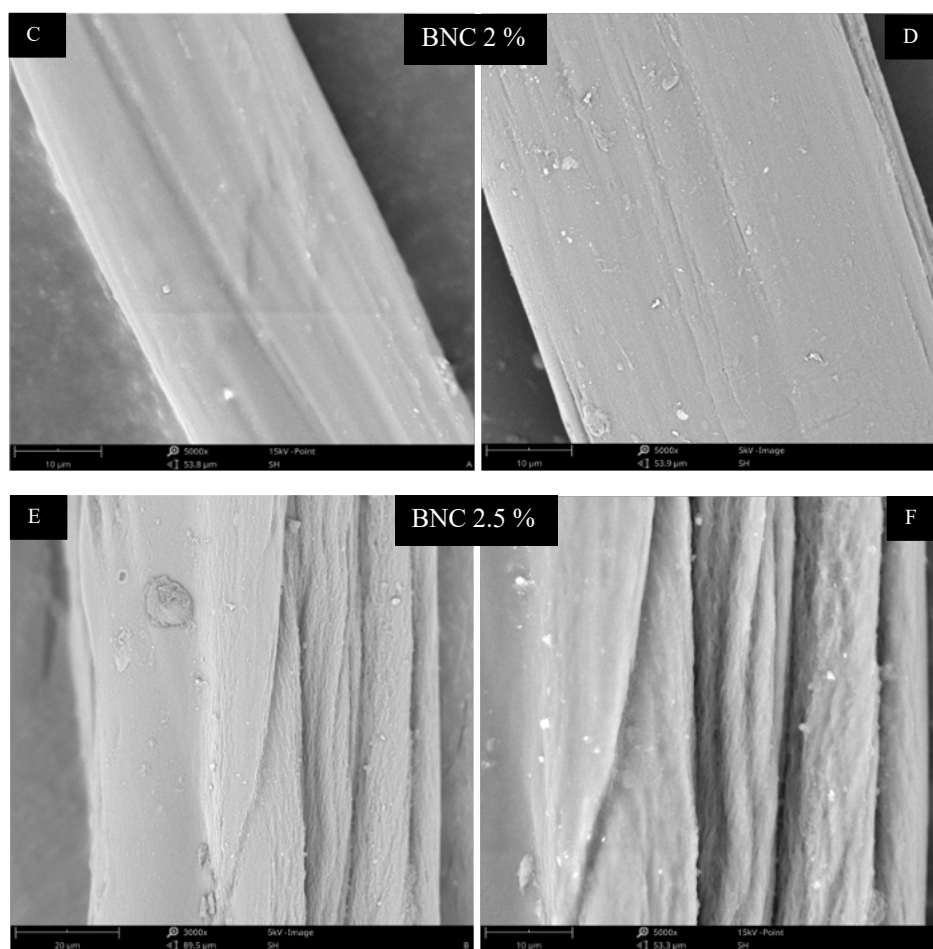


Figure 14. BNC filaments observed by scanning electron microscope (SEM) – scale is 50 µm for A, 20 µm for B and E, and 10 µm for C, D and F.

Due to their lower viscosities, the dopes with BNC concentrations of 1 and 2 %, could be spun with the 600 and the 800 µm needles. The 900 µm needle was used for all (1, 2, 2.5, 3, 3.5 and 4 % BNC) samples. For 1 % BNC, SEM images show some irregularities (lumps) on the surface of the filament, possibly due to remnants of NMMO that were not removed during washing, even after intensive washing. This concentration is too low for this syringe spinning process, thus these filaments weren't analysed further. For the highest BNC concentrations (2 and 2.5 %), this was not observed, as the washing steep was more efficient. In all samples, especially at 2.5 % BNC, the surface showed some roughness, possibly due to some BNC that was not well dissolved, as previously discussed.

Except for 1 % BNC, the obtained filaments were characterized for their mechanical properties (figure 15 and table 9 in the annexes). All filaments obtained with a needle of 900 µm yielded higher Young's modulus and tensile strength properties for lower BNC concentrations, as shown in figure 15. The elongation was higher for BNC 3 %. It should be

noted that the properties of filaments produced with the syringe can vary widely, due to the variable applied speed of (manual) extrusion and drying.

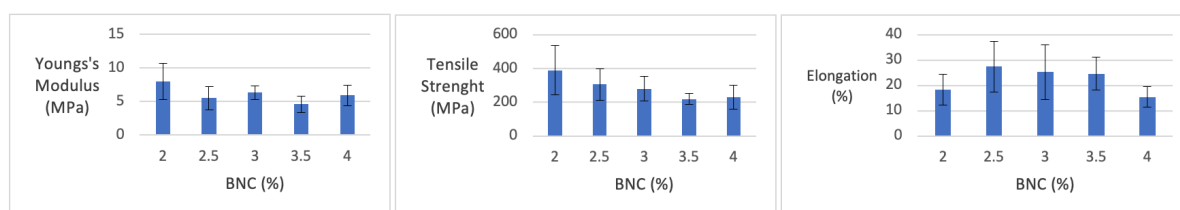
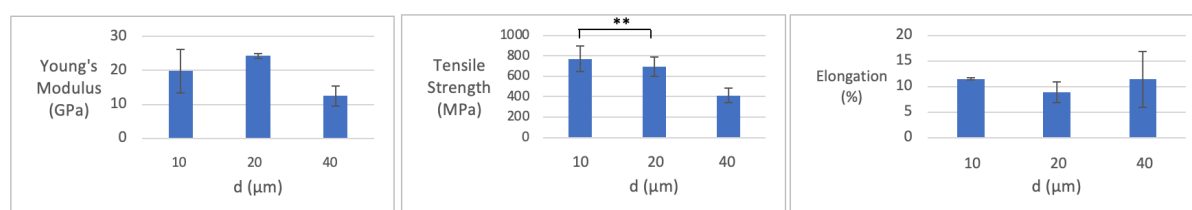


Figure 15. Mechanical properties of BNC with a 900 µm syringe.

Filaments obtained with 2 % BNC using the 800 and 600 µm needles were also analysed and the results are presented in figure 16 and 17 respectively as in the table 10 and 11 in the annexes. As the needle diameter was smaller, filaments with lower diameter (10 µm) were produced, improving the mechanical properties. Comparing the outcome of the different needles, the filaments obtained with the 600 µm needle had the highest tensile strength $1201,9 \pm 149,2$ MPa (for filaments of 10 µm obtained using a 2 % BNC solution). On the other hand, Young's modulus was not improved by lowering the needle diameter. The highest value obtained was $24,3 \pm 0,7$ GPa (for filaments of 20 µm obtained using a 2 % BNC solution).



** the differences are significant ($P < 0.05$)

Figure 16. Mechanical properties of BNC (2 %) with a 800 µm syringe.

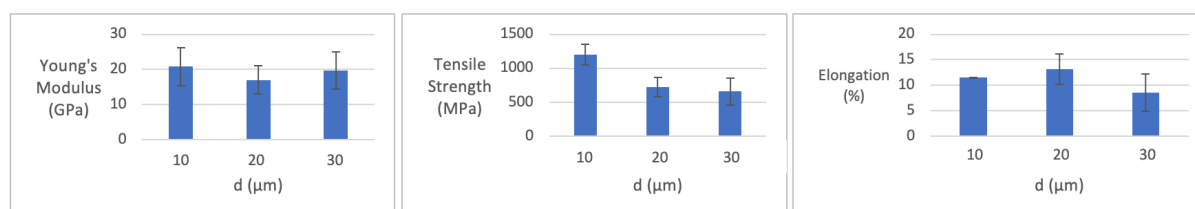


Figure 17. Mechanical properties of BNC (2 %) with a 600 µm syringe.

Comparing the results obtained with those by Makarov et al., (Young's Modulus of 20,2 GPa, tensile strength of 420-495 MPa and elongation of 5.5-6.5 % (table 1)), in this work superior mechanical properties were obtained (Young's modulus, tensile strength and elongation) (figures 15-17). BNC concentrations tested (2-4 %) were lower than those used by Makarov (6 %). When comparing filaments with the same diameter, the difference in mechanical properties are even higher, being the ones obtained in this work quite superior (table 1 and figure 17). Fibres with 2 % BNC concentration and smaller needle diameter (600 μ m) yielded better mechanical properties (Young's Modulus of $20,8 \pm 5,4$ GPa and tensile strength of $1201,9 \pm 149,2$ MPa). The mechanical properties obtained in this work are also superior to those of commercially available products (table 1). However, additional results under more controlled conditions, yielding more consistent results, are necessary in order to make definitive conclusions.

The 2 % dope is less viscous comparative to higher BNC concentrations, which means is easier to extrude manually using a syringe than higher concentrations, while facilitating fibre alignment inside the needle. Another important aspect is the length of the needle, which is considerably longer than those used in commercial extruders, increasing the BNC fibres alignment. This aspect is measured through the L/D of the spinneret, in this work was ~ 50 and in commercial extruder is between 2 and 10 (Hudson & Cuculo, 2005). BNC filaments with higher BNC concentrations (> 4 %) could not be tested, due to the poor mixture between NMMO, BNC and water. One way to overcome this issue would be to use a LIST Kneader Reactor that, having high pressure capacity and high torque, could possibly allow a homogeneous mixture (LIST, 2020). Although being produced in a not very controlled way (syringe), the properties of these filaments were better than traditional Lyocell fibres (table 1), suggesting that optimization may lead to promising results regarding the possibility of using these filaments for textile applications.

4.2 BNC dissolution and dry-jet wet-spinning

In this work, a dry-jet wet-spinning equipment was also tested. In order, to overcome the limitations in BNC dissolution, found using the solid-phase method, Lyocell process (excess of water and swelling in the dissolution stage) was carried out at CeNTI facilities. The excess water allowed a better mixture of the components and no lumps were visible by the end of the process, which suggests full BNC dissolution. BNC solutions with concentration of 3 , 4 , 5 and 6 % were successfully prepared within a few hours (~ 5 h); expectably, the higher the BNC

concentration, the longer the dissolution time. All samples were analysed in a rotational rheometer. The viscosity profiles of the dopes were measured at 80 °C, using a cone and plate geometry and the results are shown in figure 18. The viscosity remained constant up to a shear rate of $0,1 \text{ s}^{-1}$ in all samples. At low shear rates it is possible to estimate the zero shear viscosity of the different samples prepared: ~ 70 , ~ 280 , ~ 1000 and $\sim 1700 \text{ Pa.s}$, respectively for BNC at 3, 4, 5 and 6 %. Then, at shear rates higher than 0.1 s^{-1} , the viscosity decreased, characteristic of a shear thinning fluid. The increase in viscosity is lower in the 6 % BNC sample, this may be due to higher entanglement of molecular chains (Z. Jiang et al., 2019). The viscosity obtained for BNC 6 % was very different from that obtained by Makarov (10000 Pa.s), although the DP of the used BNC does not differ much (DP 2000) (Makarov et al., 2020).

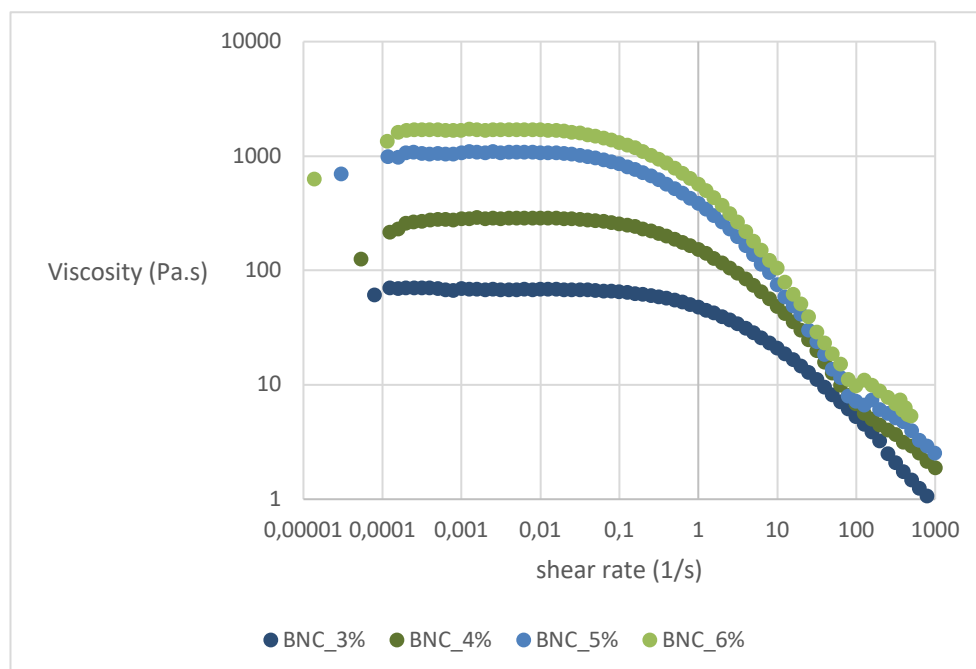


Figure 18. Dope viscosity in a rotational rheometer at 80 °C.

Dopes comprising 3 and 5 % BNC were prepared (500 mL) and extruded in the dry-jet wet-spinning equipment. Filaments with several meters long were formed. Although the equipment allows washing and drying steps, the former wasn't long enough to provide proper removal of the NMMO residues. Therefore, the filaments were further washed with distilled water until they became transparent and observed by SEM (figure 19).

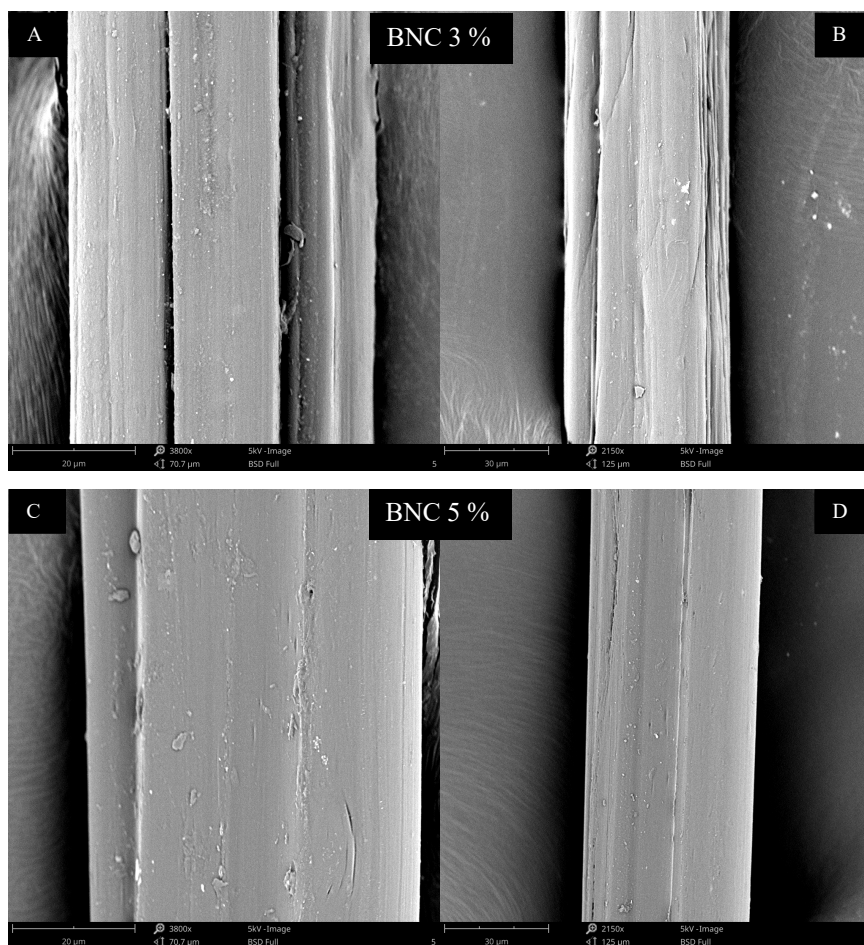


Figure 19. Dry-jet wet-spinning BNC filaments observed by scanning electron microscope (SEM) – scale is 20 μm for A and C, and 30 μm for B and C.

As in the solid-phase dissolution method (figure 14), the 3 % BNC Lyocell SEM images (figure 19), shows some bumps and the filaments are not completely cylindrical, they present some deformations. With the increase of BNC concentration, filaments have a more cylindrical form as in 5 % BNC SEM images in figure 19, that presents a smoother surface. In figure 20 various filaments, produced with 5 % BNC are shown. Their mechanical properties are shown in table 5.

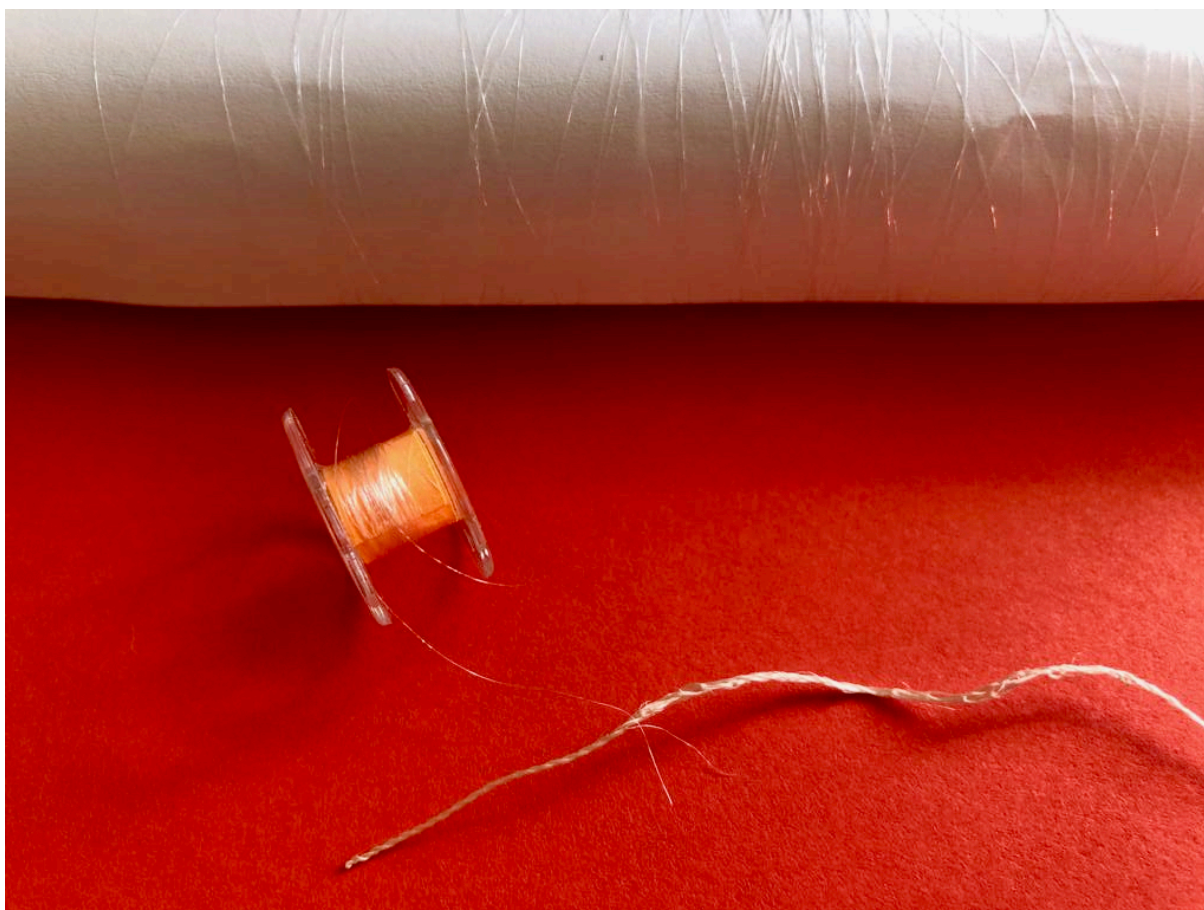


Figure 20. Dry-jet wet-spinning 5 % BNC filaments – BNC Lyocell fibre.

Table 5. Mechanical properties of BNC filaments (3 and 5 %) through the Lyocell method and dry-jet wet-spinning

BNC %	d (μm)	Young's Modulus (GPa)	Tensile Strength (GPa)	Elongation (%)
3	10-30	22,5 ± 7,4 *	771,9 ± 266,5	5,0 ± 1,5 **
5	20-40	35,0 ± 17,2 *	1103,0 ± 481,4	6,8 ± 4,0 **

** the differences are significant (P < 0.05)

Filaments with 5 % BNC showed better mechanical properties compared to those with 3 %. The filaments extruded (5 % BNC) were also more resistant to hand manipulation and the NMMO washing was easier. There is a significant difference between the two concentrations for the Young's Modulus and elongation. More concentrated solutions can be used if a more advanced equipment is used, as an integrated system of dissolution and extrusion. At CeNTI,

the main observed experimental difficulty concerned with the impossibility of pouring the dope in the dry-jet wet-spinning at higher viscosities. Comparing the solid phase dissolution (figures 15-17) to the Lyocell method (table 5), the Young's modulus is superior in the later, while the tensile strength of the 5 % BNC traditional Lyocell is almost as high as the one obtained with 2 % BNC using a 600 μm needle (1201,9 MPa). Both processes allowed the production of BNC fibres with better mechanical properties than those currently used in the market (table 1).

4.3 BNC depolymerization: mechanical treatment

A mechanical process was tested, to lower the DP of BNC, while obviating the use of alkaline solutions, thus reducing its environmental impact. For this, two mechanical treatments were performed – wet defibrillation and dry grinding. Defibrillated samples, at different processing times (1, 5, 10 and 30 min) were observed by optical fluorescence microscopy (figures 21-24) to compare the impact of the disintegration time on the morphology and bundle size (figure 25 and table 13 in the annexes). The bundles sizes dropped from 342,8 μm to 117,9 μm , with the disintegration time, albeit the large size distribution observed.

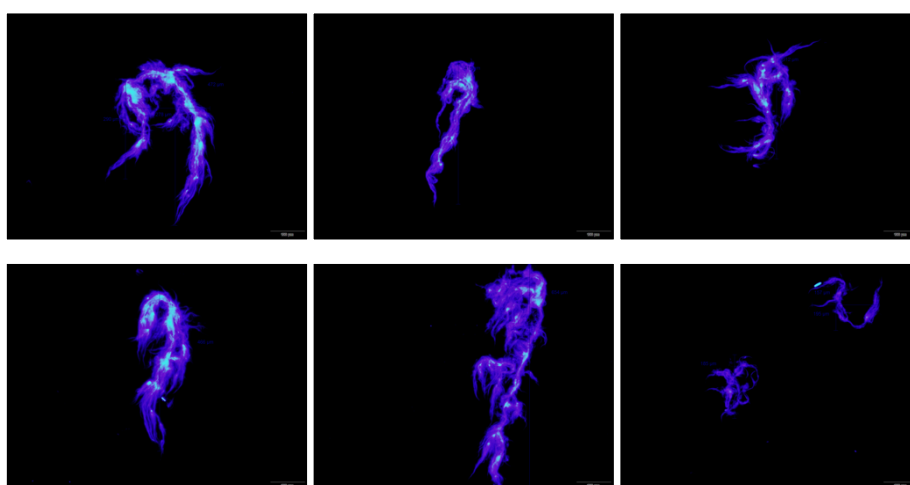


Figure 21. Fluorescence microscopy of BNC bundles with 1 min of wet defibrillation – scale is 100 μm .

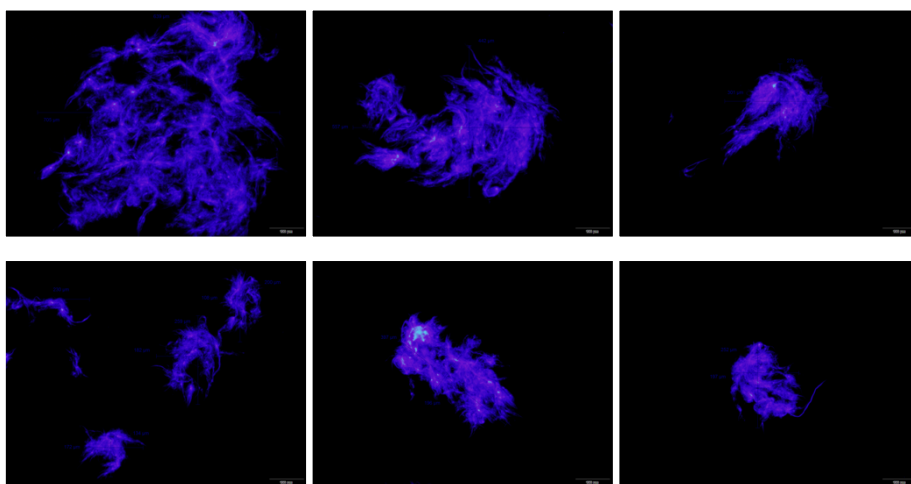


Figure 22. Fluorescence microscopy of BNC bundles with 5 min of wet defibrillation – scale is 100 μm .

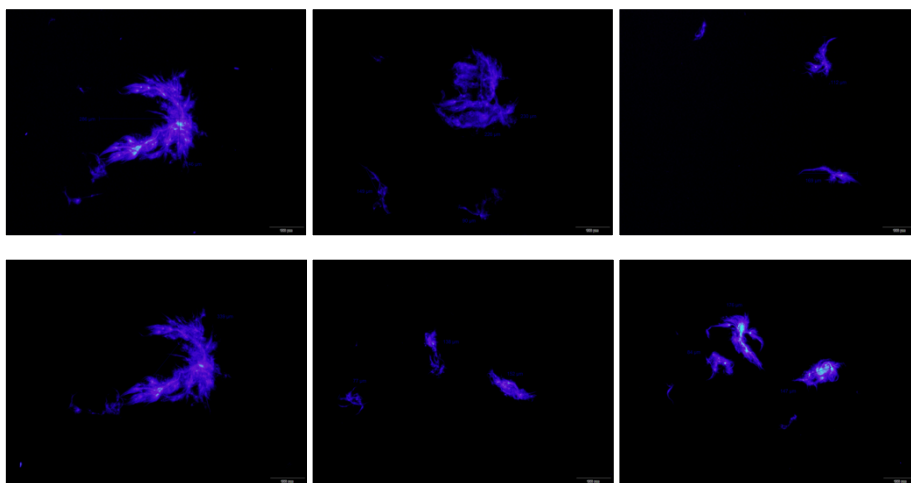


Figure 23. Fluorescence microscopy of BNC bundles with 10 min of wet defibrillation – scale is 100 μm .

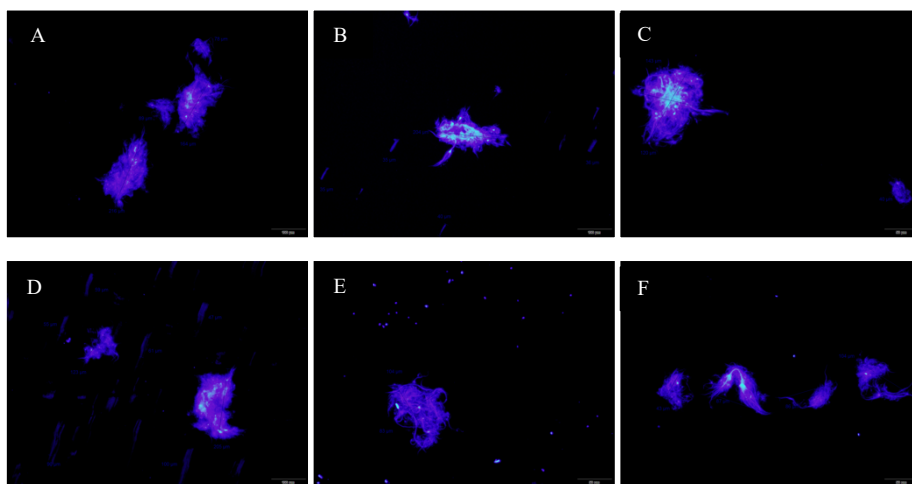
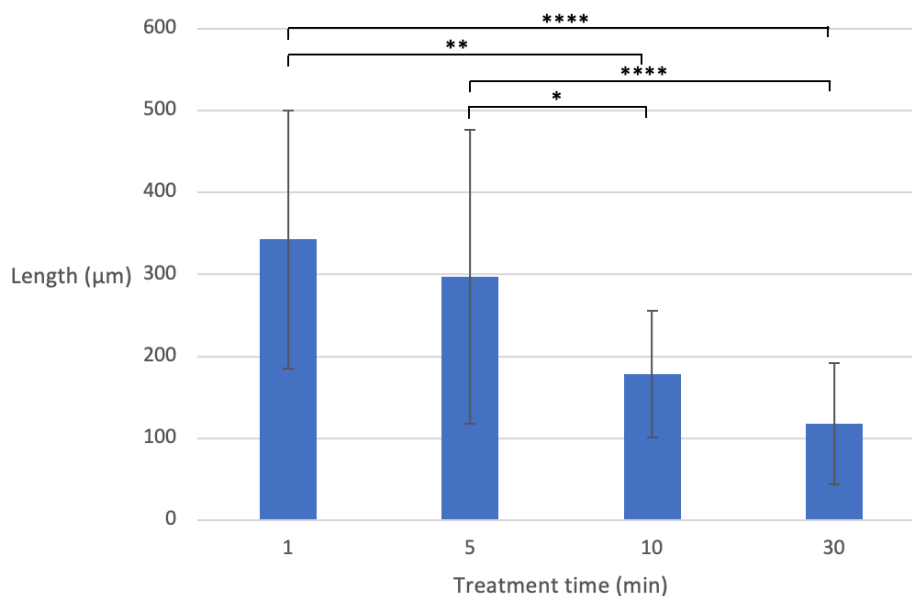


Figure 24. Fluorescence microscopy of BNC bundles with 30 min of wet defibrillation – scale is 100 μm for A, B and D, and 50 μm for C, E and F.

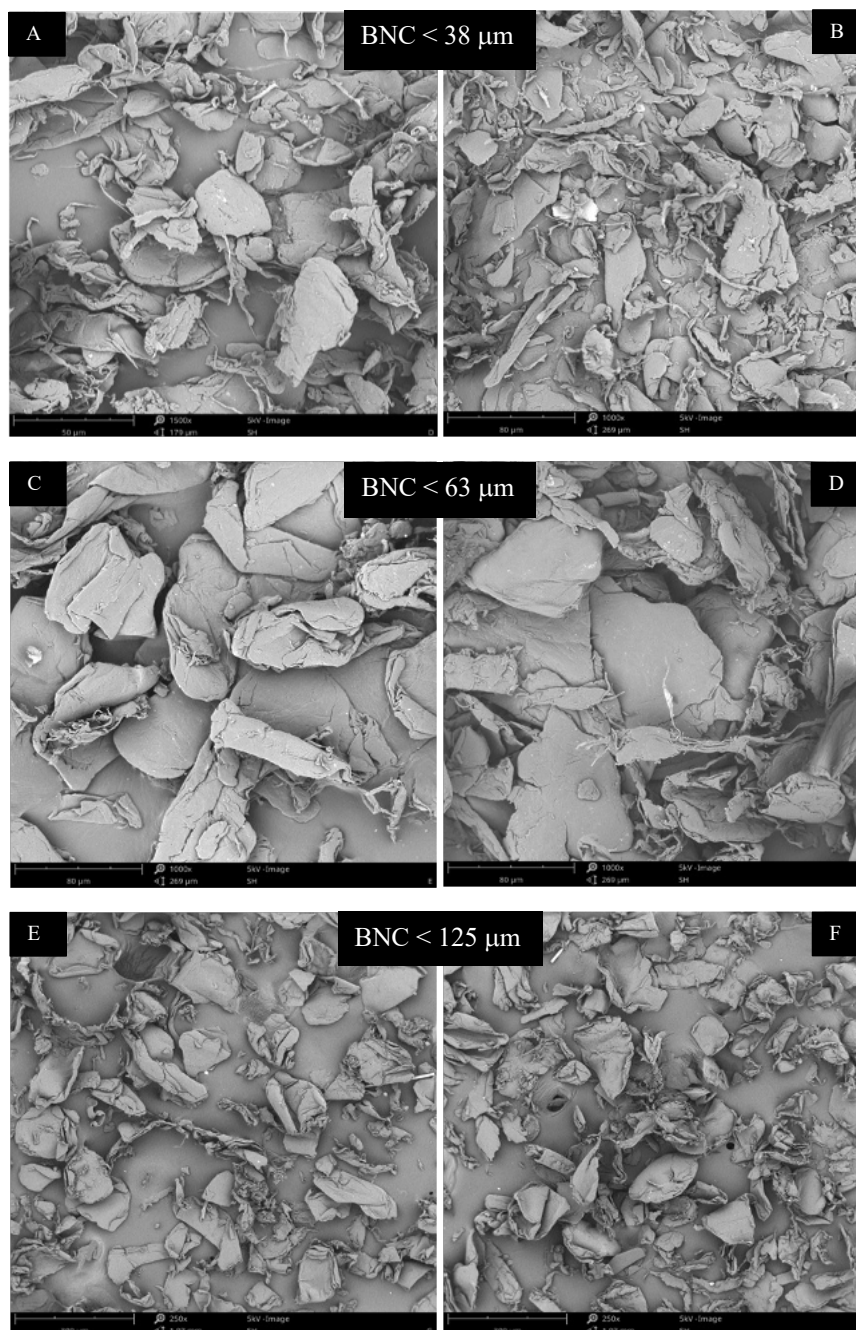
As shown in figures 21-24, BNC bundles have more light intensity, which suggests a higher BNC density, in 1 min wet defibrillation (in the firsts instants, when the fibres are defibrillated they may also be curling). The light intensity decreases with higher defibrillation time until the 30 min wet defibrillation which increases.



*, **, **** the differences are significant ($P < 0.05$)

Figure 25. BNC (0.5 %) bundles length with different wet defibrillation times.

The second mechanical treatment – dry grinding – was performed. After particle size separation ($< 38\ \mu\text{m}$, $< 63\ \mu\text{m}$, $< 125\ \mu\text{m}$ and $< 500\ \mu\text{m}$) the BNC powder fractions were analysed by scanning electron microscope (SEM) (figure 26).



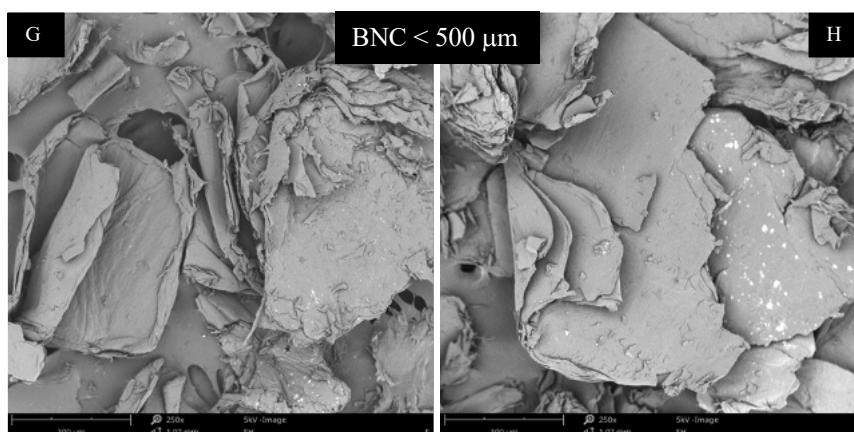
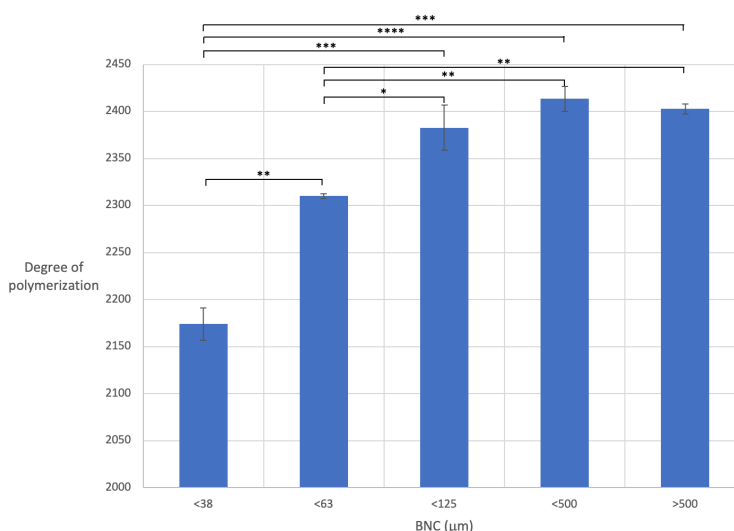


Figure 26. Powder BNC samples with different particle size in scanning electron microscope (SEM) – scale is 50 μm for A, 80 μm for B, C and D and 300 μm for E, F, G and H.

Only the dry grinding method (composed of wet defibrillation and subsequent dry grinding) (figure 26) was further studied. Since it allowed higher particle size range, it would be expected better results in terms of depolymerization. The viscosities of the powdered BNC were analysed to determine the DP, according to ISO 5351:2012. The results, shown in figure 27 and table 14 in the annexes, revealed a significant decrease in DP with the decrease in particle size. The efflux time (s) for BNC ($< 38\mu\text{m}$) is higher, due to the higher mass concentration (table 14 in the annexes).



*, **, ***, **** the differences are significant ($P < 0.05$)

Figure 27. DP of Powdered BNC with different particle size.

As observed, for environmental reasons, the mechanical treatment would be preferred, as no chemicals are used. Yet, as seen in figure 27, the lowest DP (2174) was observed for BNC with particle size lower than 38 μm , a value still far from the target value (DP $\sim$ 600). This is probably not achievable even with more potent equipment; thus the chemical method was adopted.

4.4 BNC depolymerization: chemical treatment

As with the Viscose method, the BNC depolymerization was performed using NaOH as a depolymerizing agent (Shaikh et al., 2012) (Jinzarli et al., 2019). Firstly, the mercerization step was studied without aging, to optimize the NaOH concentration (4.5 M-7.0 M). as compared to the control, a significant decrease ($p < 0.05$) in DP was visible at this stage (table 7), but using alkaline concentrations above 4.5 M did not induce further depolymerization ($p > 0.05$), thus the NaOH concentration seems not to be limiting. NaOH 5.0 M was thus chosen for the following tests. New samples were mercerized and further aged. The results may be found in figure 28 and table 15 in the annexes, showing a noticeable decrease in DP only when the samples had an aging time.

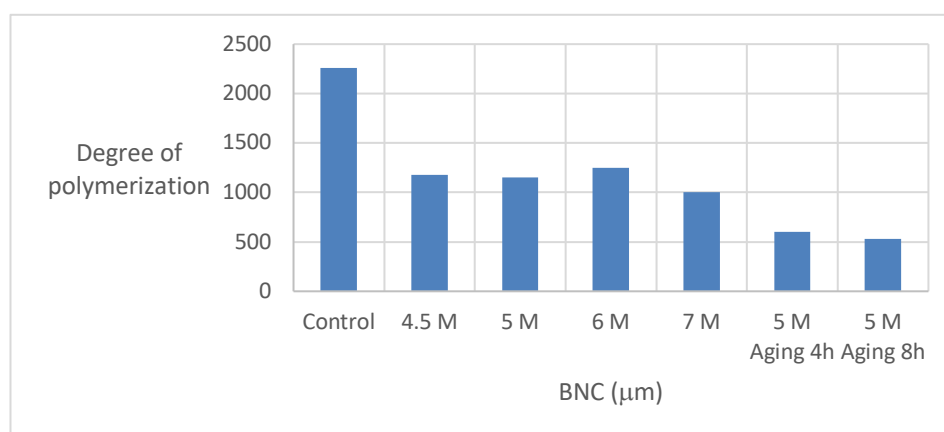


Figure 28. BNC DP for different depolymerization conditions.

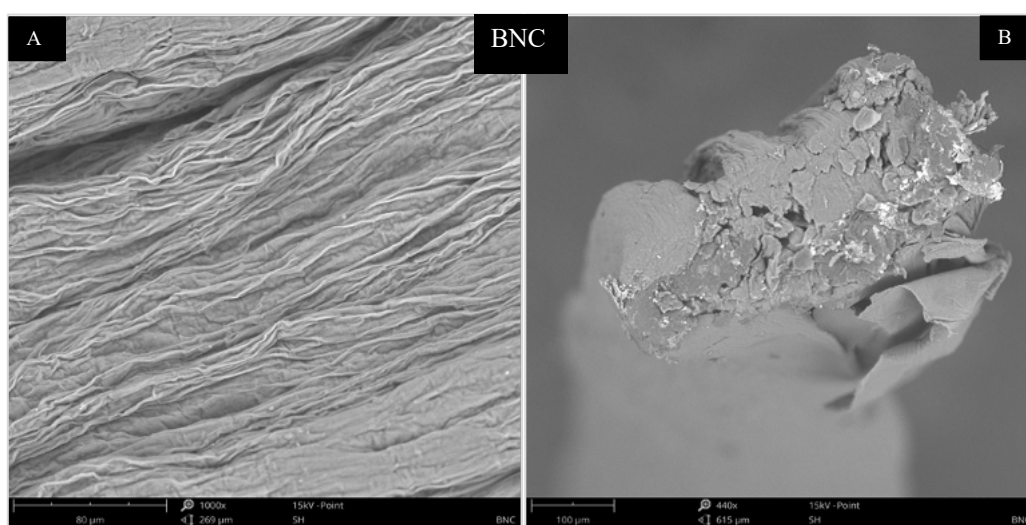
After aging, a large decrease in DP was observed for the two samples produced, the one that endured the longest aging time (8 h) showing the higher DP reduction (figure 28). These samples had DP's of 531 and 602, respectively, being the sample of 4 h aging time in the desired DP range for Lyocell production. These results were obtained from a single experiment. With replicate assays, the impact of NaOH concentration on the DP of BNC would be better assessed.

From these results, it is reasonable to assume that a 4h treatment would be sufficient to lower the DP.

With this study, it was shown that it is possible to have a BNC DP compatible with the requirements of the Lyocell process. However, having demonstrated that the BNC depolymerization is possible, environmental problems arise. The Lyocell process appear to solve some of the environmental problems related to the Viscose process, such as the use of large amounts of NaOH (Shen et al., 2010). Therefore, while technically feasible, from the environmental point of view, it would be preferable not to use this reagent to dissolve the fibres. There are alternatives to BNC depolymerization, such as enzymatic methods, that could be explored (Kosan et al., 2020).

4.5 Dry-spinning

Due to environmental reasons, processes that avoid the use of chemicals are preferable. Dry-spinning BNC, BNC – CMC and BNC – glycerol samples allowed to produce BNC filaments without BNC dissolution. Samples with 3, 5 and 10 % BNC were prepared and extruded in a Capillary Rheometer at CeNTI facilities, but only the 3 % BNC allowed the formation of a filament. Also, tests using 3 % BNC + 1 % glycerol and 3 % BNC + 1 % CMC were performed. These filaments were characterized morphologically (see figure 29) and mechanically by tensile tests (see table 6). The Young's modulus, tensile strength and elongation were similar for the samples of BNC, BNC – CMC and BNC – glycerol.



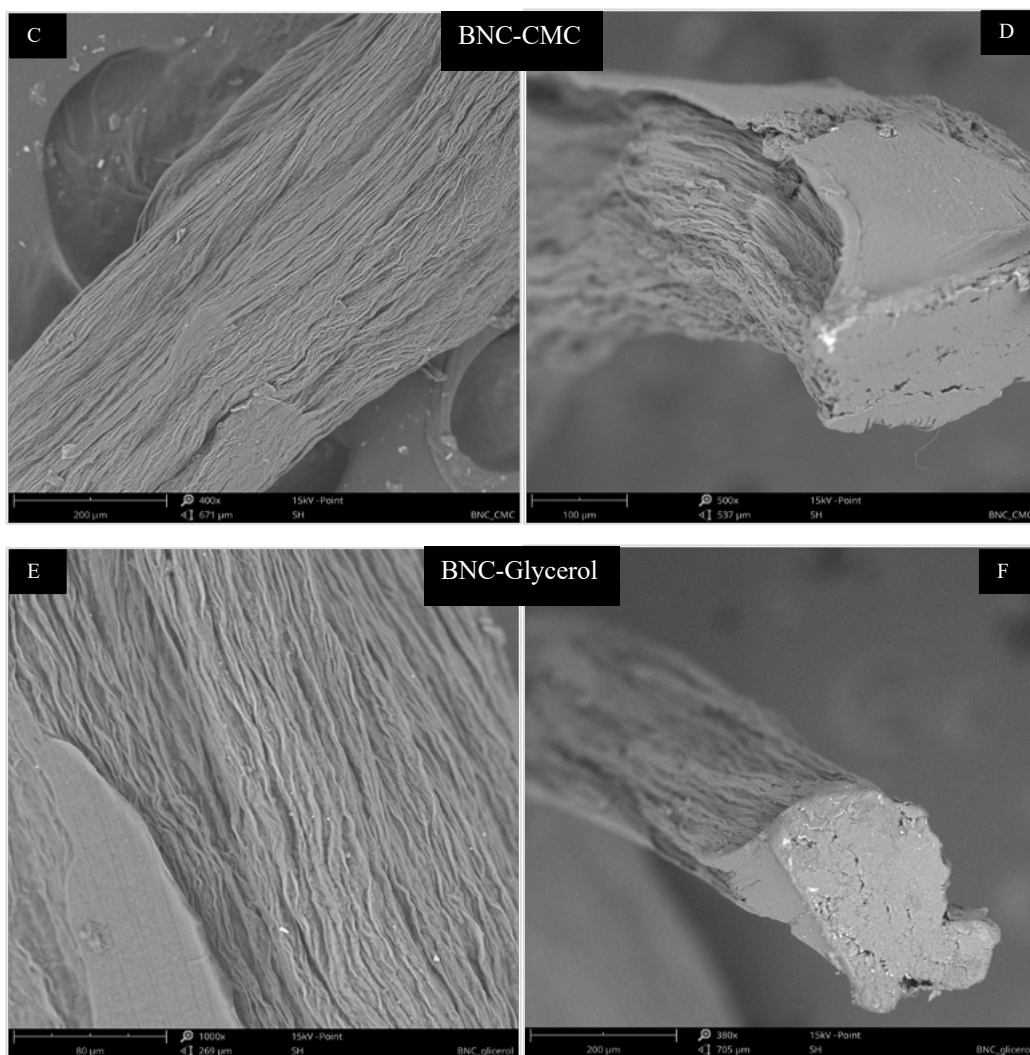


Figure 29. Dry-spinning BNC filaments in scanning electron microscope (SEM) – scale is 80 μm for A and E, 100 μm for B and D, and 200 μm for C and F.

Table 6. Mechanical properties of dry-spinning BNC filaments

Dry-spinning	d (μm)	Young's Modulus (GPa)	Tensile Strength (MPa)	Elongation (%)
BNC		$5,4 \pm 2,2$	$194,6 \pm 53,2$	$9,1 \pm 6,3$
BNC – CMC	200-300	$5,5 \pm 1,8$	$138,3 \pm 36,5$	$8,6 \pm 6,4$
BNC – glycerol		$5,6 \pm 2,0$	$164,67 \pm 34,7$	$8,1 \pm 4,2$

The SEM images (figure 29) are quite different from those obtained by syringe spinning and the dry-jet wet-spinning (figure 22 and 27, respectively), which are smoother since the BNC was dissolved. Also, the dry spun BNC fibres showed a good fibre alignment but presented many surface irregularities, which compromised the mechanical properties. Still, similar results were obtained to those of plant cellulose dry-spinning filaments (table 2) (Ghasemi et al., 2017; Hooshmand et al., 2015). Filaments produced through wet-spinning shows better properties (table 1) although SEM images shows less aligned BNC fibres (Kafy et al., 2017; Yao et al., 2017). Samples with CMC and glycerol lowered the fibres tensile strength being the better properties obtained using only BNC (3 %) This BNC filaments are very stiff. The addition of glycerol and CMC, prevents this aggregation of fibres; if on the one hand it can improve flexibility, on the other it could reduce the mechanical properties, as observed (Martins et al., 2020). It was not possible to form filaments using higher concentrations as the BNC could not align well in order to form a filament with some mechanical resistance. In this work was evaluated the BNC concentration on the production of filaments through dry-spinning, various other parameters also need optimization as defibrillation time, drying temperature (Ghasemi et al., 2017) and spinning rate (Hooshmand et al., 2015). The biggest disadvantage of this filaments, compared to Lyocell, is their hydrophilicity (defibrillating in the presence of water) that can be overcome with a hydrophobic coating. There is plenty of room to improve the mechanical properties obtained with the 3 % BNC sample, such as the extrusion speed and the addition of other rheological modifiers.

4.6 Wet-drawing

The wet-drawing method also does not require chemicals for BNC dissolution, nor requires the defibrillation of the BNC, which means that the properties of the native BNC are fully preserved. The mechanical properties of the macrofibres obtained were analysed and the results are presented in tables 7 and 8. It is noteworthy the difference between the Young's modulus of neat BNC and BNC – glycerol samples, being the latter the one with better properties. Regarding tensile strength and elongation, similar values were obtained. For different % of wet-drawing, it is visible the increase of the mechanical properties with the increase of % of wet-drawing for both BNC and BNC – glycerol samples. Samples of BNC – glycerol with 30 % wet-drawing had the highest Young's modulus ($7,9 \pm 3,4$ GPa) although an increase in tensile strength was not observed.

Table 7. Mechanical properties of wet-drawing BNC macrofibres

	%	Young's Modulus (GPa)	Tensile Strength (MPa)	Elongation (%)
BNC	0	1,1	57,2	10,0
	10	1,7	82,5	13,2
	20	1,0	264,3	12,5
	30	3,1	247,4	8,5

Table 8. Mechanical properties of wet-drawing BNC – glycerol macrofibres

	%	Young's Modulus (GPa)	Tensile Strength (MPa)	Elongation (%)
BNC – glycerol	10	3,2 ± 1,8	219,3 ± 104,7	9,6 ± 0,7
	20	4,2 ± 3,4	171,0 ± 59,3	12,7 ± 4,4
	30	7,9 ± 3,4	220,2 ± 98,4	14,3 ± 1,8

It would be expected to have better mechanicals properties as the membrane properties are maintained but that did not occur, the maximum Young's modulus was $7,9 \pm 3,4$ GPa and tensile strength of $220,2 \pm 98,4$ MPa for fibres with 30 % stretching and glycerol. Others had obtained superior results using this process (Young's modulus of 65,7 GPa and tensile strength of 826 MPa (table 2)) (S. Wang et al., 2017).

5. CONCLUSION

Several types of fibres have been produced to fulfill people's needs and demands, polyester, cotton and Viscose being the most used. However, these fibres have environmental implications during raw material processing and transport, filament manufacture, product and byproducts disposal. Current trends include the development of filaments without solvents, the development of new solvents and new sources of fibres, which include different nanocelluloses, namely BNC.

In order to minimize the use of chemicals in the filament production, BNC filaments without depolymerization were produced, using the Lyocell method, and high mechanical properties were obtained, being superior to those currently commercialized. BNC depolymerization was then studied and achieved using NaOH. Commercial Lyocell DP parameters were obtained.

Filaments without BNC dissolution, that is, without the use of chemicals harmful to the environment, were also produced. The mechanical results of these filaments weren't as good as BNC Lyocell filaments, but they can still be greatly improved.

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ANNEXES

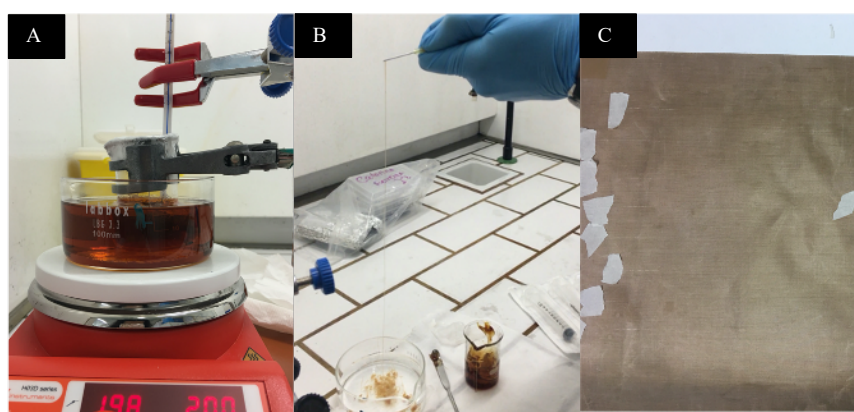


Figure 30. BNC solid-phase dissolution (A), spinning (B) and drying (C).

Table 9. Mechanical properties of BNC dope spun with a 900 μm syringe

BNC (%)	Young's Modulus (GPa)	Tensile Strength (MPa)	Elongation (%)
2	$8,0 \pm 2,7$	$390,4 \pm 144,8$	$18,4 \pm 6,2$
2.5	$5,5 \pm 1,7$	$306,2 \pm 93,3$	$27,5 \pm 10,0$
3	$6,3 \pm 1,0$	$280,9 \pm 71,5$	$25,3 \pm 10,8$
3.5	$4,6 \pm 1,2$	$219,8 \pm 31,9$	$24,6 \pm 6,5$
4	$5,9 \pm 1,5$	$229,5 \pm 70,1$	$15,4 \pm 4,1$

Table 10. Mechanical properties of BNC (2 %) with a 800 μm syringe

d (μm)	Young's Modulus (GPa)	Tensile Strength (MPa)	Elongation (%)
10	$19,8 \pm 6,4$	$768,2 \pm 125,4$	$11,45 \pm 0,2$
20	$24,3 \pm 0,7$	$691,5 \pm 94,7$	$8,9 \pm 2,0$
40	$12,50 \pm 3,0$	$411,6 \pm 69,3$	$11,4 \pm 5,5$

Table 11. Mechanical properties of BNC (2 %) with a 600 μm syringe

d (μm)	Young's Modulus (GPa)	Tensile Strength (MPa)	Elongation (%)
10	$20,8 \pm 5,4$	$1201,9 \pm 149,2$	$11,5 \pm 0,1$
20	$17,0 \pm 4,0$	$724,2 \pm 141,0$	$13,2 \pm 3,0$
30	$19,7 \pm 5,3$	$662,2 \pm 198,5$	$8,6 \pm 3,7$

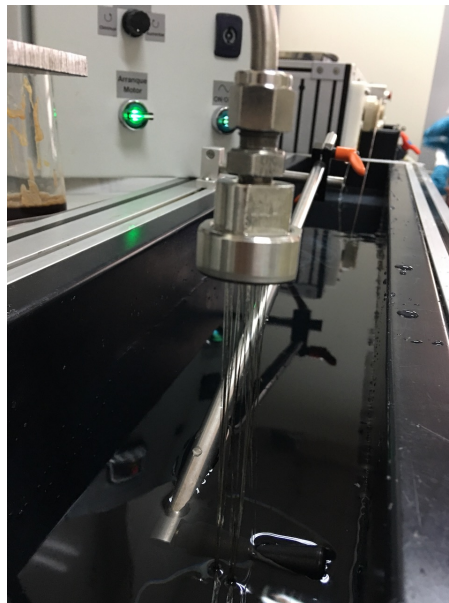


Figure 31. BNC dry-jet wet-spinning.

Table 12. Values of $[\eta] \times \rho$ corresponding to different values of the viscosity ratio η_{ratio}

η_{ratio}	0,0	0,01	0,02	0,03	0,04	0,05	0,06	0,07	0,08	0,09
1,0	0,000	0,010	0,020	0,030	0,040	0,049	0,059	0,069	0,078	0,088
1,1	0,097	0,107	0,116	0,125	0,134	0,144	0,153	0,162	0,171	0,180
1,2	0,189	0,198	0,207	0,216	0,224	0,233	0,242	0,250	0,259	0,268
1,3	0,276	0,285	0,293	0,302	0,310	0,318	0,326	0,335	0,343	0,351
1,4	0,359	0,367	0,375	0,383	0,391	0,399	0,407	0,415	0,423	0,431
1,5	0,438	0,446	0,454	0,462	0,469	0,477	0,484	0,492	0,499	0,507
1,6	0,514	0,522	0,529	0,537	0,544	0,551	0,558	0,566	0,573	0,580
1,7	0,587	0,594	0,601	0,608	0,615	0,622	0,629	0,636	0,643	0,650
1,8	0,657	0,664	0,671	0,678	0,684	0,691	0,698	0,705	0,711	0,718
1,9	0,725	0,731	0,738	0,744	0,751	0,757	0,764	0,770	0,777	0,783
2,0	0,790	0,796	0,802	0,809	0,815	0,821	0,827	0,834	0,840	0,846
2,1	0,852	0,858	0,865	0,871	0,877	0,883	0,889	0,895	0,901	0,907
2,2	0,913	0,919	0,925	0,931	0,937	0,943	0,949	0,954	0,960	0,966
2,3	0,972	0,978	0,983	0,989	0,995	1,001	1,006	1,012	1,018	1,023
2,4	1,029	1,035	1,040	1,046	1,051	1,057	1,062	1,068	1,073	1,079
2,5	1,084	1,090	1,095	1,101	1,106	1,111	1,117	1,122	1,127	1,133
2,6	1,138	1,143	1,149	1,154	1,159	1,164	1,170	1,175	1,180	1,185
2,7	1,190	1,196	1,201	1,206	1,211	1,216	1,221	1,226	1,231	1,236
2,8	1,241	1,246	1,251	1,256	1,261	1,266	1,271	1,276	1,281	1,286
2,9	1,291	1,296	1,301	1,306	1,310	1,316	1,320	1,325	1,330	1,335
3,0	1,339	1,344	1,349	1,354	1,358	1,363	1,368	1,373	1,377	1,382
3,1	1,387	1,391	1,396	1,401	1,405	1,410	1,414	1,419	1,424	1,428
3,2	1,433	1,437	1,442	1,446	1,451	1,455	1,460	1,464	1,469	1,473
3,3	1,478	1,482	1,487	1,491	1,496	1,500	1,504	1,509	1,513	1,517
3,4	1,522	1,526	1,531	1,535	1,539	1,544	1,548	1,552	1,556	1,561
3,5	1,565	1,569	1,573	1,578	1,582	1,586	1,590	1,595	1,599	1,603
3,6	1,607	1,611	1,615	1,620	1,624	1,628	1,632	1,636	1,640	1,644
3,7	1,648	1,653	1,657	1,661	1,665	1,669	1,673	1,677	1,681	1,685
3,8	1,689	1,693	1,697	1,701	1,705	1,709	1,713	1,717	1,721	1,725
3,9	1,729	1,732	1,736	1,740	1,744	1,748	1,752	1,756	1,760	1,764
4,0	1,767	1,771	1,775	1,779	1,783	1,787	1,790	1,794	1,798	1,802
4,1	1,806	1,809	1,813	1,817	1,821	1,824	1,828	1,832	1,836	1,839
4,2	1,843	1,847	1,851	1,854	1,858	1,862	1,865	1,869	1,873	1,876
4,3	1,880	1,884	1,887	1,891	1,894	1,898	1,902	1,905	1,909	1,912
4,4	1,916	1,920	1,923	1,927	1,930	1,934	1,937	1,941	1,944	1,948
4,5	1,952	1,955	1,959	1,962	1,966	1,969	1,973	1,976	1,979	1,983
4,6	1,986	1,990	1,993	1,997	2,000	2,004	2,007	2,010	2,014	2,017
4,7	2,021	2,024	2,028	2,031	2,034	2,038	2,041	2,044	2,048	2,051
4,8	2,054	2,058	2,061	2,064	2,068	2,071	2,074	2,078	2,081	2,084
4,9	2,088	2,091	2,094	2,098	2,101	2,104	2,107	2,111	2,114	2,117

Table 12. Continued.

η_{ratio}	0,0	0,01	0,02	0,03	0,04	0,05	0,06	0,07	0,08	0,09
5,0	2,120	2,124	2,127	2,130	2,133	2,137	2,140	2,143	2,146	2,149
5,1	2,153	2,156	2,159	2,162	2,165	2,168	2,172	2,175	2,178	2,181
5,2	2,184	2,187	2,191	2,194	2,197	2,200	2,203	2,206	2,209	2,212
5,3	2,215	2,219	2,222	2,225	2,228	2,231	2,234	2,237	2,240	2,243
5,4	2,246	2,249	2,252	2,255	2,258	2,261	2,264	2,267	2,270	2,273
5,5	2,276	2,280	2,283	2,286	2,288	2,291	2,294	2,297	2,300	2,303
5,6	2,306	2,309	2,312	2,315	2,318	2,321	2,324	2,327	2,330	2,333
5,7	2,336	2,339	2,342	2,345	2,347	2,350	2,353	2,356	2,359	2,362
5,8	2,365	2,368	2,371	2,374	2,376	2,379	2,382	2,385	2,388	2,391
5,9	2,394	2,396	2,399	2,402	2,405	2,408	2,411	2,413	2,416	2,419
6,0	2,422	2,425	2,427	2,430	2,433	2,436	2,439	2,441	2,444	2,447
6,1	2,450	2,452	2,455	2,458	2,461	2,463	2,466	2,469	2,472	2,475
6,2	2,477	2,480	2,483	2,485	2,488	2,491	2,494	2,496	2,499	2,502
6,3	2,504	2,507	2,510	2,512	2,515	2,518	2,521	2,523	2,526	2,529
6,4	2,531	2,534	2,537	2,539	2,542	2,545	2,547	2,550	2,552	2,555
6,5	2,558	2,560	2,563	2,566	2,568	2,571	2,573	2,576	2,579	2,581
6,6	2,584	2,587	2,589	2,592	2,594	2,597	2,599	2,602	2,605	2,607
6,7	2,610	2,612	2,615	2,617	2,620	2,623	2,625	2,628	2,630	2,633
6,8	2,635	2,638	2,640	2,643	2,645	2,648	2,651	2,653	2,656	2,659
6,9	2,661	2,663	2,666	2,668	2,671	2,673	2,676	2,678	2,681	2,683
7,0	2,686	2,688	2,690	2,693	2,695	2,698	2,700	2,703	2,705	2,708
7,1	2,710	2,713	2,715	2,718	2,720	2,722	2,725	2,727	2,730	2,732
7,2	2,735	2,737	2,739	2,742	2,744	2,747	2,749	2,752	2,754	2,756
7,3	2,758	2,761	2,764	2,766	2,768	2,771	2,773	2,775	2,778	2,780
7,4	2,783	2,785	2,787	2,790	2,792	2,794	2,797	2,799	2,801	2,804
7,5	2,806	2,809	2,811	2,813	2,816	2,818	2,820	2,823	2,825	2,827
7,6	2,829	2,832	2,834	2,836	2,839	2,841	2,843	2,846	2,848	2,850
7,7	2,853	2,855	2,857	2,859	2,862	2,864	2,866	2,869	2,871	2,873
7,8	2,875	2,878	2,880	2,882	2,885	2,887	2,889	2,891	2,894	2,896
7,9	2,898	2,900	2,903	2,905	2,907	2,909	2,911	2,914	2,916	2,918
8,0	2,920	2,923	2,925	2,927	2,929	2,932	2,934	2,936	2,938	2,940
8,1	2,943	2,945	2,947	2,949	2,951	2,954	2,956	2,958	2,960	2,962
8,2	2,964	2,967	2,969	2,971	2,973	2,975	2,978	2,980	2,982	2,984
8,3	2,986	2,988	2,991	2,993	2,995	2,997	2,999	3,001	3,003	3,006
8,4	3,008	3,010	3,012	3,014	3,016	3,018	3,020	3,023	3,025	3,027
8,5	3,029	3,031	3,033	3,035	3,037	3,040	3,042	3,044	3,046	3,048
8,6	3,050	3,052	3,054	3,056	3,058	3,061	3,063	3,065	3,067	3,069
8,7	3,071	3,073	3,075	3,077	3,079	3,081	3,083	3,085	3,087	3,090
8,8	3,092	3,094	3,096	3,098	3,100	3,102	3,104	3,106	3,108	3,110
8,9	3,112	3,114	3,116	3,118	3,120	3,122	3,124	3,126	3,128	3,130
9,0	3,132	3,134	3,136	3,138	3,140	3,142	3,144	3,147	3,149	3,151
9,1	3,153	3,155	3,157	3,159	3,161	3,163	3,165	3,166	3,168	3,170
9,2	3,172	3,174	3,176	3,178	3,180	3,182	3,184	3,186	3,188	3,190
9,3	3,192	3,194	3,196	3,198	3,200	3,202	3,204	3,206	3,208	3,210
9,4	3,212	3,214	3,216	3,218	3,220	3,222	3,223	3,225	3,227	3,229
9,5	3,231	3,233	3,235	3,237	3,239	3,241	3,243	3,245	3,247	3,249
9,6	3,250	3,252	3,254	3,256	3,258	3,260	3,262	3,264	3,266	3,268
9,7	3,270	3,271	3,273	3,275	3,277	3,279	3,281	3,283	3,285	3,287
9,8	3,288	3,290	3,292	3,294	3,296	3,298	3,300	3,302	3,303	3,305
9,9	3,307	3,309	3,311	3,313	3,315	3,316	3,318	3,320	3,322	3,324

Table 12. Continued.

η_{ratio}	0,0	0,01	0,02	0,03	0,04	0,05	0,06	0,07	0,08	0,09
10,0	3,326	3,344	3,363	3,381	3,399	3,416	3,434	3,452	3,469	3,487
11,0	3,504	3,521	3,538	3,554	3,571	3,588	3,604	3,620	3,636	3,653
12,0	3,669	3,684	3,700	3,716	3,731	3,747	3,762	3,777	3,792	3,807
13,0	3,822	3,837	3,852	3,866	3,881	3,895	3,910	3,924	3,938	3,952
14,0	3,966	3,980	3,994	4,008	4,021	4,035	4,048	4,062	4,075	4,088
15,0	4,101	4,115	4,128	4,141	4,153	4,166	4,179	4,192	4,204	4,217
16,0	4,229	4,242	4,254	4,266	4,279	4,291	4,303	4,315	4,327	4,339
17,0	4,351	4,362	4,374	4,386	4,397	4,409	4,420	4,432	4,443	4,455
18,0	4,466	4,477	4,488	4,499	4,510	4,521	4,532	4,543	4,554	4,565
19,0	4,576	4,586	4,597	4,608	4,618	4,629	4,639	4,650	4,660	4,670

Table 13. BNC (0.5 %) bundles length with different wet defibrillation times

Treatment time (min)	Length (μm)
1	$342,8 \pm 157,65$
5	$297,3 \pm 179,21$
10	$178,4 \pm 77,77$
30	$117,9 \pm 74,26$

Table 14. Powder BNC viscosity and DP with different particle size

BNC fraction	ρ mg/mL	Time (s)	$[\eta]$	DP
< 38 μm	5	$65,70 \pm 0,62$	$613 \pm 5,67$	2174 ± 17
< 63 μm	4	$56,44 \pm 0,83$	$698,63 \pm 1,59$	2310 ± 3
< 125 μm	4	$62,33 \pm 1,57$	$742,63 \pm 14,67$	2383 ± 24
< 500 μm	4	$65,01 \pm 1,17$	$761,50 \pm 8,13$	2413 ± 3
> 500 μm	4	$64,24 \pm 0,47$	$754,88 \pm 3,36$	2403 ± 5

Table 15. BNC viscosity and DP with chemical treatment

BNC sample	ρ mg/mL	Time (s)	$[\eta]$	Plant cellulose (DP > 950)	Plant cellulose (DP > 950)	DP BNC
Control	4	78,8	813	1936	2281	2259
4.5 M NaOH 120 min	5	46,6	491	1170	1176	1750
5 M NaOH 120 min	5	45,9	483	1149	1149	1734
6 M NaOH 120 min	5	50,5	515	1227	1252	1793
7 M NaOH 120 min	5	39,6	436	1038	1005	1647
5 M NaOH Aging 4 h	5	21,62	253	602	491	1249
BNC 0.5 % 5 M NaOH – Aging 8 h	5	19,5	223	531	416	1172

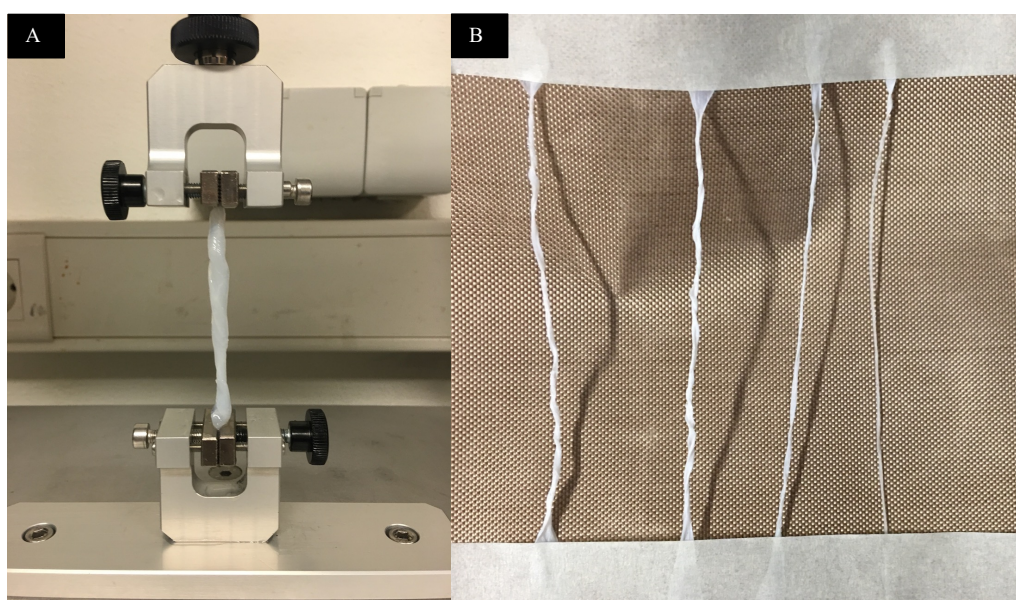


Figure 32. BNC wet-drawing process (a) and drying (B).