

Pre-treatment of pre- and post-consumer viscose textile waste for the purpose of upcycling to high quality textile fibres via Ioncell[®] process

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Preface

The work presented in this thesis was performed in Aalto University at the Department of Bioproducts and Biosystems (Finland), under the supervision of Dr. Inge Schlapp-Hackl, Dr. Marja Rissanen and Prof. Herbert Sixta, and within the frame of the Erasmus+ Program. The thesis was co-supervised in Instituto Superior Técnico (Lisbon) by Prof. Frederico Ferreira.

Declaration

I declare that this document is an original work of my own authorship and that it fulfills all the requirements of the Code of Conduct and Good Practices of the Universidade de Lisboa.

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Resumo

Dada a quantidade de desperdício de têxteis de viscose, este trabalho tem como objetivo a reciclagem da viscose usando o processo Ioncell®.

Para atingir os requisitos de viscosidade da fiação molhada de jato seco, foram realizados testes nos quais se misturou viscose de baixa viscosidade com algodão de alta viscosidade. A viscosidade das misturas resultantes foram testadas e produziram ajustes lineares com coeficiente de correlação $r^2 > 0.99$. A mistura de 80% viscose e 20% algodão atingiu a gama ideal para uma posterior operação de fiação.

Quatro soluções de celulose foram preparadas para fiação usando polpa de bétula, viscose e algodão. As fibras foram fiadas e as seguintes propriedades foram avaliadas: densidade linear, tenacidade, alongação, módulo de elasticidade e orientação total. A relação de tração 11, fibras fiadas com solução de polpa de bétula atingiram valores de 1.26 dtex, 52.58 cN.dtex⁻¹, 10.22 %, 25.50 GPa e 0.757, respectivamente. A relação de tração 5, fibras fiadas com viscose atingiram valores de 3.02 dtex, 30.49 cN.dtex⁻¹, 7.96 %, 18.88 GPa e 0.664, respectivamente. A relações de tração 6 e 7, fibras fiadas com uma mistura de 80% viscose e 20% algodão atingiram valores de 1.54 e 1.23 dtex, 23.49 e 23.55 cN.dtex⁻¹, 6.33 e 6.42 %, 17.81 e 18.93 GPa e 0.674 e 0.664, respectivamente.

Ao considerar o uso de desperdício de viscose como matéria-prima para a produção de novas fibras, é importante entender o comportamento de corantes e de técnicas de tingimento. Este trabalho providencia uma fundação teórica acerca destes tópicos e sobre métodos amigos do ambiente para descoloração.

Palavras-chave: celulose, líquido iônico, fiação molhada de jato seco, viscose, reciclagem química de têxteis

Abstract

Due to the enormous amounts of viscose textile waste, this thesis focuses on the recycling of viscose fabrics by means of the Ioncell[®] process.

To fulfill the starting material requirements for dry-jet wet-spinning, trials were performed to align the viscosity of low viscosity viscose pulp by blending with high viscosity cotton to the range of standard kraft pulp. The viscosity of the resulting blends was tested yielding linear distribution with correlation coefficients of $r^2 > 0.99$. A mixture of 80% viscose and 20% cotton reached the ideal range for posterior spinning operations.

Four cellulose solutions were prepared using virgin birch, viscose and cotton. Fibres were spun and the following properties evaluated: linear density, tenacity, elongation at break, modulus of elasticity and total orientation. At draw ratio (DR) 11, fibres were spun from birch pulp solution and achieved values of 1.26 dtex, 52.58 cN.dtex⁻¹, 10.22 %, 25.50 GPa and 0.757, respectively. At DR 5, fibres were extruded from viscose solution exhibiting properties of 3.02 dtex, 30.49 cN.dtex⁻¹, 7.96 %, 18.88 GPa and 0.664, respectively. At DRs 6 and 7, fibres were generated from 80% viscose and 20% cotton solution, revealing values of 1.54 and 1.23 dtex, 23.49 and 23.55 cN.dtex⁻¹, 6.33 and 6.42 %, 17.81 and 18.93 GPa and 0.674 and 0.664, respectively.

When considering the use of viscose waste as raw material to produce new fibres, it is important to get an understanding of colourants and dyeing techniques. This work provides a theoretical overview concerning these topics and a discussion about environmentally friendly methods of decolourization.

Keywords: cellulose, ionic liquid, dry-jet wet-spinning, viscose, chemical recycling of textiles

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Nomenclature

μ	molecular viscosity coefficient
[DBNH][OAc]	1,5-diazabicyclo [4.3.0]non-5-enium acetate
CS ₂	carbon disulphide
H ₂ SO ₄	sulphuric acid
NaOH	sodium hydroxide
Δn	birefringence
η_0^*	intrinsic viscosity
η^0	zero-shear viscosity
Γ_λ	phase difference at wavelength lambda
AC	ash content
AGU	anhydroglucopyranose
CED	cupri-ethyldiamide
COP	crossover point
DBN	1,5-diazabicyclo [4.3.0]non-5-ene
DMC	dry matter content
DP	degree of polymerization
DR	draw ratio
DS	degree of substitution
ECEAP	European Circular Economy Action Plan
f_t	total orientation
G''	loss modulus
G'	storage modulus

IL	ionic liquid
NMMO	N-methylmorpholine N-oxide monohydrate
RH	relative humidity
v_e	extrusion velocity
v_{tu}	take-up velocity
vdW	van der Waals

Chapter 1

Introduction

Textile production is associated with significant environmental impact. To relieve this burden, Circular Economy presents itself as the economic model to follow. Up to now, some efforts towards its implementation are already in practice in the European Union. However, only very few solutions completely follow the Circular Economy paradigm. The world is striving for a better future within the textile industry. There is potential in the manufacturing process of man-made cellulose fibres, especially in terms of the loncell[®] technology. Under these terms, this thesis work, which is inserted within the Finix project, attempts to extend the scope of application of the loncell[®] process by the use of pre- and post-consumer viscose textile waste as raw material for the production of fibres.

1.1 Motivation

1.1.1 Textile industry and sustainability

Global textile production was estimated at 107 million tonnes of textile products per year in 2018. Considering the growth that has been registered in the last years, global textile production is projected to reach 145 millions tonnes in 2030 [1][2].

The textile industry has a long and complex supply chain. All the process steps needed from production to disposal account for tremendous environmental impacts. This industry is responsible for 1.5 trillion litres per year of water consumption (4 % of global freshwater consumption), more than 1.7 billion tonnes per year of carbon dioxide (CO₂) emissions (10 % of total emissions), 190 000 tonnes per year of oceanic primary microplastic pollution (35% of total microplastic pollution) and more than 92 million tonnes per year of textile waste. Additionally, 20% of industrial water pollution comes from textile treatment and dyeing [3].

Polyester dominates the market with a production of 55.1 million tonnes in 2018, which corresponds to a 51.5 % market share [2]. The production of this synthetic petroleum-based fibres is well known for the use of carbon-intensive, non-renewable resources as raw material and manufacturing fuel; as such, more than 70 million barrels of oil are used to make polyester every year. Synthetic textiles are believed to be the biggest source of microplastic pollution because upon every wash, up to 1900 fibres can leach

into the water; and since this material is not biodegradable, it will persist on the environment. Despite the previous drawbacks, polyester textiles with recycled PET fibres can be made with PET bottles[4]. However, in 2018 recycled polyester represented only 13 % of the total production of polyester [2].

Cotton is the second most demanded fibre with a production of 26.05 million tonnes in 2018, which corresponds to a 24.4 % market share [2]. Prevailing problems associated with cotton cultivation are high water consumption, extensive use of fertilizers and pesticides to enhance production and large arable land requirements that compete with the production of crops ¹. Especially due to arable land requirements, cotton production growth has stagnated and currently has no prospect of increasing [5][6][7].

An increasingly important fibre category is the man-made cellulose fibres (MMCFs) with a production of 6.7 million tonnes in 2018, which corresponds to a 6.2 % market share [2]. Wood-based cellulose from sustainable forestry presents itself as a sustainable raw material with a very favorable environmental footprint. The viscose process which generates viscose fibres is still the dominating MMCF technology; it accounts for roughly 90% of total MMCF production. However, the severe impact related to the low stability of the solvent systems, the use of toxic chemicals, the generation of toxic by-products and the major energy consumption is a major drawback. The only alternative for MMCF production that bears great potential as a more eco-friendly option is the lyocell process; it only accounts for 4 % of total MMCF production. It utilises a direct solvent for cellulose that is non-toxic, biodegradable and easy to recover efficiently. However, it suffers from a potential strong exothermic reaction at high temperature and therefore requires the addition of stabilisers. Moreover, none of these processes are flexible towards the raw material, requiring highly purified cellulose that comes with environmental cost due to complex pre-treatment [5][6][8].

1.1.2 Circular Economy and European Action Plan

These impacts stress the need to reevaluate current textile industry practices, such as fast fashion, in order to mitigate the detrimental environmental consequences and to improve the long-term sustainability of the supply chain [3].

Meanwhile, as an answer to tackle sustainability issues and reduce pressure on natural resources, Circular Economy (CE) has emerged worldwide with the focus on: keeping resources in use for as long as possible, extracting their maximum value and recovering or regenerating the materials till the end of service life [9].

The European Green Deal, presented on 11 December 2019, sets an ambitious road-map centered on decoupling economic growth from resource use in which the ultimate target is the achievement of a climate-neutral circular economy by 2050. One of the main features of the previous deal is the new European Circular Economy Action Plan (ECEAP), which launches concrete actions on the seven sectors that use the most resources and where the potential for circularity is high. In particular, the textile sector is highlighted towards the new ECEAP, which sets incentives for supporting innovative solutions, circular materials, production processes and measures to ensure that textile products are designed for circularity

¹Currently, 10.6% of the total earth area (149 million km²) is used as arable land for annual crops such as grains, sugars and cotton; specifically, cultivation of cotton occupies 2.5% of the total arable land [5][6].

[10][11].

1.1.3 Future of man-made cellulosic fibres and the Ioncell[®] technology role

Cellulose fibres, including MMCFs and cotton, are characterised with superior moisture absorption, breathability and excellent mechanical properties; consequently, consumers gradually shift their preferences towards cellulose, which translates in a growth of 1.7 kg of cellulose textiles per year per capita. Furthermore, cellulose is recognized as a way of locking up CO₂ [12, p.3,8].

Despite of the previously described unique features, cellulose-based fibres cannot be replaced entirely by synthetic fibres. Since it was noticed that cotton growth appears to have stagnated and accounts for severe environmental issues, cotton production alone cannot satisfy the anticipated increase of the demand. Henceforth, a larger production of MMCFs is favoured in the near future to fulfill an anticipated need of additional 20 million tonnes of cellulose fibre by 2030 [6] [13].

Considering this market trend in the context of the ECEAP, investment in the development of sustainable technologies for the production of MMCFs is prominent. For that purpose, raw materials have to be fully sustainable, the process needs to be completely closed (no air or water emissions) and the produced product has to be fully recyclable [5] [13].

As such, the new spinning technology - Ioncell[®] - presents itself as a solution to bypass the previously mentioned limitations of MMCF production. Ioncell[®] was developed in a collaborative project between Aalto University and University of Helsinki. It is a dry-jet wet fibre spinning technology which utilises an ionic liquid (IL) 1,5-diazabicyclo [4.3.0]non-5-enium acetate ([DBNH][OAc]) as a direct cellulose solvent. This technology yields filaments with excellent properties in a process that is flexible towards the use of raw materials (cotton and newsprint have been successfully utilized as raw materials) and operates at moderate conditions without the use of additional chemicals. In short, Ioncell[®] is a very simple process that resolves the environmental concerns of the viscose process that dominates the MMCF market [5][7][13][14].

1.1.4 Finix project and contribution of this thesis

The Finix project brings together large companies, SMEs, start-ups from textile, forest and waste management along with NGOs and policymakers to establish new textile businesses in Finland that nurture all-inclusive sustainable development. For that purpose, there is strong incentive towards solid scientific basis that encompasses interlinked aspects of sustainability. The Finix project is parted into work packages and one team aims on the upcycling of textile waste, using agricultural and other waste for making fibre and closing the chemical loops [15].

Upon disposal, 73% of textiles end up in landfills, incinerated or shipped to developing countries [3]. Few of these materials are recycled which stresses the need to make improvements to their upcycling. In particular, viscose textile recycling is a challenge, mainly because of the low degree of polymerization of the fibres and the need of pre-treatment processes that causes further damage to the material.

In addition, for the use of textile waste in the production of MMCFs, pre-treatment refining stages,

before the dissolution, are needed to yield suitable fibre properties. These stages aim to increase cellulose reactivity, remove unwanted impurities, adjust cellulose viscosity and remove the colour of the waste textiles in a decolourization process.

Therefore, to close the loop in textile production according to the CE paradigm, the raw materials, the recycling technology and the pre-treatment processes used are the main focus.

Ultimately, under the scope of the Finix project, this work studies the use of pre- and post-consumer textile waste, specifically viscose textiles, as raw material for the production of fibres by means of the loncell[®] process. The proposed experimental studies include: the removal of colour of the post-consumer viscose textiles; the blending of the raw materials to adjust the intrinsic viscosity to the requirements for spinning; the assessment of the appropriate spinning conditions; and the determination of the properties of the generated fibres.

1.2 Research questions

This research work focuses on the recycling of post-consumer viscose textiles by means of the loncell[®] process. In particular, the scope of this work aims to address the following research questions:

- Can pre- and post-consumer viscose waste be used in the loncell[®] process to produce fibres?
- How to remove dyes from pre- and post-consumer viscose textiles in an environmentally friendly manner without compromising the fibres?

1.3 Thesis outline

This dissertation work is organised into the following five main chapters.

In chapter 1 - Introduction - the relevance of the subject and reasons for research were stated.

In chapter 2 - Background - an in depth literature research was presented in order to outline key concepts concerning the viscose substrate and related research areas.

In chapter 3 - Methodology - the methods used were presented.

In chapter 4 - Results and Discussion - the outcome of the experimental research was displayed along with relevant critical considerations.

In chapter 5 - Conclusions - a summary of the experimental achievements was conducted and an future work outlook was drafted with the aim of fulfilling unanswered research questions.

Chapter 2

Background

This chapter aims to examine important information for thorough comprehension of this thesis work. First, a contextualization on the cellulose polymer was provided. Then, the fibre spinning and drawing concepts were outlined as well as important fibre properties. An overview on man-made cellulose fibre production processes, characterization and colouration was also described. At last, environmentally friendly decolourization techniques were detailed.

2.1 Cellulose

2.1.1 Characterization of cellulose

Cellulose is the most abundantly biosynthesized polymer that comes from natural and renewable sources. It reaches production rates of about 1.5×10^{12} tonnes per year. It is found in the highest quantity in plants such as cotton or wood from trees; however it is also found in some fungi and algae, in the marine animal family of tunicates and as an extracellular product of some bacteria [12, p.201][16].

Cellulose is a polysaccharide with non-branched linear conformation with a molecular formula of $(C_6H_{10}O_5)_n$.

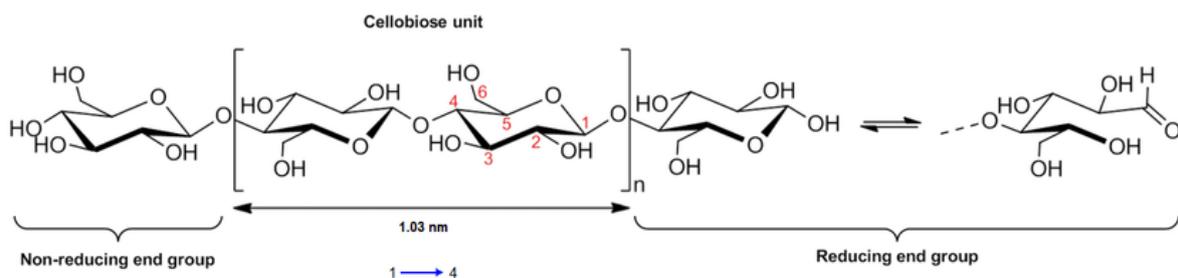
The monomer unit is anhydroglucose (AGU) - $C_6H_{10}O_5$ - and exhibits a chair conformation with secondary hydroxyl groups positioned at the C_2 and C_3 , primary hydroxyl groups at the C_6 and ether groups at the C_1 and C_4 . These substituents are positioned in sites parallel to the AGU plane (equatorial), while the hydrogen atoms are in sites perpendicular to the AGU plane (axial). These AGU monomers bridge together between the C_1 and the C_4 of an adjacent unit through β -(1-4)-glycosidic bonds. Every second AGU is rotated 180° to adjust the preferred bond angles of the β -(1-4)-glycosidic bond, forming a cellobiose unit [12, p.204][17][18, p.202-203].

The number - n - of AGU monomers in the polymer chain reflects the degree of polymerization (DP) of cellulose. Native cellulose has a DP ranging from 7000 - 15000. However, extraction methods and treatment of cellulose might degrade the polymer, and the DP of wood pulp varies between 300 - 1700 whereas regenerated fibers from cellulose have a degree of polymerization no greater than 250 - 500 [12, p.204][17][18, p.202-203].

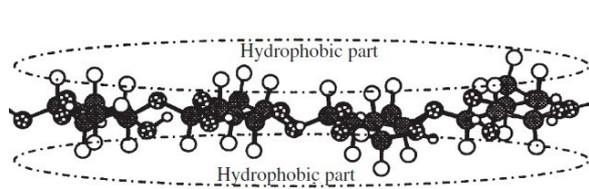
The cellulose molecule has a directional chemical asymmetry with structural anisotropy that results in sides of striking difference in polarity: in one end of the polymer, referred to as the non-reducing end, the anomeric carbon is involved in the glycosidic bond; in the other end of the polymer, referred to as the reducing end, the anomeric carbon is free to convert to an aldehyde structure. Thus, cellulose is an amphiphilic molecule in which stability is related to both hydrophobic interactions in sites parallel to the AGU plane and hydrophilic interactions in sites perpendicular to the AGU plane [19].

The cellulose polymer is densely packed in a semi ordered structure. Intramolecular O-H-O hydrogen bonds provide chain stiffness and intermolecular O-H-O hydrogen bonds allow the linear polymers to assemble in sheet structures. These sheets are further packed by intersheet interactions such as hydrophobic interactions, van der Waals (vdW) forces or C-H-O hydrogen bonds into a thin long fibrillar structure - the microfibrils. These consist of a highly ordered matrix with: crystalline regions that provide a passive framework which holds the fibres together; and the less ordered amorphous regions that provide an active region which deforms and recovers and is also the site for the entry and absorption of water. The aggregation of these microfibrils give rise to the supramolecular structure of cellulose [12, p.6][20][21].

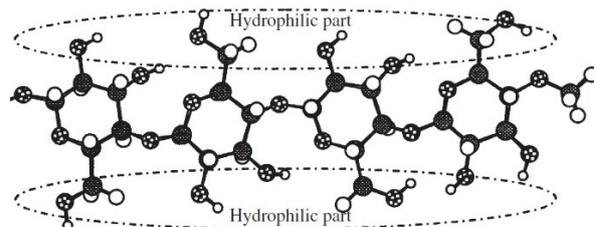
Figure 2.1 illustrates the previous considerations about the cellulose structure and interactions.



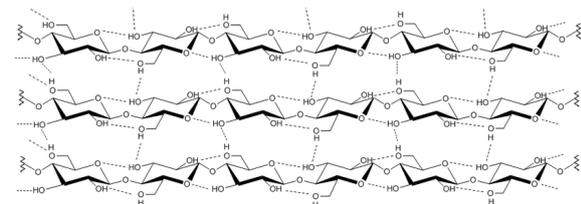
(a) Configuration of the cellulose chain with indication of the non-reducing and reducing end groups. Each cellobiose unit consists of two anhydroglucose (AGU) monomers linked by a β -(1-4)-glycosidic bond.



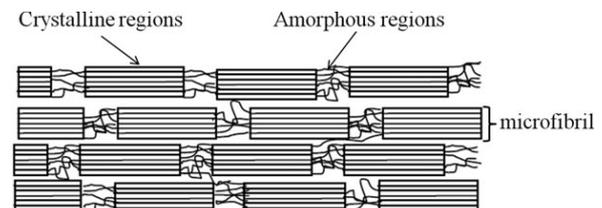
(b) Hydrophobic sites of cellulose in side view of the AGU plane with the hydrogen atoms in the axial position.



(c) Hydrophilic sites of cellulose in top view of the AGU plane with the hydroxyl groups in the equatorial position.



(d) Intra- and inter-molecular hydrogen bonding network within a cellulose sheet.



(e) Crystalline and amorphous structure regions of aggregated cellulose microfibrils.

Figure 2.1: Cellulose characterization [22].

Cellulose is a macromolecule which can twist and bend in one plane and reveals irregular conforma-

tions with different distribution of hydrogen bonds and crystalline arrangements. The cellulose crystal lattice forms - polymorphs - show different packing arrangements designated as I (I_α and I_β), II, III (III_I and III_{II}) and IV (IV_I and IV_{II}) [12, p.4]. These polymorphs can undergo reversible and/or irreversible conversions as displayed in figure 2.2.

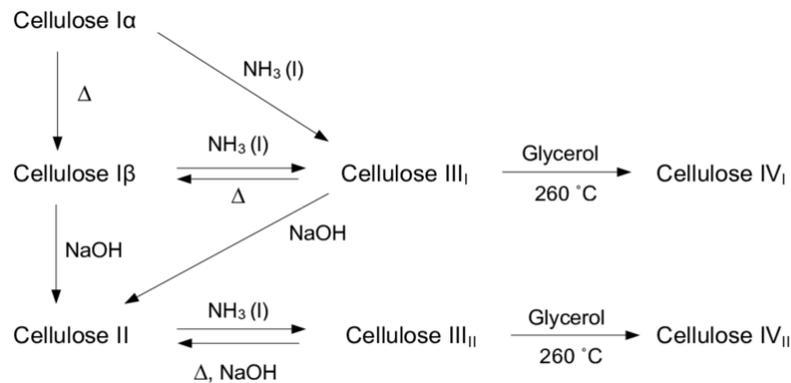


Figure 2.2: Schematic representation of cellulose transformation into its several polymorphs [23].

Cellulose I has all chains oriented parallel to each other in the same direction and exists in two distinct crystalline forms: I_α (present in bacteria, algae and plants with low complexity) crystallizes in a one-chain triclinic unit cell structure; and I_β (present in higher plants) crystallizes in a two-chain monoclinic unit cell structure. These two crystal structures are similar regarding the conformations of cellulose molecules and their inter-sheet interactions are governed by van der Waals interactions. Additionally, I_β is a more thermodynamically stable form than I_α [21].

Cellulose II can be prepared from cellulose I by dissolution and regeneration in solvents or by mercerisation through alkaline treatment. Most commercially regenerated cellulose fibres adopt cellulose II structure. It is presumed to have antiparallel chain configuration with a two-chain monoclinic unit cell structure. The inter-sheet interactions are governed by hydrogen bonds as opposed to vdW interactions in cellulose I. Moreover, the length of the hydrogen bond is shorter in cellulose II which makes them stronger and results in increased thermodynamic stability in comparison to cellulose I [12, p.6][18, pp.203-204].

Treatment of cellulose with dry liquid ammonia leads to cellulose III. Starting from native cellulose I, the conversion is denoted as cellulose III_I , since this polymorph may be converted back to cellulose I. On the other hand, if cellulose II is the starting material for the liquid ammonia treatment, cellulose III_{II} is obtained since this polymorph may be converted back to cellulose II. In cellulose III, the hydrogen bonds exist between cellulose sheets [17].

Heat treatment of cellulose III_I or cellulose III_{II} leads to cellulose IV_I or cellulose IV_{II} , respectively. Recently it was proposed that cellulose IV_I is a more disordered form of cellulose I_β [17].

All these interactions help to generate the great properties of cellulose and additionally to establish the ability to retain a highly stable semicrystalline state of aggregation even in an aqueous environment [24].

2.1.2 Dissolution of cellulose (emphasis on ionic liquids)

Cellulose is not a thermoplastic polymer as it decomposes before melting. Thus, to get the cellulose in liquid form, it has to be dissolved. Dissolution of cellulose is challenging on account of its structure and chemical composition. To achieve that, there is a need to break the ordered and extensive network of strong intramolecular and intermolecular hydrogen bonds, vdW forces and hydrophobic interactions. Consequently, effective dissolution of cellulose depends on the ability of the solvent to dismantle this network of interactions and peel away individual strands of the microfibrils resulting in a molecularly dispersed solution [16][19][21].

Cellulose solvents are divided into two groups: the derivatizing solvents (derivative methods) and the non-derivatizing solvents (direct methods). The first group relates to all the solvents that form a cellulose derivative by adding a functional group through covalent bonding to the polymer and therefore enhancing its solubility. The used solvents are carbon disulphide/sodium hydroxide [CS₂/NaOH] (viscose process), urea/NaOH (carbamate process) and dinitrogen tetroxide/N,N-dimethylformamide [N₂O₄/DMF]. The second group dissolves the polymer without chemical alteration of the cellulose chains. This is established by forming a metal complex with cellulose for instance by the addition of cuprammonium hydroxide (cuprammonium process); or by disrupting the hydrogen bond interactions of the polymer chains by the use of N-methylmorpholine-N-oxide [NMMO] (Lyocell process), N,N-dimethylacetamide/lithium chloride [DMAC/LiCl], dimethylsulfoxide/tetrabutylammonium fluoride [DMSO/TBAF] and ILs (Ioncell[®] process) [12, p.14,201-202][21][25].

A solvent for cellulose should ideally meet the following criteria: high solubility; rapid dissolution; easy solvent recyclability; minimal toxicity and flammability; and insusceptibility to side reactions between solvent and solute [21].

Furthermore, the dissolution kinetics can be manipulated through different methods. Foremost, addition of heat speeds up the process of diffusion of large molecules and also lowers the viscosity of liquids. With equivalent importance, mechanical energy in form of shear stress will decrease the length of the diffusion path from the concentrated polymer solution [12, p.14,201].

2.1.2.1 Ionic liquids

ILs are very efficient solvents for cellulose. They are defined as strongly polar ionic salts and provide several advantages over conventional solvents such as: lower volatility; high thermal stability; low flammability; general immiscibility with organic compounds; low toxicity; and electric conductivity. Additionally, they are usually able to dissolve polymers with a high degree of polymerization. Many can be recycled and can also be utilized in high concentrations in the spinning solutions [12, p.19,203].

The physicochemical properties of a IL is mainly influenced by the structure and composition of its ions. The melting point of a IL, usually below 100° C, can be tailored by selecting different cations and anions. In general, a higher symmetry between the cations and the anions results in higher melting points. ILs containing saturated side chains are thermally more stable than those with unsaturated chains. Moreover, with comparable ILs, the cation with less bulky substituents leads to ILs with higher density.

Evidently, ILs consist of an equal number of organic cations and organic or inorganic anions so that the overall structure is electrically neutral. The net basicity and polarity of the anion are key features in cellulose dissolution. Thus, pairing anions with strong hydrogen bond basicity with cations of moderate hydrogen bond acidity generates ILs that are effective as dissolution agents for cellulose [5] [6] [12, p.19] [21]. Uncountable combinations are possible and are displayed in figure 2.3.

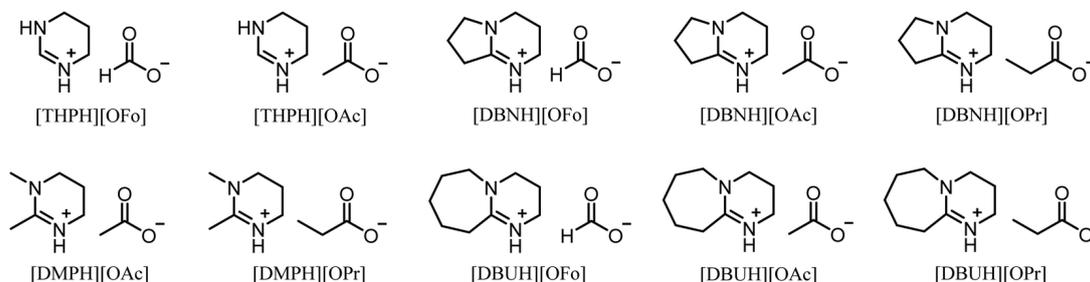


Figure 2.3: Structure of typical ionic liquids with common abbreviations [26].

The dissolution mechanism of cellulose in ILs is related to intramolecular and intermolecular hydrogen bond interaction disruption. The anion of the IL penetrates into the cellulose structure and disassembles it by competitive hydrogen bonding. The cation occupies positions at the upper and lower faces of the cellulose and interacts in a relatively non-specific and non-directional manner via hydrophobic or dispersion interactions. It might intercalate between individual cellulose strands, aiding in separation of the chains. Therefore, the anion acts as a hydrogen bond acceptor and the cation as a hydrogen bond donor [5][16][27]. Cellulose dissolution is represented in figure 2.4.

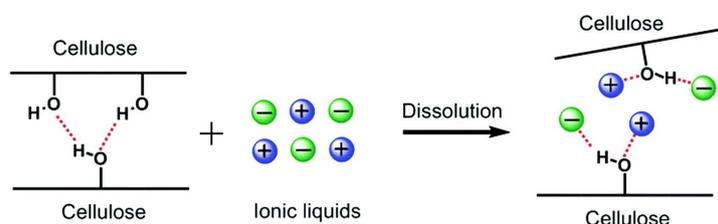


Figure 2.4: Schematic representation of ionic liquid (IL) interaction with cellulose upon dissolution [27].

Fibres produced from chloride-based ILs demonstrated stronger tenacity and lower elongation compared to fibres generated from acetate-based ILs. However, acetate-based ILs can tolerate more cellulose than chloride-based ILs, which is economically more efficient for the spinning process. Therefore, acetate-based ILs seem to be a good alternative for chloride-based ILs [6][28].

So far, the most successful IL for the production of high quality MMFCs is 1,5-diazabicyclo [4.3.0]non-5-enium acetate ([DBNH][OAc]) which is used as a solvent in the Ioncell[®] process. However, this IL still faces challenges related to solvent recycling and solvent decomposition. In the solvent recycling step, [DBNH][OAc] has to be separated from water and accumulated impurities in order to maintain appropriate cellulose dissolution capability. Via evaporation it is possible to gain [DBNH][OAc] with a water content of less than 4 wt %. Higher water content leads to a reversible hydrolysis of [DBNH][OAc] which eventually causes the loss of cellulose dissolution capability. In addition to the removal of the light components

such as water, [DBNH][OAc] has to be purified from heavy impurities originating from raw materials and possible decomposition products [5][6][29].

2.1.3 Rheological characterization of cellulose solutions

Rheology studies the correlation of the deformation of a fluid with the occurring stresses during a flow process.

Polymer solutions often show rheological characteristics of a liquid as well as of a solid. This exhibition of complex flow properties is because the viscosity is dependent on the deformation. Since both elastic and viscous behaviour are exhibited, the designation as viscoelastic is attributed to polymer solutions. These elastic and viscous properties can be determined and modified to meet the desired application requirements [30].

Cellulose chains adopt a semi-flexible conformation in solution. As such, an understanding of the concentration-dependent shear and extensional rheological properties of the cellulose-IL solutions is important to further understand the dynamic and thermodynamic properties [5][6][30][31].

The viscoelastic properties can be determined via sinusoidal small amplitude oscillatory shear measurements over the whole measuring range. This allows the polymer solution to preserve the structures, which is needed to shear and to maintain the viscoelastic properties. Cellulose and IL solutions exhibit shear thinning properties under a high shear rate. This effect is mainly due to the disentanglement and orientation of the polymer chains caused by the shear force, which leads to the reduction of the solution viscosity [32].

Via rheology measurement, the complex viscosity (η^*), complex modulus (G^*), storage modulus (G') and loss modulus (G'') of cellulose solutions are determined. G^* describes the entire viscoelastic behavior of a sample. G' and G'' relate to the energy stored elastically and dissipated through viscous flow, respectively. These values reflect the elastic and viscous behavior of the cellulose-IL solution. G' and G'' form a crossover point (COP) where the sample behavior changes from predominantly viscous to elastic. η^* is the complex modulus divided by angular frequency. To determine the zero-shear viscosity (η^0), which is the viscosity at the limit of low shear rate, the complex viscosity curves can be fitted with the Carreau or Cross viscosity models [5][6][32][33].

The rheological properties of the cellulose-IL solution can provide good information to defined the needed spinning conditions. The viscoelastic properties of the spinning dopes should fit in a defined range to guarantee good spinnability. In Ioncell[®] process the best spinning performance of the dope solutions has been realized with cellulose-IL solutions with zero-shear viscosities in the area of 27000 - 40000 Pa.s, a COP with an angular frequencies of 0.8 - 1.5 rad.s⁻¹ and with a dynamic moduli between 3000 - 6000 Pa. These characteristic ranges can be reached with dopes with a viscosity of 400 - 500 mL.g⁻¹ at an economically acceptable temperature (< 85° C) [5][6][31].

2.2 Fibre spinning and drawing

Polymeric material must be converted to a liquid or semi-liquid state to allow production of fibres, either by dissolution in a solvent or by being heated until molten. The resulting liquid is extruded through small holes known as spinnerets. The emerging filaments are solidified by cooling or coagulation. This extrusion process that yields fibres is called spinning [34].

Thereby, the spun filaments are oriented by stretching or drawing. This means in detail that the long polymer chains are pulled into alignment along the longitudinal axis of the fibre and form a dense package of crystallites. These crystallites are a result of intermolecular forces [34].

The structure of the filament is formed by the deformation of the spinning dope in the spinneret, by the regeneration of the polymer through cooling or coagulation, by the orientation and crystallization through drawing and by posterior washing and drying of the fibers [5].

Several spinning techniques are used to produce fibres, including wet spinning, dry spinning, melt spinning and dry-jet wet-spinning.

In wet spinning, the spinneret is positioned inside a coagulation bath and the polymer solution is extruded directly into a coagulation medium (anti-solvent). The polymer coagulates, regenerates and cellulose solvent and additional impurities are removed by diffusion. The resulting filament is oriented by stretching which allows the crystalline fibre structure to be assembled. The produced fibres are collected at godets and are washed with more anti-solvent [5][34].

In dry spinning, the solution of polymer is pushed through a spinneret into a heated column, where the solvent evaporates, leaving a fibre. The emerging fibre may contain solvent that may have to be removed by further heating or by washing. This operation is accompanied by stretching and collection are godets [5][34].

In melt spinning, a viscous melt of polymer is extruded through a spinneret into a process zone where molten polymer is solidified by a jet of cold air [5][34].

In the dry-jet wet-spinning, the spinneret is located outside the coagulation bath. The polymer solution is extruded by a spinneret, passes an air gap and is immersed into a coagulation bath which contains an anti-solvent (usually water). The operations are performed under tension to stretch the polymeric filament as it is collected on a godet [5][6][30].

These spinning technologies are schematized in figure 2.5.

In fiber spinning, the degree of stretching applied to the fluid filament in the drawing operation is quantified as the draw ratio (DR) [5]. The DR is defined as in equation 2.1 where v_e ($\text{m}\cdot\text{min}^{-1}$) corresponds to the extrusion velocity of the filament through the spinneret and v_{tu} ($\text{m}\cdot\text{min}^{-1}$) corresponds to the take-up velocity of the godets that collect the filament.

$$DR = \frac{v_{tu}}{v_e} \quad (2.1)$$

The spinnability of a cellulose solution (dope) can be theoretically defined by the optimum DR achieved: $DR < 2$, non-spinnable dope; $2 < DR < 8$, dope with poor spinnability; $8 < DR < 14$, dope with good spinnability; $DR > 14$, dope with excellent spinnability [31].

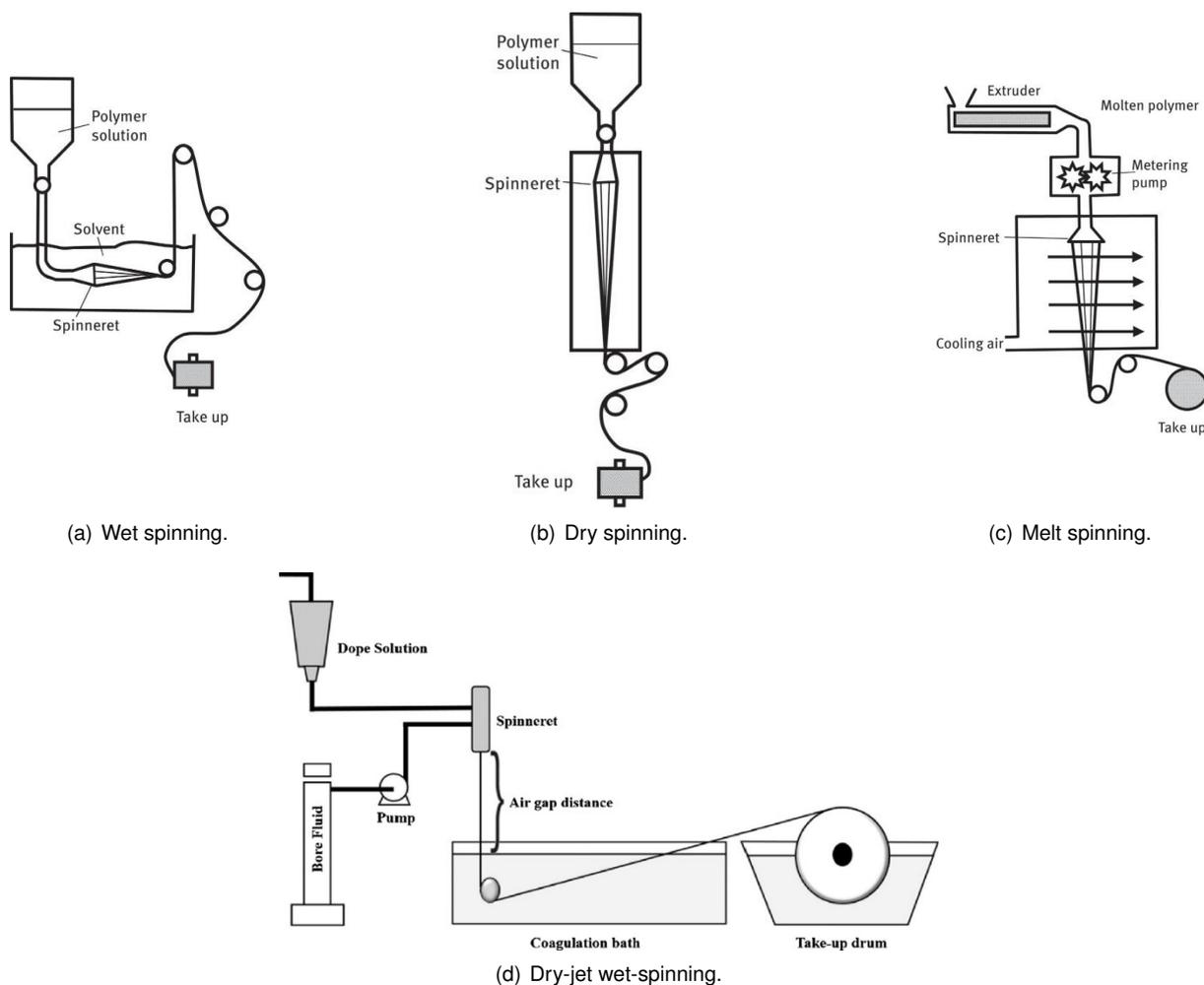


Figure 2.5: Spinning methodologies [35].

2.3 Fibre properties

Textile fibres can be defined as materials that display significantly higher length in proportion to width and exhibit properties that are of extreme importance for their ultimate end application [34].

All fibre properties correlate to several factors such as the DP, the strength of bonding between adjacent polymer chains, their degree of orientation in the direction of fibre axis and the extent of crystallinity [36].

Therefore, evaluation of fibre properties provides valuable information. A theoretical overview of tensile properties (see subsection 2.3.1) and optical properties (see subsection 2.3.2) are presented for the contextualization of the experimental part and consequent results of this thesis.

The state of cellulose fibres depends on the hydrogen bonds in the crystalline matrix. Under stress, the hydrogen bonds start to break and to reform at new places. In dry fibres, the molecules in the crystalline matrix only begin to become mobile because of thermal vibrations above 100° C. However, the fibers are not fully mobile even at 200° C. In wet fibres, there is full mobility and the matrix acts in a fluid manner. When fibres are deformed due to washing and drying, hydrogen bonds will lock the fibres in the deformed state creating wrinkles on the fabrics. Posterior ironing with steam helps to rearrange hydrogen

bonds and consequently adjust the surface to a flat disposition [18, p.230].

2.3.1 Tensile properties

The tensile properties in general help to evaluate the reaction of a fibre when forces are applied under tension. For that purpose, tensile tests are conducted by measuring the applied load and the elongation of a fibre specimen in a controlled manner. The results of a tensile test are presented via a load-elongation curve. By dividing the load by the original fibre cross-sectional area and elongation by the original fibre length, a stress-strain curve is obtained [36]. The stress-strain curve of a model fibre is shown in figure 2.6.

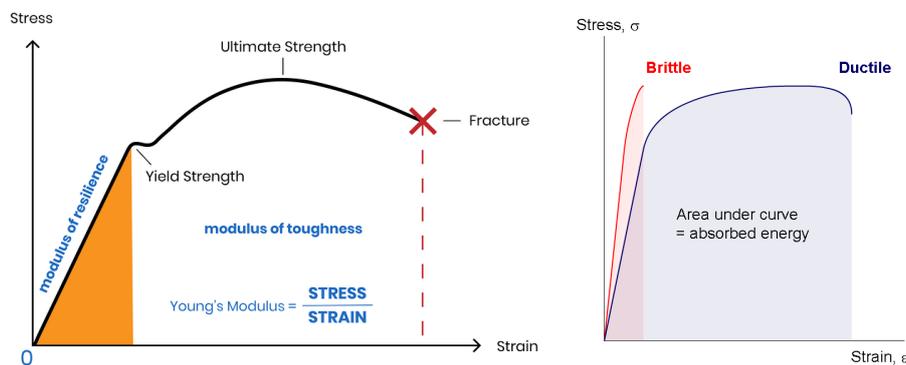


Figure 2.6: Representation of a stress-strain curve of a model fibre (left) [36]. Difference in behavior of brittle and ductile materials (right) [37].

There are many properties that can be measured through tensile testing such as linear density. In specific, through the evaluation of the produced stress-strain curves, modulus of elasticity, strain at yield point, stress at yield point, modulus of elasticity, modulus of toughness, modulus of resilience, tenacity at break and elongation at break can be determined.

It is not possible to measure the diameter of a fibre in a meaningful manner because it changes quite markedly as the fibre is compressed or elongated. Linear density is therefore the property used to evaluate fibre fineness and to quantify weight of fibre per unit length [38, p.3].

Initially, the stress and strain increase in a linear relationship. This indicates elastic deformation. In this region of the curve, Hooke's law applies and the ratio of stress to strain is constant. Therefore, when the stress is reduced, the material will return to its original shape. The slope of the curve in this region is the modulus of elasticity or Young's modulus. It defines the properties of a material as it undergoes stress, deforms and returns to the original shape as the stress is removed. Additionally, modulus of resilience is the maximum energy that can be absorbed by the fibre specimen per unit volume without creating permanent deformation [36][39].

At some point, as the strain starts to increase faster than the stress, the stress-strain curve deviates from the previous linear relationship and Hooke's law no longer applies. This is called the yield point. From this point on in the tensile test, permanent deformation occurs in the fibre specimen when load or stress are further increased. This indicates plastic deformation. The material will not return to its original,

unstressed condition when the load is removed. Moreover, modulus of toughness is the maximum energy that can be absorbed by the fibre specimen per unit volume before fracture [36].

In brittle materials, little or no plastic deformation occurs and the material fractures near the end of the elastic portion of the curve. In ductile materials, substantial plastic deformation can be withstood prior to fracture. With most materials there is a gradual transition from elastic to plastic behavior which makes the exact point at which plastic deformation begins to occur hard to determine [36].

Fibre tenacity and elongation at break are two important properties that can also be acquired from the stress–strain diagram. The strength of a material is its ability to withstand external forces without breaking. As such, tensile strength is the maximum stress reached in a tension test. Hence, tenacity at break is a measurement of same force in relation to the linear density. The deformation of a material is its ability to stretch without breaking. Therefore, strain is the ratio between the deformation and the original length. Accordingly, elongation at break is the percentage of the deformation at the breakage of the tested specimen [36][40][41].

2.3.2 Optical properties

Optical properties generally evaluate how light interacts with a fibre. Light can be partially transmitted, absorbed or reflected depending on the structure of the fibre and wave length of the light. These optical properties of fibres include birefringence and total orientation of the polymer molecules within the fibres [18, p.204].

When light falls on a textile fibre, it splits up into two refracted beams, one polarized parallel to the fibre axis and the other polarized perpendicular to the fibre axis. The birefringence value of fibre is measured by the difference between the refractive index for light that is polarized parallel to the fibre axis and the refractive index for light that is polarized perpendicular to the fibre axis. This can be expressed by two different refractive indices achieved by different polarization [42]. The birefringence (Δn) is thus defined by equation 2.2 where n_1 and n_2 are the refractive indices for light, polarized parallel and perpendicular to the fibre axis, respectively.

$$\Delta n = n_1 - n_2 \quad (2.2)$$

Furthermore, as a relative value, total orientation of fibers (f_t) is defined as in equation 3.5 where Δ_{max} is the birefringence value equivalent to 100 % orientation of cellulose fibres.

$$f_t = \frac{\Delta n}{\Delta_{max} n} \quad (2.3)$$

The extensional forces applied on the filaments upon spinning cause the cellulose polymer to align along the fibre axis, thus increasing the total orientation. High total orientation values (closer to 1) indicates that most of the molecules are lined up parallel to the fibre axis.

Moreover, the increase in total orientation of the cellulose molecules along the chain axis accounts for better fibre tensile properties. In contrast, fibres with total orientation at a maximum cannot stretch any

further and ultimately break down, which affects negatively the tensile properties.

2.4 Current man-made cellulose fibre production

MMCFs are derived from cellulose dissolving pulp and the raw materials for its production are diverse - wood, cotton or bamboo. Currently, hardwood forests are the main source of cellulose used in MMCFs production. Cellulose is transformed into dissolving wood pulp and sold to fibre producers for filament or staple fibre production [13].

All regenerated cellulose fibres may be produced as continuous filaments, containing up to a few thousand filaments or as heavier tows with millions of filaments, which are cut into staple fibres of suitable length for short or long staple spinning. About 85% of the total MMCF production is produced as staple fibres and about 15% as filaments [18, p.201][13].

The relevant industrial methods for production of MMCFs are the viscose process (see subsection 2.4.1), the modal process (see subsection 2.4.2), the acetate process (see subsection 2.4.3), the cuprammonium process (see subsection 2.4.4) and the lyocell process (see subsection 2.4.5). These processes are schematized in figure 2.7. Each of these processes generates fibres with different characteristics and account for some environmental impact (see subsection 2.4.5).

2.4.1 Viscose process

Tree harvesting, cellulose extraction and pulp conditioning [8][43]

The process begins with the harvesting of trees and the fractionation of cellulose. Tree logs are processed through barking, chipping and sorting operations. The resulting wood chips are treated, in a sulphite pulping process, with a solution of calcium bisulphite ($\text{Ca}(\text{HSO}_3)_2$) in steam and under pressure for about 14h. This treatment removes the lignin present in the wood by converting it into water-soluble sulphonated compounds without affecting the cellulose content.

The purified cellulose is then pressed and cut into sheets. These sheets, known as wood pulp, are washed with water, bleached and then dried.

After purification, the wood pulp is placed in a conditioning room with good air circulation at 30° C with the purpose of adding the desired moisture to the wood pulp.

Slurry steeping [8][18, p.37,42-43][44][45]

Wood pulp sheets are immersed in an aqueous solution of 17 - 22% sodium hydroxide (NaOH) under vigorous agitation at 45 - 55° C and allowed to soak for 1 - 14h. Due to viscosity effects, the consistency of the slurry is typically less than 6% cellulose. This treatment causes the cellulose fibres to swell and convert into its alkoxide derivative - sodium cellulosate - as in reaction 2.4.

A high degree of swelling is desirable because it opens up the pulp structure to leach out short-chain material which allows adequate penetration into the fibre structure. Thus, this enables effective conversion

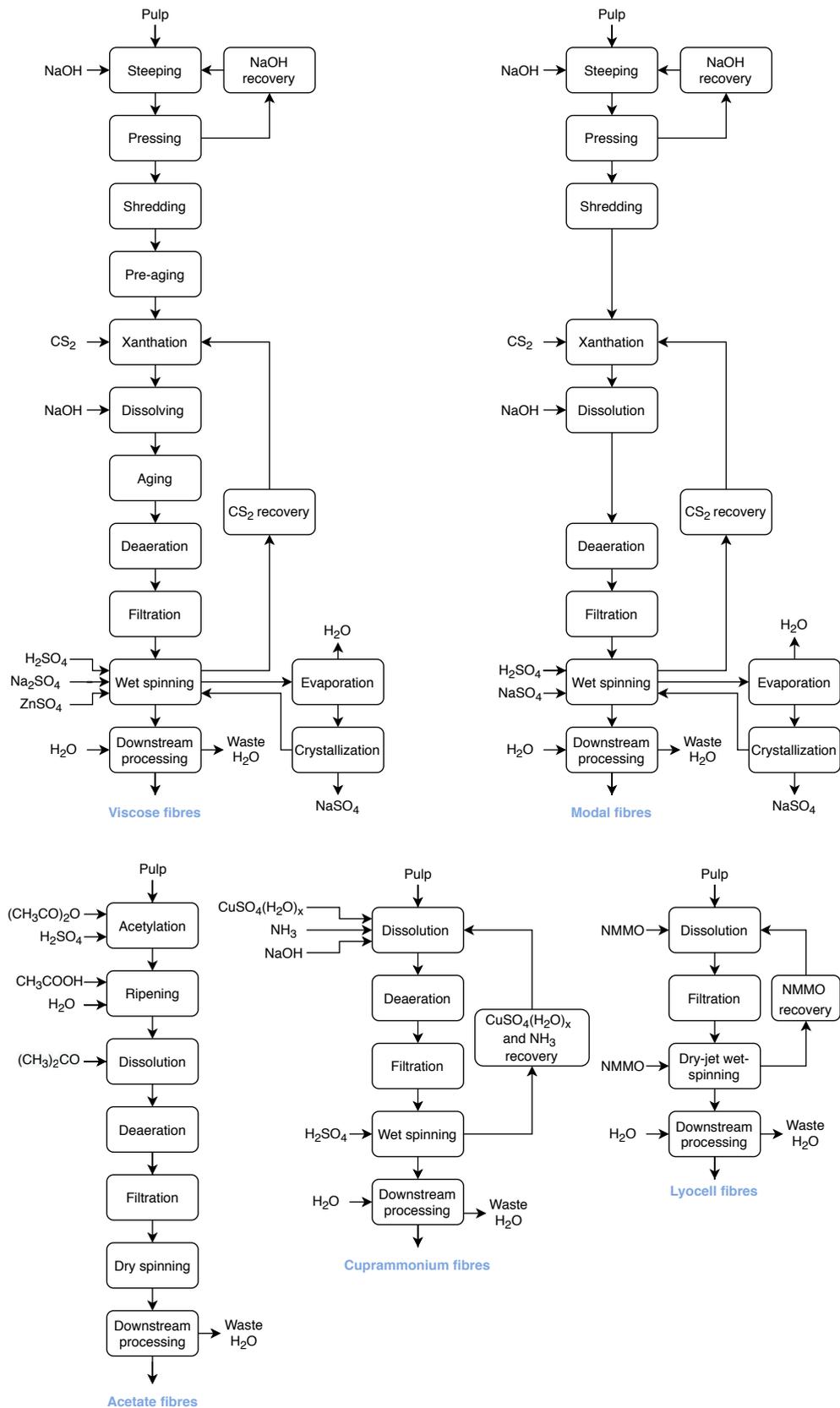
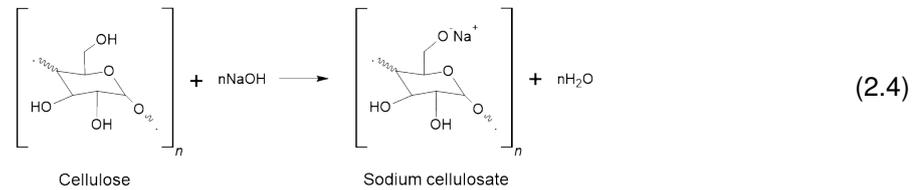


Figure 2.7: Current processes for production of man-made cellulose fibres (MMCFs): viscose process, modal process, acetate process, cuprammonium process and lyocell process.

to sodium cellulosate in both amorphous and crystalline regions of the pulp. The removal of hemicellulose and γ -cellulose present in the pulp is also achieved in this stage.



Pressing and recovery [8][18, p.37,42-43]

After steeping, mechanical presses remove the excess NaOH. The drained off fluid is returned to the steeping for reuse.

Shredding [8][18, p.37,44] [45]

The wet and dense sheets are shredded to provide adequate surface area for uniform reaction in subsequent process steps.

Leftover hemicellulose levels of up to 3% are tolerable, depending on the type of fibre to be produced. For the production of stronger fibres, extra steps such as dialysis or reverse osmosis might be needed to reduce it further.

Pre-aging or mercerizing [8][18, p.37,45][45]

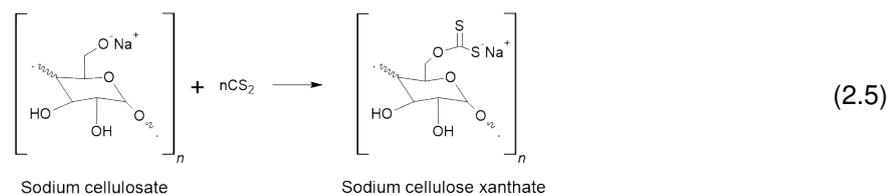
The shredded sodium cellulosate is stored for 0.5 - 5h at 40 - 50° C to allow the oxygen in the air to oxidise it.

As received, pulp typically has a DP in the range of 750 - 850. This pre-aging process reduces the molecular size of the cellulose which is necessary to obtain a spinning solution of the correct viscosity and a DP in the range of 270 - 550.

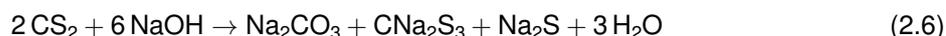
Xanthation or churning [8][18, p.37,47-48][12, p.202][45][44]

During xanthation, sodium cellulose xanthate is formed as in reaction 2.5 by treating the sodium cellulosate with carbon disulphide (CS₂) for 0.5 - 1.5h at 25 - 37° C. This reaction is performed under partial vacuum to ensure vaporisation of CS₂. The CS₂ charge is about 30% of the cellulose weight.

For regular viscose manufacture, only one of the hydroxyl groups of the sodium cellulosate needs to be replaced by a xanthate group; no matter how much CS₂ is used, the incomplete accessibility of the sodium cellulosate molecules prevents complete xanthation with replacement of each hydroxyl group with a xanthate group.



By-product formation between CS₂ and NaOH also occurs as displayed in reaction 2.6. Thereby, the sodium trithiocarbonate (CNa₂S₃) from the side reaction alters the viscose dope colour from white to orange.



The availability of free NaOH, hemicellulose or low molecular weight cellulose encourages side reactions. Hence, the amount of these materials entering this stage, which is important in achieving low consumption of CS₂ and NaOH. Higher temperatures also encourages by-product formation. However, dropping the xanthation temperature to achieve better CS₂ usage efficiency also extends the xanthation time. Therefore, a compromise is necessary between productivity and chemical use.

Dissolution [8][18, p.48][12, p.202][45]

The sodium cellulose xanthate is dissolved into dilute aqueous 5 - 8% NaOH for 4 - 5h to form sodium cellulose xanthate solution. Dissolution is more easily carried out at low temperatures in the range of 8 - 12° C are applied. Typically, the liquor contains 8.5 - 10% cellulose.

High shear mixing speed up the process but can cause local heating, which can regenerate cellulose.

Aging or ripening [8][18, p.37,48-49][12, p.202][45]

In the ripening process, the viscose solution is stored for 4 – 5 days at 10 – 18° C to redistribute the xanthate groups in the cellulose. This results in an initial decrease in viscosity and subsequent rise to the original value.

As the degree of xanthation is too high, with too many of the xanthate groups in positions dictated by their accessibility and not in the ideal positions for uniform dissolution, dexanthation, the reversal of reaction 2.5, and transxanthation, the redistribution of xanthate groups into the most favorable positions on the cellulose molecules, occurs automatically as the viscose ages.

Deaeration [8][18, p.37,50][12, p.202][45]

To ensure continuity at spinning, the viscose is held under vacuum to remove any dispersed gases that might otherwise cause small bubbles to form as the viscose is extruded into filament form. Some CS₂ and H₂O is lost at deaeration.

Filtration [8][18, p.37,49-50] [12, p.202][45]

Regardless of how well the xanthate is brought into solution, some undissolved particles will be

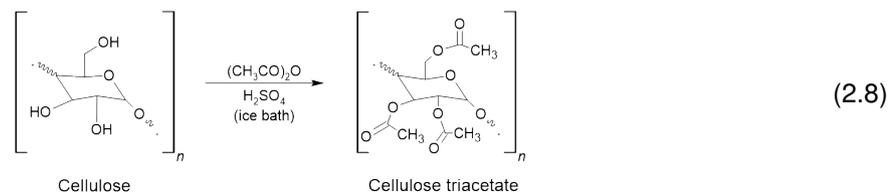
is spun into a low-acid spinning bath with a slightly lower temperature; in this way, the stretching ratio can be enhanced from 60%, as in standard viscose, to 100% [8].

2.4.3 Acetate process

The raw materials in the acetate process can be wood pulp or cotton linters.

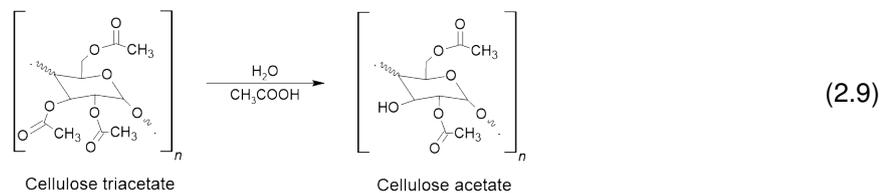
Acetylation [8][46]

Acetylation is carried out by mixing the pulp thoroughly for 7 - 8h at 25 – 30° C with glacial acetic acid (CH₃COOH), acetic anhydride ((CH₃CO)₂O) and concentrated sulfuric acid (H₂SO₄) as a catalyst, with the ratio of 1:3:5:0.1, respectively. This converts the free hydroxyl groups (OH) of cellulose into acetate ester groups (CH₃COO) with the formation of triacetate in the form of a suspension - the acid dope - as in reaction 2.8. As the acetylation reaction is an exothermic reaction, it is favored by removing heat through circulation of cold water.



Ripening [8][46]

In the ripening process, the acid dope is stored with acetic acid (CH₃COOH) and H₂O for 10 – 20h. This process partially converts the CH₃COO groups into OH groups as in reaction 2.9. White flakes of cellulose acetate are then precipitated out as a result of water addition and continuous stirring. The cellulose acetate flakes are dried after centrifugation of the excess water.



Dissolution, deaeration and filtration [8][46]

The dried acetate flakes are then slowly dissolved for 24 h in acetone ((CH₃)₂CO) with a ratio of 1:3, respectively. A thick clear dope is obtained which is then deaerated and filtered.

Dry spinning [8][46]

Using a dry spinning process, the acetate filaments are formed due to evaporation of the solvents. The filaments travel a distance of 2 – 5m vertically to a feed roller and then pass over a guide roller to

godets set to much higher speed.

2.4.4 Cuprammonium process

The raw materials in the cuprammonium process can be wood pulp or cotton linters [12, p.11].

Dissolution [12][8][47]

Hydrated copper sulphate ($\text{CuSO}_4(\text{H}_2\text{O})_x$) solution, a small amount of sugar and NaOH solution are mixed with water in a vessel at room temperature. Copper hydroxide ($\text{Cu}(\text{OH})_2$) is formed due to the reaction of $\text{CuSO}_4(\text{H}_2\text{O})_x$ and NaOH. Then, the addition of ground cellulose to the above mixture forms copper cellulose. The copper cellulose is then dissolved in a solution of 24 – 28% ammonia (NH_3) cooled below 20°C . The mixture is agitated until dissolution is complete. If necessary, air is introduced to allow oxidative depolymerization and hence a lowering of the dope viscosity.

Filtration and deaeration [8][45]

The dark blue cuprammonium solution containing 5 – 10% of cellulose with a DP of 1000 – 2000 is filtered to remove any particles that might block the spinneret holes. A few compounds are added to the cuprammonium solution to make it suitable for spinning such as glycerin, glucose, tartaric acid, citric acid, oxalic acid and cane sugar. It is then deaerated under vacuum and stored ready for spinning.

Wet spinning [8][12, p.29,203][45]

The spinning dope is discharged through the spinneret holes into the coagulation bath containing 5% sulfuric acid (H_2SO_4). This completes the regeneration of cellulose and converts the ammonia and copper residues into their sulfates. This leads to formation of relatively thick filaments, which are subsequently stretched to reduce the fineness.

Recovery [45]

The spin-bath liquor is passed through ion-exchange resins and the effluent from these resins is reused. The copper washed out of the yarn was precipitated with NaSO_4 , forming the basic copper sulfate sludge, which was reused in cellulose dissolving. Only 95% copper recovery was possible using this system.

A high percentage of the ammonia can be recovered from the spin-bath effluent and by washing prior to the final acid bath. During acidification, remaining ammonia is converted to the sulfate and recovered when the acid wash liquor is treated with carbonate to recover the copper. Ammonia residuals in the large volumes of washwater can only be removed by distillation. Overall about 75 – 80% of the ammonia required to dissolve the cellulose can be recovered.

2.4.5 Lyocell process

The raw materials for lyocell process is wood pulp from eucalyptus, though oak and birch. Furthermore, SeaCell fibres use the lyocell process to produce fibres where cellulose pulp and seaweed are mixed

together as raw material [8].

Dissolution [6] [18, p.66][47]

The pulp is fed into a shredder which cuts the pulp into small pieces. Then, it is mixed with hot N-methylmorpholine-N-oxide (NMMO) solution with large excess of water with a typical composition of 76% NMMO, 10% H₂O and 14% cellulose. The dissolution occurs when the surplus of water is evaporated under vacuum at temperatures of 70 - 90° C. This is important because the NMMO solvent in solution can undergo an exothermic degradation process if it is overheated. The resulting solution is a clear dark amber colored viscous solution of cellulose.

The excellent dissolving capacity of NMMO on cellulose is due to its strong N–O dipoles and basicity. In the dissolution process, the N–O group interacts with the hydrogen atom on the hydroxyl group of cellulose and forms new hydrogen bonds between NMMO and cellulose, thus replacing the intermolecular and intramolecular hydrogen bonds in cellulose. During the dissolution process of cellulose and the recovery of NMMO solution at high temperatures, a portion of NMMO will be thermally degraded to various compounds. To minimize NMMO degradation, some stabilizers and antioxidants can be added to the dissolving tank. Specifically, n-propyl gallate is used as an antioxidant to prevent cellulose degradation.

Filtration and dry-jet wet-spinning [12, p.29,203]

Prior to spinning it is necessary to filter various impurities out of the solution which mainly consist of undissolved pulp fibres and coarse inorganic compounds such as sand and ash.

The spinning dope is extruded via a dry-jet/wet-spinning process, conducted at high temperature which decreases the viscosity of the spinning dope and allows easy extrusion. The coagulation of the extruded filaments is carried out in the aqueous precipitation bath with dilute NMMO.

Washing and recovery [6][12, p.29,203]

The produced fibers are then washed thoroughly to remove the NMMO and dried. This process is designed to recover more than 99% of the NMMO solvent for reuse which helps to minimise the effluent.

2.4.6 Fibre characterization and sustainability

A comparative overview of the current MMCF is displayed in table 2.1.

Table 2.1: Properties of man-made cellulose fibres (MMCFs).

	viscose	modal	acetate	cuprammonium	lyocell
tenacity [cN/tex] [48][44]	17.7 - 23.0	34.0 - 36.0	10.6 - 12.4	15.0 - 23.8	39.7 - 44.2
wet	08.8 - 13.2	19.0 - 21.0	05.7 - 06.6	14.1 - 15.0	34.4 - 35.3
dry	17 - 25	8 - 12	25 - 35	12 - 13	11 - 16
wet	21 - 30	9 - 15	35 - 45	26 - 27	16 - 18
modulus of elasticity [GPa] [49]	3 - 4.5	4.2 - 4.9	2.5 - 4.5	3 - 4.5	6
cross section [18, p.201]	serrated	circular	serrated	circular	circular
properties [8][12, p.12][18, p.212]	absorbent, resistant to abrasion, high wearing comfort, good drapeability, flammable, poor resiliency, prone to wrinkle formation and shrinkage	resistant to wrinkle formation and shrinkage, more resistant to sunlight than viscose, lower moisture absorption than viscose	very good handle and comfort properties, fast drying, prone to wrinkle formation, poor durability, builds static electricity, heat sensitive	extreme fineness, degradation and weakening occur due to exposure to sunlight in the presence of oxygen and moisture, burns rapidly and chars at 180 ° C	shrink and wrinkle resistant, excellent drape and soft handle, fibrillation, flammable, biodegradable
common uses [12, p.8, 11][44][43][50][51]	household textiles, clothing, high absorption hygienic materials, bandages, surgical dressings, coated fabrics, conveyor belts, automobile tyres	sportswear, underwear, t-shirts, bed sheets	cigarette filters, clothing	lightweighth fabrics, form-fitting clothing	clothing, conveyor belts, medical dressings, specialty paper

2.4.6.1 Sustainability of current processes for the production of man-made cellulose fibres

The current processes for MMCF production have sustainability aspects that are worthwhile discussing.

As an advantageous characteristic of these processes, wood pulp from trees is the most used raw material. The trees used for this purpose grow using rainwater and do not need any other type of water supply. The land used for these forests does not cause any environmental impact. Consequently, as the trees can grow and regenerate at a high pace and cellulose from that source is widely available, these resources are considered as replenishable and sustainable [8][48].

On the other hand, these raw materials are subjected to lengthy and strenuous processes in order to produce fibres. First, the existing MMCF production processes require highly purified dissolving grade pulp, without the presence of non-cellulosic impurities, in order to guarantee the necessary dope quality and spinning stability. Furthermore, the viscose, modal, acetate and cuprammonium processes make use of solvents that cause environmental problems. At last, the consumption of energy and fossil fuel in the previous production processes, as well as in the production of the required chemicals, are also sustainability concerns [6][8][12, p.12].

Hence, attempts have been made to develop alternative processes. The lyocell process is currently the most friendly. The used solvent is N-methylmorpholine-N-oxide (NMMO) which is non-toxic and fully biodegradable. Additionally, it is a closed-loop process with no effluents or gases emitted to the atmosphere [12, p.30].

However, the lyocell process has not replaced the other MMCFs processes due to its drawbacks. First, NMMO in solution tends to degrade exothermically. This can be caused by faulty operation of equipment or chemical contamination of the solution. If this degradation occurs, the temperature of the solution increases rapidly and decomposes to volatile amines and water; in turn, pressure increases very rapidly which can cause damage to the equipment with very serious safety implications. Thus, this process requires the addition of stabilisers to avoid the runaway reaction and consequent extensive cellulose degradation. Additionally, lyocell fibres have great ease of fibrillation. Fibrillation becomes apparent when stress is applied along the fibre axis in wet state, making the surface fibrils peel away from the main body of the fibre. This imposes limitations on the use of this kind of fibres[12, p.30][18, p.66].

2.5 Ioncell[®] process

Ioncell[®], developed in the collaboration of Aalto University and University of Helsinki, is a very simple process that presents itself as a solution to bypass the previously mentioned limitations of the MMCF production processes that dominate the market.

It is a dry-jet wet fibre spinning technology which utilises an IL 1,5-diazabicyclo [4.3.0]non-5-enium acetate ([DBNH][OAc]) as a direct cellulose solvent. This technology produces filaments with excellent properties in a process that is flexible towards the use of raw materials and operates at moderate conditions without the use of additional chemicals [7][13][14].

As a first step of the process, cellulose derived from dried wood pulp is dissolved in liquefied [DBNH][OAc], to a 13 wt% cellulose consistency. The mixture is transferred into a vertical kneader, where the temperature, pressure and shearing rate is controlled. The dissolution process is typically conducted at 80° C with the shearing of 30 rpm for 90 minutes. The resulting solution is a clear amber viscous solution of cellulose. Subsequently, the resulting dope is filtered by means of a hydraulic filtration unit at 80° C to remove impurities from the solution which mainly consist of undissolved pulp fibres. From the prepared dope, the cellulose fibers are spun using a piston spinning unit. First, the spinning cylinder is filled with the solidified solution that has to be molten and then the temperature is set to the desired value depending upon the characteristics of the prepared dope, between 70 - 85° C. Afterwards, the dope is extruded through a spinneret, the filament passes an air-gap of 0,5 cm, is immersed into a coagulation bath and is collected at godets (dry-jet wet-spinning method). Next, the produced fibers are washed thoroughly to remove the [DBNH][OAc] and dried [6][52]. This process is schematized in figure 2.8.

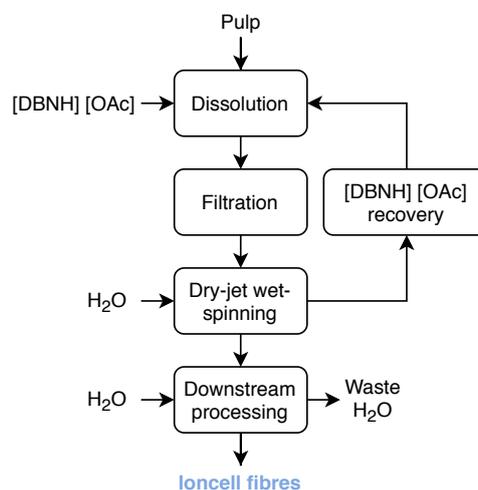


Figure 2.8: Schematic representation of Ioncell[®] process.

2.6 Colouration of man-made cellulose fibres

In general, textiles are coloured by dyeing and/or printing. Table 2.2 displays some characteristics of the referred processes.

Table 2.2: Characteristics of dyeing and printing processes.

	dyeing	printing
colour	single colour application	single or multiple colour application
application form	liquid	paste
colouration treatment	colour penetrates the substrate	colour remains on the surface
substrate structure	fibre, yarn, fabric (open width or rope form)	fabric (open width form)

Both processes aim to achieve an acceptable durability of colour and to reproduce the desired shades consistently. Thereby the treatments have to assure a reasonable operation time and price while following ecological and safety requirements.

The used colourants can be parted into two types, dyes and pigments. The characteristics of the two types are summarized in short in table 2.3.

Table 2.3: Characteristics of dyes and pigments.

	dyes	pigments
colour	intense	intense
solubility	soluble during dyeing stage	insoluble in water and common solvents
substantivity^a	substantive during dyeing stage	not substantive
molecular size	small (can penetrate the fibre structure and get fixed inside)	small to large
stability	stable	stable
durability	depends upon chemical bonds	depends upon binders

^a Difference between the chemical potential of the dye in its standard state in the fibre and the corresponding potential in the dye bath or the tendency of a dye to move from the dye bath and penetrate into the inner molecular structure of the fibre.

In ancient times colourants were extracted from natural resources; whereas, nowadays the colourants are synthesized from petroleum based intermediates. These synthetic colourants are classified according to the chemical structure or the type of application. The chemical structure method makes a distinction between the type of chromophore responsible for the colour of the dye. However, a classification by type of application is more common and is the principal system adopted by the Colour Index ¹ [53, pp.1-12;339-349].

In principle, the same colourants can be used for viscose and cotton. However, usually the same colourant produces deeper and more brilliant colours attached to viscose rather than cotton. Reactive dyes, direct dyes, vat dyes and sulphur dyes are used for viscose dyeing. Pigment colours, azoic colours and reactive dyes are the most used for viscose printing [53, pp.1-12;339-349]. In table 2.4 some properties of the previous referred colourants are summarized.

¹The unique and definitive classification system for dyes and pigments used globally by manufacturers, researchers and users of dyes and pigments.

Table 2.4: Characteristics of colourants used for viscose fibres.

colourants	reactive dyes	direct dyes	vat dyes	sulphur dyes	pigment colourants	azoic colourants
solubility	soluble	soluble	insoluble	insoluble	insoluble	insoluble
range of colour	wide	wide	wide	limited	wide	limited
brightness of shade	bright	bright	dull	dull	bright	bright
cost	inexpensive	inexpensive	expensive	inexpensive	inexpensive	inexpensive
washing fastness^a	very good	poor	excellent	very good	good	excellent
light fastness	good	good	very good	good	good	poor to good
rubbing fastness	good	poor	poor	good	poor	poor
chlorine fastness	poor	poor	very good	poor	poor	poor
application process	easy	easy	difficult	easy	easy	difficult
dye-fibre interaction	covalent bond	hydrogen bonds, van der Waals forces, secondary valence forces and dye aggregation	mechanical entrapment by redox reaction	mechanical entrapment by redox reaction	mechanical entrapment by use of binders	mechanical entrapment by generation of the chromophore inside the fabric

^a Colour fastness is defined as the durability of the colour against fading forces; these can be further classified into colourfastness to washing, light, rubbing and chemical treatments.

2.6.1 Reactive Dyes

[53, pp.113–132;349–357] [54]

The general structure of a reactive dye molecule, as in figure 2.9, is composed of the following elements:

- the reactive group, which is an electrophilic functional group that reacts with the cellulose fibres; can be a halogen derivative of a nitrogen heterocycle compound with a reduced π -electron density (triazine, pyrimidine, quinoxaline) or activated vinyl compound (vinyl sulphone, vinyl acrylamide, vinylsulphonamide).
- the bridging group, which connects the reactive group to the chromophore containing group.
- the chromophore containing group.
- the solubilizing group.

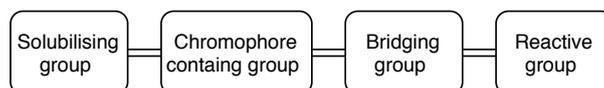


Figure 2.9: Chemical structure of a reactive dye.

However, some reactive dyes do not contain all of these elements.

Reactive dyes interact with the fibre by the formation of a covalent bond.

The dyeing mechanism for the reactive dyes consists of the following stages: exhaustion, fixation or reaction and aftertreatment.

Exhaustion or dye absorption

Once the fabric is immersed in a dye bath, the fibres acquire a negative ionic charge. The reactive dye in the bath is also negatively charged. This causes a repulsive force called zeta potential between the fibre and the dye². As such, an electrolyte (sodium chloride or sodium sulphate) is added to neutralize the negative charges of the fibre and to decrease the hydrolysis rate of the dye; this increases the affinity and therefore adsorption of the dye to the fibres occurs.

Fixation or reaction

In the fixation stage the reactive group of the dye reacts with the terminal hydroxyl group of the cellulose fibre forming a covalent bond. Thus, the dye becomes an integral part of the fibre and is much less likely to be removed by washing than dyes, which adhere by adsorption. For that purpose, alkali (sodium hydroxide, sodium carbonate or sodium bicarbonate) is used to create proper pH in the dye bath and act as a dye-fixing agent to fix the dye inside the fibre.

Two alcoholysis reaction mechanisms can occur to attach the dye to the fibre: an addition reaction as in figure 2.10 (a); and a substitution reaction as in figure 2.11 (a). Simultaneously, a hydrolysis of the reactive group happens as in figures 2.10 (b) and 2.11 (b). There is a greater nucleophilicity of cellulose compared to water which results in the preference of the reactive group for the fibre.

²Degree of electrostatic repulsion between adjacent, similarly charged particles in a dispersion.

Aftertreatment or washing

To remove the excess of dye, the reaction by-products and impurities, the substrate is first rinsed with cold water, then washed at boiling temperature with soap and finally cleaned with hot and further cold water.

Stripping of reactive dyes

The reactive dye cannot be totally stripped from fibre due to the established covalent bond. Partial stripping can be obtained by treating the dyed fabric with a dilution of acetic acid or a dilution of formic acid at high temperatures.

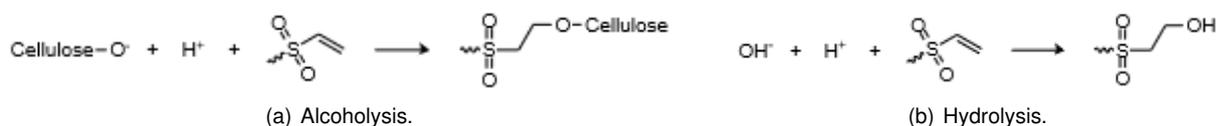


Figure 2.10: Addition reactions of a vinylsulfone reactive group of a reactive dye.

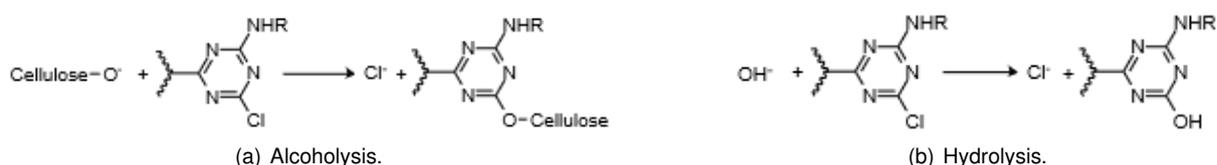


Figure 2.11: Substitution reactions of a monochlorotriazine reactive group of a reactive dye.

2.6.2 Direct or Substantive Dyes

[53, pp.158-178;358-361]

The direct dye molecule displays structural linearity along its entire length with a long chain of conjugated double and single bonds for the development of resonance forms and coplanarity of the benzene rings for the contact of the dye molecule with the cellulose fibre. It contains solubilizing sulphonic acid groups which gives the dye a negative charge in aqueous solution.

The dye is attached to the fibre by different forces such as: hydrogen bonds between the hydrogens of the amino groups of the dye with the oxygen of the hydroxyl groups of the cellulose or the nitrogens of the azo groups of the dye with the hydrogen of the hydroxyl groups of the cellulose; van der Waals forces that create intermolecular attraction by generation of a temporary dipole moment; secondary valence forces that allow the interaction between the conjugated system of π -electrons and the hydrogen atoms of the hydroxyl groups of cellulose; and aggregation of the dye molecules. The combination of all these interactions explain the excellent substantivity of these dyes.

The dyeing mechanism for the direct dyes consists of the following stages: exhaustion and aftertreatment.

Exhaustion or dye absorption

This stage is carried out in a similar manner as described above in the reactive dye exhaustion stage, with the following differences: a neutral or alkaline bath is required due to hydrolysis of cellulose in acidic

conditions; the temperature is adjusted at or near boiling point due to aggregation of the dye at room temperature.

Aftertreatment

Direct dyes are bound to the fiber by the weak previously mentioned forces. Consequently, at dyeing equilibrium, the rate of absorption is equal to the rate of desorption. Without additional measures, the strength of these bonds is low and most of these dyes can be washed out of the fiber. Therefore, the treatments to improve fastness include diazotization, chelation with salts of metals (copper or chromium), treatment with formaldehyde or with a cationic dye-complexing resin.

Stripping of direct dyes

Most direct dyes can be stripped without harmful effects on the fibres by the use of stripping salts (sodium hydrosulphite) or by using a chlorine bleaching agent (sodium hypochlorite).

2.6.3 Vat Dyes

[53, pp.178-214;362-369]

Depending upon their chemical nature, vat dyes can be classified in indigo or anthraquinone derivatives. The chromophore of this class of dyes is the carbonyl group.

Vat dyes are confined in the fibres in a water insoluble form.

The dyeing process involves the following stages: vatting, absorption, oxidation and after treatment.

Vatting or reduction

The insoluble vat dye is uniformly applied to the fabric surface, usually with the aid of dispersing agents (detergents). Then, a reducing agent (sodium dithionite) is added to convert the water insoluble form of the dye to a weakly acidic leuco³ vat form. At last, the dye is neutralized with an alkali (sodium hydroxide) to produce a water soluble sodium salt of the leuco vat dye. The described reactions are represented in figure 2.12.

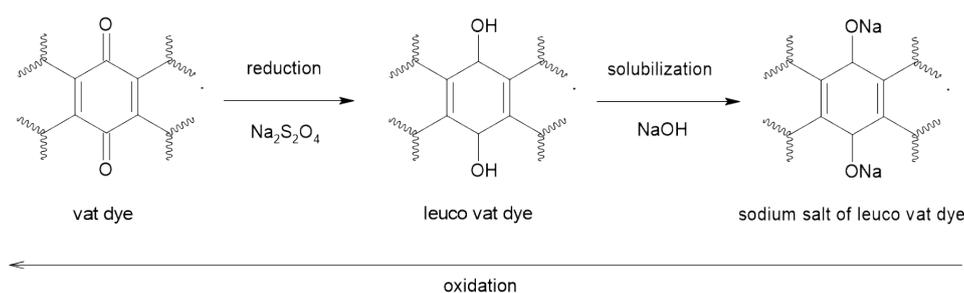


Figure 2.12: Reaction of vat dyes: vatting stage.

Absorption or dyeing

Once the dye has been converted to its soluble form, the sodium leuco vat dye present in the bath can penetrate into the fibres. Depending on the absorption rate of the dyeing process, an exhaustion agent may be needed. The textile material must be fully immersed in the dye bath with all oxygen removed to prevent oxidation of the leuco compound.

³A leuco dye is a dye that can switch between two chemical forms with different colour and solubility.

Oxidation

After adequate time for penetration, the soluble leuco form of the dye is converted to the original insoluble form by oxidation and thus fixed to the fiber. Oxidation can be achieved by airing (atmospheric oxygen) or by chemical treatment with the addition of oxidants to the liquor (hydrogen peroxide or sodium perborate). Once the vat dyes have been regenerated inside the fiber, they are very insoluble.

Aftertreatment

Next, the textile material is treated in mildly alkaline conditions with boiling soap or other detergent solutions. This allows the aggregation of smaller dye particles into bigger ones to provide optimum hue and improved fastness properties.

Stripping of vat dyes

Stripping of vat dyes is very difficult due to the need of reduction to convert the dye to the soluble form. This makes the fibres lose their strength.

2.6.4 Sulfur Dyes

[53, pp.70-84;215-226;370-375]

The sulfur dye is a complex organosulfur heterocyclic molecule with high molecular weight in which sulfur is present as sulphide bridges or thiazole groups. These dyes are synthesized by heating aromatic or heterocyclic compounds with sulfur or alkali metal polysulfides.

Sulfur dyes are confined in the fibre in a water insoluble form.

The dyeing process involves the following stages: reduction, absorption, washing, oxidation and aftertreatment.

Reduction

Similarly to the vat dyeing technique, a reducing agent (sodium sulphide) is added to the dye bath at elevated temperatures. As such, cleaving of the disulfide groups of the insoluble sulfur dye into mercapto groups occurs. An alkali (sodium hydroxide) is applied to produce a water soluble sodium salt of the leuco sulfur dye. This reaction is represented in figure 2.13.

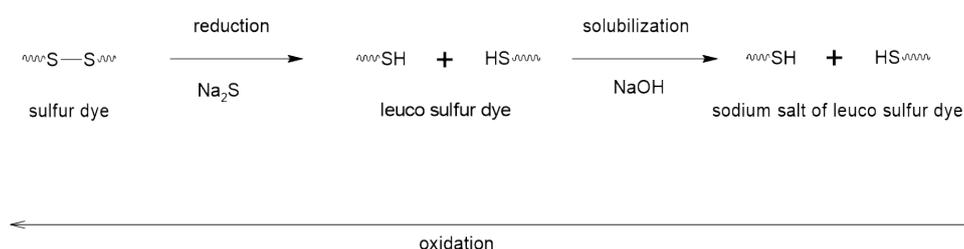


Figure 2.13: Reaction of sulfur dyes: reduction stage.

Absorption or dyeing

Once the dye has been converted to its soluble form, the dye can penetrate into the fibres. Next, the electrolyte is added and elevated temperatures are maintained to promote exhaustion of the dye to the fibre.

Washing

After getting the correct shade, the material is washed and rinsed several times with fresh water to remove loose residual dye, alkali or reducing agent.

Oxidation

The oxidation is performed to reconvert the dye from its soluble form to its insoluble form; therefore, the dye is fixed to the fibres. Oxidation can be achieved by exposing the dyed material to atmospheric oxygen, contact with dissolved oxygen in fresh water or chemical oxidation with oxidation agents (sodium perborate, hydrogen peroxide and a combination of potassium bicarbonates and acetic acid).

Aftertreatment

After oxidation, alkylating agents are applied for cross-linking and enlargement of the dye molecule to increase their fastness properties. Then, the substrate is washed at high temperatures to remove excess oxidation agent and, possibly, detached dye.

Stripping of sulfur dyes

Faulty sulfur dye can be stripped by treatment with sodium hypochlorite.

2.6.5 Azoic or naphthol colourants

[53, pp.227-250;375-375]

Azoic colours are mechanically entrapped and held in the fiber in a water insoluble form. They are generated inside the polymer matrix by applying the coupling component - naphthol - and the diazo component - diazo base or diazo salt. The azo group is part of the chromophore.

The reaction of azoic dyes is composed of the following stages: naphtholation, diazotization, coupling or developing and aftertreatment.

Naphtholation

The coupling component or naphthol is solubilised by the addition of an alkali (sodium hydroxide) forming the corresponding naphtholate ion as in figure 2.14 (a). Then, this solution is applied to the fibres in the presence of an electrolyte to promote exhaustion of the naphtholate ion onto the substrate. Thus, the textile becomes naphtholated.

Diazotization

The base or salt containing an amino group reacts with sodium nitrite in presence of excess hydrochloric acid at low temperature. A solution or paste of diazonium chloride of that base is formed as in figure 2.14 (b).

Coupling or developing

The naphtholated fibres are padded by treatment with the diazotized base paste. As such, coupling of the naphthol and the diazo base occurs and generates a coloured azo group inside the fabric as in figure 2.14 (c).

Aftertreatment

The fabric is left to dry and then the print can be washed to remove unconsumed naphthol.

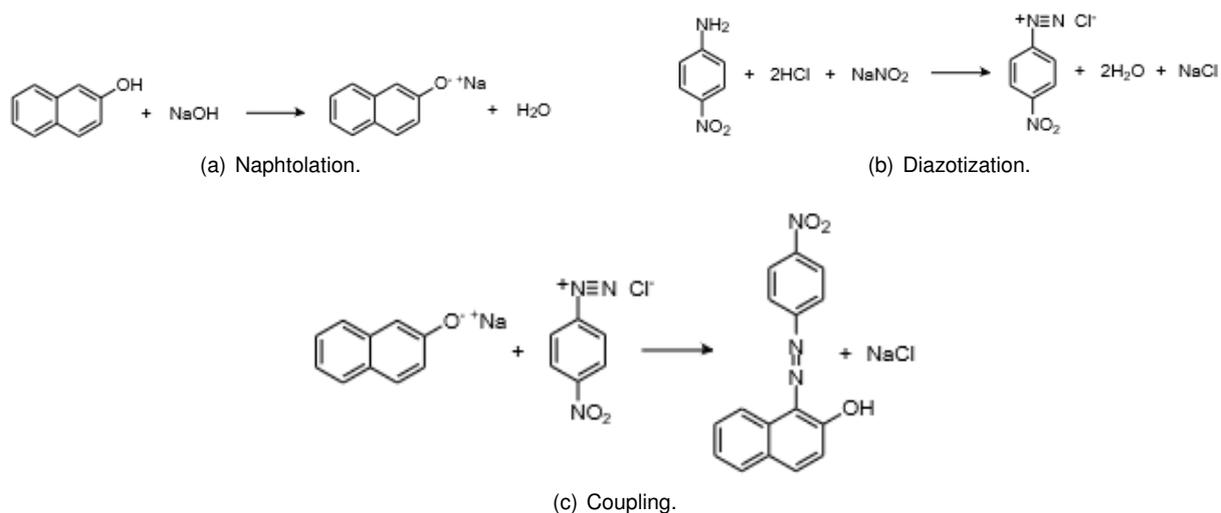


Figure 2.14: Reaction of azoic colourants.

2.6.6 Pigment printing

[53, pp.380-381][55]

Pigments require no chemical reactions between the colourant and the fabric. As they are insoluble and have no substantivity, they cannot penetrate the fibres. Hence, they attach mechanically on the surface of the fibre structure by means of special chemicals.

The pigment printing process is composed of the following stages: printing paste preparation, printing and fixation.

Printing paste preparation

The printing paste consists of the pigment to provide the colour; a binder to fix the pigments on the fibre by creating a coating between the fabric and the pigment; a thickener to give the required viscosity to the paste so it may be applied without bleeding; a fixing agent helps in strengthening the binder to hold onto the pigment; and a solvent.

Printing

The printing paste is applied to the fabric through several possible routes such as block, roller, screen, and heat transfer printing to print a design onto the fabric. Afterwards, the fabric is left to dry.

Fixation

The printed fabrics are treated by steaming or heating at 150 °C. The heat activates the binder to adhere the pigments onto the surface of the cloth. Fabrics printed with pigments do not require washing after fixation. Therefore, any thickening agent remains on the printed cloth and stiffens the printed areas.

2.7 New environmentally friendly decolouration techniques

In the context of increasing the amount of textile waste used as a raw material for production of new fibres, it is important to have in focus feasible ways to manage the colours of the recycled textile waste.

Several options are available to handle this matter, such as: the removal of the colour before fibre production; the collection and sorting of waste textiles based on their colour while retaining it throughout the further stages of fibre production; the blending of waste textiles, ignoring their colour, subsequent production of the fibres and posterior removal of colour or colouration with darker colour to even the shade. All these mentioned options for colour management include challenges; however, the most likely method to be applied in the textile industry would be the removal of the colour of the waste before fibre production [56].

Decolourization is the removal of colour by either solubilization or destruction of the chromophoric sites in the coloured textile in order to produce a material with a clean white appearance. This may be carried out either by reductive or oxidative decolourization agents; however, most agents used are oxidative [57].

When employing a decolourization process it is important to consider the type of colourant present in the textile fibres as well as the process of decolourization applied which may influence specific cellulose properties. It is important to mention the low degree of polymerization of viscose fibres; because of this characteristic, it is necessary to apply decolourization methods with limited aggressiveness in order to minimize fibre degradation.

The most common methods for this purpose are sodium hypochlorite (NaOCl) and sodium chlorite (NaClO_2). NaOCl is cheap and can be used at room temperature; but, the process produces absorbable organic halogens (AOX), chloroform which is toxic for sea life and fabrics turn yellow on storage. NaClO_2 is expensive, generates ClO_2 gas which is toxic and highly corrosive to normal stainless steel. Therefore, these methods possess some serious drawbacks that make them harmful to the environment [58].

The increasing demand for conservation of natural resources and environmental protection creates an interest in developing processes that do not use harsh chemicals, are short in duration, low in energy and low in water consumption. All these requirements have to be fulfilled while producing the desired whiteness and quality targets. So, in the context of recycling and the establishment of a closed loop process on textile production, the decolourization techniques applied have to fulfill CE expectations in an attempt to mitigate environmental impacts. Hydrogen peroxide and ozone present themselves as viable options for this purpose [56].

2.7.1 Hydrogen peroxide

[59][60][61][62]

Decolourization with hydrogen peroxide (H_2O_2) yields permanent results since fibres do not turn yellow on storage; furthermore, it is environmentally friendly because there is no formation of toxic and dangerous byproducts (the products formed are H_2O and O_2). However, H_2O_2 is a highly corrosive compound and it is damaging to fibres.

Decolourization is achieved due to H_2O_2 ionization as in equation 2.10; the perhydroxyl anion (HO_2^-) formed in the reaction is the active species responsible for the decolourization.



H_2O_2 can also decompose as in equation 2.11; this reaction causes oxidative degradation by lowering the degree of polymerization of the fibre polymer and leading to strength reduction. Moreover, water for the decolourization process has to be free from metal ions, such as iron and copper, because they act as catalyst for the same decomposition reaction.



It is very difficult to specify strict guidelines for optimum decolourization conditions using H_2O_2 . However, efficient decolourization makes use of alkaline conditions and high temperature to promote the dissociation of H_2O_2 to HO_2^- as in equation 2.12. Moreover, parameters such as liquor composition and concentration, pH, temperature and time are crucial for this reaction.



The decolourization liquor for this purpose requires H_2O_2 at 1 - 4%, an activator and a stabilizer. Activators, such as NaOH, Na_2CO_3 or Na_3PO_4 , are used to generate HO_2^- . Stabilizers, such as MgSO_4 , sodium silicate and phosphonic acids, are used to prolong the action of HO_2^- by avoiding its decomposition to O_2 and by controlling the formation of free radicals that would damage cellulose, by a buffering action that controls the pH at optimum level and by forming a complex with trace metals which can catalyse the degradation of the fibres.

H_2O_2 is stable at pH 2 - 3. Therefore, under acid or neutral pH conditions, its dissociation to HO_2^- is very slow. Therefore, the optimum pH for decolourization lies in the 10.5 - 10.8 range; this is where the rate of decomposition of H_2O_2 to HO_2^- is equal to the rate of HO_2^- consumption for decolourization. At pH above 11, the formation of HO_2^- is so rapid that it becomes unstable with the formation of oxygen gas which has no decolourizing properties. Above pH 11.8, all H_2O_2 is converted to HO_2^- and the non utilized HO_2^- may damage the fibres. At pH below 10, H_2O_2 is the major species and so no decolourization occurs.

Ideal decolourization temperature falls in the range of 95 - 100° C. Below 80° C the decomposition to HO_2^- is very slow. The increase in temperature increases the rate of decolourization; at the same time this makes the reaction more unstable and increases fibre degradation.

Common decolourization time falls in the range of 60 - 90 minutes. The time of decolourization is inversely proportional to the temperature applied and also depends on the fibre type and the equipment used.

2.7.2 Ozone

[63][64][65][66][67]

Ozone (O₃) is an irritating pale blue gas, heavier than air, highly reactive and with high oxidation potential. Therefore, it is capable of participating in many chemical reactions with inorganic and organic substances.

It is generally produced using a O₃ generator by passing dry air or oxygen through a very strong electric field, which splits the diatomic oxygen molecule (O₂) into two highly excited oxygen atoms (O[•]). These unstable O[•] atoms combine with other O₂ molecules to form O₃ as in equation 2.13.



Decolourization with O₃ is environmentally friendly because there is no need to use harmful chemicals, it uses a minimal quantity of water, it does not require any heating or cooling energy and does not produce any dangerous byproducts. However, O₃ is a very reactive and chemically unstable for storage and transportation so it has to be generated *in situ*; furthermore, this process can damage cellulose fibres.

The effectiveness of the O₃ decolourization process is dependent on the pH, O₃ dose, treatment time, temperature and cellulose moisture content. The pH has the greatest effect on whiteness of the decolourized fibres, followed by O₃ dose and treatment time.

Depending upon the pH, O₃ may react with the colouring matter present in cellulose fibres in two ways. Either reaction occurs directly with molecular O₃ or by reaction with radical species. In acidic, neutral and mildly alkaline solutions with a pH below 9, the reaction occurs predominantly by means of the highly selective O₃ molecules; this reaction occurs rapidly at sites of high electron density (such as aliphatic and aromatic double bonds) and slowly at less reactive sites (such as C–H bonds of saturated hydrocarbons). In strong alkaline solutions with a pH above 9, O₃ undergoes catalytic decomposition to a variety of products including hydroxyl radical (•OH) and superoxide anion (O₂^{•-}); •OH radicals have less selectivity and high oxidation potential so they react not only with the colouring matter present in cellulose but also with other intermediates formed during the decomposition of O₃. When increasing pH from 2 to 9, there is a marginal decrease in the whiteness of fibres and a further increase in pH from 9 to 12 results in a rapid decrease in whiteness. Additionally, strongly acidic conditions with pH below 3 is ineffective for improving whiteness and causes hydrolysis of the cellulose with damage to the cellulose fibers. In view of this effect of pH on O₃ decomposition, a better degree of whiteness is expected in acid, neutral and mild alkaline solutions than in strong alkaline solutions. Additionally, the rate of bleaching is much faster in acidic conditions than in strongly alkaline conditions. Strength loss mainly depends on treatment time; therefore, strength loss is minimum in acidic medium because decolourization can occur in a short time period.

The increase in O₃ dose increases the whiteness obtained. This is due to the enhancement of the mass transfer efficiency that causes an increased O₃ concentration.

The whiteness increases with increased O₃ treatment time. The rate of O₃ reaction is very quick during the first 15 min because it readily cleaves the double bonds and other functional groups of the

chromophores. Exposure times longer than 45 minutes marginally improve the whiteness while also increasing mechanical and chemical damage to the cellulose fibres.

O₃ is susceptible to high temperatures and can decompose in a short time at temperatures of 50 – 52° C.

Moisture content of the fibres also correlates with decolourization effectiveness. This is due to the ease of dissolution and penetration of O₃ into the fibres when a certain level of moisture is present. 8% moisture content has very little decolourization effect, but it increases rapidly as the percentage of moisture increases up to 24%; then, a further increase up to 80% in moisture content retards the decolourization action and thereafter, the amount of moisture present seems to have no effect on decolourization outcome.

When taking into consideration the previous described parameters and their influence in O₃ decolourization, optimum values differ in the literature because different conditions might produce satisfactory results [67].

Chapter 3

Methodology

This chapter introduces an experimental work to recycle pre- and post-consumer viscose waste by means of Ioncell® technology. Cellulose material from wood pulp, which served as reference sample, and from textile samples was ground, dissolved in ionic liquid and spun into new fibres. The properties of the spun fibers have been determined.

3.1 Samples

The cellulosic wood and textile materials used in this experimental work were the following:

- Pre-hydrolyzed birch kraft pulp sheets from Stora Enso Enocell mill, Enocell pure - sample Eno.
- Virgin viscose fibre samples - samples VV1 and VV2.
- Virgin cotton fabric sample from Lindström group - sample VC.
- Post-consumer viscose fabric samples from Lahti University - samples V01 to V15.

3.1.1 Microscope analysis

A Leica DM750 optical microscope was used to observe the post-consumer viscose textile samples. Therefore, the yarn of each post-consumer viscose fabric (V01 to V15) was unraveled with the purpose of observing the fibre structure under 20 x objective.

3.1.2 Grinding

Wiley mills were used to process the sheets of Eno and the textile samples into a fine pulp (60 mesh sieve).

3.1.3 Dry matter content

Dry matter content (DMC) determination was performed by drying the samples in a Memmert oven at 105 °C. This procedure was conducted for all the ground textile samples in triplicate.

The data was analyzed, evaluated and statistical analysis was performed in compliance with the Grubbs test.

3.1.4 Ash content

Ash content (AC) determination was conducted by incinerating the samples in a Selecta Horn muffle furnace at 575 °C. This procedure was conducted for all the ground textile samples in triplicate.

The data was analyzed, evaluated and statistical analysis was performed in compliance with the Grubbs test.

3.1.5 Viscosity

Intrinsic viscosity (η) determination was assessed by dissolving an appropriate sample amount in a dilution of cupri-ethylenediamine (CED) and measuring the correspondent efflux time of the solution in a capillary-tube viscometer. The standard method SCAN-CM 15:99 was followed [68]. This procedure was conducted for all ground textile samples and for selected blends of those textiles in triplicate.

The data was analyzed, evaluated and statistical analysis was performed in compliance with the Grubbs test.

3.2 Dope production and analysis

3.2.1 Solvent synthesis

IL 1,5-diazabicyclo[4.3.0]non-5-ene acetate ([DBNH][OAc]) was prepared by the gradual addition of an equimolar amount of acetic acid (glacial, 100%, Merck, Germany) to 1,5-diazabicyclo[4.3.0]non-5-ene base (DBN, 99%, Fluorochem, UK) in a 6 L reactor at 80 °C with constant stirring. Afterwards, the IL was stored at room temperature in glass bottles.

3.2.2 Dissolution

The crystallized IL was melted in a water bath at 70 °C.

For the preparation of four dopes - Eno, VV1, Blend₁ and Blend₂ - an appropriate amount of ground cellulose was dissolved in IL for a cellulose content of 13 dry wt%. Table 3.1 characterizes each prepared dope.

Subsequently, stirring was conducted in a kneader for 90 minutes at 80 °C with an angular velocity of 30 rpm.

Table 3.1: Characterization of the prepared dopes Eno, VV1, Blend₁ and Blend₂: total dry weight ($m_{\text{total,dw}}$), intrinsic viscosity of the cellulose ($[\eta]$), composition, cellulose additives with respective ratio and dry weight (m_{dw}) and ionic liquid with respective dry weight.

dope		Eno	VV1	Blend ₁	Blend ₂
$m_{\text{total,dw}}$ [g]		30	30	30	23
$[\eta]_{\text{cellulose}}$ [mL.g ⁻¹]		400 - 500	172	471	471
composition [%]	cellulose	13	13	13	13
	ionic liquid	87	87	87	87
cellulose	additive ₁	Eno ^a	VV1 ^b	VV1	VV1
	ratio	1	1	0.8	0.8
	m_{dw} [g]	3.90	3.90	3.12	2.39
	additive ₂	-	-	VC ^c	VC
	ratio	-	-	0.2	0.2
	m_{dw} [g]	-	-	0.78	0.60
ionic liquid [DBNH][OAc] ^d	m_{dw} [g]	26.1	26.1	26.1	20.01

^a Enocell Pure. ^b Virgin viscose. ^c Virgin cotton. ^d 1,5-diazabicyclo[4.3.0]non-5-ene acetate.

After dissolution, the dope was filtered through a hydraulic press filter (metal filter mesh with 5 μm absolute fineness, from Gebr. Kufferath AG, Germany) at 2 MPa and 80 ° C.

The resulting dope was shaped to fit the dimensions of the spinning cylinder and solidified upon cooling at 5 - 7° C.

3.2.3 Dissolution studies

A Leica DM2500M optical microscope was used to evaluate the dissolution of the selected cellulose pulp in the IL through time; four samples for each dope were prepared for observation at: 30 min of dissolution, 60 min of dissolution, 90 min of dissolution and post filtration. Each sample was placed on a Linkam LTS420 hot stage at 80 ° C. Cross-polarized light was used to increase the contrast between the solvent and the undissolved particles and to improve the luminosity of those undissolved traces.

Python Microscope Analyzer, developed at Aalto University, was used to calculate an indicative value for percentage of dissolution. This calculation is based on the proportions between white and black pixels of the microscopic pictures of each sample.

This procedure was conducted for all prepared dopes.

3.2.4 Rheology

An Anton Paar MCR 300 Rheometer with a parallel plate geometry (25 mm plate diameter, 1 mm measuring gap) was used to determine the viscoelastic behaviour of the prepared dopes under shear stress. Storage modulus (G'), loss modulus (G'') and complex viscosity (η^*), were determined by dynamic frequency sweep with a 0.5% strain of temperatures ranging between 50 - 100 ° C over an angular frequency of 0.1 - 100 rad.s⁻¹.

RheoCompass software was used to determine the crossover point between the curves of G' and G'' and the zero-shear viscosity (η_0^*) was determined by fitting Carreau-Galeitner regression to the complex

viscosity data.

This procedure was conducted for all prepared dopes.

3.3 Fibre spinning and analysis

3.3.1 Spinning

Fibre spinning was conducted with a dry-jet wet-spinning system with a single spinneret hole. The spinning temperature was selected according to the rheology data in order to achieve the desired viscoelastic properties of the dope; experimental adjustments of the ideal temperature might have been necessary for spinning improvement.

The dope was extruded from a cylinder through a single hole spinneret (diameter of 0.1 mm and length of 0.2 mm); the extruded filament passes an air gap (0.5 cm) and is immersed in a water coagulation bath at 5 ° C; after exiting the coagulation bath, the filament was led over a guide roller and attached to a motor-driven godet couple where it was collected for further tests.

The filament extrusion velocity (v_e) in $\text{m}\cdot\text{min}^{-1}$ was kept constant while the take-up velocity (v_{tu}) in $\text{m}\cdot\text{min}^{-1}$ was adjusted according to the targeted draw ratios (DRs). DR is calculated as in equation 3.1.

$$DR = \frac{v_{tu}}{v_e} \quad (3.1)$$

The collected fibers were washed three times with water at 80 ° C and air dried.

This process was conducted for all prepared dopes.

3.3.2 Fibre characterization

3.3.2.1 Tensile strength

A Favigraph instrument (Textechno, Germany) was used to determine linear density, tenacity and elongation at break. The test parameters were the following: 20 cN load cell, 20 mm gauge length and 20 $\text{mm}\cdot\text{min}^{-1}$ test speed; pretension weights between 50 - 250 mg were used depending upon the linear density of the given sample.

For the dry measurement, the fibres were previously conditioned in an environment at 20 ° C and 65 % relative humidity (RH). Twenty measurements were performed for all collected DRs of each spun dope.

For the wet measurement, the fibres were previously immersed in water for 10 s. Twenty measurements were performed with the fibre immersed in water for one selected DR of each spun dope.

3.3.2.2 Modulus of elasticity

Modulus of elasticity was determined from the slope of the elastic part of the stress-strain curve of the fiber according to the ASTM D2256 standard. The stress-strain curve data was obtained from the tensile strength measurements and the calculation was performed using a MATLAB script (MathWorks, Inc.).

3.3.2.3 Birefringence

Vibroskop 400, Lenzing Instruments GmbH & Co KG, Austria was used to measure the linear density (D) in dtex of each selected fibre in triplicate, permitting 1.5 % variation. Assuming 1.5 g.ml⁻¹ as the density (ρ), the diameter (d_s) in nm was calculated as in equation 3.2 [69].

$$D = \frac{\pi\rho}{100} \left(\frac{d_s}{2} \right)^2 \quad (3.2)$$

Each fibre was extended between two pieces of double-sided tape on a microscope slide. Zeiss Axio Scope A1 microscope equipped with a Leica B 5λ-Berek tilting compensator was used to determine the position vertical to the propagation of the light (i) in triplicate from a selected spot. The compensator plate has a thickness (d) of 1.52×10⁶ nm and at the wavelength (λ) of 541.6 nm has a refractive index of the extraordinary wave (n_e) of 1.39043 and a refractive index of the ordinary wave (n_o) of 1.37859. The phase difference or optical retardation (Γ_λ) in nm was calculated as in equation 3.3 [70].

$$\Gamma_\lambda = d \cdot n_o \left(\sqrt{1 - \frac{\sin^2 i}{n_e^2}} - \sqrt{1 - \frac{\sin^2 i}{n_o^2}} \right) \quad (3.3)$$

Birefringence (Δn) was calculated as in equation 3.4.

$$\Delta n = \frac{\Gamma_\lambda}{d_s} \quad (3.4)$$

Assuming 0.062 as the maximum Δn of cellulose (equivalent to 100 % orientation), total orientation of fibers (f_t) was determined as in equation 3.5.

$$f_t = \frac{\Delta n}{\Delta_{max}n} \quad (3.5)$$

For a selected DR of each spun dope, three filaments were analysed.

Chapter 4

Results and discussion

The Ioncell[®] technology, developed at Aalto University, establishes a novel and promising process for MMCF production. The exceptional properties of the fibers spun from a cellulose and [DBNH][OAc] solution and the low sensitivity of the process towards the use of different cellulose raw materials present an interesting prospect to investigate the applicability of other cellulose based materials as raw materials, such as viscose textile waste.

This chapter describes and discusses the results obtained the experimental work in which Ioncell[®] technology was utilized to recycle pre- and post-consumer viscose waste. First, the viscosity of viscose starting materials was adjusted to the needs of the process (see section 4.1). Then, several dopes were prepared for spinning operations and the solution properties were analysed (see section 4.2). At last, spinning of the prepared dopes was carried out and the resulting fibres were tested (see section 4.3).

4.1 Viscosity adjustment

Ioncell[®] technology show an effective spinning ability for cellulose materials with a viscosity in the range of 400 - 500 mL.g⁻¹ [5]. However, viscose material typically has a very low viscosity, located below this range. Tables A.1 and A.2 in Appendix A detail the viscosity results of the used materials. The viscosity of the analysed virgin and post-consumer viscose materials fit in the range of 7 - 205 mL.g⁻¹.

Hence, there was a necessity to increase the viscosity of the viscose materials to get closer to the material properties of standard Ioncell[®] pulps. The most readily available solution for that purpose was to blend the viscose material with a high viscosity virgin cotton sample. To match the appropriate viscosity range, blending tests were conducted. As such, one virgin viscose sample (sample VV1) with a viscosity of 172±7 mL.g⁻¹ and one post-consumer viscose sample (sample V04) with a viscosity of 31±1 mL.g⁻¹ were blended with virgin cotton (sample VC) with a viscosity of 1667±19 mL.g⁻¹. Tables A.3 and A.4 in Appendix A show the measured data points and figure 4.1 displays the results.

The blending tests for both mixtures follow linear adjustments with very good correlations ($r^2 > 0.99$). Therefore, it was possible to accurately adjust the viscosity of the viscose material, either virgin or post-consumer to fit in the range for standard spinning.

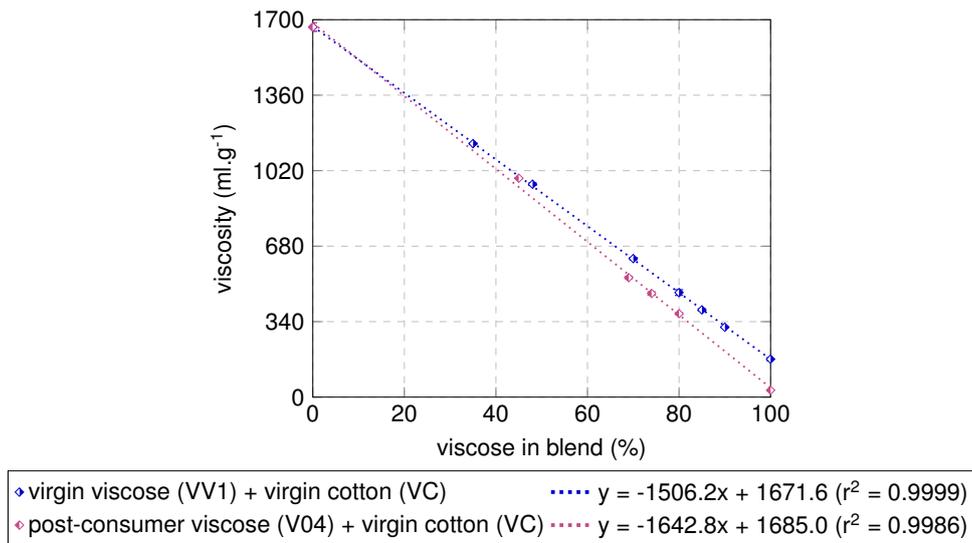


Figure 4.1: Viscosity data points of different mixtures of viscose - VV1 or V04 - with cotton - VC - and respective standard deviations. Linear adjustment of the data points of each mixture.

4.2 Dope production and analysis

Four distinct cellulose solutions (dopes) with a content of 13 % cellulose were produced.

Enocell Pure dope - Eno - was prepared as a control.

Virgin viscose dope - VV1 - was prepared to evaluate the limits of the Ioncell® technology by the use of a low viscosity material.

At last, dopes with two 80 % virgin viscose (VV1) + 20 % virgin cotton (VC) - Blend₁ and Blend₂ - were prepared. The ratio of 80 % VV1 to 20 % VC reveals a viscosity of $471 \pm 13 \text{ mL.g}^{-1}$ which is in the range for effective Ioncell® spinning (see figure 4.1).

In table 3.1 from chapter 3, further details of the prepared dopes are summarized.

4.2.1 Dissolution studies

The homogeneity of the prepared dope is an imperative characteristic to predict a consistent spinning operation and to ensure uniform cellulose distribution. Therefore, the dopes were analysed by microscope measurements to evaluate the time dependent dissolution behaviour of the cellulose materials in the IL. Table 4.1 describes the results from this analysis.

Table 4.1: Results of the dissolution (D) of the dopes of Enocell Pure - Eno -, virgin viscose - VV1 - and 80% virgin viscose (VV1) + 20% virgin cotton (VC) - Blend₁ and Blend₂ - at the stages of 30 min, 60 min and 90 min dissolution and after filtration with respective standard deviations (σ).

dope	30 min D		60 min D		90 min D		after filtration	
	D [%]	σ [%]	D [%]	σ [%]	D [%]	σ [%]	D [%]	σ [%]
Eno	96.977	3.162	98.115	1.932	99.881	0.153	99.974	0.042
VV1	99.997	0.004	99.999	0.001	99.853	0.135	99.999	0.002
Blend ₁	99.865	0.086	99.860	0.028	99.819	0.013	99.997	0.004
Blend ₂	98.498	0.542	99.889	0.030	99.300	0.557	97.599	2.499

Overall, all analysed dopes achieved an excellent dissolution.

The trend for the Eno dope shows an increase in dissolution and decrease in standard deviation according to the stage of measurement. Therefore, every stage of dissolution and further filtration contributes to a better homogenization of the final dope.

The VV1 dope shows no significant variation of the dissolution according to the stages of measurement. The significantly lower viscosity and consequently lower degree of polymerization of the cellulose chains of the viscose material might facilitate IL interactions, which can accelerate the dissolution process.

The remaining Blend₁ and Blend₂ dopes show similar results when taking into account the standard deviations. Contrarily to Eno dope, these blends show a less significant variation of dissolution according to the stages of measurement. However, a slightly increased variation of dissolution can be noticed compared to VV1 dope. The presence of a small percentage of high viscosity cotton material in the dope with high degree of polymerization might affect the IL interactions, which can slightly hinder dissolution.

4.2.2 Rheology

The rheological properties of the dopes are essential for the prediction of the spinnability. As such, rheological measurements were conducted to determine the visco-elastic properties. Table A.5 in Appendix A shows the analysis of the measurements and figure 4.2 displays two of the measurements in detail.

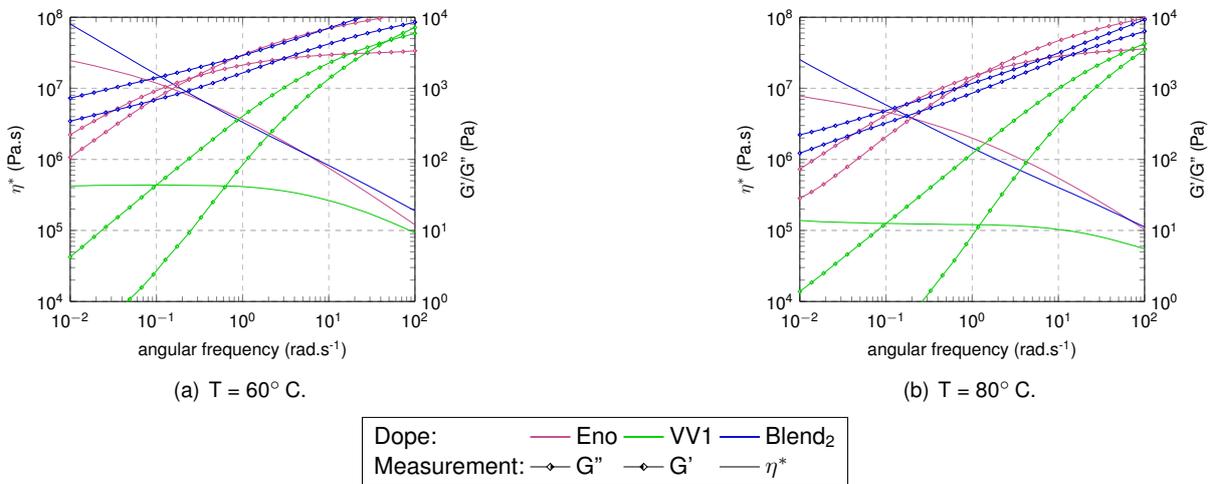


Figure 4.2: Rheological measurements of spinning dopes of Enocell Pure - Eno -, virgin viscose - VV1 - and 80% virgin viscose (VV1) + 20% virgin cotton (VC) - Blend₂ - at 60° C (a) and 80° C (b): complex viscosity (η^*), storage modulus (G') and loss modulus (G'').

For the best spinning performance, the zero-shear viscosity needs to be between 27000 - 40000 Pa.s, the COP should be at an angular frequency between 0.8 - 1.5 rad.s⁻¹ and at a dynamic moduli between 3000 - 6000 Pa [5, 6, 31]. These characteristic ranges predict an effective spinning of a dope with a viscosity in the range of 400 - 500 mL.g⁻¹ at an economically acceptable temperature (< 85° C) [5].

For the Eno dope, according to table A.5 in Appendix A, the zero-shear viscosity fits in the range at 60 - 75° C. The angular frequency at COP fits to the range at 70 - 85° C and the modulus at COP does not fit to the range at any temperature. From these observations, ideal spinning might be achieved at 70 - 75° C.

Regarding VV1 dope, according to table A.5 in Appendix A, no COP is detected above 65 °C. Moreover, the complex viscosity has very low values. Therefore, this rheological measurement did not give any useful information according to the spinning temperature. Probably the analysed temperature range was too high.

Due to a failure of the equipment during a measurement Blend₁, no rheological data was received for.

Lastly, Blend₂ was expected to have a similar behaviour as Eno dope. However, according to table A.5 in Appendix A, the rheological behaviour was very peculiar: the zero-shear viscosity has much higher values than Eno and no COP has been detected at any temperature. Hence, this rheological measurement did not give any reliable information which indicates the ideal spinning temperature.

Figure 4.2 displays the rheological data for two specific temperatures of the measurements. The expected behaviour of Eno dope is displayed by a COP between G' and G'' in both temperatures. In contrast, the VV1 dope displays much lower viscosity, as expected, and a COP between G' and G'' only at the lowest temperature. Finally, the Blend₂ dope displays a higher viscosity as intended, approaching the range of Eno dope. However, the dope behaviour is still very different with no COP at any temperature.

4.3 Fibre spinning and analysis

All of the prepared dopes were spun by the use of the mono filament dry-jet wet spinning system. The fibers were collected at different DRs according to the performance of each dope. Tables 4.2, 4.3, 4.4 and 4.5 summarize the spinning operation details of the trials.

Table 4.2: Spinning data of Enocell Pure dope - Eno: spinneret pressure ($P_{\text{spinneret}}$), spinneret temperature ($T_{\text{spinneret}}$), extrusion velocity (v_e), take-up velocity (v_{tu}) and draw ratio (DR).

$P_{\text{spinneret}}$ [bar]	$T_{\text{spinneret}}$ [° C]	v_e [m.min ⁻¹]	v_{tu} [m.min ⁻¹]	DR
nm	69.0	1.3	14.0	11
nm	79.0	1.3	15.3	12
nm	79.0	1.3	16.6	13

^{nm} no measurement.

Table 4.3: Spinning data of virgin viscose dope - VV1: spinneret pressure ($P_{\text{spinneret}}$), spinneret temperature ($T_{\text{spinneret}}$), extrusion velocity (v_e), take-up velocity (v_{tu}) and draw ratio (DR).

$P_{\text{spinneret}}$ [bar]	$T_{\text{spinneret}}$ [° C]	v_e [m.min ⁻¹]	v_{tu} [m.min ⁻¹]	DR
10.1 - 10.2	45.2 - 45.7	2.5	5.1	2
10.9 - 13.5	40.0 - 40.1	1.3	5.1	4
10.2 - 10.8	40.3 - 40.9	1.3	6.4	5

4.3.1 Dope spinnability

DR and tensile properties of the produced fibres are crucial for the determination of the dope spinnability. As such, figure A.1 and tables A.6 and A.7 in Appendix A display the values of all the tensile

Table 4.4: Spinning data of 80% virgin viscose (VV1) + 20% virgin cotton (VC) dope - Blend₁: spinneret pressure ($P_{\text{spinneret}}$), spinneret temperature ($T_{\text{spinneret}}$), extrusion velocity (v_e), take-up velocity (v_{tu}) and draw ratio (DR).

$P_{\text{spinneret}}$ [bar]	$T_{\text{spinneret}}$ [° C]	v_e [m.min ⁻¹]	v_{tu} [m.min ⁻¹]	DR
6.6 - 7.1	79.5 - 80.0	1.3	5.1	4
6.2 - 6.4	85.2 - 86.3	1.3	6.4	5
5.8 - 5.9	86.7 - 87.5	1.3	7.6	6

Table 4.5: Spinning data of 80% virgin viscose (VV1) + 20% virgin cotton (VC) dope - Blend₂: spinneret pressure ($P_{\text{spinneret}}$), spinneret temperature ($T_{\text{spinneret}}$), extrusion velocity (v_e), take-up velocity (v_{tu}) and draw ratio (DR).

$P_{\text{spinneret}}$ [bar]	$T_{\text{spinneret}}$ [° C]	v_e [m.min ⁻¹]	v_{tu} [m.min ⁻¹]	DR
9.2 - 9.3	76.9 - 77.7	1.3	5.1	4
7.4 - 7.9	84.0 - 86.0	1.3	6.4	5
7.2 - 7.3	86.1 - 86.6	1.3	7.6	6
7.1 - 7.2	87.3 - 87.6	1.3	8.9	7

properties. Meanwhile, figure 4.3 compares the values of three important properties - linear density, tenacity and elongation - at different DRs.

By stretching of the fibers in longitudinal direction, orientation of the cellulose chains occur. Until optimum DR, the cellulose chain becomes more aligned and consequently, elongation and especially tenacity values tend to increase. Above the optimum DR, further stretching weakens the cellulose chain. No alignment is possible anymore and therefore, tenacity and elongation values start to decrease. With increased DR, the fibre stretches more, producing a thinner filament with decreased linear density. The standard linear density for MMCF is around 1.3 dtex.

In case of the Eno fibres (figure 4.3 (a)), tenacity and elongation decrease at DRs 12 and 13. This demonstrates that the cellulose chain was already overstretched at those DRs, compromising fibre strength and elasticity. Furthermore, DR 11 already exhibits the intended linear density. The optimum DR for fibre spinning of this dope would be DR 11.

With regards to VV1 fibres (figure 4.3 (b)), DR 4 shows the highest tenacity, with slightly higher tenacity and elongation compared to DR 5. However, the difference between the values of DRs 4 and 5 fall within the error of the measurements and the linear density was the lowest at DR 5. The optimum DR for fibre spinning would be DR 5.

The Blend₁ fibres (figure 4.3 (c)) show very similar results of the tenacity and elongation for all DRs. The linear density presents the lowest value at DR 6. Therefore, the optimum DR for fibre spinning would be the highest, DR 6.

The Blend₂ fibres (figure 4.3 (d)) show similar tenacity and elongation for all DRs with the exception of DR 7, which has the highest tenacity. DR 7 also shows a linear density value close to 1.3 dtex. Accordingly, the optimum DR for fibre spinning would be DR 7.

Blend₁ and Blend₂ exhibit the same dope characteristics. Hence, the outcome was similar and the fibres of the highest DRs from both dopes demonstrated identical tenacity and elongation values. However, the linear density of Blend₁ displays higher values probably due to the lower DR.

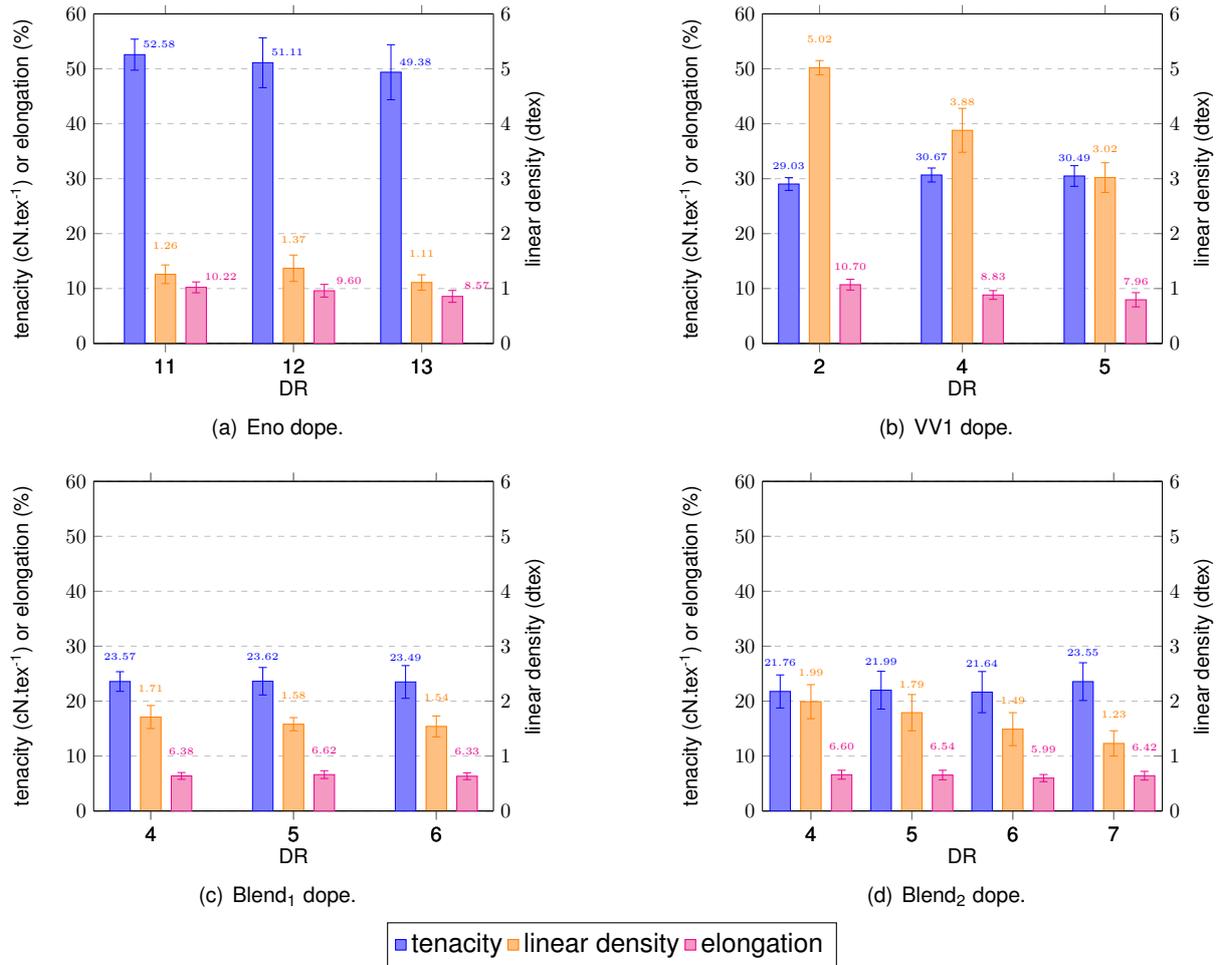


Figure 4.3: Fibre tenacity, linear density and elongation under dry conditions of all collected DRs (draw ratios) from Enocell Pure dope - Eno (a) -, virgin viscose dope - VV1 (b) - and 80% virgin viscose (VV1) + 20% virgin cotton (VC) dopes - Blend₁ (c) and Blend₂ (d).

The spinnability of a dope can be theoretically evaluated by the optimum DR achieved: for DR<2, non-spinnable dope; for 2<DR<8, dope with poor spinnability; for 8<DR<14, dope with good spinnability; for DR>14, dope with excellent spinnability. Accordingly, table 4.6 represents the conditions that allowed spinning of the optimum DRs and the evaluation of the dope spinnabilities. [31].

Table 4.6: Spinnability data of Enocell Pure dope - Eno -, virgin viscose dope - VV1 - and 80% virgin viscose (VV1) + 20% virgin cotton (VC) dope - Blend₁ and Blend₂: maximum draw ratio (DR), optimum DR, temperature ($T_{Opt DR}$), pressure ($P_{Opt DR}$) and qualitative considerations regarding spinnability (Spinnability_{Opt DR}).

	Maximum DR	Optimum DR	$T_{Opt DR}$ [°C]	$P_{Opt DR}$ [bar]	Spinnability _{Opt DR}
Eno	13	11	69	nm	good
VV1	5	5	40.3 - 40.9	10.2 - 10.8	poor
Blend ₁	6	6	86.7 - 87.5	5.8 - 5.9	poor
Blend ₂	7	7	87.3 - 87.6	7.1 - 7.2	poor

^{nm} no measurement.

4.3.2 Fibre characterization

Figure A.2 and tables A.8 and A.9 in Appendix A summarizes all measured properties of the optimum DRs. Meanwhile, figure 4.4 compares the most important measured fibre characteristics - tenacity, elongation, modulus of elasticity, linear density and total orientation - achieved at optimum DRs.

When fibres are immersed in water, swelling occurs. The swelling drives cellulose chains far from each other, which breaks the hydrogen bonds. Less bonds results in reduced strength and an increased elasticity of the fibres, which implies that less force is needed to deform the chains. This means lower tenacity, higher elongation and lower modulus of elasticity values, respectively. Figure 4.4 (a), (b) and (c) confirms this statement: the wet measurements show lower tenacity, higher elongation and lower modulus of elasticity values than the dry measurements.

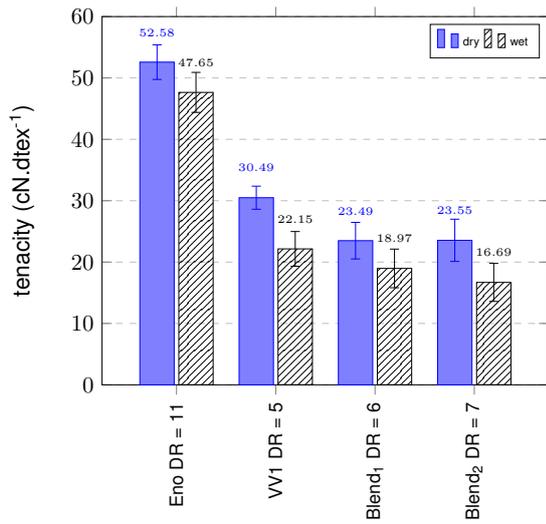
The extensional forces applied on the filaments upon spinning cause the cellulose polymer to align along the fibre axis, thus increasing the total orientation. Figure 4.4 (e) shows that the fibres of Eno dope achieved the highest total orientation, as well as the highest DR (DR 11). Furthermore, the fibres from VV1, Blend₁ and Blend₂ dopes achieved similar total orientation while exhibiting similar DRs. So, total orientation increases with DR.

Moreover, the increase in the orientation of the cellulose molecules along the chain axis accounts for better fibre tensile properties. In contrast, fibres with maximum orientation cannot be stretched any further and break, which affects negatively the tensile properties. Figure 4.4 confirms that the Eno dope fibres, with the highest total orientation, display the highest value of tenacity, elongation and modulus of elasticity; accordingly, in the VV1, Blend₁ and Blend₂ dope fibres, the tensile properties decreased values is caused by a low orientation of the cellulose chains.

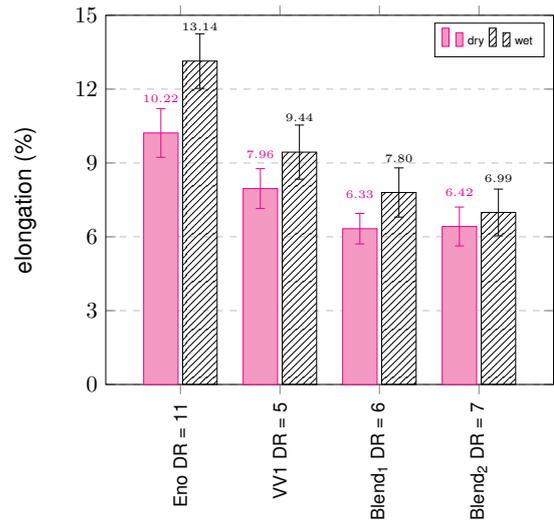
In figure 4.4 (a) and (b), VV1 dope fibres show slightly higher tenacity and elongation compared to the Blend₁ and Blend₂. This means that although the average chain length of the Blend fits the optimum range, the existence of two different cellulose chains lengths affects negatively the final properties of the fibres.

Furthermore, in figure 4.4 (d), VV1 fibres show the most discrepant linear density value, far from the intended value of 1.3 dtex. The low chain length of the VV1 dope raw material changes the alignment of the fibril structure.

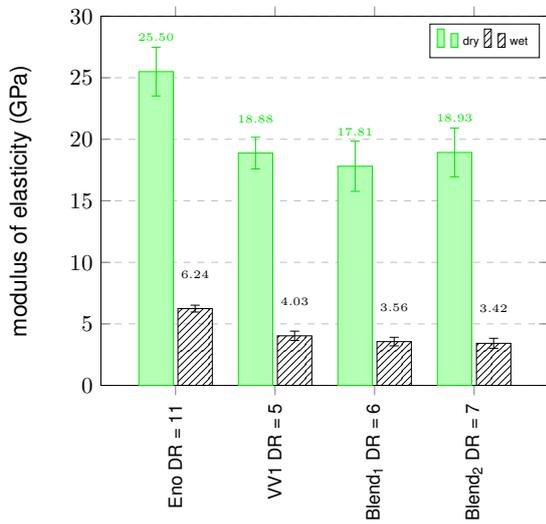
Blend₁ and Blend₂ show the same dope characteristics and overall, these two blends display similar fibre characteristics.



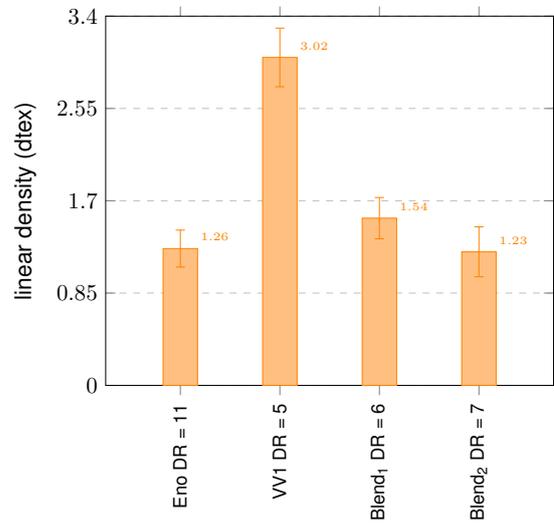
(a) Tenacity.



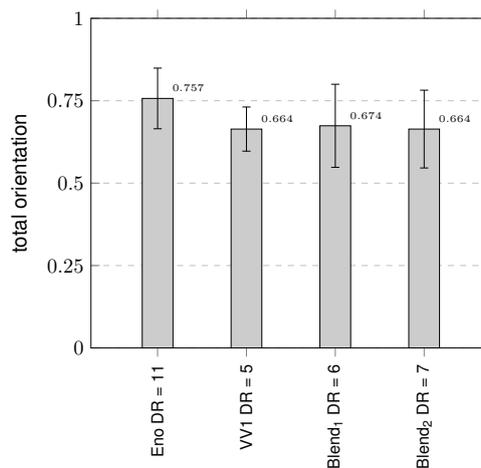
(b) Elongation.



(c) Modulus of elasticity.



(d) Linear density.



(e) Total orientation.

Figure 4.4: Fibre characterization of the optimum DRs (draw ratio) from Enocell Pure dope - Eno -, virgin viscose dope - VV1 - and 80% virgin viscose (VV1) + 20% virgin cotton (VC) dopes - Blend₁ and Blend₂: tenacity (a), elongation (b) and modulus of elasticity (c) under dry and wet conditions; linear density (d) and total orientation (e).

Chapter 5

Conclusions

This thesis work is parted into two main objectives. The first objective was to assess if pre- and post-consumer viscose waste could be utilized to produce fibres with the Ioncell® process. This objective will be addressed in the achievements (see section 5.1). The second objective was the removal of dyes from post-consumer viscose textiles in an environmentally friendly manner without compromising the fibres. Due to the COVID-19 situation, this objective was not experimentally fulfilled and will be discussed in the future work proposal (see section 5.2).

5.1 Achievements

The upcycling (recycling) of waste textiles is a topic of great interest due to the negative environmental impact of textile production and consumption. In that context, this work studied the utilization of pre- and post-consumer viscose waste textiles as starting materials for the production of MMCF using the Ioncell® process. Therefore, a comprehensive assessment of the dissolution behaviour and viscoelasticity of the resulting spinning dopes and the structural and mechanical properties of the spun fibers was performed.

Low viscosity viscose was blended with high viscosity cotton. Viscosity tests were performed to evaluate the effect of different quantities of cotton. A ratio of 80% viscose and 20% cotton fulfilled the requirements for posterior spinning operations regarding to the viscosity properties. Additionally, the results showed linear adjustments with correlation coefficients of $r^2 > 0.99$.

The dissolution behaviour of the starting materials Eno, VV1, Blend₁ and Blend₂ in [DBNH][OAc] was determined, dopes generated and the rheological behavior analyzed. For each dope, a dissolution above 99% was established. Regarding the rheology, apart from Eno, the viscoelastic property values were outside the usual spinning range.

The produced dopes were spun and subsequently the spinnability and the properties of the resulting fibres were analysed. Eno dope achieved good spinnability. VV1, Blend₁ and Blend₂ dopes achieved only poor theoretical spinnability.

Eno fibres produced at DR 11 reached a linear density, tenacity, elongation at break, modulus of elasticity and total orientation of 1.26 dtex, 52.58 cN.dtex⁻¹, 10.22 %, 25.50 GPa and 0.757, respectively.

VV1 fibres produced at DR 5 reached a linear density, tenacity, elongation at break, modulus of elasticity and total orientation of 3.02 dtex, 30.49 cN.dtex⁻¹, 7.96 %, 18.88 GPa and 0.664, respectively. Blend₁ and Blend₂ fibres produced at DRs 6 and 7 reached a linear density, tenacity, elongation at break, modulus of elasticity and total orientation of 1.54 and 1.23 dtex, 23.49 and 23.55 cN.dtex⁻¹, 6.33 and 6.42 %, 17.81 and 18.93 GPa and 0.674 and 0.664, respectively. So, fibres produced from the VV1, Blend₁ and Blend₂ dopes showed poor tensile properties and total orientation in comparison to standard Eno fibres.

Despite the viscoelastic values, the VV1, Blend₁ and Blend₂ dopes were spinnable and fibres were produced. Therefore, the first objective of this work was fulfilled. The outcome of these investigations are a good starting point for further studies to recycle viscose textile waste by Ioncell®.

5.2 Future work proposal

The achievements of this work reveal the potential of the Ioncell® technology for the recycling of viscose waste.

The VV1, Blend₁ and Blend₂ dopes obtained in this work were spinnable and fibres were produced. Despite not matching the quality displayed by the Eno fibres, viscose still has the potential to be used as a raw material. The properties may be improved by blending the low viscosity viscose with a material other than cotton.

The cellulose concentration in every prepared dope was 13%. In general, an increase of the cellulose concentration is associated with an increase of the pre-orientation of the cellulose chains; in turn, this may result in better fibre tenacities (dry and wet) and modulus of elasticity. Therefore, using a higher cellulose concentration in the VV1, Blend₁ and Blend₂ dopes could lead to better outcomes in the resulting fibre characteristics.

The dissolution time for every prepared dope was 90 min. Dissolution was found to occur more rapidly in VV1, Blend₁ and Blend₂ dopes than in the Eno dope due to the presence of short chain cellulose material which facilitates solvent interactions. As such, the dissolution time could be reduced and therefore optimized for the dopes in which viscose is used as starting material.

When considering the use of viscose waste as raw material for the production of new fibres, it is important to have in focus feasible ways to manage colourants. In section 2.6, an overview on colourants used in MMCFs and their interactions with fibres was provided. In section 2.7, a summary of methods for decolourization that meet CE environmental standards was presented. These theoretical sections provide the foundation necessary for future experimental studies that aim to fulfill the second objective of this work: the removal of colourants by the use of different decolourization agents.

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Appendix A

Appendix

Table A.1: Characteristics of the samples of virgin cotton textile (VC) and virgin viscose fibre (VV1 and VV2): dry matter content (DMC), ash content (AC), viscosity ($[\eta]$) and respective standard deviation (σ).

sample		DMC [%]	σ [%]	AC [%]	σ [%]	$[\eta]$ [mL.g ⁻¹]	σ [mL.g ⁻¹]
VC		96.36	0.07	0.45	0.07	1667	19
VV1	virgin viscose fibre	91.85	0.27	0.40	0.06	172	7
VV2	virgin viscose fibre	93.45	0.02	0.30	0.04	165	2

Table A.2: Characteristics of the samples of post-consumer viscose (V1 to V15): sample image, dry matter content (DMC), ash content (AC), viscosity ($[\eta]$) and respective standard deviation (σ).

sample		DMC [%]	σ [%]	AC [%]	σ [%]	$[\eta]$ [mL.g ⁻¹]	σ [mL.g ⁻¹]
V01		93.21	0.22	1.75	0.10	128	2
V02		92.84	0.20	0.42	0.01	174	5
V03		93.54	0.09	0.28	0.01	8	0
V04		92.95	0.10	2.59	0.05	31	1
V05		92.96	0.10	1.12	0.00	150	2
V06		93.08	0.03	0.54	0.00	7	1
V07		93.15	0.09	0.28	0.01	159	5
V08		92.22	0.16	0.78	0.01	172	4
V09		92.86	0.14	0.48	0.02	205	5
V10		93.24	0.16	0.68	0.01	27	5
V11		93.43	0.14	0.71	0.04	101	1
V12		93.48	0.16	0.26	0.02	12	2
V13		93.31	0.12	0.72	0.07	148	2
V14		93.62	0.08	1.58	0.06	166	5
V15		92.66	0.19	0.43	0.01	169	3

Table A.3: Viscosity (μ) data points of different percentages of mixture of virgin viscose - VV1 - with virgin cotton - VC - and respective standard deviation (σ).

VV1 in blend	0%	35%	48%	70%	80%	85%	90%	100%
$[\mu]$ [mL.g ⁻¹]	1667	1142	959	624	471	393	315	171
σ [mL.g ⁻¹]	19	4	6	5	13	5	2	7

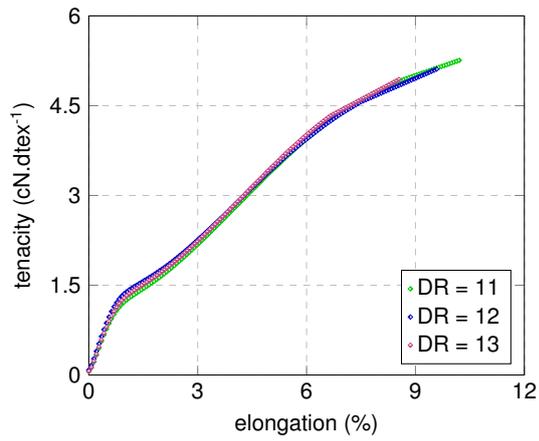
Table A.4: Viscosity (μ) data points of different percentages of mixture of post-consumer viscose - V04 - with virgin cotton - VC - and respective standard deviation (σ).

V04 in blend	0%	45%	69%	74%	80%	100%
$[\mu]$ [mL.g ⁻¹]	1667	986	538	467	376	31
σ [mL.g ⁻¹]	19	3	5	8	4	1

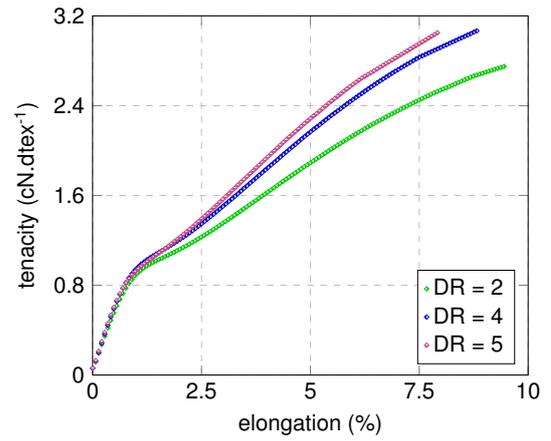
Table A.5: Rheology data analysis results at all measured temperatures of Eno cell Pure dope - Eno -, virgin viscose dope - VV1 - and 80% virgin viscose (VV1) + 20% virgin cotton (VC) - Blend₂: zero-shear viscosity (η_0^*), angular frequency at crossover point (ω_{COP}) and modulus at crossover point (G_{COP}).

T [°C]	Eno		VV1		Blend ₂	
	η_0^* [Pa.s]	ω_{COP} [s ⁻¹]	G_{COP} [Pa]	η_0^* [Pa.s]	ω_{COP} [s ⁻¹]	G_{COP} [Pa]
50	nm	nm	nm	nm	nm	nm
55	nm	nm	nm	nm	nm	nm
60	50323	0.26786	1417.5	433.95	47.781	4624.9
65	37656	0.45263	1523.9	286.45	76.826	4961.3
70	26250	0.68021	1566.2	211.10	-	-
75	18519	0.98480	1616.5	162.80	-	-
80	13191	1.37110	1655.9	129.96	-	-
85	9865	1.83380	1678.3	106.01	-	-
90	7202	2.43720	1707.7	87.09	-	-
95	5630	3.34570	1738.5	69.79	-	-
100	4577	4.66280	1776.2	54.44	-	-

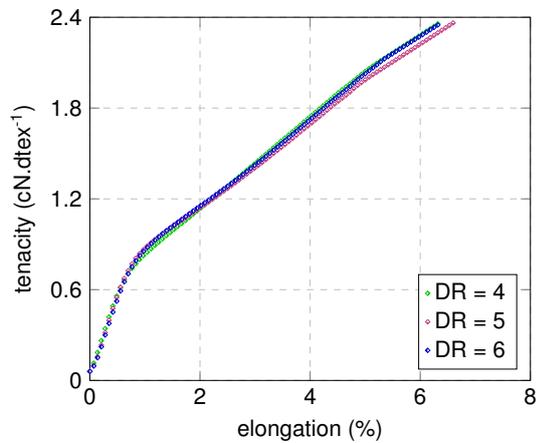
nm no measurement. * no crossover point (COP).



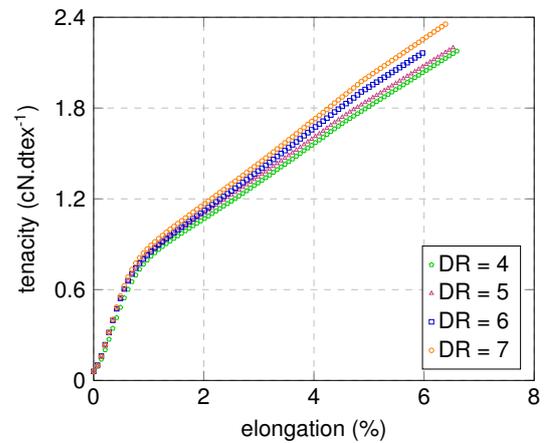
(a) En4 dope.



(b) VV1 dope.



(c) Blend₁ dope.



(d) Blend₂ dope.

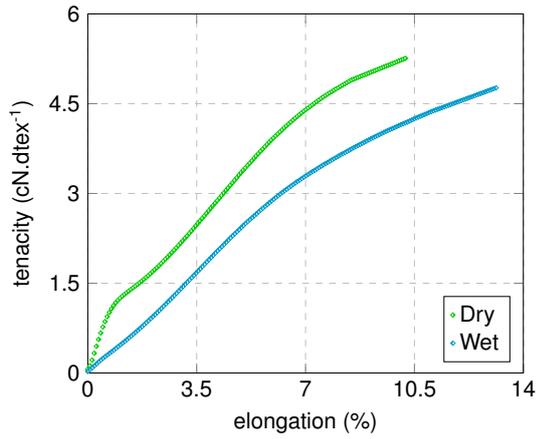
Figure A.1: Fibre testing results under dry conditions of all collected draw ratios (DRs) from Enocell 4 dope - En4 (a) -, virgin viscose dope - VV1 (b) - and 80% virgin viscose (VV1) + 20% virgin cotton (VC) dope - Blend₁ (c) and Blend₂ (d).

Table A.6: Tensile properties under dry conditions and respective standard deviation (σ) of all the collected draw ratios (DRs) of Enozell Pure fibres - Eno - and virgin viscose fibres - VV1.

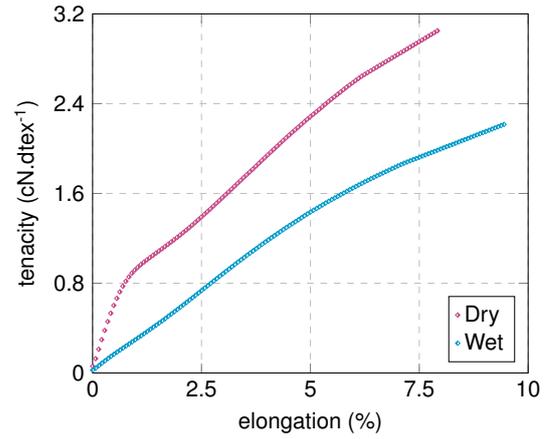
fibres	DR=11		Eno DR=12		DR=13		VV1 DR=4		DR=5	
	linear density [dtex]	1.26	1.37	1.11	5.02	3.88	3.02	3.88	3.02	3.02
σ [dtex]	0.17	0.24	0.14	0.13	0.40	0.27	0.13	0.40	0.27	0.27
diameter [μm]	10.32	10.73	9.68	20.64	18.15	16.01	18.15	16.01	16.01	0.72
σ [μm]	0.72	0.93	0.6	0.27	0.94	0.72	0.94	0.72	0.72	0.72
tenacity [cN.tex ⁻¹]	52.58	41.11	49.38	29.03	30.67	30.49	30.67	30.49	30.49	1.88
σ [cN.tex ⁻¹]	2.82	4.54	5.01	1.16	1.27	1.88	1.27	1.88	1.88	1.88
elongation [%]	10.22	9.60	8.57	10.7	8.83	7.96	8.83	7.96	7.96	0.81
σ [%]	0.99	1.16	1.08	0.98	0.80	0.81	0.80	0.81	0.81	0.81
modulus of elasticity [GPa]	25.50	27.54	26.38	16.69	18.34	18.88	18.34	18.88	18.88	0.72
σ [GPa]	1.98	0.78	0.89	0.84	0.79	0.72	0.79	0.72	0.72	0.72
strain at yield point [%]	0.86	0.78	0.89	0.84	0.79	0.72	0.79	0.72	0.72	0.03
σ [%]	0.18	0.08	0.24	0.14	0.13	0.03	0.13	0.03	0.03	0.03
stress at yield point [MPa]	140.86	164.92	150.38	109.17	101.62	105.95	101.62	105.95	105.95	7.6
σ [MPa]	16.23	23.43	28.07	15.72	13.58	7.6	13.58	7.6	7.6	7.6
modulus of toughness [MPa]	50.72	46.61	39.00	31.13	25.84	22.71	25.84	22.71	22.71	3.60
σ [MPa]	6.76	9.16	8.46	3.88	3.44	3.60	3.44	3.60	3.60	3.60
modulus of resilience [MPa]	0.47	0.60	0.55	0.44	0.42	0.36	0.42	0.36	0.36	0.04
σ [MPa]	0.11	0.21	0.24	0.15	0.13	0.04	0.13	0.04	0.04	0.04

Table A.7: Tensile properties under dry conditions and respective standard deviation (σ) of all the collected draw ratios (DRs) of 80% virgin viscose (VV1) + 20% virgin cotton (VC) fibres - Blend₁ and Blend₂.

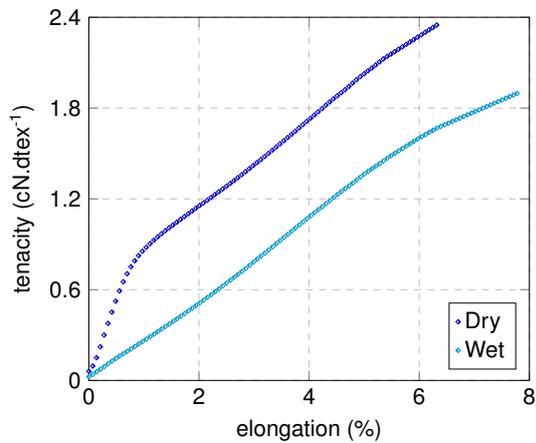
fibres	Blend ₁			Blend ₂			
	DR=4	DR=5	DR=6	DR=4	DR=5	DR=6	DR=7
linear density [dtex]	1.71	1.58	1.54	1.99	1.79	1.49	1.23
σ [dtex]	0.21	0.12	0.19	0.31	0.33	0.30	0.23
diameter [μm]	12.03	11.56	11.42	12.95	12.27	11.18	10.18
σ [μm]	0.74	0.44	0.71	1.01	1.12	1.15	0.98
tenacity [cN.tex ⁻¹]	23.57	23.62	23.49	21.76	21.99	21.64	23.55
σ [cN.tex ⁻¹]	1.79	2.50	2.98	3.01	3.44	3.75	3.44
elongation [%]	6.38	6.62	6.33	6.60	6.54	5.99	6.42
σ [%]	0.62	0.71	0.62	0.81	0.87	0.65	0.79
modulus of elasticity [GPa]	17.34	18.08	17.81	16.19	17.58	17.79	18.93
σ [GPa]	1.49	1.61	2.04	1.99	2.31	2.45	1.98
strain at yield point [%]	1.01	0.76	0.82	0.87	0.78	0.75	0.87
σ [%]	0.08	0.10	0.11	0.15	0.12	0.13	0.17
stress at yield point [MPa]	93.94	102.44	100.96	96.46	101.86	91.02	101.11
σ [MPa]	8.21	14.80	24.79	14.73	20.28	17.09	13.59
modulus of toughness [MPa]	14.34	15.04	14.18	13.87	14.08	12.65	14.66
σ [MPa]	1.72	2.76	2.57	3.12	3.46	3.20	3.46
modulus of resilience [MPa]	0.31	0.36	0.37	0.36	0.37	0.30	0.33
σ [MPa]	0.06	0.12	0.16	0.12	0.14	0.11	0.07



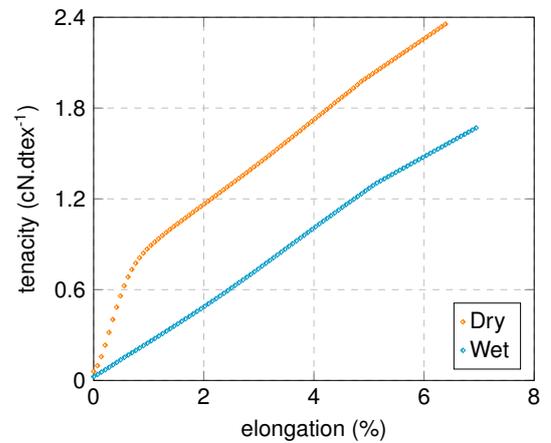
(a) DR = 11 of En4 dope.



(b) DR = 5 of VV1 dope.



(c) DR = 6 of Blend₁ dope.



(d) DR = 7 of Blend₂ dope.

Figure A.2: Fibre testing results under dry and wet conditions of the optimum draw ratio (DR) from Enocell 4 dope - En4 (a) -, virgin viscose dope - VV1 (b) - and 80% virgin viscose (VV1) + 20% virgin cotton (VC) dope - Blend₁ (c) and Blend₂ (d).

Table A.8: Characterization of the optimum draw ratio (DR) of Enocell Pure fibres - Eno -, virgin viscose fibres - VV1 - and 80% virgin viscose (VV1) + 20% virgin cotton (VC) fibres - Blend₁ and Blend₂: comparison of fibre properties data of dry and wet measurements and respective standard deviation (σ).

fibres	Eno DR = 11		VV1 DR = 5		Blend ₁ DR = 6		Blend ₂ DR = 7	
	dry	wet	dry	wet	dry	wet	dry	wet
linear density [dtex]	1.26	1.27	3.02	2.94	1.54	1.38	1.23	1.33
σ [dtex]	0.17	0.18	0.27	0.33	0.19	0.18	0.23	0.26
diameter [μm]	10.32	10.37	16.01	15.76	11.42	10.81	10.18	10.56
σ [μm]	0.72	0.74	0.72	0.89	0.71	0.70	0.98	1.01
tenacity [cN.tex ⁻¹]	52.58	47.65	30.49	22.15	23.49	18.97	23.55	16.69
σ [cN.tex ⁻¹]	2.82	3.26	1.88	2.83	2.98	3.15	3.44	3.10
tenacity [MPa]	788.70	714.75	457.35	332.25	352.35	284.55	353.25	250.35
σ [MPa]	42.30	48.90	28.20	42.45	44.70	47.25	51.6	46.50
tenacity _{wet} /tenacity _{dry}	0.91		0.73		0.81		0.71	
elongation [%]	10.22	13.14	7.96	9.44	6.33	7.80	6.42	6.99
σ [%]	0.99	1.11	0.81	1.10	0.62	1.00	0.79	0.95
modulus of elasticity [GPa]	25.50	6.24	18.88	4.03	17.81	3.56	18.93	3.42
σ [GPa]	1.98	0.28	1.29	0.38	2.04	0.35	1.98	0.41
strain at yield point [%]	0.86	2.35	0.72	2.27	0.82	2.31	0.87	2.27
σ [%]	0.18	0.15	0.03	0.17	0.11	0.18	0.17	0.26
stress at yield point [MPa]	140.86	131.35	105.95	86.36	100.96	73.88	101.11	70.24
σ [MPa]	16.23	12.04	7.60	11.74	24.79	11.39	13.59	15.77
modulus of toughness [MPa]	50.72	56.56	22.71	18.45	14.18	12.57	14.66	9.64
σ [MPa]	6.76	8.60	3.60	3.94	2.57	3.84	3.46	3.06
modulus of resilience [MPa]	0.47	1.32	0.36	0.87	0.37	0.74	0.33	0.73
σ [MPa]	0.11	0.20	0.04	0.18	0.16	0.17	0.07	0.26

Table A.9: Characterization of the optimum draw ratio (DR) of Enocell Pure fibres - Eno -, virgin viscose fibres - VV1 - and 80% virgin viscose (VV1) + 20% virgin cotton (VC) fibres - Blend₁ and Blend₂: birefringence (Δ_n), total orientation (f_n) and respective standard deviation (σ).

fibres	Eno DR = 11	VV1 DR = 5	Blend₁ DR = 6	Blend₂ DR = 7
Δ_n	0.0469	0.0400	0.0418	0.0411
σ	0.0057	0.0041	0.0078	0.0073
f_n	0.757	0.644	0.674	0.664
σ	0.092	0.067	0.126	0.118