

# Development of Cellulose-Based Nonwovens

Treatment Methods for Solution Blown Nonwovens from  
Cellulose Dissolved in EMIMAc

Master's thesis in Materials Chemistry

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Cover: Scanning electron microscopy image of sample S22 (Neutral®, isopropanol, vacuum suctioning) at x100 magnification.

## Abstract

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The purpose of this project was to investigate treatment methods for bio-based nonwovens produced via solution blowing of cellulose dissolved in 1-Ethyl-3-methylimidazolium acetate (EMIMAc). The produced nonwovens should have desirable characteristics, such as a high level of softness and flexibility. In order to achieve the right properties, different treatment methods used after the solution blowing step were explored. A 3<sup>3</sup>-factorial design was applied in which three parameters corresponding to a first washing bath, a second washing bath, and a drying step were varied. The first washing bath tested the effect of surfactants at three levels, the second washing bath tested three different solvents, and the drying step tested three different drying methods. The 28 samples produced underwent several evaluations, the most prominent being a subjective fabric hand evaluation in which the hand feel of the samples was investigated with the help of a test panel. Other methods used for evaluation were thickness measurements, bending length measurements, air permeability measurements, light microscopy, and scanning electron microscopy (SEM).

The results showed that the drying method with the largest impact on the examined properties was a method based on vacuum suctioning. This method created more fluffy and bendable materials with a more textile-like feel compared to the other methods. It was also shown that it was, in general, more beneficial to use a surfactant than just water during washing, and that the best surfactant for the task of creating more textile-like cellulosic nonwovens was the cationic fabric softener Neutral®. When it comes to washing the samples in different solvents, it was clear that isopropanol or acetone was to be preferred over water. In some of the pictures of the eight samples evaluated with SEM, interesting fibre structures were shown. Several of the samples dried through vacuum suctioning displayed curly fibres, a phenomenon which was more abundant in the samples that had been treated with isopropanol or acetone. These samples were also some of the highest graded in the hand evaluation, indicating a possible connection between curly fibres and textile-like properties.

A few additional samples testing the effects of ethanol in the second washing bath, the effect of drying directly from a surfactant, or the effect of freeze-drying were also created. These served as trial-tests for further development of treatment methods for cellulosic nonwovens produced through solution blowing.

Keywords: solution blowing, solution blow spinning, EMIMAc, cellulose nonwovens.



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# 1 Introduction

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Sustainability is an important topic in today's society, and renewable bio-based products are of high interest in the quest for more environmentally sustainable materials [1]. One source for renewable materials is the Swedish forest which can provide bio-based materials such as cellulose and lignin. The raw materials from the forest industry can be used to create renewable materials that otherwise would be produced from chemicals from a depleting source [1]. One such product group is nonwovens, most of which are currently made of fossil-based polymers [2]. If cellulose is used as a raw material instead, a potentially more environmentally sustainable nonwoven material can be created which might also have the benefit of being biodegradable. Switching from fossil-based to renewable bio-based materials is one of the keys needed to create a better environment and to promote a more environmentally sustainable future [1]. Another key is to create materials that can easily be recycled, reused, or repurposed in a circular economy [3]. This is challenging for nonwoven products, but a problem which has to be solved in order to make the nonwoven industry more sustainable.

Nonwoven materials consist of entangled fibres or filaments bonded into web or sheet structures [4]. They can be used in a wide range of different products such as diapers, wet wipes, isolation materials, filters, and geotextiles due to the variety of properties achievable through alternation of fibre type, fibre length, and production method [5]. In the year 2019, there was an increase with 4.2 % in the production of nonwovens from the previous year, resulting in 18.4 million tons of nonwovens being produced [6]. The demand for functionalised nonwovens is predicted to increase even further in the future due to high interest in competitive, multi-functional, and flexible materials [2]. Examples of possible functionalised nonwovens include antibacterial or electrically conductive materials [4]. One advantage with nonwoven materials is that they do not require the fibres to be transformed into yarns before production of the material, making low cost production through single step processing possible. Since it is currently of great interest to find new areas in which cellulose can be used, research on cellulose based nonwovens is of high importance and there exists a potential for these materials to become a new big cellulose based product group [2].

Cellulose has a long history of being used in fibre manufacturing, with one example being the cellulose-based fibre viscose which has been of high importance for the textile industry for a long time [4]. Fibres from cellulose or cellulose derivatives can be used to create nonwovens through several different techniques such as dry-laying, wet-laying, and polymer-laying [5]. Solution blowing, which is a type of polymer-laying technique, will be used in this project. Methods based on research conducted by Jedvert et.al [2] will be used as a foundation in regard to cellulose dissolution and solution blowing parameters. The cellulose used in this project will be directly dissolved in an ionic liquid, thus avoiding derivatisation steps which could make the process less environmentally sustainable. The produced nonwoven material should have certain properties depending on the intended application of the material. How to treat the cellulose based nonwoven to get textile-like properties will be investigated in this master thesis project.

## **1.2 Purpose and Aim**

The purpose of this project is to investigate treatment methods for bio-based nonwovens from cellulose produced via solution blowing. The current problem is that this type of material is too stiff and cardboard-like, making the areas in which they can be used limited. The produced nonwovens should instead have desirable characteristics, such as a high level of softness and flexibility. An experimental design will be used to direct the properties of the material through variation of how the material is washed and dried. The effect of surfactants will be included in the experimental matrix as well. The aim of the project is to find a treatment method for cellulosic nonwovens produced through solution blowing which can generate materials with improved properties regarding, primarily, softness and flexibility. However, this must not come at too great of a loss of certain mechanical properties such as strength and resilience. Preferably, the materials should have more textile-like properties in order to fit potential future applications such as for example wound care.

### **1.2.1 Limitations**

The methods for producing nonwoven materials will only be investigated at a laboratory scale. The cellulose source is a dissolving grade pulp (Buckeye, Georgia-Pacific), which will be dissolved in the ionic liquid 1-Ethyl-3-methylimidazolium acetate (EMIMAc). No other types of solvents will be tested. The only media used for coagulation will be water due to safety precautions. All of the solution blowing parameters such as extrusion rate, collection time and air heat will be set, and the analysis is thus limited to the after-treatment steps introduced. It will only be possible to examine a few samples with scanning electron microscopy due to limitations regarding time and availability.

## **1.3 Specification of Issue Under Investigation**

The project aims to answer the following research questions in order to produce more textile like samples of nonwovens from EMIMAc-dissolved cellulose through solution blowing.

- How can the nonwoven material be treated in order to get the right properties and how do the different steps in the process influence the properties?
  - Surfactants: how does the material react to surfactants and what type of surfactant is the most effective?
  - Washing solution: how does the material react to different washing solutions and what type has the most effect?
  - Drying: in what way can the material be dried and how does the material react to different drying techniques?
- How can the desirable properties be evaluated?

A 3<sup>3</sup>-factorial design will be applied in which the three parameters mentioned above will be varied in three different ways. The experimental design will be used to evaluate the results generated from the testing of the materials to see if there are any significant differences between the sample treatments tested in the experimental matrix.

## 2 Theoretical Background

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A literature study has been conducted in order to gain understanding about the areas the project covers and to find support for the decisions made regarding the materials used in the project. The findings of this literature study are reported in this section of the report along with the basic knowledge required to understand the materials and techniques used within the project.

### 2.1 Nonwoven Materials

As the name suggests, nonwoven materials are not woven or knitted, but rather consists of natural or man-made fibres put together by a chemical or mechanical process resulting in a material intrinsically lacking an organised geometrical structure [5], see Figure 1 for an example. According to ISO standard 9092, a nonwoven material is defined as an “engineered fibrous assembly, primarily planar, which has been given a designed level of structural integrity by physical and/or chemical means, excluding weaving, knitting or papermaking” [7]. Fibre length and fibre type are important factors influencing the properties of the nonwoven material [5]. Properties that a nonwoven can have include high absorbency, flame resistance, and water resistance, while also being light-weight. The application decides what properties the nonwoven should be designed to have and the large amount of possibilities make nonwovens popular within areas such as clothing, hygiene, packaging, and filtration [5].



Figure 1: An example of a cellulose-based nonwoven material produced with solution blowing.

There are several types of processes for manufacturing of nonwovens. The three main categories are wet-laying, dry-laying, and polymer-laying, the last of which includes techniques such as melt-blowing and electrospinning [5]. The drylaid technique stems in large part from the textile industry and constitutes the largest group of nonwovens. In this technique, the fibres are processed in a dry state before the fibres are bonded by a thermal, chemical, or mechanical method [8]. The wetlaid technique was developed from the paper industry and the nonwovens produced from this technique are paper-like, with the difference from paper being the amount of synthetic fibres used [9]. In this technique, short fibres are suspended in a liquid which is later drained causing the fibres to form a web [9]. The polymer-laid techniques are based on polymer extrusion methods derived to fit fibre processing. There are several different methods of polymer-laid manufacturing, but in general it is a process in which a polymeric material is extruded through a spinneret [8]. Continuous filaments are formed and stretched before falling

onto a collector surface, creating a random web structure [8]. A method from the polymer-laid category called solution blowing will be used in this project to produce nonwovens of cellulose.

Most of the nonwovens produced today are made of man-made fibres which can be sorted into three categories [5]:

- synthetic polymer-generated fibres,
- natural polymer-generated fibres,
- fibres generated from inorganic materials.

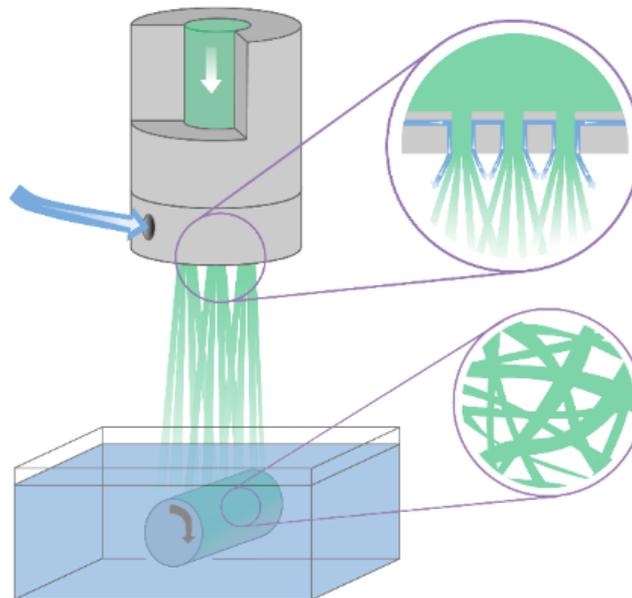
Some popular fibres used for the manufacturing of nonwovens are polypropylene, polyester, and polyamide [8]. Regarding natural polymers, cellulose is one of the most commonly used [5]. From cellulose, continuous fibres for textile applications such as for example viscose rayon and Lyocell can be produced either through derivatisation of the cellulose or by dissolution in an appropriate solvent [4]. This project investigates how cellulose dissolved in an ionic liquid can be used to create nonwovens with textile like properties through solution blowing.

## **2.2 Solution Blowing**

One innovative method for producing fibres in the micro- and nano range is solution blowing [10]. In this method, which is displayed in Figure 2, a polymer solution is forced through a nozzle while pressurised gas is supplied in a concentric manner around the capillary tips of the nozzle [10]. The gas, which often is air, is fast-moving and stretches the polymer solution into fibres before they fall into the coagulation bath and onto a collector surface. The stretching produces thin fibres in the micro- and nanometre-range [10]. Volatile solvents are evaporated in the gas stream, leaving a structure consisting mostly of the polymer behind [11]. However, for cellulose dissolved in an ionic liquid, the residual solvent is washed away both during the coagulation step and during the washing steps after the spinning is completed. Upon exiting the spinneret, the fibre structure begins to coagulate, forming a nonwoven structure which is collected on a drum or a conveyor belt in a coagulation bath where the cellulose filaments coagulate [11]. This bath consists of a liquid acting as a solvent for ionic liquids but as a non-solvent for the cellulose structure. The nonwoven material can be further processed, e.g. in washing steps where surfactants are added.

The process of solution blowing is similar to that of melt blowing, with the main difference being that in solution blowing a polymer solution is used instead of a polymer melt [4]. Consequently, solution blowing is more appropriate for polymers that do not melt, such as for example cellulose. Both methods are suitable for one-step spinning of webs made of fibres [10]. A similar method is electrospinning, which can produce even thinner fibres. However, only low concentrations of cellulose can be used in this technique [4] and only a single jet is commonly used [2]. This generates a low speed of production which is problematic when it comes to upscaling of the method. Making larger amounts of nonwovens using electrospinning is thus costly which pushes the quest for cheaper alternatives forward. Solution blowing can more easily be upscaled since the amount of jets can be increased by using a larger spinneret, making it possible to produce larger pieces of material more quickly [2]. Additionally, a higher

concentration of cellulose in the spinning solution can be used in solution blowing, further increasing the speed of production.



**Figure 2: The solution blowing process.** The polymer solution, depicted in green, is extruded through the thin capillaries which are concentrically surrounded by the high-speed gas (blue arrows) stretching the fibres. Upon collection in the coagulation bath, a nonwoven material is created.

## 2.3 Properties of Cellulose

Nonwoven materials can be made of several different kinds of fibres [5]. In this project, the focus will be on cellulose which is a fibre that can be found in abundance in nature. It is the main constituent of plant cell walls, contributing with rigidity and strength to the plant [4]. Cellulose consists of D-glucose monomers linked by  $\beta$ -1,4-glycosidic bonds (Figure 3) forming a complex and strong molecule with a linear and highly crystalline structure with a slightly negative charge [12]. Intra- and intermolecular hydrogen bonding forms a network which, along with the  $\beta$ -1,4-glycosidic bond, makes the molecule very stable, giving it its crystalline structure [12]. There are also hydrophobic interactions between hydrogen and carbon atoms further contributing to the complicated nature of cellulose molecules [4]. The cellulose fibre is made up of cellulose aggregates, which in turn are made of long D-glucose chains called microfibrils. These microfibrils aggregate into structures of even higher order, forming the fibres that can be viewed through, for example, scanning electron microscopy [4]. Surrounding these aggregates are the other main constituents of plant cell walls, such as lignin and hemicelluloses [12]. Pulping processes separates the cellulose from the other components of the plant cell wall generating cellulose pulp that can be used for the production of various different materials [4].

Cellulosic materials can experience a phenomenon called hornification, a process which occurs upon water removal and which generates a material with increased brittleness and decreased fibre flexibility and water retention properties [13]. One common explanation for this phenomenon is the irreversible hydrogen bonding occurring both intra- and intermolecularly,

facilitated by the large amount of oxygen atoms present in cellulosic materials [13]. Due to this bonding, the cellulosic material becomes stiff and brittle, offering a plausible explanation for the properties of the cellulosic nonwoven material this project aims to improve.

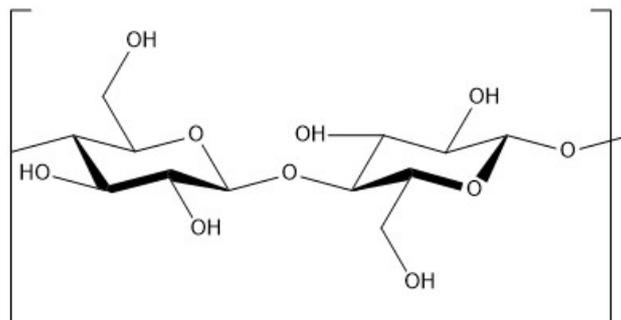


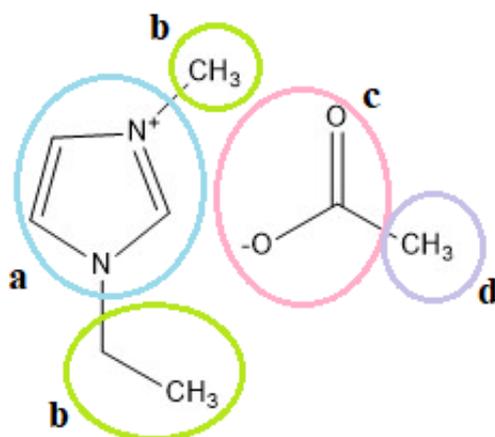
Figure 3: Structure of cellulose. Two D-glucose units are linked through a  $\beta$ -1,4-glycosidic bond. The repeating units form long chains called microfibrils which in turn form cellulose fibres [12]

Cellulose does not melt at higher temperatures the way synthetic polymers often do, but instead decomposes causing the polymer chain to be destroyed [4]. In order to process cellulose into filaments or nonwovens with e.g. wet spinning, solution blowing, or electrospinning, the cellulose pulp has to be dissolved. However, cellulose is insoluble in water and common organic solvents due to its amphiphilic nature promoting hydrophobic interactions [4]. The complex structure of the cellulose polymer along with its many hydroxyl groups makes it problematic to find an efficient solvent. Depending on the process and the source of the cellulose two categories of solvents can be used, namely derivatising or nonderivatising solvents [4]. These two groups differ in the way the solvent interacts with the polymer, for example if covalent bonds are formed or if there are intermolecular interactions only. One example of a derivatising solvent is carbon disulphide in sodium hydroxide which is commonly used in the viscose process [14]. An example of a nonderivatising solvent can be found in the Lyocell process, where the solvent N-methylmorpholine-N-oxide (NMMO) is commonly used [4]. Ionic liquids, which belong to the non-derivatising category and have the potential to be efficient and “green” solvents for cellulose, will be used in this project.

## 2.4 Ionic Liquids as Solvents for Dissolution of Cellulose

Ionic liquids are molten organic salts with melting points under 100 °C [4]. They are composed of four parts: an anion core, anion substituents, a cation core, and cation substituents [15]. An example of this can be seen in Figure 4, in which the chemical structure of the ionic liquid used in this project is displayed. The different coloured circles (marked with letters a-d) represent the four different parts of the ionic liquid. The four parts can be changed, generating a large number of ionic salts possible to manufacture [15]. Ionic liquids are nonderivatising and work as solvents by breaking intramolecular hydrogen bonds [16] and likely also through hydrophobic interactions [17]. There are typically three categories of ionic liquids: heterocyclic amines, superbases, and quaternary cations [15]. The currently most popular cation used in ionic liquids is imidazolium, which belongs to the heterocyclic amines-group [17]. Cellulosic systems based on ionic liquids can be sensitive to water content, temperature fluctuations, and

the cellulose content [15]. If the viscosity of the system becomes too high, it will be difficult to extrude the fibres through the spinneret. However, if the viscosity becomes too low, a cohesive drawing in the air gap between the nozzle tips and the coagulation bath will not occur [15]. How the ionic liquid is designed can have great impact on the cellulosic material produced, generating a large amount of opportunities for further development of novel cellulosic materials.



**Figure 4:** The chemical structure of the ionic liquid EMIMAc (1-Ethyl-3-methylimidazolium), which is used in this project. The blue circle (a) marks the cation core of the ionic salt, the green circles (b) mark the cation substituents, the pink circle (c) marks the anion core, and the purple circle (d) marks the anion substituent.

Although discovered in the beginning of the 20<sup>th</sup> century, ionic liquids did not attract interest as possible solvents for dissolution of cellulose until 2002 when an article was published on the topic [16], [17]. As mentioned earlier, cellulose is insoluble in water and common organic solvents, making it difficult to utilize the full potential of cellulose as a sustainable material, which motivates research into novel solvents suitable for the task. Ionic liquids are considered to be “greener” than many organic solvents partly due to their low vapour pressure and high thermal stability [2]. Additionally, ionic liquids can be used under ambient conditions, which is beneficial from an energy-preservation point of view. However, there are still challenges to overcome in regard to using ionic liquids as solvents for dissolution of cellulose at an industrial scale, with the main challenge being recovery and recycling of the solvent [2].

The ionic liquid used as solvent in this project is 1-Ethyl-3-methylimidazolium acetate (EMIMAc), which has proven to be effective at small scale dissolution of cellulose [17]. Furthermore, it has been investigated for the production of sustainable solution blown nonwovens with good results in regard to spinnability and capability for generating a nonwoven material [2]. EMIMAc is an imidazolium based ionic liquid and thus belongs to the heterocyclic amines-group. The blue circle (marked with a) in Figure 4 marks the imidazolium cation with its two methyl groups marked in green (b), serving as the cation substituents. The anion core and its substituent forms an acetate ion, marked in the picture in pink and purple (c and d, respectively). It can be noted that the cation is asymmetrical, which contributes to making the viscosity appropriate for the application of EMIMAc as a solvent for cellulose [17].

## 2.5 Surfactants and Fabric Softeners

Surfactants are surface active agents that adsorb to surfaces and interfaces in order to decrease the free energy of the boundary between phases [18]. They are amphiphilic, meaning that they consist of at least two parts, a head and a tail, one being soluble and the other insoluble in a specific liquid. If the liquid is water, the surfactant consists of a hydrophilic head group and a hydrophobic tail. The tail may be linear or branched, usually consisting of eight to eighteen carbon atoms [18]. The head group is polar and can be either ionic or non-ionic. The size of the head group for an ionic surfactant depends on the type of ion used, while for non-ionic surfactants the size can be chosen more freely when the surfactant is designed. The relationship in size between tail and head has a great impact on the physiochemical behaviour of the surfactant, more so than the individual sizes of the parts themselves [18].

The classification system of surfactants is based on the head group; typically surfactants are separated into the categories non-ionic, anionic, cationic, and zwitterionic [18]. Anionic surfactants are the most common type, typically found in detergents and soaps. The polar groups usually found in anionic surfactants are sulphate, phosphate, sulfonate, and carboxylate, paired with counterions such as sodium, ammonium, or potassium [18]. The second most used group of surfactants are the non-ionics, which have either a polyhydroxyl or polyether unit functioning as the polar group. In third place is the cationic surfactants, which are common in fabric softeners [18]. Most cationic surfactants have nitrogen as the cation, commonly in the form of amines or quaternary ammonium compounds ('quats'). Zwitterionic surfactants are the least common but are sometimes used in personal hygiene products. The head group consists of two oppositely charged groups, with the negative charge often being carboxylate and the positive being ammonium [18]. In this project, both a cationic and an anionic surfactant will be tried for the purpose of making a softer cellulose nonwoven.

The cationic surfactant used in this project is a common fabric softener consisting of a quaternary ammonium compound ('quat'). Quats are the most commonly used cationics for fabric softeners and consists of a positively charged nitrogen atom with four covalently bonded organic groups [19]. A fabric softener provides a fabric with a soft feel and sometimes a pleasant scent, and, additionally, works as an anti-static agent by preventing entanglement of the fibres in the fabric. The positive charge of the cation as well as the typically long chains of the organic groups are responsible for the adsorption of the surfactant to the fabric surface [19]. When some types of fabrics are repeatedly washed and dried in a machine, parts of the fibres begin to protrude from the surface like fine spikes, causing the surface of the fabric to have a rough feel. A fabric softener smooths the surface by interrupting the electrostatic repulsion holding the spikes in place [19]. This is typical for fabrics made of for example cotton, however, synthetic fibres do not experience this. They are instead prone to suffer from a build-up of static electricity when dried in a machine which can be reduced by the addition of a fabric softener [19]. Along with a quat, fabric softeners often include a non-ionic surfactant working as a levelling agent to encourage a uniform quat deposition upon the fabric. Additionally, the non-ionic surfactant also works as a buffering system to secure the low pH-value needed for optimal quat efficiency [19].

## **2.6 Methods for Evaluation**

The methods for evaluation of the materials produced in this project include subjective fabric hand evaluation, optical microscopy, and scanning electron microscopy (SEM). Additional measurements common for textile testing such as surface weight and sample thickness were performed, as well as evaluations of sample rigidity and air permeability. Some of the methods used for evaluation are described in this subsection of the report.

### **2.6.1 Subjective Fabric Hand Evaluation**

In order to determine the feel of a fabric or material when held in a person's hand, a subjective type of evaluation can be performed. The method for subjective fabric hand evaluation used in this project is inspired by the American Association of Textile Chemists and Colorists' (AATCC's) Evaluation Procedure 5 [20] and will be further detailed in the "Materials and Methods" section of this report. The purpose of this type of evaluation is to quantify the sensation that occurs when a material is touched or handled, which is defined as fabric hand [21]. A group of evaluators will assess the samples and give grades on a scale from 1 to 4 for each sample on the three physical attributes compression, bending, and surface. The samples are anonymised in order to make the evaluation unbiased. The evaluators are given instructions so that the procedure has as little variation from person to person as possible. The guidelines from AATCC [20] are used to minimise the variation in conditions and procedure to get as reliable results as possible.

### **2.6.2 Air Permeability**

For the measuring of the air permeability of the samples, ISO standard 9237:1995 will be used as a reference [22]. In this standard, air permeability is defined as "velocity of an airflow passing perpendicularly through a test specimen under specified conditions of test area, pressure drop and time". The rate of an air flow passing through a circular area of each sample will be measured at a set pressure difference of 2 mbar, giving an indication of which samples have more closely packed fibre structures and which have a more open arrangement. This will be compared to the results from the subjective fabric hand evaluation, thickness measurements, and rigidity measurements.

### **2.6.3 Evaluating Rigidity through Bending Length Measurements**

In order to evaluate the rigidity of the samples, the bending length can be used. ISO standard 9073-7:1998 describes a cantilever bending method for measuring of the bending length of nonwoven materials and will be used as a guideline for bending length measurements in this project [23]. In this standard, the bending length is defined as the "length of a rectangular strip of fabric, fixed at one end and free at the other, that will bend under its own weight" [23]. The strip of fabric, or nonwoven material, acts as a cantilever beam which is defined as an elastic beam fixed horizontally at one end [24]. The longer the beam is, the more its weight will cause it to bend downwards. To measure the bending length, the sample is placed at the edge of a platform with a weighted disk on top, see Figure 5 [23]. The disk moves at a constant rate, pushing the sample over the edge of the platform. At a certain length, depending on the rigidity of the sample, the sample will begin to bend downwards [23]. The bending length can be

calculated from the overhang length measured when the sample has reached a bending of  $41.5^\circ$  according to Equation 1 [24].

$$\text{Bending length} = \frac{\text{Overhang length}}{2} \quad [\text{length unit}] \quad (1)$$

From the bending length, the flexural rigidity can be calculated according to Equation 2 [24].

$$\text{Flexural rigidity} = \text{Area weight} * \text{Bending length}^3 * 10^3 \quad [\text{g/unit width}] \quad (2)$$

Flexural rigidity is defined in the ISO standard as a “ratio of small changes in bending moment per unit width of the material to corresponding small changes in curvature” [23]. A low flexural rigidity indicates a sample with more desirable textile like properties.

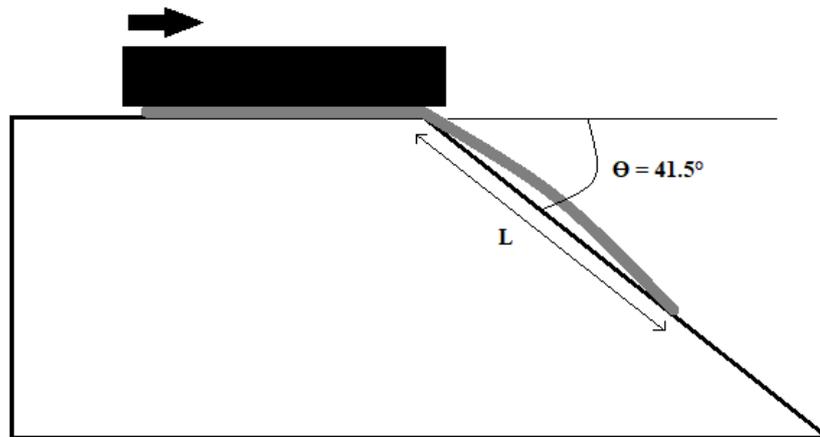


Figure 5: Cantilever bending test used for the evaluation of bending length and flexural rigidity through the measuring of the overhang length ( $L$ ) when a sample (in grey) is being pushed over the edge of a platform in the direction of the arrow until it bends to an angle of  $41.5^\circ$ .

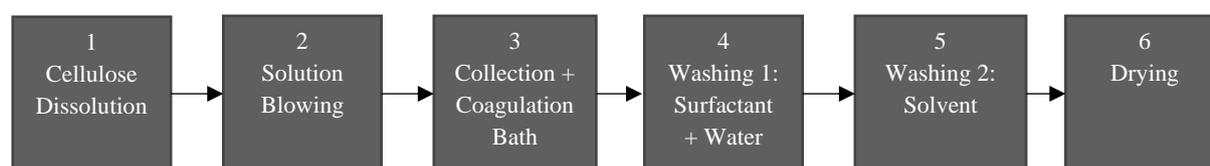
## 2.6.4 Optical Microscopy and Scanning Electron Microscopy

Two types of microscopy will be used in this project, namely optical microscopy, and scanning electron microscopy (SEM). Both methods will serve as additional ways to compare the samples, especially in regard to fibre diameter and fibre arrangement. All samples will be studied using optical microscopy, however, only a select few will be studied using SEM due to constraints regarding time and availability. These samples will be selected based on the results from the subjective fabric hand evaluation. One of the worst graded samples and a few of the best graded samples will be the ones studied with SEM.

## 3 Materials and Methods

In this section of the report, the experimental design used for planning and evaluation of the results is presented along with the experimental steps needed for the production of cellulosic nonwovens through solution blowing. Furthermore, the methods for evaluation of the materials produced are described including both subjective and objective procedures.

The steps used for the production of nonwovens of cellulose are displayed in Figure 6. These steps consist of cellulose dissolution, solution blowing, collection of sample and coagulation of fibre structure, washing with water and surfactant, washing with a non-solvent (water, isopropanol, or acetone), and drying. This segment of the report will further expand on the different steps in the sample production and will also include the materials and pieces of equipment used as well as descriptions of the evaluation methods used to examine the samples.



**Figure 6:** The steps for production of cellulosic nonwovens used within this project. Firstly, the cellulose is dissolved in EMIMAc. Secondly, the fibres are spun using solution blowing before being coagulated in a bath in the third step. The fourth step constitutes washing the fibre structure in a surfactant-water mixture. A second washing step is introduced in step five, in which the fibre structure is soaked in water, isopropanol, or acetone. The last step is drying of the material.

### 3.1 Materials and Equipment

The materials and chemicals used in this project are listed below:

- Pre-hydrolysis Kraft softwood dissolving grade pulp (Buckeye, Georgia-Pacific, USA)
- 1-Ethyl-3-methylimidazolium acetate,  $\geq 95.0$  % (HPLC) Sigma Aldrich, (CAS: 143314-17-4), used as received
- Propan-2-ol,  $\geq 99.8$  %, Fisher Scientific, (CAS: 67-63-0), used as received
- Acetone,  $\geq 99$  %, Fisher Scientific, (CAS: 67-64-1), used as received
- Ethanol, 95 %, KiiltoClean, (Ethanol (85-95 %) CAS: 64-17-5, Ethyl acetate (1-5 %) CAS: 141-78-6), used as received
- Praelanol® BG, Bozzetto GmbH, used as received
- Neutral® 0% Fabric Conditioner, Unilever, used as received

The equipment and software used in the project can be found in the list below:

- Solution blowing nozzle, Biax Fiberfilms, Greenville, WI, USA
- Flower press, plywood, [NORDIC brands]
- Polarized light microscope, Nikon Eclipse Ci POL, Japan
- ImageJ 1.52a, Wayne Rasband, National Institutes of Health, USA
- NIS-Elements BR 4.51.00, Nikon, Japan
- Funnel construction for vacuum drying, originally made to separate berries from leaves and dirt, in this project repurposed using duct tape, Marjukka

- Digital Micrometer 49-56-00-0028, Testing Machines Inc., DE, USA
- FRL Cantilever Bending Tester, Testing Machines Inc., DE, USA
- Air permeability tester L14 DC, Karl Schröder KG, Germany
- Scanning electron microscope, JEOL Ltd. (JSM-7800F), Japan

Pictures of the flower press setup and the funnel construction used for vacuum drying can be seen in Appendix A.1.

### **3.2 Preparation of Cellulose Solution**

The cellulose solution was prepared according to the method used by Jedvert et.al [2]. Before dissolution, the pulp was grinded and then dried for four hours at 105°C. Dried cellulose pulp was then dissolved in EMIMAc at a pulp concentration of 5 wt.-% in a glass reactor placed in a preheated oil bath. The solution was stirred at 100 rpm for one hour at a constant temperature of 70°C. Thereafter, the solution was allowed to cool and was then stored at room temperature until it was used in solution blowing experiments. For a more detailed description of the protocol used for cellulose dissolution, see Appendix A.2.

### **3.3 Solution Blowing and Coagulation Bath**

The cellulose solution was loaded into a piston attached to the spinneret. The piston was heated to a temperature of 45°C for a minimum of 20 minutes to allow the cellulose solution to heat up and become less viscous and thus sink further down into the piston. This also allowed for venting of the air bubbles present in the solution. An airflow with 1 bar pressure was heated to about 45°C and was attached to the spinneret. A pump was connected to the piston rod so that the cellulose solution could be extruded through the spinneret at a rate of 2.23 ml/min.

After the extrusion, the fibres were stretched in the airgap before falling into the coagulation bath consisting of deionised water placed under the spinneret. The nonwoven material was collected on a drum with a diameter of 32 cm placed in the coagulation bath 30 cm below the spinneret. The drum was spinning with a rate of 5.22 revolutions per minute.

The amount of time used for solution blowing and collection was 6 minutes, after which the process was paused, the sample removed and split into two parts which were placed in the first washing baths. The solution spinning process was started again and was run for another 6 minutes, generating a new piece of sample which was split into two smaller pieces and placed in washing baths in the same manner. This process was then repeated a third time. This means that six samples could be produced per 80 ml batch of cellulose solution.

### **3.4 Variation of Processing Parameters**

There are several parameters in the process of solution blowing of cellulose that can be varied. Examples include cellulose concentration, rate of extrusion, temperature, and distance between nozzle and coagulation bath. The three parameters chosen to be adjusted in this project all include steps taken after the solution blowing is finished. They include:

- One washing step where the effects of different surfactants are tested
- One washing step where the solvent used as washing media is altered

- Different drying methods

All other parameters were set. Preparatory tests were made in order to decide the set levels of the parameters as well as to make sure the chosen levels of the parameters were reasonable and would generate a result of interest.

When deciding the levels of the parameters, benign materials and methods were focused on. In order to make a potential upscale from research level to pilot and industrial level production go smoother, care was taken to use materials and methods functional at a larger scale. When designing new processes, it is of great value to consider the “greenness” of the process as a whole [25]. If safe materials can be used, such as water for example, that is to be preferred. Less energy intensive methods are to be preferred over methods with a high energy requirement. An example of this is choosing pathways performed at ambient temperatures and pressures over pathways requiring intense heat or cold [25]. These ideas were taken into consideration when the solvent, surfactants, solutions, and drying methods were chosen.

### 3.4.1 The Parameter Levels – Surfactants in the First Washing Bath

It was decided that one of the parameters to be tested should involve surfactants since they are surface active compounds known for their ability to have an effect on textile-like materials [18]. Since the cellulose molecule has a slightly negative charge, it can be anticipated that a cationic surfactant will have a stronger interaction with the fibres. To test this, both an anionic and a cationic surfactant were included in the project. The three levels of surfactants tested are no surfactant, a common cationic fabric softener, and the anionic surfactant Praelanol®. The fabric softener was chosen because of its well-known softening properties. It is also benign and commonly used in close contact to skin which can become important in a future application of the material. The softener consists of the cationic surfactant dihydrogenated tallowoyethyl hydroxyethylmonim methosulfate (Figure 7) which is a quaternary ammonium compound. The second surfactant, Praelanol® BG, is a sulfonated anionic surfactant containing nitrogen used mainly for viscose staple fibres. The producer claims that the surfactant imparts smoothness and softness to the fibre, properties which are of interest for this project.

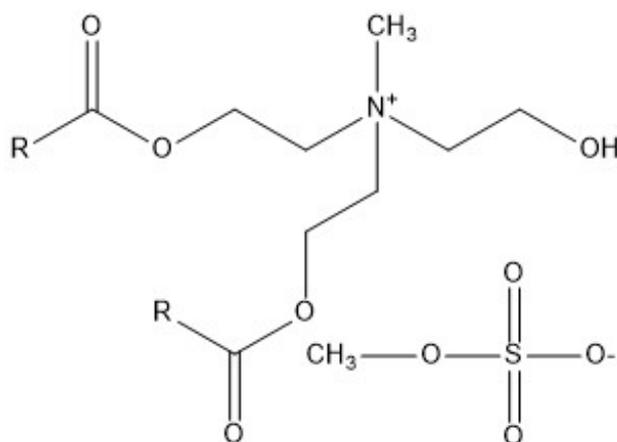


Figure 7: The cation surfactant dihydrogenated tallowoyethyl hydroxyethylmonim methosulfate which is a quaternary ammonium compound with methosulfate as a counterion. This system is the active ingredient in the fabric softener used in this project.

### **3.4.2 The Parameter Levels – Solvents in the Second Washing Bath**

Different solvents can have different effects on the hydrogen bonding occurring in a cellulosic material [26]. One parameter was chosen to test the effect of different solvents when cellulosic nonwovens are washed. The three levels of different solvents tested are water, isopropanol, and acetone. Water was selected partly as a reference to compare the other levels to, and partly because of its benign properties. In preparatory tests, ethanol and acetone generated interesting results in regard to softness of the material produced. Due to this, acetone was selected as one of the levels used in the experimental matrix. Acetone is a commonly used solvent which hopefully will have an effect on the intermolecular hydrogen bonding of the samples. Instead of ethanol, isopropanol was chosen as the third washing media mainly because a slightly stronger coagulation effect was expected from it compared to ethanol [26]. Isopropanol is also a commonly used solvent and will hopefully, just as acetone, have an effect on the hydrogen bonding within the nonwoven material.

### **3.4.3 The Parameter Levels – Drying Methods**

It is necessary to hold the samples into place during the drying step to prevent shrinking of the sample. In the “original” drying method used during the preparative testing, needles were used to attach the samples to a planar surface where they were allowed to dry in room temperature. This generated wrinkly materials which shrunk a lot during the drying step. It is, therefore, of interest to find a better method for keeping the material in place during the drying step so that it can keep its original size better and have a smoother surface. Two of the three drying methods investigated are based on pressing the material in a flower press during the drying time. One of the methods takes place in room temperature, and the other in an oven at 105°C. The press was chosen mainly because of its convenience. Since drying at room temperature would be convenient from an energy preservation point of view, this was chosen as one of the levels. 105°C was chosen to be on the other end of the spectrum, while still being far below the degradation temperature for cellulose. Having two different temperatures creates an opportunity to study the effect of temperature on the drying and potential hornification of the cellulose in the material. The third drying method involves using vacuum to draw the liquid out of the samples while the samples simultaneously are held in place, possibly making the material keep some of its original shape and size. This method is based on the vacuum suctioning of air through the sample and is performed at room temperature (22°C) in this project. It is quick and can easily be performed at a larger scale.

Another drying method of interest is freeze drying, which was not used for the experimental matrix samples due to limitations regarding equipment availability. However, two additional samples were freeze-dried to serve as a trial of the method. One of the samples was washed in two water baths, the other in a first bath containing fabric softener followed by a second bath consisting of water. One problem with freeze drying is its high energy requirements, making an upscaling of the method expensive and less “green” [27]. The process is also time consuming, further making the method unavailable for easy upscaling [27].

### 3.5 Experimental Design

A 3<sup>3</sup>-factorial design was implemented in order to plan out the experimental work and to evaluate the results. This design is presented in Table 1, in which the three parameters ‘Surfactant’, ‘Washing Media’, and ‘Drying Method’ can be seen. The three parameters are alternated at three different levels. For ‘Wash Bath 1: Surfactant’, the three levels are no surfactant, a common cationic fabric softener (Neutral®), and the anionic surfactant Praelanol® BG. The three levels of ‘Wash Bath 2: Solvent’ are water, isopropanol, and acetone. The three ‘Drying Methods’ used are drying in a flower press at room temperature, drying in a flower press in an oven at 105°C, and drying through vacuum suctioning. A total of 27 samples were created according to the experimental design, see Appendix A.3 for a complete list. An additional sample, S0, was created to represent the “original” treatment method. This sample was washed in two water baths before it was dried in room temperature by being pinned to a flat surface.

Table 1: The experimental design used to plan out the laboratory work and to evaluate the results.

Wash Bath 1: Surfactant	Wash Bath 2: Solvent	Drying Method
No surfactant	Water	In press at room temperature
Fabric Softener (Neutral®)	Isopropanol	In press at 105°C
Praelanol® BG	Acetone	Vacuum suctioning

#### 3.5.1 First Washing Step: Washing with Surfactant

The produced samples were washed in a first washing step in either deionised water or a mixture of deionised water and surfactant at room temperature for a minimum of 24 hours. The amounts of surfactant used were 17 g/litre for the fabric softener and 0.267 g/litre for Praelanol® BG. The fabric softener has a lower concentration of the active surfactant, hence the large difference in amount needed compared to Praelanol® BG to achieve similar amounts of the two surfactants in the finished washing solutions. For more details regarding the preparation of the surfactant solutions, see Appendix A.4. Each sample was placed in its own bath according to the experimental design matrix. After washing, some of the excess liquid was allowed to drop off before the sample was moved to the second washing bath.

#### 3.5.2 Second Washing Step: Washing with Non-Solvent

The second washing step was performed at room temperature for at least 24 hours. Each of the samples were washed in water, isopropanol, or acetone according to the experimental design matrix.

#### 3.5.3 Drying Methods

After the second washing steps, the samples were dried using one of three methods according to the experimental design matrix. In the first method, the samples were pressed in a flower press for a minimum of 48 hours at room temperature. In the second method, the samples were pressed in a flower press for a minimum of 2 hours at a temperature of 105°C. In the third method, the liquid in the samples was removed through vacuum suctioning at room temperature (22°C).

### **3.5.4 Extra Samples**

Six additional samples, displayed in Appendix A.2, were produced to expand on the original experimental design. Two of the extra samples were washed with ethanol in the second washing step and were, thereafter, dried using the vacuum suctioning method. Ethanol was expected to have a similar effect on the material as isopropanol and was used in order to test this expectation. Another two of the extra samples were washed a single time, in a water bath containing Neutral®. They were then dried directly from the first bath by either vacuum suctioning or by being pressed in a flower press at room temperature. These samples were created in order to test the effect of having surfactant still attached to the sample instead of being, more or less, washed away in the second washing step. Neutral® was chosen due to it showing greater effects compared to Praelanol® in the subjective fabric hand evaluation. The last two extra samples were washed in a first bath either with Neutral® or without surfactant and were then washed in a second bath containing water. These samples were freeze dried by being submerged in liquid nitrogen and then placed in a vacuum chamber for sublimation. It was not possible to use the freeze-drying equipment for a larger group of samples, but the method was considered interesting enough to warrant a small trial with two samples. The idea was to test if freeze drying could be a viable option for drying and to see what effect it could have on the material.

## **3.6 Evaluation Methods**

The samples were evaluated according to the methods described in this section of the report. These methods include subjective fabric hand evaluation, thickness measurements, air permeability measurements, flexural rigidity evaluation through bending length measurements, light microscopy, and scanning electron microscopy.

### **3.6.1 Subjective Fabric Hand Evaluation**

The instructions given to the ten participants of the subjective fabric hand evaluation are detailed in Appendix A.5. Before the evaluation began, the samples were placed in anonymous bags to prevent bias from interfering with the results. The evaluation took place in a controlled environment with a relative humidity of 65 % and a temperature of 22°C in which the samples had been conditioned for twenty hours before the beginning of the evaluation. Each participant filled out a questionnaire in which they gave grades between 1 and 4 for each sample on the three hand components ‘compression’, ‘bending’, and ‘surface’. ‘Compression’ is defined as the sensation occurring when pressing a sample between the fingers, ‘bending’ is the feeling experienced when carefully bending the sample back and forth, and ‘surface’ corresponds to the feeling of stroking the sample or rubbing it between thumb and index finger.

### **3.6.2 Measuring Sample Thickness**

The sample thickness was measured by a digital micrometre which measures the distance between the flat surface upon which the sample is loaded, and a circular disk pressing down on the sample with a pressure of 0.5 kPa. The thickness was measured at three points on each sample; two points at the two ends of each sample, and one point located in the middle. The samples were cut into rectangles of 1.5 cm times 12 cm and were conditioned in a controlled

environment (22°C, 65 % relative humidity) before the start of the evaluation. Two of the samples, S10 and S16, were too small to be cut into exactly the right dimensions but were considered to be close enough in size to still be evaluated. The areas of these samples were estimated using the image processing program ImageJ. The samples were photographed along with a ruler and the area of each sample was measured relative to the ruler with the help of ImageJ.

### **3.6.3 Measuring Air Permeability**

A sample holder with a circular hole with a diameter of 1.1 cm was used for the measurement of air permeability. Each sample was clamped in place with the sample holder and an air flow was forced perpendicularly through the sample being measured and the hole in the sample holder. The air flow rate was measured at a pressure difference of 2 mbar. With the equipment used in this project, the flow had to be adjusted with a multiplication factor of 21.05 to adjust for the area of the hole in the sample holder, which was selected to fit the width of the samples (1.5 cm). Every sample was measured at three different places, two points close to each end of the sample and one in the middle. Samples E5 and E6 could not be evaluated due to their brittleness.

### **3.6.4 Measuring Sample Bending Length**

The sample bending length was measured using a set up similar to the one displayed in Figure 5. A sample was placed on the platform and a weighted disk was placed on top of the sample. As the disk moved rightwards at a rate of 0.6 cm/s, the sample slid over the edge of the platform. At a certain overhang length, the sample began to bend downwards. When the sample had bent enough to hit the marker at the 41.5° angle, the disk was stopped, and the overhang length was measured using the ruler on the disk. Four measurements were performed per sample, one per end and side of the sample. An average bending length could then be calculated using Equation 1 and the flexural rigidity could be calculated using Equation 2.

### **3.6.5 Evaluation through Light Microscopy and SEM**

A light microscope was used to evaluate the thickness of the fibres in the samples. Pictures of the samples were taken, and fibre diameters were measured using the NIS-Elements Br software. The purpose of this evaluation was to compare the ranges of fibre thickness displayed by the different samples to see whether different washing and drying methods had a large impact on this parameter. The samples were viewed at magnifications of 4x and 10x.

The first four samples selected for SEM were S0, S13, S23 and E5. S0 was the worst graded sample in the subjective fabric hand evaluation, while samples S13 and S23 were among the highest graded samples. The large differences between these samples made them the most interesting targets for SEM evaluation. E5 was selected due to the interesting properties displayed by the samples when studied; it is thick, fluffy, and soft, but falls into pieces easily. Since it proved impossible to perform several of the other evaluations on the freeze-dried samples due to their brittleness, SEM serves as one of the few ways in which these samples can be studied in this project. Due to the interesting fibre structures displayed by samples S13 and S23, four more samples were selected for SEM. These were S15, S18, S22, and S27, and were

selected based on the method used to dry them as well as on the results from the subjective fabric hand evaluation.

Before the samples could be viewed with SEM, they had to be coated with a thin layer of carbon to reduce build-up of charge and to avoid beam damage. Small sample pieces were cut and taped to a sample holder, before the samples were sputter coated with carbon particles resulting in a layer a few nanometres thick. The samples could then be loaded into the microscope and were viewed at magnifications of 50x, 100x, 300x, and 1000x. The voltage used was 6kV and low vacuum SEM was selected to keep the amount of charging low.

## 4 Results and Discussion

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This section of the report presents and discusses the results achieved during the evaluation of the cellulosic nonwoven samples produced in this project. For pictures of the samples, see Appendix B.1. It is notable that the samples differ from each other regarding shape and size. This is in part due to the differences introduced in the experimental matrix, but also in part due to the handling of the material. It was noted during the production of the samples that the way in which they were removed from the baths impacted the shape they received upon drying. Additionally, when the solvent used in the second washing bath consisted of acetone or isopropanol, a tendency for the sample to maintain its shape from the point of being dropped into the washing bath was noted. It was almost like the structure and shape of the sample was “frozen” or congealed upon the encounter with the different solvent. It is thus of high importance to ensure the same handling of the samples in order to get samples with as similar shapes as possible. However, this is difficult with the current setup where each sample piece goes through several steps of individual handling, each having the potential to introduce differences between the samples. At a larger production scale, this problem can be avoided by using a conveyor belt for bringing the material through the different washing baths.

The number of samples that were possible to produce in this project was limited by time constraints and, therefore, only one sample per level in the experimental matrix was created. This affects the statistical analysis of the study, especially in regard to reproducibility. This project must therefore be viewed as an introduction to the topic of which treatment methods are appropriate for making cellulose based nonwovens less papery and more textile like.

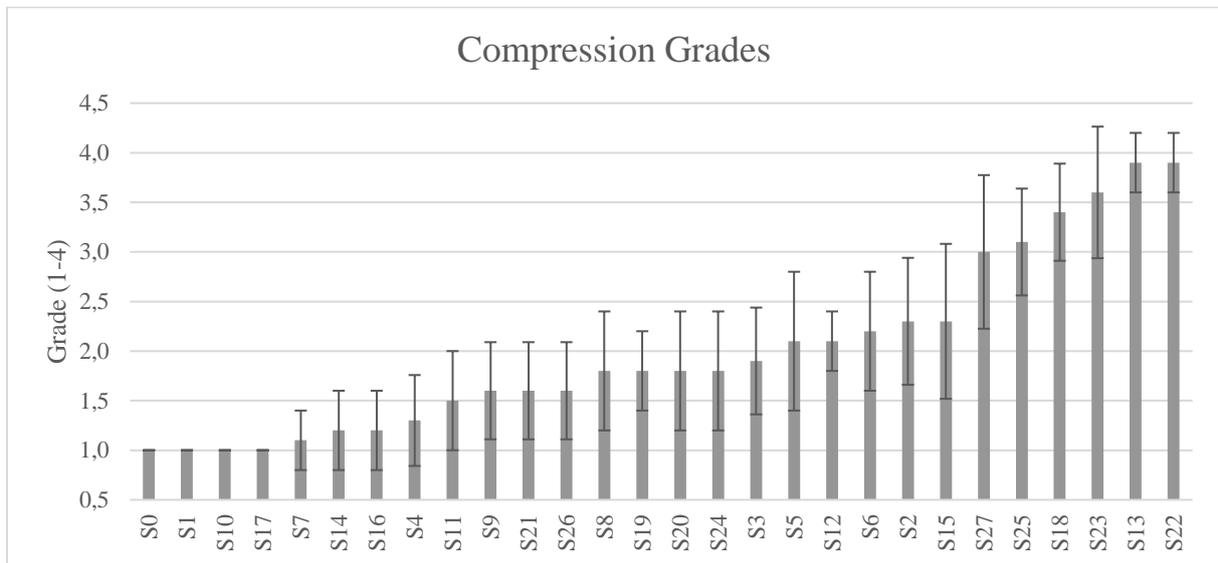
### 4.1 Subjective Fabric Hand Evaluation Results

The data from the subjective fabric hand evaluation is presented in detail in Appendix B.2. It can be noted that the sample which represents the “original” treatment method, S0, received the lowest grades for all the components evaluated. This indicates that all of the tested treatment methods had at least some positive impact on the hand feel of the materials, although some less than others. Additionally, it can be noted that the whole grade range (1-4) is represented among the results, meaning that there is a wide spread of grades. Large differences in grade indicates large differences in sample properties, proving that the different treatment methods have had various effects on the nonwoven material.

#### 4.1.1 The Compression Component

The results from the evaluation of the hand component ‘compression’ are displayed in Figure 8, sorted from lowest to highest grade, with the standard deviations marked in the form of error bars in the diagram. In this diagram, it can be seen that all of the seven most highly graded samples (S15, S27, S25, S18, S23, S13, S22) were dried using the vacuum suctioning method. This indicates that this drying method is the most suitable for production of materials aimed to have a soft compression feel, which likely is due to the fibres in these samples having a relatively airy arrangement. This in turn allows space for compression when the samples are evaluated. The coefficient plot for the ‘compression’ component, displayed in Figure 9, also

points to the importance on this drying method for the compression feel. The other two drying methods, both based on pressing the sample, generated samples with lower grades, signalling that these materials were perceived as firmer and more unyielding. This is likely due to the fibres in these samples being more pressed together, leaving little room for further compression when evaluated. The coefficient plot indicates that the elevated temperature press-method is the least suitable for making samples with a soft compression feel.



**Figure 8:** Results from the subjective fabric hand evaluation for the component ‘compression’. The samples are sorted from lowest to highest grade. The standard deviations are indicated with error bars.

Regarding the first washing bath, there seem to be no major trends indicating that the use of a surfactant is highly important for the compression feel. There is a slight tendency for higher grades being given to samples treated with Neutral®, considering that three (S22, S23, S18) of the four most highly graded samples were treated with this surfactant. This is also indicated by the coefficient plot in Figure 9. However, there are also highly graded samples that were treated with Praelanol® or just water as well. Considering this, it can be concluded that the presence of a surfactant is not the most important parameter for the production of materials with a soft compression feel.

When it comes to washing with a solvent, it becomes clear that it is more beneficial to use acetone or isopropanol compared to water. Out of the eight lowest graded samples (S0, S1, S10, S17, S7, S14, S16, S4, S11) all except for one sample (S14) were washed with water. This, along with the fact that only one sample (S18) washed with water was placed among the fifty percent of the samples with the highest grades, shows that samples washed in water were less compressible compared to the other samples. The coefficient plot in Figure 9 further proves this statement, showing that water has a negative impact compared to the other levels of the parameter. If comparing acetone and isopropanol, it seems that isopropanol is better at creating compressible materials than what acetone is. This is indicated by the fact that only one sample (S8) out of nine washed with isopropanol was placed among the fifty percent of the samples with the lowest grades, compared to four out of nine washed with acetone (S14, S9, S21, S26). This is also indicated in the coefficient plot. A possible explanation for these results

could be that both acetone and isopropanol, to varying degrees, hinder some of the hydrogen bond formation which is more commonly present when water is used.

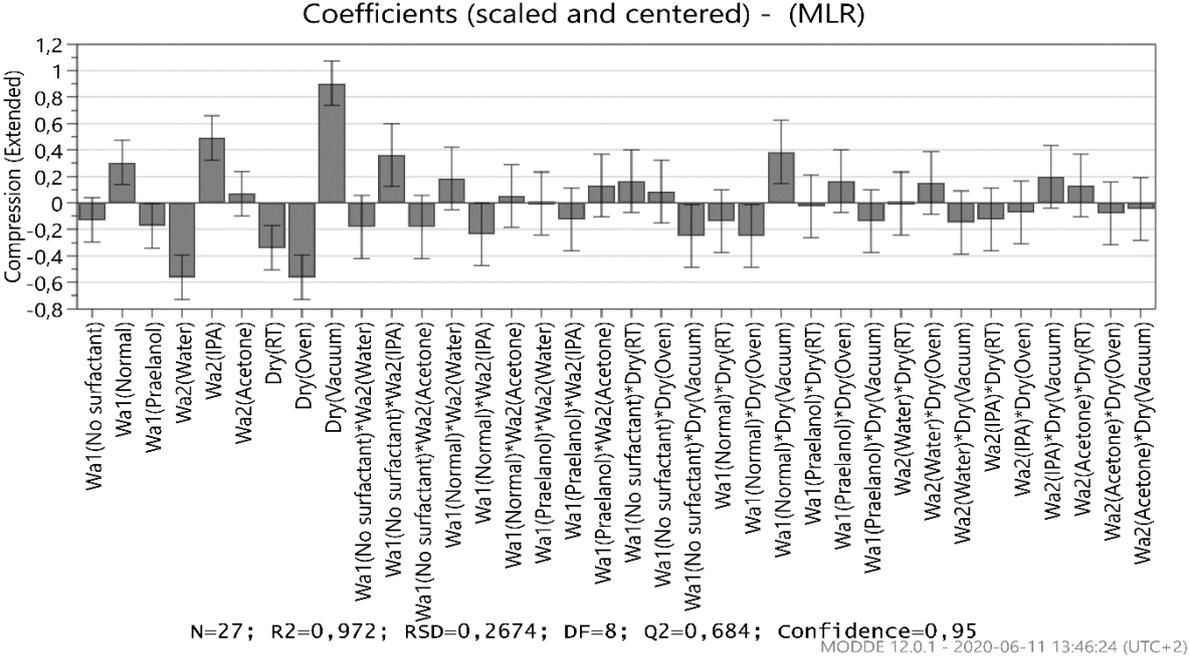


Figure 9: Coefficient plot for the ‘compression’ component.

### 4.1.2 The Bending Component

In Figure 10, the results from the evaluation of the component ‘bending’ can be seen, with the samples sorted from lowest to highest grade. A similar trend regarding drying methods can be seen for the results for the ‘bending’ component as with the results for the ‘compression’ component. In the bending evaluation, just as in the compression evaluation, the seven most highly graded samples were dried using vacuum suctioning (S15, S25, S27, S18, S13, S22, S23). This, along with the coefficient plot for the ‘bending’ component displayed in Figure 11, marks the vacuum suctioning method as the best for making bendable samples. It can also be seen in Figure 10 that, if S0 is disregarded, out of the eight lowest graded samples (S10, S7, S17, S16, S14, S26, S24, S20), only one sample (S7) was not dried in a press at 105°C. This indicates that an elevated temperature is less beneficial for the production of easy-to-bend cellulosic nonwoven materials compared to a lower temperature, at least when a press is used during the drying step. This is further proven by the coefficient plot, in which it can be seen that elevated temperature press-method has a more negative impact on the bending feel compared to both of the other methods.

The trend regarding the influence of surfactants on the bending feel is similar to the influence of surfactants on compression feel. In general, the data suggests that having the surfactant Neutral® present in the first washing bath generates samples that can be bent more easily. Again, out of the four highest graded samples (S18, S13, S22, S23), only one (S13) was not treated with Neutral®, suggesting that this surfactant is the most impactful for the types of materials this project treats. This is also indicated in the coefficient plot in Figure 11. In this plot, it can also be seen that Praelanol® seems to have a bit of a negative impact on the

component. However, the surfactant parameter as a whole has a lower impact on the ‘bending’ component compared to the drying method parameter.

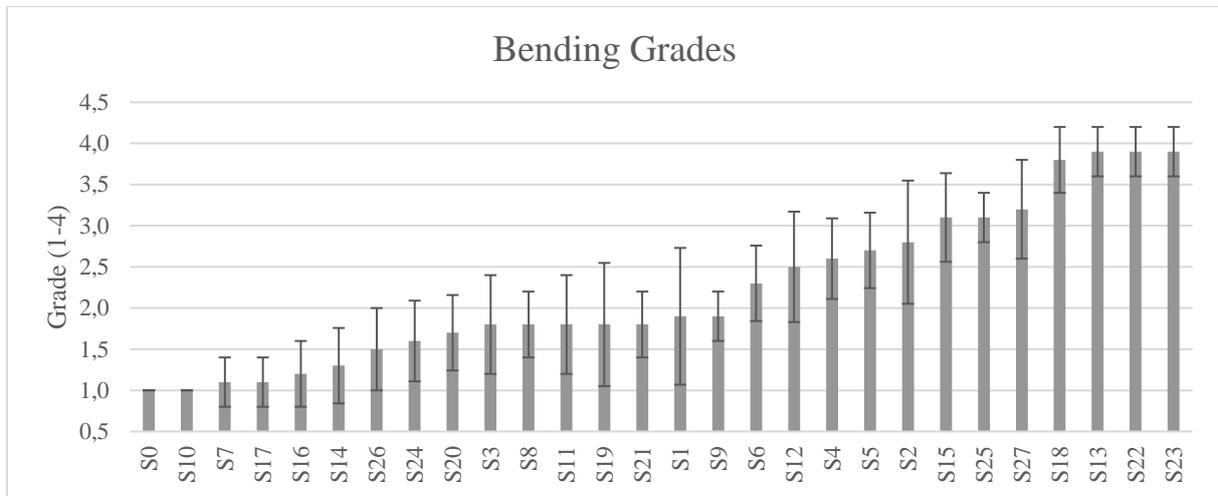


Figure 10: Results from the subjective fabric hand evaluation for the component ‘bending’. The samples are sorted from lowest to highest grade. The standard deviations are indicated with error bars.

When it comes to the solvent used in the second washing bath, the trend indicating water being less favourable than acetone or isopropanol is not as strong for the ‘bending’ component as for the ‘compression’ component. Nevertheless, samples treated with acetone or isopropanol still received higher scores in general compared to water-treated samples. The disadvantage of using water is also proven by the coefficient plot in Figure 11. Again, isopropanol-treated samples are graded slightly higher compared to acetone-treated samples, but the difference between the methods is less pronounced for this component than for the ‘compression’ component. This can be seen in the coefficient plots for both of the components. Again, the second washing bath-parameter seem to be of less importance for the ‘bending’ component than what the drying method-parameter is.

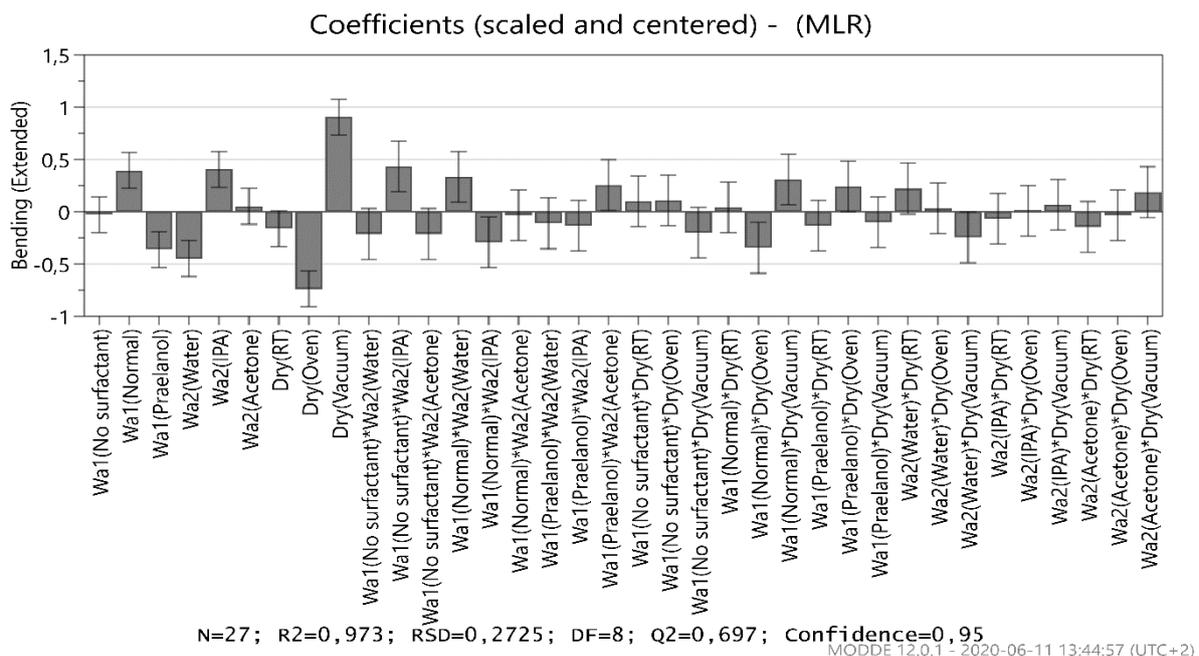


Figure 11: Coefficient plot for the ‘bending’ component.

### 4.1.3 The Surface Component

The results from the evaluation of the ‘surface’ component are displayed in Figure 12, sorted from lowest to highest grade. It can be noted that the average grade for all the samples is at a higher level for this component than for the other two, indicating that the evaluators overall tended to grade the samples more highly on ‘surface’ than on ‘compression’ or ‘bending’. It is possible that the samples, in general, were perceived as quite smooth, making it more difficult to distinguish the different samples from each other regarding the ‘surface’ component compared to the other components.

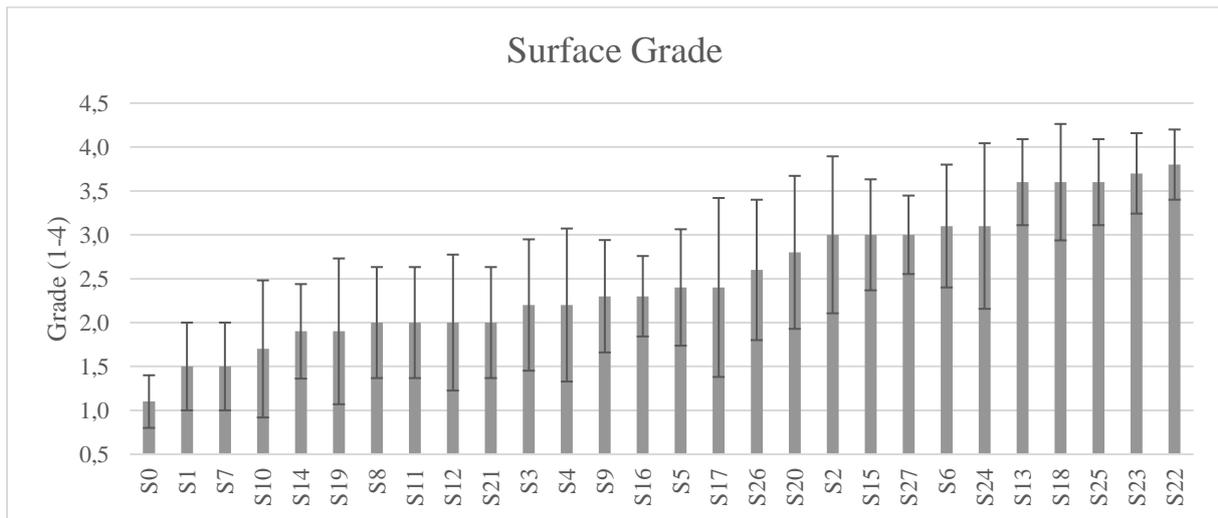


Figure 12: Results from the subjective fabric hand evaluation for the component ‘surface’. The samples are sorted from lowest to highest grade. The standard deviations are indicated with error bars.

Just as for the other two components, the trend for the drying methods suggests that the vacuum suctioning method is the most beneficial for generating samples with a high grade for the component. However, the trend is not as strong for the ‘surface’ component as it is for the other two. Of the seven most highly graded samples (S6, S24, S13, S18, S25, S23, S22), five (S13, S18, S25, S23, S22) were dried using the vacuum suctioning method. It is notable, however, that there is a difference between the level of the grades received by S6 and S24, and the five more highly graded, vacuum dried, samples. This serves as an indication of the importance of the vacuum drying method’s impact on the ‘surface’ component, which is also proved by the coefficient plot for the ‘surface’ component displayed in Figure 13. Regarding the press-based drying methods, no major differences in effect can be observed. Both methods are similarly as capable at creating both rougher and smoother surfaces, however, the coefficient plot indicates that they both have overall negative impacts on the surface feel of the samples compared to the vacuum suctioning method. This is interesting, considering that it could possibly have been expected that the press-based methods would have caused the fibres at the surface to be more densely packed, generating a softer surface-feel. However, this does not seem to correspond to the evaluators’ perception of what a soft or smooth surface-feel is. It is possible that the evaluators had different ideas of how to judge this component, which would mean that the results are more difficult to analyse.

The trend indicating the importance of the presence of surfactants for the hand feel properties is stronger for the ‘surface’ component than for the other two components. Of the ten samples

washed with only water in the first washing bath (S0, S1, S10, S14, S11, S12, S3, S2, S15, S13), seven can be found among the fifty percent of samples with the lowest grade. This can be compared to three out of nine for Neutral®, and four out of nine for Praelanol®. Additionally, it can be noted that Neutral® has a more distinct positive impact on the surface-feel compared to what it has for the other two components. Praelanol® generates samples with grades all over the range, indicating that this surfactant by itself is not the most important factor for generating materials with a soft feel. These trends can also be seen in the coefficient plot in Figure 13.

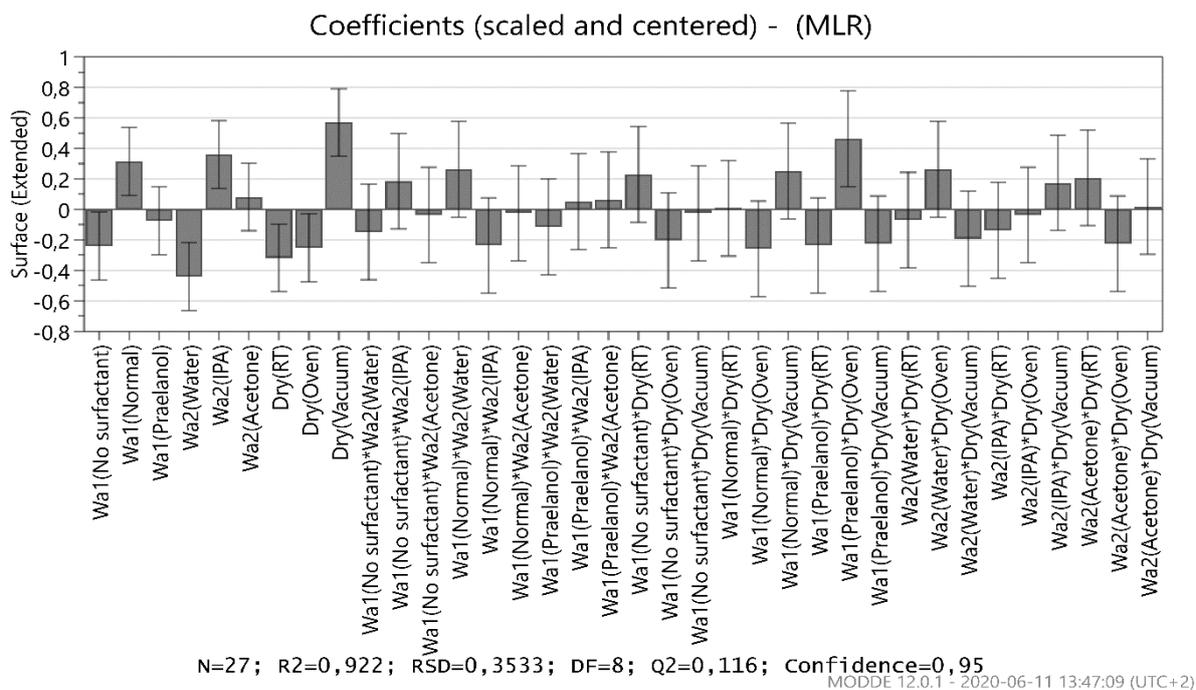


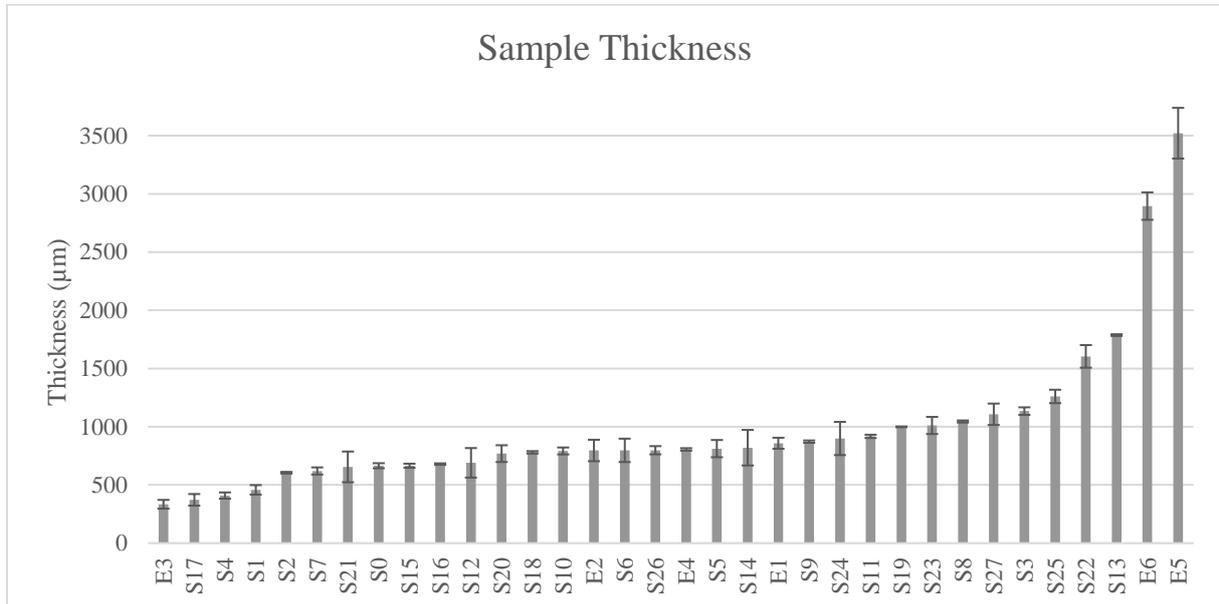
Figure 13: Coefficient plot for the 'surface' component.

Regarding the solvent used in the second washing bath, it is once again clear that water is the less suitable option for generating samples with higher grades on the component. Of the ten samples washed with water in the second washing bath (S0, S1, S7, S10, S19, S11, S4, S16, S17, S18), all except for two (S17, S18) can be found among the fifty percent lowest graded samples. Six of these samples are among the eight lowest graded. The coefficient plot in Figure 13 further displays this trend. Once again, the samples treated with isopropanol are slightly higher graded than those treated with acetone, but the trend is not as pronounced as for the 'compression' component. The coefficient plot indicates that isopropanol is the most beneficial solvent overall for creating samples with a soft surface feel.

## 4.2 Sample Thickness Results

The data from the sample thickness measurements are displayed in Appendix B.3. An average thickness was calculated for each sample from the three measurements performed. These average thicknesses are displayed in Figure 14, sorted from thinnest to thickest, with the standard deviations marked in the form of error bars in the diagram. It can be noted that the freeze-dried samples, E5 and E6, are a lot thicker compared to the rest. This drying method clearly has an impact on the fluffiness, and thus the thickness, of the cellulosic nonwoven. The sample corresponding to the original treatment method (S0) is placed among the thinner

samples in the diagram, close to other samples washed in one or two water baths. Other samples in the same thickness range were dried using one of the methods based on pressing, which is more similar to the “pinning-to-surface”-method used for S0 than what the vacuum suction method is. The placement of S0’s thickness in the thickness range is thus not surprising.



**Figure 14: Sample thickness expressed in µm. The thickness is calculated as an average from three measurements per sample. The standard deviations are indicated with error bars.**

Of the nine thickest samples from the experimental matrix (S11, S19, S23, S8, S27, S3, S25, S22, S13), all except for two (S3, S8) were dried using the vacuum suctioning method. This data suggests that, in general, thicker materials are produced when the vacuum suctioning method is used. The six thinnest samples from the experimental matrix (S17, S4, S1, S2, S7, S21) were dried using a flower press. Two of the samples (S17, S21) were dried at 105°C and the remaining four at room temperature. However, more of the samples dried at 105°C can be found among the fifty percent of the thinnest samples compared to those dried at room temperature. Consequently, it can be assumed that the pressing method itself has the capability to produce both thinner and thicker materials, while the temperature during drying is of less importance to the thickness property.

It can be suspected that the differences in thickness between the vacuum suction-dried samples, in large part, can stem from differences in handling during the drying step. Since the process used for vacuum suctioning in this project is quite manual, unintentional differences in handling might have occurred. This could have had the result that some samples retracted in area size more than in thickness, and vice versa. To test this theory, more experiments would be needed in which the area is estimated or measured both before and after drying. It could also be of interest to test the effect of different air temperatures as well.

Regarding the effect of surfactants used in the first washing bath, there is a small trend indicating that samples washed with Praelanol® (S17, S7, S26, S9, S24, S19, S8, S27, 25) are thicker compared to the other samples. Neutral®, on the other hand, seem to be connected to thinner samples. Most of the samples from the experimental matrix washed with the fabric softener (S4, S21, S16, S20, S18, S6, S5, S23, S13) can be found among the fifty percent of the

thinnest samples. The trends are, however, not clear enough that any solid conclusions can be drawn regarding the effects of surfactants on sample thickness. It could be said, however, that these results suggest that there are no large amounts of surfactant residues on the surfaces of the samples, at least not enough to have an effect on the thickness of the samples.

When it comes to the solvents used in the second washing bath, the diagram in Figure 14 shows that of all ten samples from the experimental matrix washed with water (S17, S4, S1, S7, S0, S16, S18, S10, S11, S19), eight can be found among the thirteen thinnest. From this, it can be deduced that water, in general, generates thinner samples compared to acetone and isopropanol. Acetone and isopropanol seem to have similar effects on sample thickness overall, but it can be noted that the three thickest samples (S25, S22, S13) were all washed in isopropanol. Regarding the two samples washed in ethanol (E2, E1), they are placed in the middle of the thickness diagram and thus not showing any unexpected effects on this parameter. Regarding the samples dried directly from surfactant (E3, E4), they are placed in different areas of the thickness range. Although the sample size is too small for any conclusion to be made, this indicates that the second washing bath might have little effect on the sample thickness unless a solvent such as acetone or isopropanol is used.

### **4.3 Surface Weight and Density**

Data detailing weight, average volume, surface weight, and average density for each of the samples can be found in Appendix B.3. The average volume of each sample was calculated by multiplying the sample areas with the average thicknesses displayed in Table B.2. The surface weights were calculated as weight divided by area in grams per square meter, and the average densities were calculated as weight divided by average volume in grams per cubic meter.

The surface weight data shows a wide spread of results for all of the parameters and levels tested. It is thus not possible to draw any solid conclusions on the influence of the three processing parameters and their three levels on the sample surface weight. A small trend indicates that Praelanol® might generate samples with a slightly higher surface weight. Out of the nine samples washed with Praelanol® (S7, S26, S9, S27, S25, S8, S19, S24, S17), only three (S19, S24, S17) can be found among the fifty percent with the lowest surface weight, including the extra samples. It is possible that more of that surfactant stayed on the surface of the samples through the second washing bath compared to Neutral® and water, resulting in a higher surface weight.

Figure 15 shows the densities of the samples sorted from lowest to highest. It can be noted that the two freeze-dried samples (E5, E6) have much lower densities compared to the rest of the samples. This stems in part from the fact that these samples are much thicker compared to the others, but it must also be noted that the areas of these samples were estimated with ImageJ and not measured. It is thus possible that the areas differ a bit from reality, which can have an effect on the densities calculated from the areas.

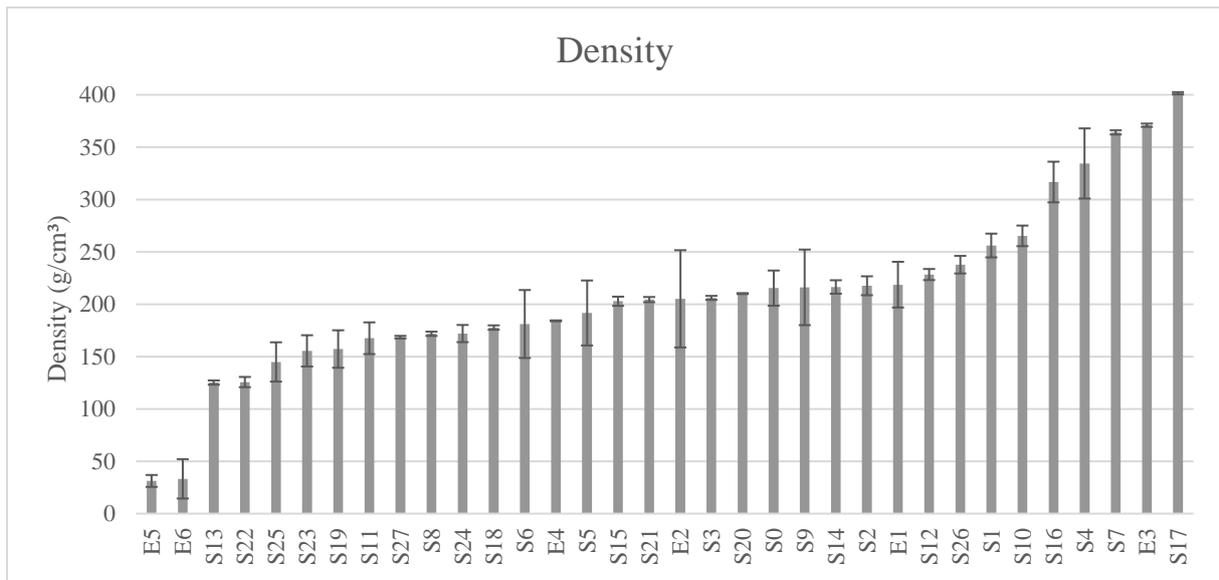


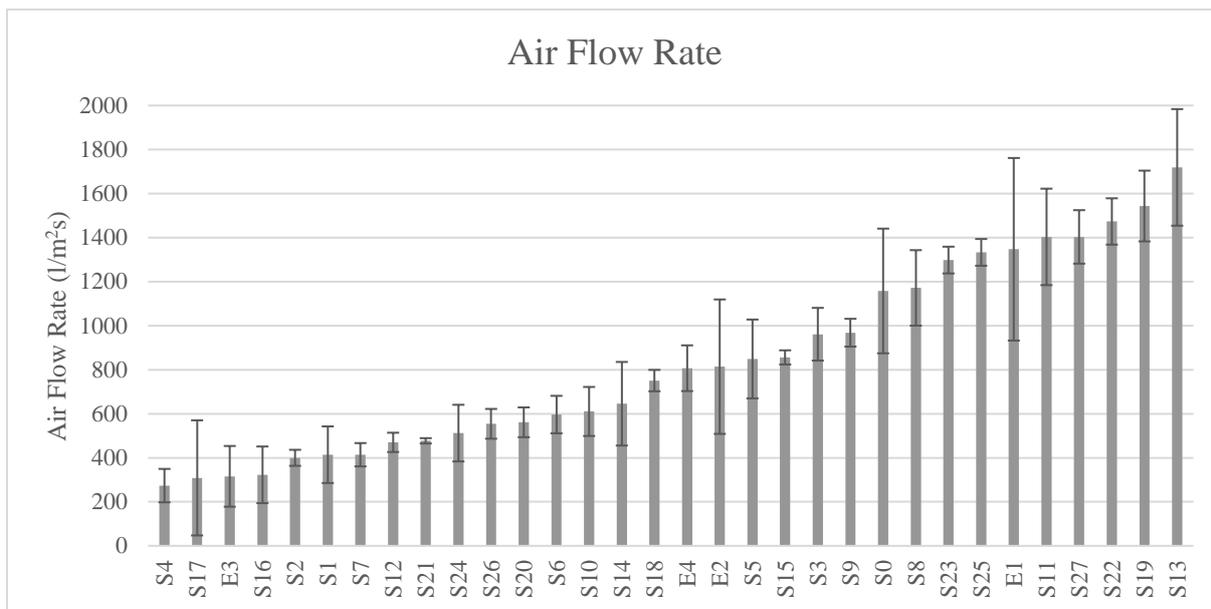
Figure 15: Average density for each sample in  $\text{g/cm}^3$ . Standard deviations are indicated with error bars.

In the graph in Figure 15, it can be noted that the density data follows the data from the thickness measurements, but in reverse. It can, in general, be seen that the thicker samples have lower densities, which comes as no surprise considering that roughly the same amount of cellulose solution was used in the production of the samples. However, some samples deviate from this trend which can be due to a number of reasons. Firstly, due to the turbulent nature of the solution blowing process, some samples might have experienced more waste of solution during the spinning process compared to others. Secondly, some of the samples treated with a surfactant might have more residues left on the samples, which can affect the weight of the sample. Thirdly, differences in density can be introduced through differences in thickness. As discussed above, it is possible that differences in thickness can stem from differences in handling during the drying step, especially during the vacuum suction-drying.

#### 4.4 Air Permeability

The data from the air permeability measurements are displayed in Appendix B.4. The samples were measured at three points, two close to each end and one in the middle, from which an average air flow rate could be calculated. The air flow rates had to be adjusted by multiplication with a factor of 21.05 to adjust for the size of the sample holder. Samples E5 and E6 could not be evaluated due to their brittleness.

A graph of the results from the air permeability measurements can be seen in Figure 16. In this graph, the air flow rates passing through the samples at a 2 mbar pressure difference are displayed, with standard deviations between the three measurements indicated with error bars. It can be noted that the results from this evaluation in many ways follow the results from the thickness measurement and density calculations. This is not surprising considering that less dense, and thus “fluffier”, samples should be more permeable to air as the fibres in these samples are less densely packed allowing for a higher flow of air to pass through.



**Figure 16: Average air flow for each sample expressed in l/m<sup>2</sup>s. Standard deviations between three measuring points per sample are indicated with error bars.**

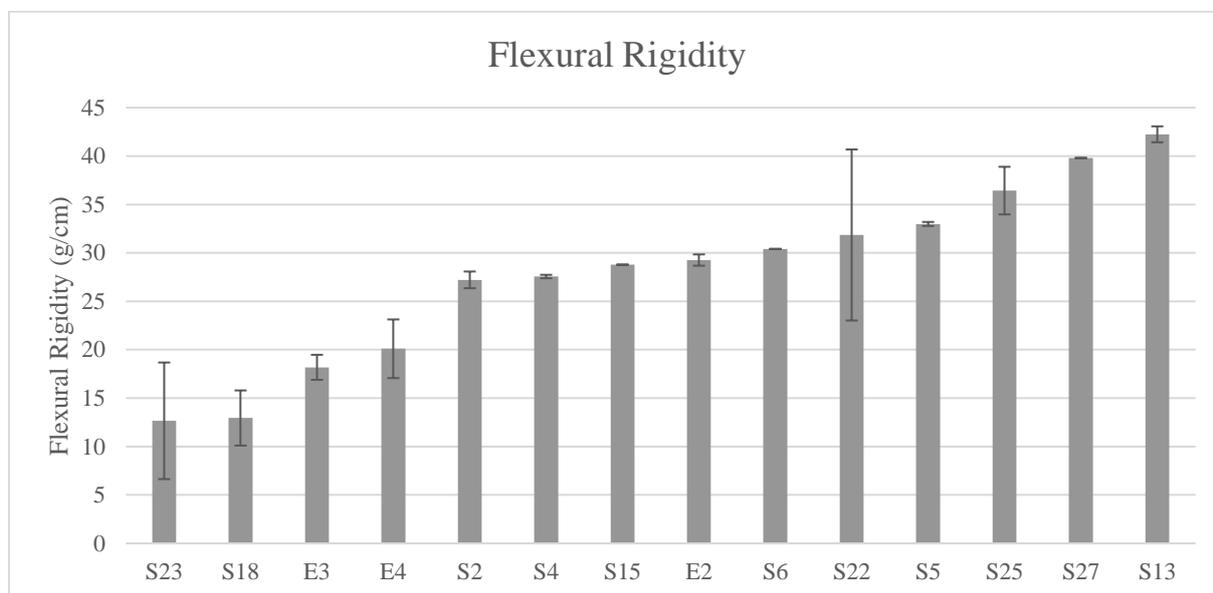
It can be seen clearly in Figure 16 that the drying method with the largest impact on the air permeability of the samples is the vacuum suctioning method. All of the eight samples with the highest air permeability (S23, S25, E1, S11, S27, S22, S19, S13) were dried using this method. All of the samples dried using this method, including the extra samples, are placed in the upper half of the air permeability range. One explanation for this behaviour could be that these samples display higher porosities compared to the other samples. Regarding the two press-based methods, the trend is not as clear. No samples dried in a press at 105°C (S17, S16, S12, S21, S24, S26, S20, S10, S14) can be found among the samples with highest air permeability, while four (S5, S3, S9, S8) of the ten samples dried in a press at room temperature can. This indicates that samples dried at an elevated temperature are slightly more prone to be less air permeable than samples dried at room temperature, at least when a press is used.

It is not possible to see any strong trends regarding the effect of surfactants on the air permeability of the samples. Samples washed in just water (S2, S1, S12, S10, S14, S15, S3, S0, E1, S11, S13) in the first washing bath can be found all over the air permeability range. Samples washed in Neutral® (S4, E3, S16, S21, S20, S6, S18, E4, E2, S5, S23, S22) seem to be connected to lower air flow rates while samples washed in Praelanol® (S17, S7, S24, S26, S9, S8, S25, S27, S19) seem connected to higher air flow rates. The trends are, however, not strong enough that any solid conclusions can be drawn.

Neither is it possible to see any strong trends regarding the effect of different solvents in the second washing bath. Samples washed in water seem to be vaguely connected to a lower air permeability, while samples washed in either acetone or isopropanol seem to be spread out over the air flow rate range. It is thus not possible to say that any of the levels of the second washing bath parameter has more effect on sample air permeability than the others.

## 4.5 Bending Length and Flexural Rigidity

The data collected from the deflection measurements can be found in Appendix B.5. Only fourteen of the samples were flexible enough to bend or bend enough to reach an angle of 41.5°, these are displayed in Figure 17. Of the 28 samples included in the experimental matrix, only eleven can be found in the graph.



**Figure 17:** Flexural rigidity (g/cm) for the samples that could bend to a 45.1° angle. Standard deviations between four measuring points per sample are indicated with error bars.

The clearest trend is that no samples dried in a press at 105°C could be measured since they were too stiff. Nine (S23, S18, E4, S15, E2, S22, S25, S27, S13) of the fourteen samples displayed in Figure 17 were dried using the vacuum suctioning method, while the remaining five were dried in a press at room temperature. Twelve samples overall were dried using the vacuum suctioning method. This indicates that the most beneficial drying method for the production of bendable cellulosic nonwoven materials is the vacuum suctioning method. This agrees with the results from the ‘bending’ component in the subjective fabric hand evaluation.

Most samples in Figure 17 were treated with Neutral® in the first washing bath (S23, S18, E3, E4, S4, E2, S6, S22, S5). This indicates that this surfactant is the most beneficial level of the first washing bath parameter for the production of bendable materials. However, the number of samples is small, so it is not possible to be certain of any conclusions. The other two levels, water or Praelanol®, are also represented in the graph with three samples having been washed in just water (S2, S15, S13) and two in Praelanol® (S25, S27). Most of these samples can be found among the samples with the highest flexural rigidity, further indicating the importance of Neutral® for the production of easy-to-bend cellulosic nonwovens.

Isopropanol is the most abundant solvent used in the second washing bath represented in the bending measurement data. However, only five samples (S2, S22, S5, S25, S13) out of the fourteen were washed with this solvent, and most of these can be found among the least bendable of the fourteen. Three of the samples (S15, S6, S27) were washed with acetone, and two were washed with water (S18, S4). The remaining three samples consist of the extra

samples, with one (E2) washed in ethanol and two (E3, E4) dried directly from the first washing bath. This makes it impossible to draw any conclusions regarding the effect of the solvents used in the second washing bath on the bendability of the samples.

## 4.6 Light Microscopy Pictures

The light microscopy pictures of the samples can be seen in Appendix B.6. These images are taken at 4x magnification and gives a general idea of what the samples' fibre structures look like. It is, however, difficult to draw any concise conclusions regarding the properties or behaviours of the samples from these pictures. All pictures are quite similar and displays similar structures at this level of magnification, making it difficult to attribute certain characteristics measured in the other evaluation methods to a certain kind of fibre structure or style of fibre aggregation. An example of what the samples look like can be seen in Figure 18, which displays sample S7. The nature of the samples makes it difficult to take good pictures, a problem which increases with increasing magnification. The samples are too thick, and in some cases also too “fluffy”, to photograph well, with the result that large areas of the pictures sometimes end up being out of focus due to the fibres being at different levels. This is especially noticeable for the freeze-dried samples, E5 and E6. The samples dried in a flower press, however, were easier to get into focus due to them being flatter.

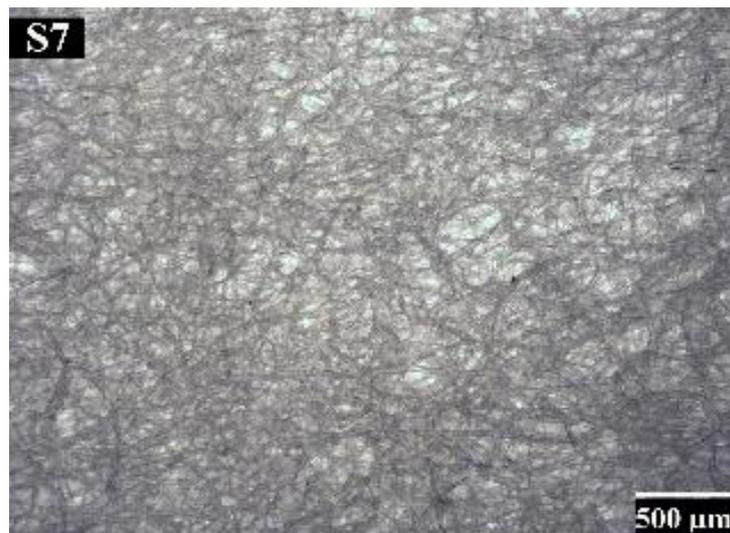


Figure 18: Light microscopy picture for sample S7.

When fibre thickness was measured, no large differences between the samples could be observed. All samples displayed fibres ranging from about 1  $\mu\text{m}$  to 50  $\mu\text{m}$  in thickness. A similar fibre thickness distribution between the samples was to be expected considering that the same production method was used for all the samples up until the after treatment.

It was not possible to draw any conclusions using light microscopy regarding the way the fibres within one sample behaved in relation to each other. What is apparent is that the fibres have formed a typical nonwoven material where they have fallen in a random pattern, but more than that is not possible to say with this technique.

## 4.7 Scanning Electron Microscopy Pictures

Scanning electron microscopy (SEM) pictures of samples S0, S13, S15, and S18 can be seen in Figure 19, and pictures of samples S22, S23, S27, and E5 can be seen in and Figure 20. At first, only samples S0, S13, S23, and E5 were selected for SEM analysis. However, the images from the vacuum suction-dried samples (S13, S23) displayed such interesting fibre structures that a few more samples were selected for evaluation. To get a more comprehensive understanding of the fibre structures, all samples should be studied with SEM. This was, however, not possible due to time constraints.

The sample corresponding to the “original” sample treatment method, S0, displays a broad range of fibre diameters, with clusters of very thin fibres. An edge of one of these clusters can be seen in the lower left corner in Figure 19 (a). It can be noted that the fibres are more or less straight and are arranged in a typical nonwoven style with fibres laying randomly in all directions.

The image of sample S13 in Figure 19 (b) looks a bit different than the image of S0. Sample S13 was washed with water in the first washing bath, isopropanol in the second washing bath, and was dried using the vacuum suctioning method. While the fibre range distribution in this sample is similar to the distribution in S0, the fibres look less densely packed. This makes it difficult to get a picture with a good sharpness; in order to get a few fibres into focus, a lot of other fibres end up being out of focus. This sense of fibre separation agrees with the results from the thickness and air permeability measurements. It makes sense for a “fluffier” sample to have a less densely packed fibre structure at a microscopic level. It can also be noted that several of the fibres shown in Figure 19 (b) are more curly than straight, which might contribute to the “fluffiness” of the sample.

Some curliness can also be seen in sample S15, which is displayed in Figure 19 (c). This sample was washed in water in the first washing bath, acetone in the second washing bath, and was dried using the vacuum suctioning method. The fibres in this sample are not as curly as in S13, but some curly tendencies are still displayed. The image of S15 more closely resembles the image of S0 than S13 does, which agrees with the fact that S15 is very close in thickness to S0. They are also closer in air permeability, however, S15 could bend enough to be measured in the bending length measurement while S0 could not. Regarding fibre diameter range, S15 overall displays a similar distribution as S0 and S13.

The fourth sample that was studied with SEM was S18, which can be seen in Figure 19 (d). This sample was washed with Neutral® in the first washing bath, water in the second washing bath, and was dried using the vacuum suctioning method. This sample does not display a large amount of curly fibres, although a few can be observed. The fibre diameter range, once again, matches that of the three previously discussed samples. A few fibres that are seemingly more flat than round can be observed.

When it comes to curliness, samples S22 and S23 are the most notable of the samples studied using SEM. S22, which can be seen in Figure 20 (a), was washed in Neutral® in the first washing bath, isopropanol in the second washing bath, and was dried using the vacuum suctioning method. S23, visible in Figure 20 (b), was treated similarly, but was washed with

acetone instead of isopropanol in the second washing bath. Both of these samples display very curly fibres with fibre diameter ranges similar to the previously observed samples. The surface of the fibres in S23 seem to be smoother than in the other samples observed, and the fibres look more round. It is difficult to know why that is, but it is important to note that this sample was one of the overall highest graded for all components in the subjective fabric hand evaluation and the most flexible of the samples observed, so the fibre curliness and smoothness might be contributing factors to these results.

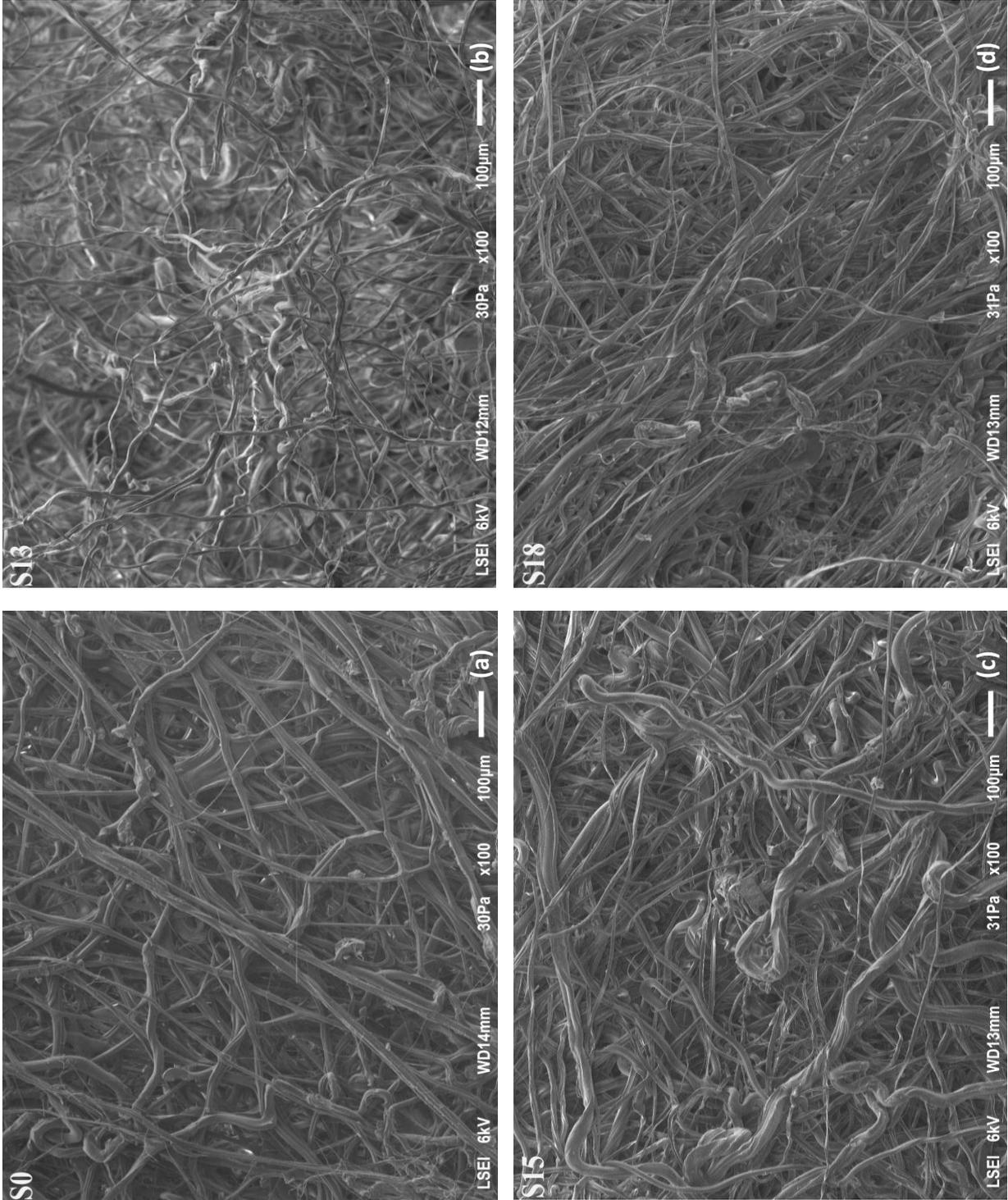


Figure 19: Scanning electron microscopy pictures at x100 magnification of samples S0, S13, S15, and S18.

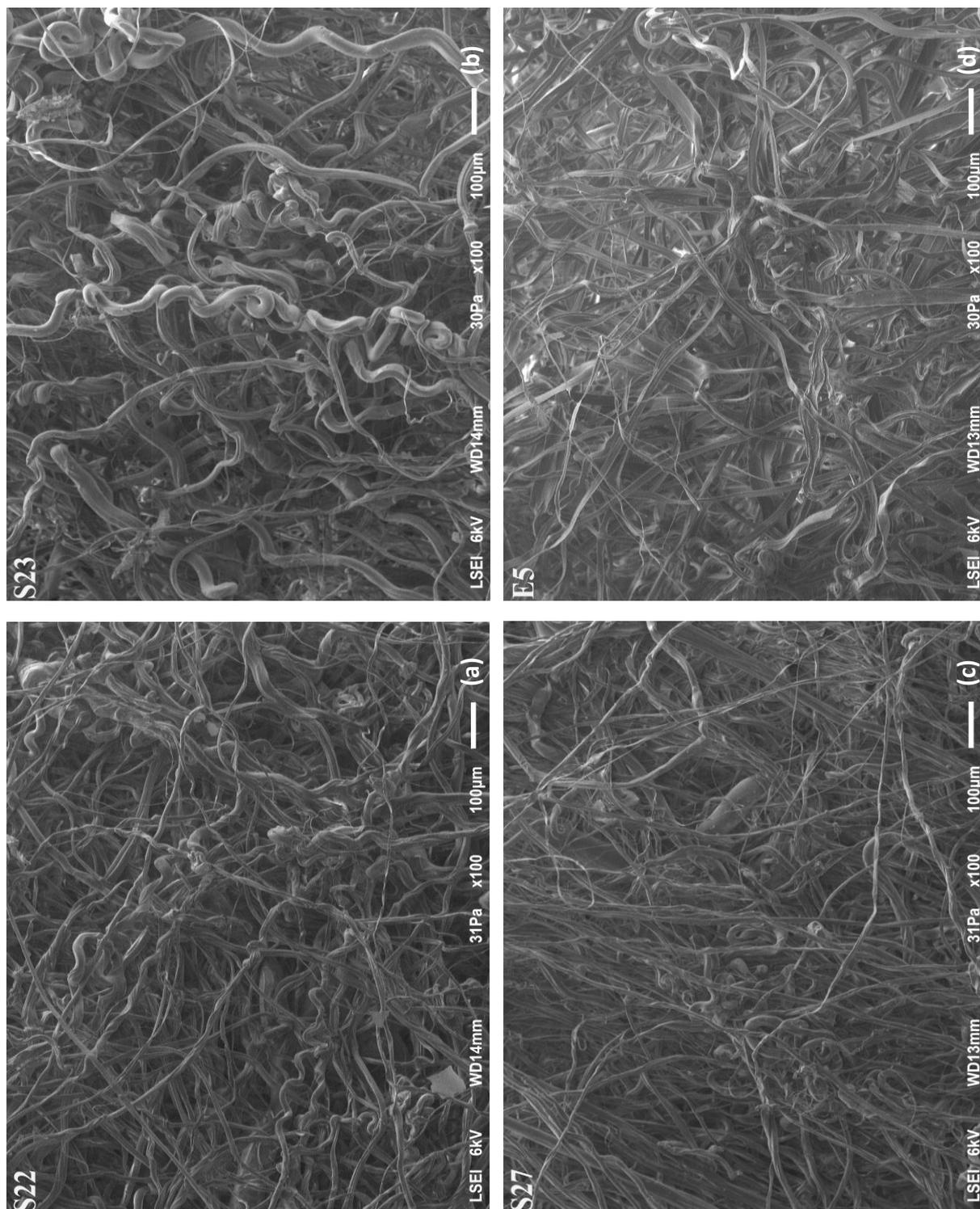


Figure 20: Scanning electron microscopy pictures at x100 magnification of samples S22, S23, S27, and E5.

A sample which shows a similar curly tendency is S27, which can be seen in Figure 20 (c). This sample was washed with Praelanol® in the first washing bath, acetone in the second washing bath, and was dried using the vacuum suctioning method. Both curly and straight fibres can be seen, some with smoother surfaces and some with more rough. Again, the fibre diameter range is similar to those previously observed. It can be noted that curly fibres are clearly present in all of the samples washed with either isopropanol or acetone and dried using vacuum

suctioning, but only to a small degree or barely at all in the water-washed and vacuum suction-dried samples. This indicates that the solvent used in the second washing bath has an impact on the fibre structure and has the power to make fibres more or less curly. Further studies would have to be performed to decipher why, but one reason could be that the solvent creates forces along the surface of the fibre which can make some parts of the fibre surface expand while other parts shrink. The curliness could also stem from some surfaces being more available for solvent exchange than others, causing the fibre to curl upon the changing of washing baths. It is also possible that fibres are attached to each other at connection points, and that the solvent exchange occurring during the second washing step makes it so that the fibres are drawn in different directions, causing tensions and creating a curly structure upon drying. It can also be noted that the two most curly samples, S22 and S23, were both treated with Neutral®. It is possible that the combination of the surfactant and acetone or isopropanol has an effect on the curliness and the smoothness of the fibres as well.

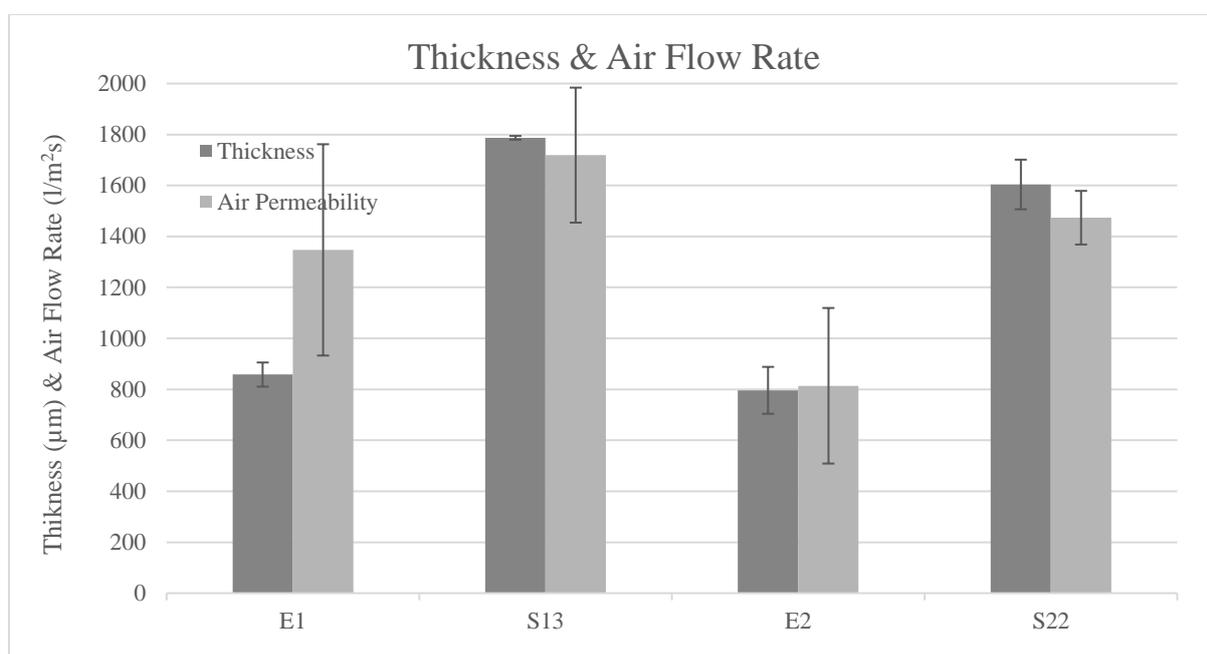
The last sample that was studied with SEM is E5, which is displayed in Figure 20 (d). This sample was washed in two water baths and was then dried using freeze-drying. The most noticeable difference in the picture of E5 compared to the other samples is that the fibres appear to be flat, almost ribbon-like. Most of the fibres in the other samples were more round, although only S23 displayed an abundance of really round fibres. It is possible that the fibres were flattened during the freezing step if the water retained in the fibre structure suddenly needed to expand and was limited by the shape of the fibre, causing the fibre to break and become flat. To further understand this phenomenon, the fibre structure of a non-dried sample should be studied. This would be possible, yet difficult, to do with a light microscope.

## **4.8 The Extra Samples**

The two extra samples washed with ethanol in the second washing bath (E1, E2) can be compared to the samples washed in isopropanol that otherwise had the same levels on the parameters first washing bath and drying method (S13, S22 respectively). Both samples washed with ethanol displayed lower air permeability compared to the isopropanol-treated samples, see Figure 21. They are also clearly thinner than their isopropanol-treated counterparts. Regarding flexural rigidity, only E2 from the two ethanol-treated samples could bend enough to be measured. Both E2 and S22 display similar bending lengths. S13 could bend enough to be measured, however, it is still the stiffest of the samples that could bend enough. It can thus be noted that neither E1 nor S13 are very flexible compared to some of the other samples, such as S23 for example. It is not possible to draw any certain conclusions from the results from only two samples, but the data indicates that isopropanol might be more suitable for the production of textile-like cellulosic nonwovens compared to ethanol. However, more tests are needed to confirm this.

The two samples dried directly from a bath containing Neutral® (E3, E4) can be compared to the other samples washed in Neutral® and dried with the same drying methods (S4, S5, S6, and S18, S22, S23). Both of the two samples, E3 and E4, could bend enough to be measured in the evaluation of flexural rigidity. The same goes for samples S4, S6, S18, S22, and S23. As mentioned before, this is indicative of the softening properties of the surfactant. Samples E3,

S4, S5, and S6 were dried in a flower press at room temperature and are thus, in general, on the thinner side of the thickness spectra. They place in the lower portion of the air permeability range indicating that the fibres in these samples are, in general, more densely arranged than in other samples. Especially E3 is noticeable as this sample is the second to least air permeable of all evaluated samples. An explanation for this could be that residues of surfactant hinder the air flow. Samples E4, S18, S22, and S23 were dried using the vacuum suctioning method. These samples are on the thicker side of the thickness range and are also among the most air permeable. The vacuum suctioning drying method seem to have a dominant effect on air permeability compared to the second washing bath for these samples, so no conclusions can thus be made regarding the effects of drying directly from surfactant. Again, more samples would be needed to test this method further.



**Figure 21:** Thickness and air flow rate for the two samples treated with ethanol in the second washing bath (E1, E2) and their isopropanol-treated counterparts (S13, S22). Thickness is measured in  $\mu\text{m}$  and air flow rate in  $\text{l/m}^2\text{s}$ , standard deviations are marked with error bars.

The two freeze dried samples (E5, E6) displayed interesting properties such as “fluffiness” and ribbon-like fibre structures. It was decided to attempt this drying method to see if it was even possible for this type of material to be dried in this way. The attempts were successful in that the samples display a high level of softness and “fluffiness”, but the freezing method has to be further developed so that the samples do not break for this method to be a viable option.

## 4.9 The Effects of the Treatment Methods

It is difficult to deduce exactly why the samples display the properties they do when the number of samples, and thus the amount of data, is limited. With more repeats of certain samples and with more types of evaluations, a more thorough analysis could be made. However, the results from the evaluations can still give an indication of why the samples show certain properties and which properties that seem to be more important for production of textile-like cellulosic nonwovens.

The seemingly most impactful treatment method parameter of the ones tested in this project is the drying method. Which drying method that was used impacted the thicknesses and densities of the samples, and also the air permeability, bendability, and perceived softness. This indicates that the different drying methods generate differences in not only fibre morphology, but also in the amount of connection points existing between the fibres in the samples. More SEM pictures displaying samples dried with different methods would be needed to study this further and would also generate a possibility to study the amount of fibre connection points between samples. Fewer connection points between fibres would mean more space for each fibre to move, making the material less rigid and leaving more pathways open for air to pass thorough the sample which mean a higher air permeability. This might, however, have an effect on the tensile strength of the material if there are fewer points holding the sample together. The samples dried in a flower press had their fibres pressed closer together during the drying step, making it possible for the fibres to create more densely packed arrangements. The fibres in the samples dried with vacuum suctioning, on the other hand, were allowed more space during the drying step, resulting in a more airy structure.

The usage of different solvents during the second washing step seemingly has an effect on the fibre morphology. This can be seen in the SEM pictures of some of the vacuum suction-dried samples which display a larger amount of curly fibres in the samples washed with acetone or isopropanol. The solvent exchange occurring upon the changing of washing baths might be one of the causes for the curly fibres. This, in turn, might be one of the reasons why these samples, in general, showed more textile-like properties. Both acetone and isopropanol can have effects on the intramolecular hydrogen bonding in the samples, generating materials with less strongly bonded fibres compared to samples washed in water. Just as with fewer connection points, fewer hydrogen bonds between fibres can cause more bendable and air permeable materials when the fibres can move more freely in relation to each other.

Regarding the effect of surfactants, the results indicate that the cationic fabric softener has had the largest positive effect on the samples. This was expected since a cationic surfactant presumably should interact better with the slightly negatively charged cellulose structure compared to what an anionic surfactant should. More interactions between the fibres and the surfactant could reduce the number of hydrogen bonds and could also have possible effects on hydrophobic interactions. One of the actions of a fabric softener is also to smooth surfaces of fabrics by interrupting electrostatic repulsion which is making fibres protrude from the surface of the material. This generates a softer surface feel, which the samples treated with the fabric softener in this project seem to experience as well, according to the results from the hand evaluation.

#### **4.10 Future Outlook and Additional Evaluation Methods**

A subjective method to evaluate the hand feel of the samples had to be developed for this project so that the hand feel properties of the samples could be compared and the treatment methods' influence on the hand feel properties evaluated. There exist objective methods for measuring compression, bending, and surface feel of fabric, however, not all of those were available for this project. Bending length, and thus flexural rigidity, could be measured and the results could

be compared to those from the subjective evaluation of the ‘bending’ component. It could be of interest for further studies to explore methods to measure compression and surface feel in an objective way which would also enable the properties to be compared to other nonwoven materials.

Another additional evaluation method that could be of interest is tensile testing, which can give information on the strength, stiffness, and elongation properties of a material [28]. It would be of interest to compare different treatment methods’ effect on the stress response of a sample if this type of nonwoven material is to be further developed. Again, this would make it easier to compare the samples to other nonwoven materials.

It would also be of interest to further study the samples, and future samples, with SEM to get a better understanding of the treatment methods’ effect on the shape of the fibres. Additionally, it would be beneficial to study the fibre shape of a non-dried sample using light microscopy in order to gain understanding of what happens during the drying step. This is especially interesting in regard to the ribbon-like shape of the fibres in the freeze-dried samples. SEM pictures could also be used to study fibre connection points.

The method of freeze-drying of cellulosic nonwovens was only briefly tested in this project. The samples dried with this method are fluffy and soft, which makes this drying method interesting. It would be interesting to further dive into this topic and to find a way to freeze the material without it breaking. A possibility would be to attempt drying from another solvent than water. Freeze-drying is an expensive and time-consuming drying method; however, it could still be of value to study this method further to gain more understanding of cellulosic nonwoven materials.

In order to make larger pieces of cellulosic nonwoven material, a larger nozzle has to be used. For further development of cellulosic nonwovens beyond this project, using a larger nozzle is recommended. Having larger pieces of material to evaluate would make further development easier. It would also be of interest to attempt a different sort of collection surface, such as a conveyor belt instead of a spinning drum. When the drum spins, the material is collected in layers. On a conveyor belt, the material would instead be collected in a single layer, which could have possible effects on the properties of the material.



## 5 Concluding Remarks and Conclusion

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The purpose of this project was to study treatment methods for cellulosic nonwovens produced through solution blowing of cellulose dissolved in the ionic liquid EMIMAc. Three different treatment steps were tested: two consecutive washing baths and a drying step. These three steps were treated as parameters in a 3<sup>3</sup>-factorial design and thus had three levels each which corresponded to different treatment methods. The first washing bath tested the effects of anionic and cationic surfactants, the second washing step tested the influence of different solvents, and the last step tested three different approaches to drying of the samples. A few extra samples were also created to get an idea of the effect of other possible treatment methods to look at in the future.

The treatment step with the largest impact on the evaluated properties is the drying method. The vacuum suctioning method stands out as the most beneficial method for drying of samples when the aim is to get more textile-like materials. This drying method generated the most highly graded samples in the subjective fabric hand evaluation for all the evaluated components. The samples dried with this method are, in general, thicker and more air permeable than the samples dried in a flower press. They also tend to bend more easily which, along with a soft surface feel, makes them more textile like. The samples dried in a flower press at an elevated temperature showed properties that were more paper like, especially in the bending test and in the hand evaluation. Most of the samples dried at room temperature in a flower press show similar properties as those dried at 105°C on several of the evaluation, however, this method also generated some samples with more textile like properties.

The presence of a surfactant did not appear to be highly important for the thickness, density, and air permeability of the samples. Neither did the presence of a surfactant seem to be of high importance for the feel of the components ‘compression’ and ‘bending’ in the subjective fabric hand evaluation. Neutral® appeared to be connected to slightly higher grades, but the greatest take-away is that having a surfactant is better than just using water. However, for the third component in the hand evaluation, ‘surface’, the presence of a surfactant seems to be of higher importance. It is specifically Neutral® which stands out as more connected to higher grades and thus to a more textile like feel.

Which type of solvent that is used in the second washing bath (water, acetone, or isopropanol) does not seem to have a large impact on thickness and air permeability. However, it becomes clear in the subjective fabric hand evaluations that samples washed in either acetone or isopropanol are connected to higher grades for all of the three components evaluated. Both acetone-treated and isopropanol-treated samples received high grades; however, there is a small indication that isopropanol is slightly more beneficial for the production of samples with textile like hand properties. SEM picture of the samples showed curly fibres being present in vacuum dried samples washed in either acetone or isopropanol. The samples with the most curly fibres visible had been treated with Neutral®, indicating a connection between surfactant and solvent. These are interesting tendencies that need further testing to be understood.

## **5.1 Conclusion**

The treatment methods used after solution blowing of cellulosic nonwovens can have large impacts on the properties of the material produced. In order to produce materials with textile-like rather than paper-like properties, the most important step is the drying method. Vacuum suction-based drying can create bendable materials with a textile-like hand feel in an efficient and sustainable way. This drying method does not require any additional chemicals and can easily be upscaled from the laboratory scale used in the project. The textile-like properties of the material can be further improved if a surfactant is used during the washing of the material after solution blowing. A common, cationic, fabric softener such as Neutral® is suitable for this task. It is also beneficial for the properties of the material if a bath containing a solvent such as acetone or isopropanol is introduced.

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# Appendices

# Appendix A – Protocols

This appendix details some of the pieces of equipment used in this project. Furthermore, protocols for dissolution of cellulose and for surfactant preparations can be found here. The experimental design and the extra samples are detailed in full, as well as the instructions for the subjective hand evaluation.

## A.1 Equipment

Figure A.1 a) depicts one of the flower presses used in the project. The press was loaded with several layers of absorbent paper tissues (in blue), a thinner layer of white paper tissue, and two layers of wire mesh between which the samples were placed. The white paper tissues were used to prevent staining of the samples from the blue paper tissues.



Figure A.1: a) One of the flower presses used during the drying of some of the cellulosic nonwoven samples produced in the project. b) The funnel construction used for vacuum drying of the samples. A vacuum machine was used to draw the liquid out of the samples placed on top of a mesh on top of the funnel.

Figure A.1 b) shows the funnel construction used for vacuum drying of the samples. The funnel is originally designed to be used with a vacuum machine to separate berries from dirt but was repurposed in this project. A wire mesh of metal was placed on top of the funnel with an additional layer of finer wire mesh on top. The meshes were taped into place using duct tape, which was also used to secure tight seals between all the connecting parts. When a sample was being dried, a twice folded piece of tissue paper was placed on top of the sample to ensure that as little air as possible would be leaking past the sample.

## A.2 Cellulose Dissolution Protocol

This is the protocol for the dissolution of cellulose in EMIMAc, from which an 80 ml sample with 5-wt % cellulose concentration can be generated. The cellulose pulp had been grinded and dried at 105°C for 4 hours before dissolution.

1. Measure the dryness percentage (DP) of the cellulose and calculate the weight of cellulose ( $w_{\text{cellulose}}$ ) that needs to be added to get a 5-wt % cellulose concentration in the finished solution according to Equation A.1. The ideal cellulose weight ( $w_{\text{ideal}}$ )

corresponds to the weight of cellulose needed to get a 5-wt% cellulose concentration if the DP was 1. For the production of 80 ml of sample,  $w_{ideal} = 4$  grams.

$$w_{cellulose} = \frac{w_{ideal}}{DP} \quad (A.1)$$

2. Calculate the amount of EMIMAc according to Equation A.2.

$$w_{EMIMAc} = 80 - w_{cellulose} \quad (A.2)$$

3. Place the cellulose and the EMIMAc in a glass reactor placed in an oil bath heated to 70°C. Stir for 1 hour at 100 rpm.
4. Let the cellulose solution cool before transferring to a second vial for storage in room temperature until solution blowing.

### A.3 Experimental Design

The 3<sup>3</sup>-experimental design used in this project is displayed in Table A.1. The table shows which sample corresponds to which level of the three variables ‘Wash Bath 1: Surfactant’, ‘Wash Bath 2: Solvent’, and ‘Drying method’. For the surfactant variable, the three levels are no surfactant, the common fabric softener Neutral®, and Praelanol®. For the solvent variable, the three levels are water, isopropanol, and acetone. For the drying method variable, the three levels are pressing at room temperature, pressing in an oven at 105°C, and vacuum suctioning at room temperature (around 22°C). A sample representing the original methods for washing and drying was included as well to be used as a reference during evaluation.

Table A.1: The 3<sup>3</sup>-experimental design used in the project, which describes which sample correspond to which level of the three variables. A sample called S0 is included as a representative of the “original” washing and drying methods.

Sample Name	Wash Bath 1: Surfactant	Wash Bath 2: Solvent	Drying Method
S0	No surfactant	Water	Pinning to surface at room temperature
S1	No surfactant	Water	Press at room temperature
S2	No surfactant	Isopropanol	Press at room temperature
S3	No surfactant	Acetone	Press at room temperature
S4	Neutral®	Water	Press at room temperature
S5	Neutral®	Isopropanol	Press at room temperature
S6	Neutral®	Acetone	Press at room temperature
S7	Praelanol®	Water	Press at room temperature
S8	Praelanol®	Isopropanol	Press at room temperature
S9	Praelanol®	Acetone	Press at room temperature
S10	No surfactant	Water	Press at 105°C
S11	No surfactant	Water	Suctioning
S12	No surfactant	Isopropanol	Press at 105°C
S13	No surfactant	Isopropanol	Suctioning
S14	No surfactant	Acetone	Press at 105°C
S15	No surfactant	Acetone	Suctioning
S16	Neutral®	Water	Press at 105°C
S17	Praelanol®	Water	Press at 105°C
S18	Neutral®	Water	Suctioning

<b>S19</b>	Praelanol®	Water	Suctioning
<b>S20</b>	Neutral®	Isopropanol	Press at 105°C
<b>S21</b>	Neutral®	Acetone	Press at 105°C
<b>S22</b>	Neutral®	Isopropanol	Suctioning
<b>S23</b>	Neutral®	Acetone	Suctioning
<b>S24</b>	Praelanol®	Isopropanol	Press at 105°C
<b>S25</b>	Praelanol®	Isopropanol	Suctioning
<b>S26</b>	Praelanol®	Acetone	Press at 105°C
<b>S27</b>	Praelanol®	Acetone	Suctioning

### A.3.1 Extra Samples

Table A.2 displays the six extra sample produced to expand on the original experimental matrix. For these samples, additional methods for cellulosic nonwovens were tried such as freeze drying, washing with ethanol, and drying directly from a washing bath containing a surfactant.

**Table A.2:** The six extra samples produced to expand the original experimental design.

Sample Name	Wash Bath 1: Surfactant	Wash Bath 2: Solvent	Drying Method
<b>E1</b>	No surfactant	Ethanol	Suctioning
<b>E2</b>	Neutral®	Ethanol	Suctioning
<b>E3</b>	Neutral®	-	Press at room temperature
<b>E4</b>	Neutral®	-	Suctioning
<b>E5</b>	No surfactant	Water	Freezing
<b>E6</b>	Neutral®	Water	Freezing

## A.4 Protocol for Preparation of Surfactants

These protocols describe the preparations of the surfactant solutions used in the project. Each of the protocols are calculated for one sample bath. In the instances where several baths could be prepared at the same time, the amounts used in the protocols were multiplied accordingly.

**Fabric softener:** 12.75 g of fabric softener was diluted with deionised water to a total volume of 0.75 litres. This generated a surfactant concentration of 17 g/litre.

**Praelanol®:** 0.2003 g of the Praelanol® paste was dissolved in 0.75 litre deionised water at a temperature of 50°C with moderate stirring. This generated a Praelanol®-concentration of 0.267 g/litre.

## A.5 Subjective Fabric Hand Evaluation Instructions

The instructions given to the participants of the subjective fabric hand evaluation were inspired by AATCC's Evaluation Procedure 5 [20]. Below follow the instructions given to the participants at the place of evaluation. Before the evaluators were allowed to participate, the samples were anonymised in order to prevent the evaluation being affected by bias. The evaluation took place in a controlled environment (22°C, 65 % relative humidity).

### A.5.1 Instructions for Evaluators

Every sample (1-28) should be given a grade from 1-4 for the three categories (constituent elements of hand) listed under “Terminology”. The words in Table A.3 can be used as a reference for an easier evaluation of the different categories.

Be careful with the samples! Do not bend them so much so that they cannot return to their original shape.

Wash your hands before the evaluation begins and do not use hand crème.

#### Give a grade according to:

The goal material in this project should be soft and easy to bend, with more textile like properties than paper like properties. A low grade in this evaluation corresponds to a more paper-like material, while a high grade corresponds to a more textile like material.

**Follow the instructions below to judge the categories and mark your answer with a circle in the questionnaire. See “Terminology” below for examples of words which can be used to describe the materials according to the categories.**

1. Compression: Carefully press the sample between thumb and index finger repeatedly.
2. Bending: Hold the sample in one hand and bend it carefully back and forth, without bending it sharply.
3. Surface: hold the sample in one hand and stroke along the surface of the sample with the index finger of the other hand or rub the sample carefully between thumb and index finger.

#### Terminology:

Hand – “the tactile sensations or impressions which arise when fabrics are touched, squeezed, rubbed, or otherwise handled”

Constituent elements of hand – those components, qualities, attributes, dimensions, properties, or impressions which make the sensation of touching one material different from that of touching another. Categories used in this evaluation: compression, bending, and surface.

Table A.3: Constituent Elements of Hand.

Compression	Bending	Surface
Soft	Springy	Smooth
Springy	Soft	Soft
Hard	Limp	Fuzzy
Firm	Papery	Scratchy
	Boardy	Coarse
	Firm	Rough
	Stiff	Raspy

# Appendix B – Results

This appendix contains the results achieved during the evaluation of cellulosic nonwoven samples produced with solution blowing in this project. Pictures of the samples along with detailed data from the evaluations are presented in this appendix.

## B.1 Pictures of the Samples

Pictures of the samples before they were cut into strips are displayed in Figure B.1, with figure (a) displaying samples S0 to S6. Sample S0 represents the “original” methods for washing and drying and was used as a reference during the evaluation of the other samples. Samples S7 to S13 are displayed in Figure B.1 (b), samples S14 to S20 in Figure B.1 (c) and samples S21 to S27 in Figure B.1 (d).

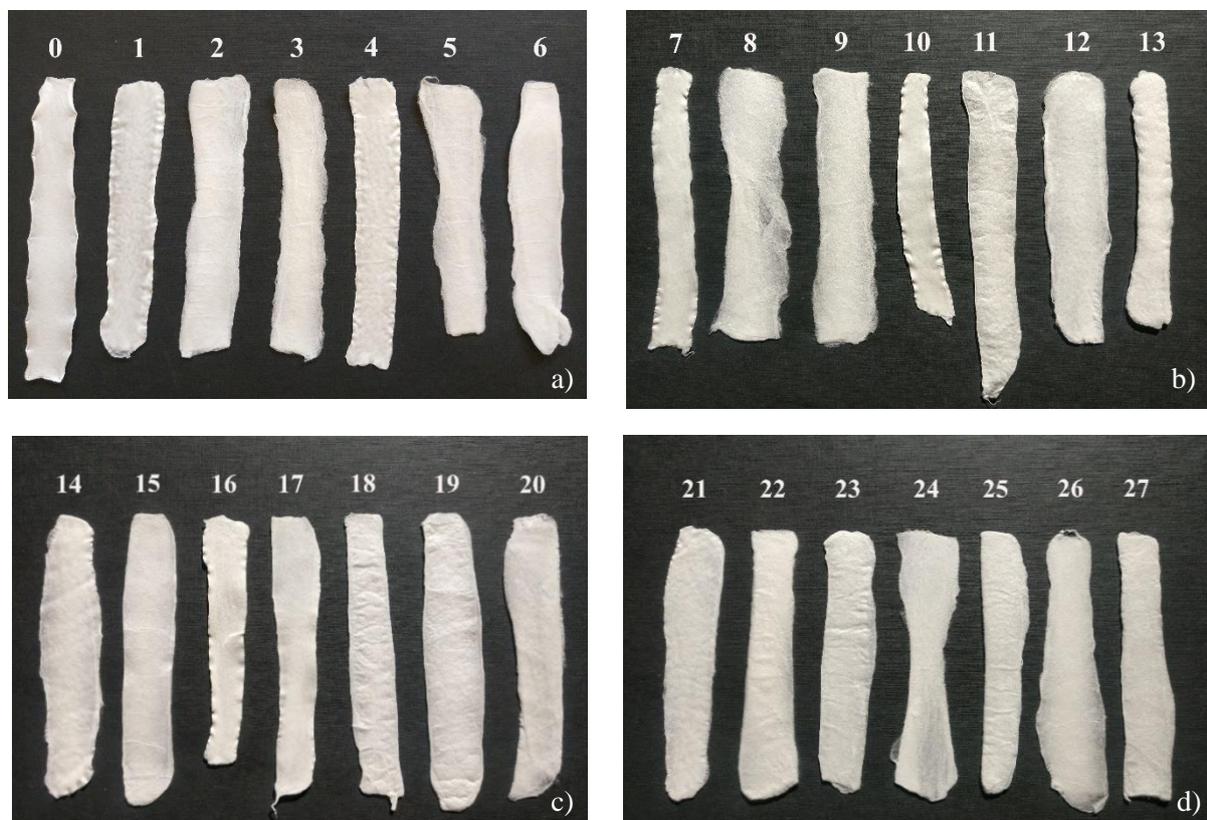


Figure B.1: a) Samples S0 to S6. Sample S0 was washed and dried according to the “original” method and is included as a reference material when evaluating the samples in the experimental matrix. b) Samples S7 to S13. c) Samples S14 to S20. d) Samples S21 to S27.

Pictures of the additional samples are displayed in Figure B.2. These samples were added after the subjective fabric hand evaluation had been conducted and serves as an expansion of the original experimental matrix.



Figure B.2: The six extra samples produced as an expansion of the original experimental matrix.

## B.2 Subjective Fabric Hand Evaluation Results

The results from the subjective fabric hand evaluation are presented in Table B.1. The values displayed are the calculated averages from 10 evaluators. The standard deviations, SD, for each of the three components are included in the table as well.

Table B.1: Results from the subjective fabric hand evaluation. Displayed are the average values collected from 10 participants allowed to evaluate the samples regarding compression, bending, and surface texture. The standard deviations for the three components are included as well.

Sample	Compression	SD <sub>Comp</sub>	Bending	SD <sub>Bend</sub>	Surface	SD <sub>Surf</sub>
S0	1.0	0.00	1.0	0.00	1.1	0.30
S1	1.0	0.00	2.0	0.83	1.4	0.50
S2	2.3	0.64	2.8	0.75	2.9	0.89
S3	1.9	0.54	1.9	0.60	2.2	0.75
S4	1.3	0.46	2.7	0.49	2.1	0.87
S5	2.0	0.70	2.8	0.46	2.3	0.66
S6	2.2	0.60	2.3	0.46	3.0	0.70
S7	1.1	0.30	1.1	0.30	1.6	0.50
S8	1.8	0.60	1.8	0.75	1.9	0.77
S9	1.6	0.49	1.9	0.30	2.3	0.46
S10	1.0	0.00	1.0	0.00	1.7	0.78
S11	1.4	0.50	1.8	0.40	2.0	0.63
S12	2.0	0.30	2.6	0.67	2.0	0.63
S13	3.9	0.30	3.9	0.30	3.6	0.66
S14	1.2	0.40	1.3	0.46	1.8	0.83
S15	2.3	0.78	3.0	0.54	3.0	0.63
S16	1.2	0.40	1.2	0.40	2.2	0.64
S17	1.0	0.00	1.1	0.30	2.2	1.02
S18	3.4	0.49	3.8	0.40	3.6	0.49
S19	1.8	0.60	1.8	0.60	1.9	0.54
S20	1.8	0.40	1.7	0.46	2.7	0.87
S21	1.6	0.49	1.8	0.40	2.0	0.63
S22	3.9	0.30	3.9	0.30	3.8	0.40
S23	3.6	0.66	3.9	0.30	3.7	0.46

<b>S24</b>	1.8	0.60	1.7	0.49	3.0	0.94
<b>S25</b>	3.0	0.54	3.0	0.30	3.6	0.49
<b>S26</b>	1.6	0.49	1.4	0.50	2.6	0.80
<b>S27</b>	3.0	0.77	3.2	0.60	3.0	0.45

### B.3 Data for Sample Thickness, Surface Weight and Density

The thicknesses of the samples were measured by a digital micrometre which was run three times for each sample: at the two ends of the sample in question as well as in the middle. Table B.2 displays the results from the three runs and the calculated average thickness. The table also includes the standard deviation between the three measurements.

**Table B.2: Sample thickness measured in  $\mu\text{m}$ . Three measurements per sample were performed, and average thickness and standard deviation were calculated for each sample.**

Sample	Thickness			Average Thickness ( $\mu\text{m}$ )	Standard deviation
	Test 1 ( $\mu\text{m}$ )	Test 2 ( $\mu\text{m}$ )	Test 3 ( $\mu\text{m}$ )		
<b>S0</b>	652	690	652	665	21.72
<b>S1</b>	500	418	458	458	40.94
<b>S2</b>	600	602	613	605	7.08
<b>S3</b>	1096	1150	1154	1134	32.49
<b>S4</b>	379	432	417	409	26.92
<b>S5</b>	869	729	839	812	74.01
<b>S6</b>	765	910	717	797	100.35
<b>S7</b>	630	644	585	620	30.88
<b>S8</b>	1050	1034	1050	1045	9.04
<b>S9</b>	863	872	883	872	10.06
<b>S10</b>	788	824	764	792	29.87
<b>S11</b>	921	928	901	917	14.22
<b>S12</b>	833	592	644	690	126.80
<b>S13</b>	1781	1784	1795	1787	7.40
<b>S14</b>	993	763	704	820	152.81
<b>S15</b>	666	682	647	665	17.58
<b>S16</b>	686	673	679	679	6.51
<b>S17</b>	415	318	384	372	49.88
<b>S18</b>	791	777	771	780	10.22
<b>S19</b>	1002	995	998	999	3.56
<b>S20</b>	829	788	689	769	71.90
<b>S21</b>	518	781	664	655	131.95
<b>S22</b>	1495	1683	1634	1604	97.25
<b>S23</b>	952	1094	988	1011	73.42
<b>S24</b>	1055	774	869	899	142.62
<b>S25</b>	1324	1213	1243	1260	57.52
<b>S26</b>	773	838	782	798	35.18
<b>S27</b>	1021	1204	1096	1107	91.72
<b>E1</b>	904	810	858	858	47.36

<b>E2</b>	708	892	788	796	92.07
<b>E3</b>	301	375	325	334	37.64
<b>E4</b>	817	800	797	805	10.60
<b>E5</b>	3300	3527	3735	3521	217.64
<b>E6</b>	3014	2779	2891	2895	117.83

Weight, average volume, surface weight, and average density for each of the samples are displayed in Table B.3. The samples were cut into rectangles measuring 1.5 cm times 12 cm, resulting in a surface area of 18 cm<sup>2</sup>, before the thickness measurements. However, samples S10 and S16 were too small to be cut in perfect rectangles; the areas of these samples had to be estimated using the image processing program ImageJ. The areas of the samples were estimated to be 17.75 cm<sup>2</sup> for S10 and 17.50 cm<sup>2</sup> for S16. The areas of samples E5 and E6 had to be estimated in the same way due to it not being possible to cut these samples without them breaking into smaller pieces. The average volume of each sample was calculated by multiplying the sample areas with the average thicknesses displayed in Table B.2. The surface weights were calculated as weight divided by area in grams per square meter, and the average densities were calculated as weight divided by average volume in grams per cube meter.

**Table B.3: The weight, average volume, surface weight, and average density for the samples.**

<b>Sample</b>	<b>Weight (g)</b>	<b>Average Volume (cm<sup>3</sup>)</b>	<b>Surface Weight (g/m<sup>2</sup>)</b>	<b>Average Density (g/m<sup>3</sup>)</b>
<b>S0</b>	0.258	1.197	143.22	215.37
<b>S1</b>	0.211	0.824	117.28	256.07
<b>S2</b>	0.237	1.089	131.67	217.63
<b>S3</b>	0.421	2.041	233.67	206.06
<b>S4</b>	0.246	0.736	136.78	334.42
<b>S5</b>	0.280	1.462	155.61	191.64
<b>S6</b>	0.260	1.435	144.33	181.10
<b>S7</b>	0.406	1.116	225.72	364.07
<b>S8</b>	0.323	1.881	179.50	171.77
<b>S9</b>	0.339	1.570	188.44	216.11
<b>S10</b>	0.373	1.406	210.08	265.26
<b>S11</b>	0.277	1.651	153.61	167.51
<b>S12</b>	0.284	1.242	157.56	228.34
<b>S13</b>	0.403	3.217	223.67	125.16
<b>S14</b>	0.320	1.476	177.50	216.46
<b>S15</b>	0.243	1.197	134.89	202.84
<b>S16</b>	0.376	1.188	215.03	316.68
<b>S17</b>	0.269	0.670	149.33	401.43
<b>S18</b>	0.250	1.404	138.61	177.71
<b>S19</b>	0.283	1.798	157.06	157.21
<b>S20</b>	0.291	1.384	161.61	210.16
<b>S21</b>	0.241	1.179	133.89	204.41
<b>S22</b>	0.363	2.887	201.56	125.66

<b>S23</b>	0.283	1.820	157.17	155.46
<b>S24</b>	0.278	1.618	154.61	171.98
<b>S25</b>	0.329	2.268	182.56	144.89
<b>S26</b>	0.342	1.436	189.72	237.75
<b>S27</b>	0.336	1.993	186.56	168.52
<b>E1</b>	0.338	1.544	187.61	218.66
<b>E2</b>	0.282	1.373	163.30	205.16
<b>E3</b>	0.223	0.601	123.89	370.92
<b>E4</b>	0.267	1.449	148.22	184.13
<b>E5</b>	0.483	15.467	109.98	31.23
<b>E6</b>	0.520	15.635	96.23	33.24

## B.4 Air Permeability

The results from the air permeability measurements are displayed in Table B.4. Three tests were performed per sample, two close to each end and one in the middle of the sample. From the three tests, an average air flow rate could be calculated. Before this, however, the air flow rates had to be multiplied by a factor of 21.05 to adjust the results to fit the correct area of the sample holder. Samples E5 and E6 could not be evaluated due to their brittleness.

**Table B.4:** Results from the air permeability measurements. Samples E5 and E6 could not be evaluated due to their brittleness. An average air flow rate could be calculated from the three measurements performed per sample. The table also includes the standard deviation for the three tests, for each sample.

Sample	Air flow rate			Average air flow rate (l/m <sup>2</sup> s)	Standard deviation
	Test 1 (l/m <sup>2</sup> s)	Test 2 (l/m <sup>2</sup> s)	Test 3 (l/m <sup>2</sup> s)		
<b>S0</b>	1474	1074	926	1158	283.20
<b>S1</b>	526	274	442	414	128.62
<b>S2</b>	442	379	379	400	36.46
<b>S3</b>	926	1095	863	961	119.70
<b>S4</b>	211	358	253	274	75.90
<b>S5</b>	1053	779	716	849	179.03
<b>S6</b>	610	505	674	596	85.07
<b>S7</b>	358	421	463	414	52.97
<b>S8</b>	1053	1095	1368	1172	171.44
<b>S9</b>	1031	905	968	968	63.15
<b>S10</b>	526	737	568	611	111.39
<b>S11</b>	1474	1579	1158	1403	219.10
<b>S12</b>	484	421	505	470	43.82
<b>S13</b>	1684	2000	1474	1719	264.87
<b>S14</b>	632	463	842	646	189.84
<b>S15</b>	884	863	821	856	32.15
<b>S16</b>	463	295	211	323	128.62
<b>S17</b>	610	147	168	309	261.51
<b>S18</b>	779	779	695	751	48.61
<b>S19</b>	1579	1684	1368	1544	160.77

<b>S20</b>	484	589	610	561	67.67
<b>S21</b>	484	463	484	477	12.15
<b>S22</b>	1579	1368	1474	1474	105.25
<b>S23</b>	1263	1368	1263	1298	60.77
<b>S24</b>	653	484	400	512	128.62
<b>S25</b>	1368	1368	1263	1333	60.77
<b>S26</b>	632	526	505	554	67.67
<b>S27</b>	1474	1474	1263	1403	121.53
<b>E1</b>	1684	884	1474	1347	414.64
<b>E2</b>	1116	505	821	814	305.29
<b>E3</b>	463	189	295	316	138.03
<b>E4</b>	737	926	758	807	103.84
<b>E5</b>	No data				
<b>E6</b>	No data				

## B.5 Results from Bending Length Measurements

The results from the bending length measurements are displayed in Table B.5. Several samples did not bend or did not bend enough to reach a 41.5° angle. These samples, therefore, have lines (-) in Table B.4 in place of numbers. Samples E5 and E6 could not be evaluated due to their brittleness. The overall mean bending length was calculated using Equation 1, utilizing the average overhang value calculated from the four tests performed per sample. The flexural rigidity was calculated using Equation 2. The table also includes the standard deviation between the four tests measured per sample.

**Table B.5:** Results from the bending length measurements used to evaluate the rigidity of the samples. The table includes the results from four tests performed per sample, the standard deviation between the tests, the overall mean bending length calculated from the four test, and the mean flexural rigidity calculated from the overall mean bending length. The samples that could not bend enough are marked with (-). Samples E5 and E6 could not be evaluated.

Sample	Overhang Length				Standard deviation	Overall mean bending length [cm]	Flexural rigidity [g/cm]
	Test 1 (cm)	Test 2 (cm)	Test 3 (cm)	Test 4 (cm)			
<b>S0</b>	-	-	-	-	-	-	-
<b>S1</b>	-	-	-	-	-	-	-
<b>S2</b>	-	-	11.70	11.95	0.125	5.91	27.21
<b>S3</b>	-	-	-	-	-	-	-
<b>S4</b>	-	-	11.75	11.70	0.025	5.86	27.56
<b>S5</b>	11.90	11.95	-	-	0.025	5.96	32.99
<b>S6</b>	11.90	11.90	-	-	0.000	5.95	30.40
<b>S7</b>	-	-	-	-	-	-	-
<b>S8</b>	-	-	-	-	-	-	-
<b>S9</b>	-	-	-	-	-	-	-
<b>S10</b>	-	-	-	-	-	-	-
<b>S11</b>	-	-	-	-	-	-	-
<b>S12</b>	-	-	-	-	-	-	-
<b>S13</b>	11.50	11.50	11.55	11.35	0.075	5.74	42.24

<b>S14</b>	-	-	-	-	-	-	-
<b>S15</b>	11.95	-	-	-	0.000	5.98	28.77
<b>S16</b>	-	-	-	-	-	-	-
<b>S17</b>	-	-	-	-	-	-	-
<b>S18</b>	8.40	9.00	8.80	10.10	0.630	4.54	12.95
<b>S19</b>	-	-	-	-	-	-	-
<b>S20</b>	-	-	-	-	-	-	-
<b>S21</b>	-	-	-	-	-	-	-
<b>S22</b>	11.65	11.95	9.85	9.80	0.993	5.41	31.85
<b>S23</b>	7.85	10.60	7.40	8.70	1.234	4.32	12.66
<b>S24</b>	-	-	-	-	-	-	-
<b>S25</b>	11.45	11.40	11.95	11.95	0.263	5.84	36.43
<b>S26</b>	-	-	-	-	-	-	-
<b>S27</b>	11.95	-	11.95	11.95	0.000	5.98	39.79
<b>E1</b>	-	-	-	-	-	-	-
<b>E2</b>	-	-	11.35	11.20	0.075	5.64	29.26
<b>E3</b>	-	-	10.30	10.80	0.250	5.28	18.18
<b>E4</b>	9.80	9.80	11.00	10.50	0.507	5.14	20.10
<b>E5</b>	No data						
<b>E6</b>	No data						

## B.6 Light Microscopy Pictures

The light microscopy pictures of the samples are displayed in Figures B.3-B.7. The pictures were taken at 4x magnification. Figure B.3 displays samples S0-S7, Figure B.4 displays samples S8-S15, Figure B.5 displays samples S16-S23, Figure B.6 displays samples S24-S27, and, Figure B.7 displays the extra samples E1-E6.

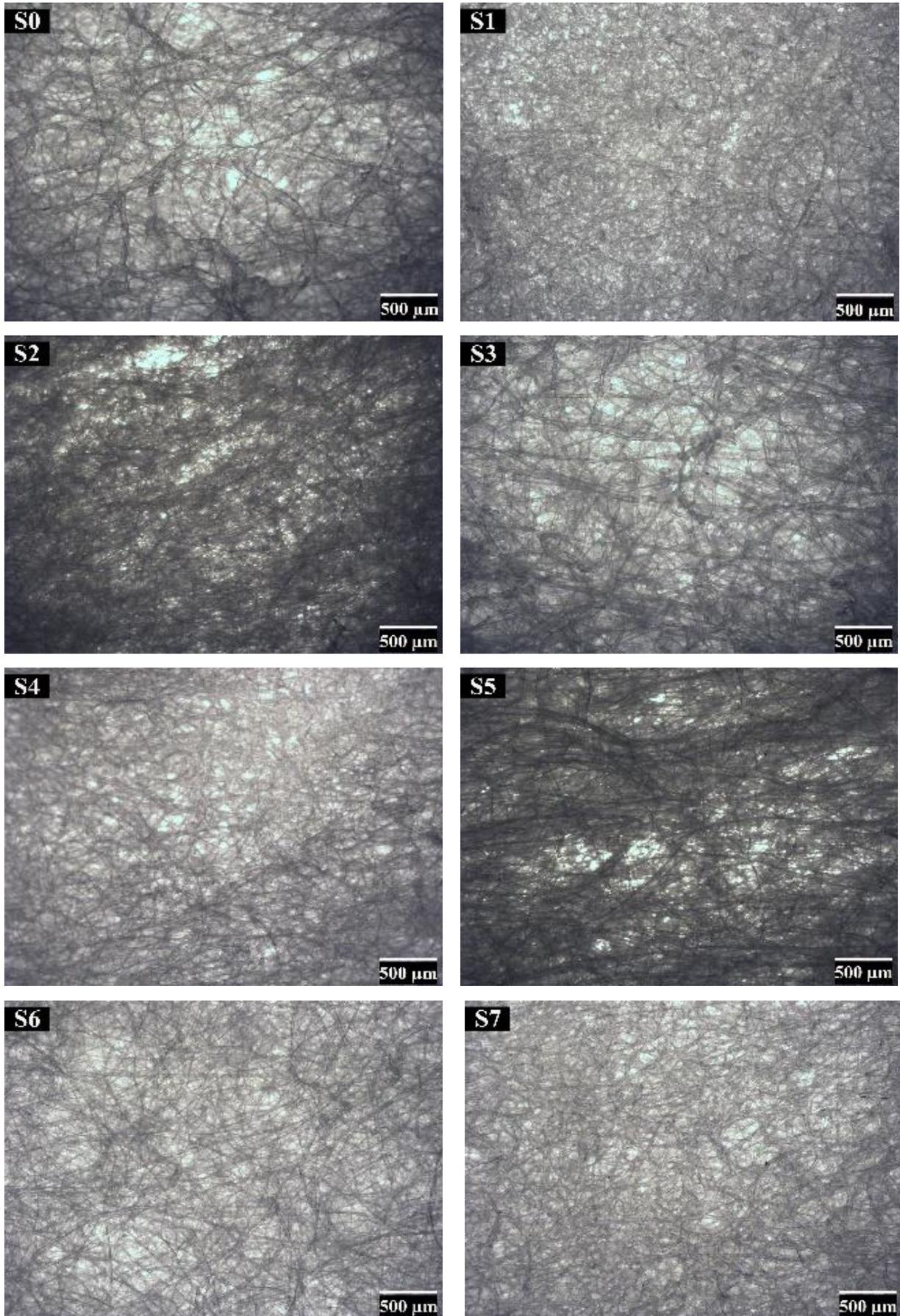


Figure B.3: Light microscopy pictures of samples S0-S7. The images were taken at 4x magnification, the scalebars represent 500  $\mu\text{m}$ .

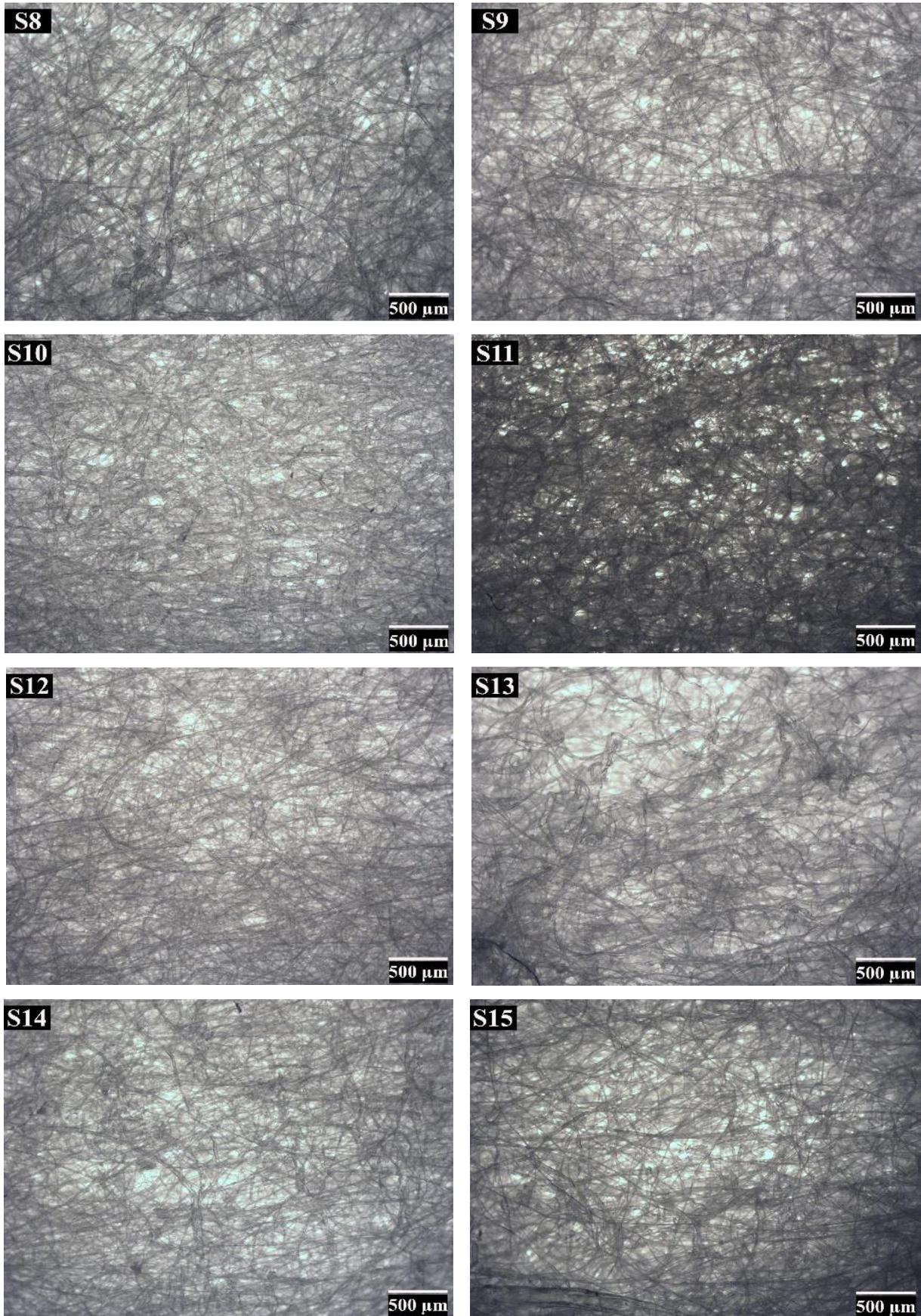


Figure B.4: Light microscopy pictures of samples S8-S15. The images were taken at 4x magnification, the scalebars represent 500  $\mu\text{m}$ .

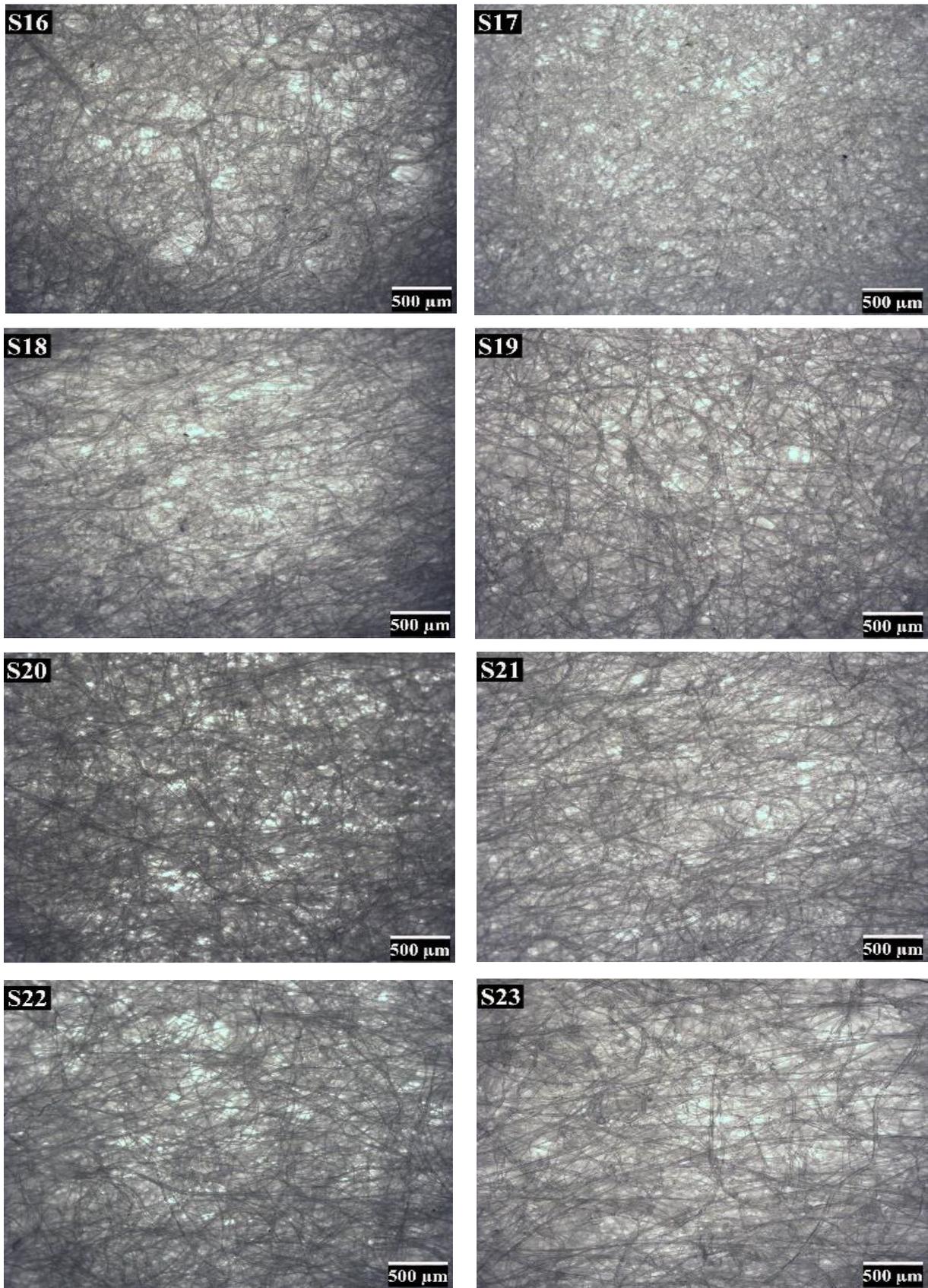


Figure B.5: Light microscopy pictures of samples S16-S23. The images were taken at 4x magnification, the scalebars represent 500  $\mu\text{m}$ .

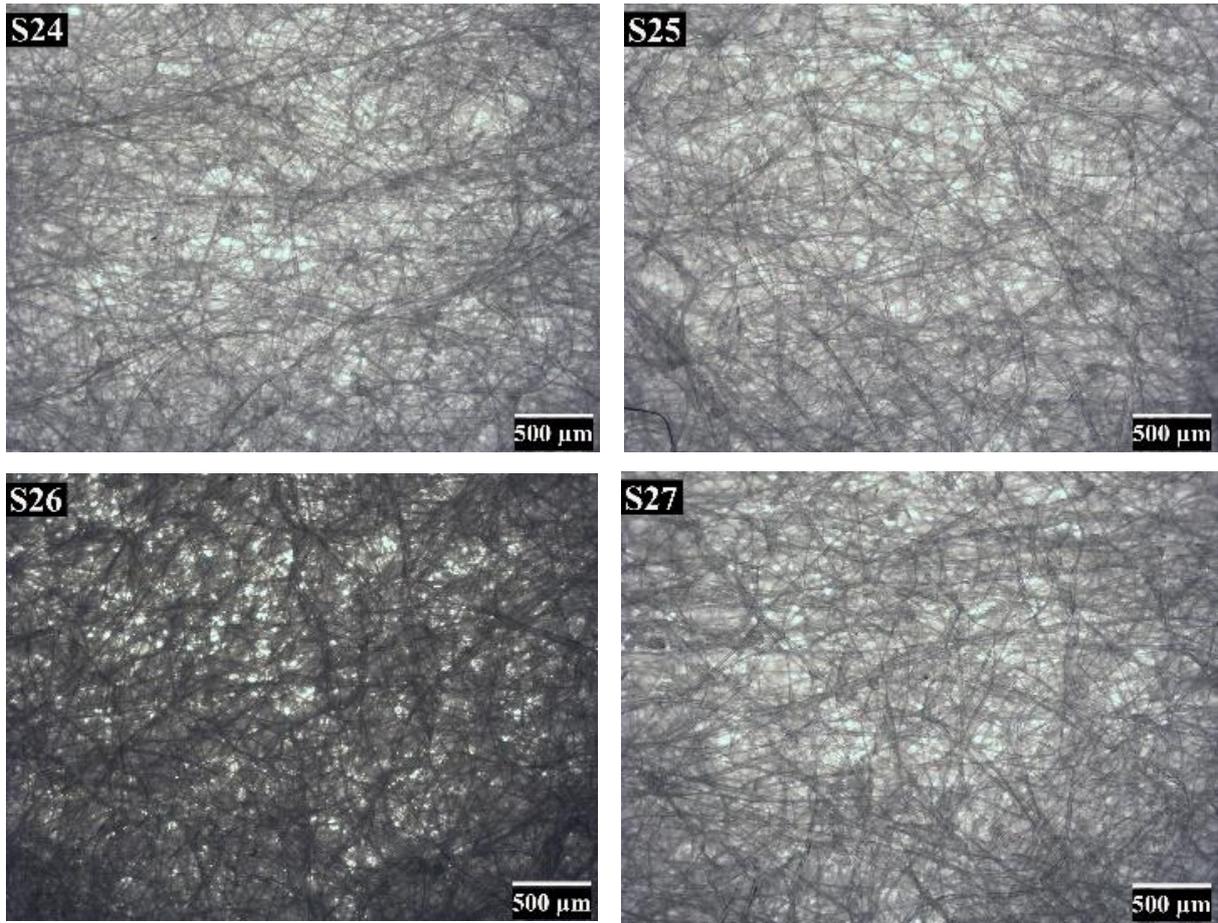


Figure B.6: Light microscopy pictures of samples S24-S27. The images were taken at 4x magnification, the scalebars represent 500  $\mu\text{m}$ .

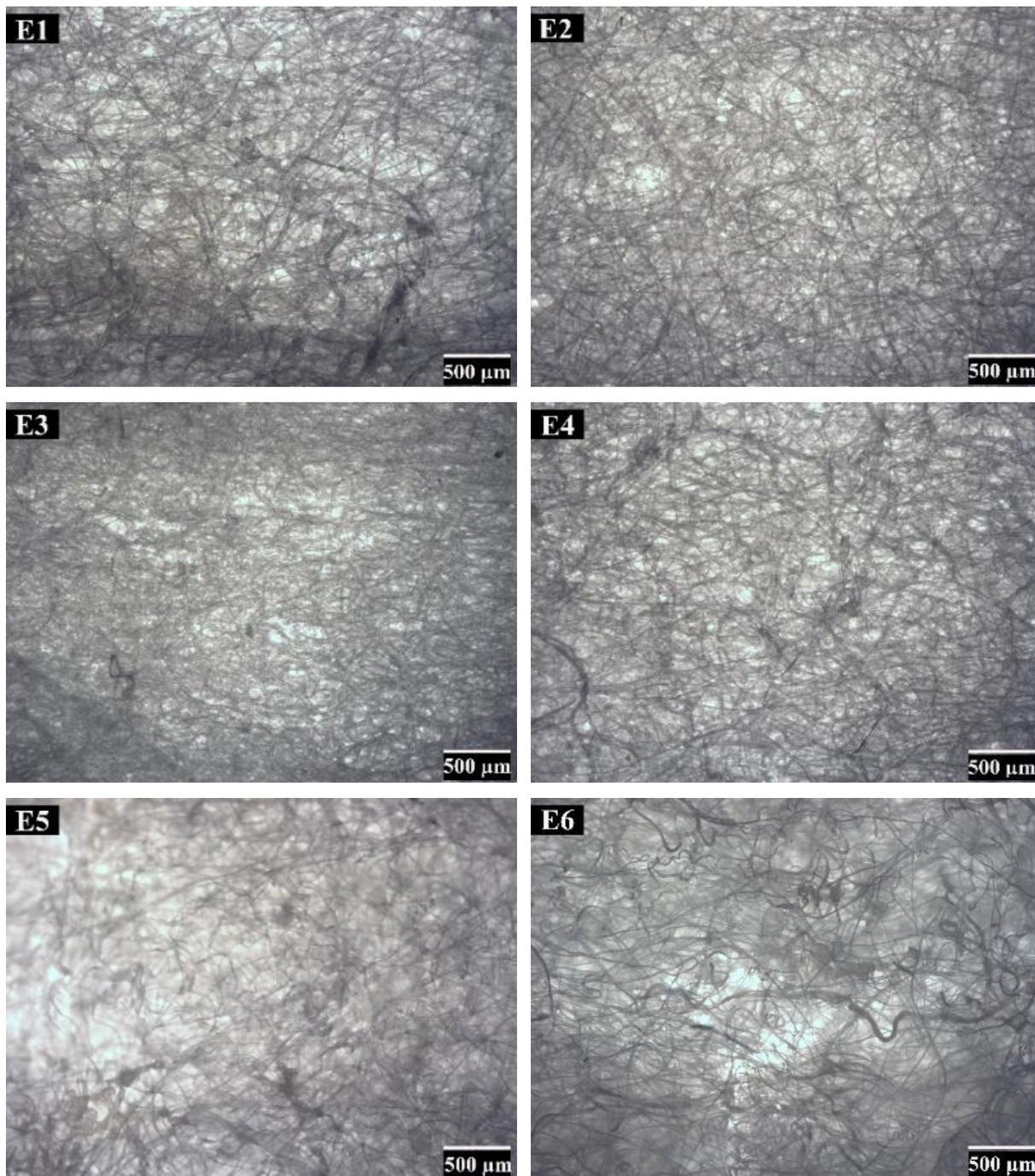


Figure B.7: Light microscopy pictures of samples E1-E6. The images were taken at 4x magnification, the scalebars represent 500  $\mu\text{m}$ .

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