A microscopic study of cellulosic fibre networks

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Chapter 1

Introduction

Paper and paperboard are used in a wide range of applications, each having specific requirements with respect to mechanical or surface properties. For example, packaging paper requires high strength whereas printing paper needs a smooth surface and tissue paper should be soft and absorbing. These macroscale properties are determined by the underlying microstructure formed during the production process.

The microstructure is created from individual cellulose fibres that are mechanically or chemically released from wood. The individual fibres are diluted in water, resulting in a mixture called pulp. The highly diluted fibres are dropped onto a moving wire mesh. A thin sheet of fibres remains on the wire while the water passes through. Pressing and heating removes the remaining water from the sheet. Dropping the pulp onto a moving wire mesh results in more fibres oriented in machine direction (i.e. the moving direction of the wire) than in cross-direction (perpendicular to the moving direction).

The resulting microstructure is a complex structure of individual fibres bonded together at some points. A continuum model cannot describe the mechanical properties sufficiently accurate based on this microstructure, therefore a mesoscopic model, shown in Figure 1.1, was developed in [1]. In order to be able to analyse the relation between mechanical properties of a single fibre and those of the fibre network, the model requires structural parameters of the microstructure.

This study will focus on characterizing the microstructure of paper based on microscopic images obtained with various techniques. Our objective is to obtain structural parameters, such as characteristic fibre length, distance between fibre bonds, and the fibre orientation distribution. Microscopy techniques such as optical microscopy (OM), environmental scanning electron microscopy (ESEM), confocal laser scanning microscopy (CLSM), and X-ray computed microtomography ($\mu$CT) are explored to determine the possibilities of each technique to visualize the fibre network of paper. A three-dimensional image of the microstructure is preferable since it provides the most information on the fibre network. From this perspective $\mu$CT is expected to produce the most useful images.

This report will first present an elaborate study of the available literature on the microscopy techniques used in paper research in Chapter 2. It will give the basic principles of each technique and an overview of the current applica-
Figure 1.1: Mesoscopic model with a unit cell highlighted. Source [1].

bility of the technique in paper research. Experimental details for each tech-
nique are then described in Chapter 3 followed by presenting and discussing
the experimental results in Chapter 4. In Chapter 5 several conclusions and
recommendations are given.
Chapter 2

Literature study

A variety of imaging techniques has been used to characterize the microstructure of paper and paperboard. Since each technique has its particular advantages, several imaging techniques have been investigated in this study. This chapter briefly describes the current research status of microscopic measurement techniques for paper, such as optical microscopy, scanning electron microscopy, confocal laser scanning microscopy, and X-ray computed microtomography. X\(\mu\)CT will be described elaborately since this is the main technique used in our own study (Chapter 3).

2.1 Optical microscopy

Optical microscopy is a two-dimensional imaging technique. Visible light is used to illuminate an object. Light emanating from the object passes through a set of lenses that form an enlarged virtual image which can be seen through the eyepiece. There are two methods to illuminate a sample, episcopic (reflected) or diascopic (transmitted). Stereo microscopy adds a perception of depth to the image by visualizing the object through two instead of one eyepiece.

Optical microscopy is rarely used in fibre network research. To the best of the author’s knowledge it is only mentioned in [2], which describes a study in which STFI Packforsk created a digitized paper sample by cutting 1\(\mu\)m slices of paper embedded in a polymer and manually placing these under an optical microscope. The result is shown in Figure 2.1. Although this appears to be a useful result, an important disadvantage is that the reconstruction of a three-dimensional object proved to be too complicated due to the manual placing of each slice. This imaging technique was therefore abandoned by the authors.

2.2 Environmental scanning electron microscopy

Environmental scanning electron microscopy is essentially a two-dimensional imaging technique used in a wide variety of applications. In a scanning electron microscope (SEM) an electron beam is focused by condenser lenses to a spot size of several nanometres in diameter. A final lens deflects the beam in the two in-plane directions to scan a rectangular grid on the sample surface. Various
detectors measure various interactions between the electrons and the sample’s atoms.

Inelastic scattering interactions cause secondary electron (SE) emission. These low energy electrons stem from the sample material and are shot out of the sample by the beam electrons. Since SE’s have a low energy, an electrically-biased grid is able to attract them to a detector. Signal intensity is dependent on the angle of the incidence beam; a larger angle causes more secondary electrons to escape the sample. Thus steep surfaces and edges appear brighter on the image, which results in images with depth perception.

Elastic scattering interactions on the other hand cause backscattered electrons (BSE). These electrons originate from the electron beam and are backscattered out of the sample. BSE are high energy electrons and cannot be attracted, therefore the detector is placed in a donut shape around the electron beam. Since heavy elements reflect electrons more strongly than light elements, BSE is able to detect contrast between regions of different materials.

Besides imaging, SEM can also be used to create light emission spectra and to examine optical and electrical properties of semiconductor materials.

Conventional SEM requires samples to be completely dry and electrically conductive, since the sample chamber is at high vacuum and to prevent accumulation of electrostatic charge at the surface, respectively. The Environmental SEM solves both problems. Operating at low vacuum, ‘wet’ samples can be scanned while the gaseous environment prevents the sample from charging, since the gas is conductive.

Aronsson [2] developed a tool for characterizing individual wood fibres in a three-dimensional image. Microtomography and ESEM were combined to obtain a stack of two-dimensional images which were later reconstructed into a three-dimensional image. Producing the two-dimensional images required cutting thin slices from the sample in cross-machine direction. The paper sample was first embedded in an epoxy resin to make a stable block. Between two
imaging steps, 5 µm was cut from the block. This was done in five steps to reduce the forces acting on the knife. In order to prevent the slice from breaking apart while cutting, it was floated on water. The surface of the remaining sample was imaged using backscatter mode to take advantage of the fact that the epoxy resin and fibre material have different densities. A resulting cross-section is shown in Figure 2.2.

The segmentation tool is a programme that lets the user identify lumens in a two-dimensional cross-section and fills the lumen accordingly. With this method all nearly machine directional fibres are segmented. Cross-machine directional fibres have to be identified by hand.

Coeurjolly and Svensson [3] used the same imaging approach as Aronsson [2] for developing a discrete curve estimator to analyse three-dimensional fibre networks. Using this method a fibre is converted into a string of single voxels, as shown in Figure 2.3, representing the fibre. Radii of curves in the string are determined by circumscribing a triangle consisting of the two straight lines from the centre of the curve to both ends and the connection of these ends.
Table 2.1: Shape measures of fibres. All measures are in [µm]. Source [3]

<table>
<thead>
<tr>
<th>fibre</th>
<th>L</th>
<th>∆x</th>
<th>∆y</th>
<th>∆z</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>538.21</td>
<td>7.0</td>
<td>10.5</td>
<td>504.0</td>
<td>1.07</td>
</tr>
<tr>
<td>2</td>
<td>536.10</td>
<td>84.7</td>
<td>11.2</td>
<td>504.0</td>
<td>1.05</td>
</tr>
<tr>
<td>3</td>
<td>562.56</td>
<td>142.8</td>
<td>23.8</td>
<td>504.0</td>
<td>1.07</td>
</tr>
<tr>
<td>4</td>
<td>442.40</td>
<td>123.2</td>
<td>2.1</td>
<td>388.5</td>
<td>1.09</td>
</tr>
<tr>
<td>5</td>
<td>546.04</td>
<td>43.4</td>
<td>21.7</td>
<td>504.0</td>
<td>1.08</td>
</tr>
<tr>
<td>6</td>
<td>540.83</td>
<td>10.5</td>
<td>4.2</td>
<td>504.0</td>
<td>1.07</td>
</tr>
<tr>
<td>7</td>
<td>574.91</td>
<td>143.5</td>
<td>23.1</td>
<td>504.0</td>
<td>1.10</td>
</tr>
<tr>
<td>8</td>
<td>187.81</td>
<td>63.7</td>
<td>2.1</td>
<td>149.1</td>
<td>1.16</td>
</tr>
<tr>
<td>9</td>
<td>564.61</td>
<td>21.7</td>
<td>4.2</td>
<td>504.0</td>
<td>1.12</td>
</tr>
<tr>
<td>10</td>
<td>431.04</td>
<td>32.2</td>
<td>7.0</td>
<td>383.6</td>
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</tr>
<tr>
<td>11</td>
<td>267.42</td>
<td>4.9</td>
<td>18.9</td>
<td>254.1</td>
<td>1.05</td>
</tr>
<tr>
<td>12</td>
<td>288.74</td>
<td>56.7</td>
<td>1.4</td>
<td>254.1</td>
<td>1.11</td>
</tr>
<tr>
<td>13</td>
<td>234.89</td>
<td>133.7</td>
<td>48.3</td>
<td>119.0</td>
<td>1.27</td>
</tr>
<tr>
<td>14</td>
<td>571.85</td>
<td>92.4</td>
<td>9.8</td>
<td>499.1</td>
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</tr>
<tr>
<td>15</td>
<td>87.91</td>
<td>30.1</td>
<td>1.4</td>
<td>68.6</td>
<td>1.17</td>
</tr>
<tr>
<td>16</td>
<td>581.34</td>
<td>83.3</td>
<td>4.2</td>
<td>504.0</td>
<td>1.14</td>
</tr>
<tr>
<td>17</td>
<td>216.34</td>
<td>44.8</td>
<td>16.1</td>
<td>193.9</td>
<td>1.08</td>
</tr>
</tbody>
</table>

A measure often used is the dimensionless fibre curl (C) which indicates the global curvature of a fibre. It is defined as the length of the fibre divided by the distance between its end-points. Table 2.1 shows that most fibres are rather straight, since C is close to unity. To indicate how well fibres are aligned in z-direction (machine direction), the fibre conformation in x- (cross-machine direction), y- (thickness direction) and z-direction (∆x, ∆y, ∆z) are also given in Table 2.1. Small ∆y values indicate a layered structure, while high ∆z values indicate an orientation in machine direction.

### 2.3 Confocal laser scanning microscopy

Confocal laser scanning microscopy (CLSM), described by Goel et al. [4] and Jang et al. [5], is another technique to visualize the fibre network of paper. This method is non-destructive and provides three-dimensional images, although penetration depths over 50 µm prove to be difficult [4] due to optical interference of the layers above the focal plane.

In CLSM laser light is focused in the focal plane within or on the surface of a sample. Reflected as well as any fluorescent light from the focal spot is collected by the detector. Before reaching the detector, the light passes through an aperture, which is positioned in the confocal plane. This physically excludes any light emanating from regions above and below the focal plane, reducing out-of-focus blur. Scanning a focal plane point by point creates an image of the plane. In this study fluorescence mode and profiling mode CLSM were investigated. Both modes use the above described procedure to obtain a focal plane image. However, fluorescence mode can only be used on fluorescent objects whereas profiling mode can only be used on opaque objects. Profiling mode CLSM detects reflected light to create an image of the focal plane. By scanning
a finite number of focal planes, each representing a single height, a height map of the sample surface can be created. Fluorescence mode CLSM detects fluorescent light to create an image of the focal plane. A set of focal plane images can be reconstructed into a three-dimensional image by stacking the images.

Goel et al. [4] scanned a paper sample using fluorescence mode CLSM layer by layer to a depth of 50 µm and reconstructed the images (Figure 2.4) to a three-dimensional image. To enhance image quality, the weakly auto-fluorescent pulp fibres were dyed with fluorochrome dye. After binarization, for which a dynamic threshold method was used, the area of the pores was measured by counting pore voxels in each layer to obtain a pore size distribution. It is stated that the measured pore size distribution is comparable to those obtained by mercury intrusion porosimetry.

Jang et al. [5] imaged unbleached softwood kraft pulp fibres in a machine directional plane. As mentioned in [4] the pulp must be dyed to obtain sufficient fluorescence. Images of focal plane depths up to 20 µm were of reasonable quality, higher depths resulted in weaker and noisier signals. The accuracy of fluorescence CLSM was validated by comparing the dimensions of a calibrated sphere to its dimensions resulting from image analysis. Measurements show that CLSM offers an accurate and rapid method to determine the transverse fibre dimensions. An analysis of cross-sectional images as shown in Figure 2.5 shows that fibres with thin walls almost totally collapsed.

### 2.4 X-ray computed microtomography

Computed tomography is a frequently used method in medical sciences and materials technology for three-dimensional imaging. The method consists of taking a set of tomographic images of a beam transmitted through a sample, see Figure 2.6. The sample or beam source is rotated slightly between images.
to create images from multiple viewing directions. Based on these tomographic two-dimensional images a three-dimensional representation of the sample is reconstructed. The limit between conventional tomography and microtomography is generally taken to be situated at a spatial resolution of 50 to 100 $\mu$m [6].

$\mu$CT depends on X-rays to obtain tomographic images. X-rays are produced in an X-ray tube, where high energy electrons collide with a target material [7]. An X-ray tube is an evacuated environment containing a filament and a target. The filament is heated by an electrical current and consequently releases electrons by thermionic emission. The free electrons are accelerated to the positively charged target and attain a kinetic energy equal to the tube voltage. The tube voltage is defined by the potential difference between the filament and the target and can range between 10 and 180 kV. The number of electrons traveling from the filament to the target is known as the tube current. The tube current is controlled by the electrical current through the filament.

In the rare event that a high energy electron comes close to a target nucleus and experiences attractive forces due to its positive charge, the electron is decelerated. The electron’s kinetic energy is partially or completely converted to electromagnetic radiation (X-rays) in a process called “bremsstrahlung”. The magnitude of deceleration depends on the interaction distance between the electron and the nucleus, where closer interactions cause higher X-ray photon energies. The probability of occurrence, however, decreases with decreasing interaction distance.

When produced, X-rays travel from the target in all directions, including the direction of the sample. Passing through the sample X-rays encounter atoms that attenuate the photon energy. Depending on the contrast mode the absorption diagram or the refractive diagram is detected.

Fitzgerald [8] stressed the benefits of phase contrast for light elements. Phase contrast relies on refraction of X-rays instead of absorption of X-rays. The index of refraction $n$ deviates only slightly from unity for X-rays as shown by [9]. An index of refraction $n$ of 0.999999904 at an energy of 19.4 keV, as can be found for cellulose, is sufficient to see the edge of individual fibres.

The set of tomographic images needs to be reconstructed into a three-
dimensional object. This mathematical procedure is known as an inverse Radon transformation and is widely used in tomography. The method states that if a continuous function $f$ represents an unknown density of an object, the Radon transform $Rf$ represents the data obtained from the X-ray scans. Therefore, the inverse of a Radon transform creates density function $f$.

To the best of the author’s knowledge Samuelsen et al. [9] were the first to use phase contrast X$\mu$CT to investigate the fibre network of paper. No other non-destructive method could yield a full three-dimensional representation of paper at the time, therefore X$\mu$CT was explored. It is stated (without reference) that phase contrast tomography is the only contrast technique to provide sufficient contrast in materials with light elements like cellulose. Phase contrast is more sensitive than contrast by absorption, which is the commonly used contrast method. In order to obtain phase contrast images the X-ray beam must at least be partially spatially coherent. This is a major drawback of phase contrast since it can only be achieved by using expensive third generation synchrotron X-ray sources. Images of a softwood kraft pulp hand sheet, such as the reconstructed cross-section in Figure 2.7, show ring-shaped artefacts indicating the limitations of the method. However, many details of the internal structure can be discerned. Cross-sections of individual fibres were found to have a typical size of 15 x 30 $\mu$m and a full three-dimensional analysis shows well-defined fibre tubes, called lumen. Furthermore, it is confirmed that hand sheets are highly layered structures with virtually no interconnections between layers. Paper deformation, caused by cutting with a knife, is observed at the edges.

Antoine et al. [10] presented results of a microtomography study on paper with a phase contrast X-ray source at the European Synchrotron Radiation Facility (ESRF). The imaging methods presented in [9] were used for imaging...
and the focus in this study was on post-processing of the three-dimensional images. Five laboratory hand sheets composed of different amounts of chemical and thermo-mechanical pulp, one filter paper made of cotton, one newsprint paper and a super-calendared magazine paper were studied. All images, except of the super-calendered paper, show fibres, fibre lumens and even fibrils (fine threadlike fibres) although the fibrils have a poor contrast. The dense super-calendered paper required a very high resolution to discern the small features. The ring artefacts mentioned in [9] have been resolved although quasi-ring like artefacts have emerged. These stem from fluctuations in the beam profile, while ring artefacts stem from detector inhomogeneities.

A set of routines to binarize the images was presented by the same authors. First a Butterworth filter to filter high frequency noise was applied. Seed points were then manually introduced to assist in detecting lumen and pores since they show almost equal gray values, which are difficult to distinguish by a computer. Attempts for global thresholding showed local variations in the background colour. Therefore, a local thresholding procedure using a 30 x 30 pixel window was used, giving satisfying results. Simple thresholding would have been possible if all fibre-pore interfaces were closed, which was not the case due to noise and damaged fibres. The result of the binarization procedure is shown in Figure 2.8.

Another approach was presented by Walther et al. [11]. The study focused on the quantitative and qualitative analysis of the fibre microstructure of medium-density fibreboard. Images were taken using phase contrast XμCT and reconstructed into twenty-seven sub-volumes to reduce computational cost.

Image processing resulting in segmentation of individual fibres commenced with noise removal. Uncorrelated noise was relatively easy to remove, whereas systematic errors, probably caused by a limited number of sampling points and blur in the detector system, gave difficulties. Systematic errors were hard to remove since they appeared in the same frequency range as the fibre material.
Therefore, it was assumed that all fibres are physically connected to form a solid material while systematic errors appear randomly in the image. An aggressive threshold classified all non-fibre regions as noise. After this step, three main components of the microstructure were segmented. First, the air regions were segmented from the fibre material based on voxel intensity. The lumen segmentation was more complicated since fibre walls were discontinuous due to physical damage or damage resulting from previous processing steps. Fibre wall discontinuities were solved using an erosion operator on the air regions. Luminens were then identified by their elongated shape to exclude small air pockets in resins or between fibres. Individual fibres were segmented in the last step by associating fibre material with the nearest lumen, since naturally each fibre has only one lumen. This resulted in a volume of individually segmented fibres as shown in Figure 2.9.

In the fibre analysis, the fibre orientation, volumes and surface of fibres, and the recognition of fibre bundles was examined. The fibre orientation was calculated by determining the eigenvector of all voxels belonging to a lumen. The fibre orientation is defined as the angle between the eigenvector and the original axes of the volume. Fibre bundles were characterized by examining the outside surface areas of fibres that were not or only partially in contact with an air region. If an outside surface area is not in contact with an air region, it must be in contact with other fibres. A threshold for minimal contact surface area then determines if a fibre belongs to a bundle.

Using the segmentation method, an estimated 75% of the lumens was correctly classified as such. Visual inspection further showed that about 20% of the labels were assigned to complete fibres while 70% was assigned to fragments of complete fibres. This means that a single fibre was split into several segments. The other 10% of the labels were false positives. Further research aims at decreasing the number of labels assigned to fragments of complete fibres.

Holmstad et al. [12] obtained a binarized reconstruction of 100% chemical kraft pulp hand sheet from Antoine et al. [10]. The reconstruction was used to assess the applicability of the equivalent pore concept (EPC) on fibre networks.
A set of characteristic structural parameters could be determined using the EPC presented by Silvy [13]. The EPC is presented as a method to determine transport properties, optical properties and strength properties of a fibre network. The EPC determines the fibre-to-fibre distance in a pore and calculates the mean free path length in all directions. The results are represented by an ellipsoid. The mean free path lengths in the principal directions are considered to be important structural parameters. Phase contrast X-ray microtomography is considered to be the best available three-dimensional imaging technique available. Many structural parameters can be quantified.

Ramaswamy et al. [14] performed an elaborate study to develop a non-invasive method to visualize the pore structure of paper and board. This method was used to characterize the three-dimensional structure of paper and to establish a relationship between the pore structure characteristics and the transport properties for water. Phase contrast X\(\mu\)CT images with a resolution of 1 \(\mu\)m were compared to absorption contrast X\(\mu\)CT images with a resolution of 5 \(\mu\)m. The images were obtained at ESRF and using a SkyScan-1072 laboratory scanner, respectively. It was shown that the high resolution phase contrast method preserves the topology of fibres better than the low resolution absorption contrast technique. The hydraulic pore radius, defined as the pore area divided by the pore perimeter and shown in Figure 2.10, suggests that the accuracy of structural parameters is affected by the noise and lower resolution of the absorption contrast images. The significantly smaller (up to 50\%) hydraulic pore radii in high resolution images was most probably caused by a longer parameter. All further analyses in this study were performed using the high resolution images.

To distinguish fibres and voids the images were binarized (Figure 2.11) using a dynamic thresholding method presented by Goel et al. [4]. This method
determines the thresholding value of a pixel considering a window of 7 x 7 neighbouring pixels. The high resolution images were then used to characterize transport properties such as vapour diffusivity, liquid permeability and thermal conductivity.

The effect of the production processes used on the three-dimensional structure was studied by comparing hand sheet and commercial paper. The relationship between permeability and porosity (ratio of pore volume to total volume) as illustrated in Figure 2.12 shows distinct differences between hand sheet and commercial paper, suggesting a different microstructure of the fibre network.

Almgren et al. [15] used phase contrast XµCT to investigate the role of the fibre-fibre and the fibre-matrix bonds on stress transfer in paper-reinforced plastics and plain paper. An image analysis tool to determine de fibre-fibre bonds in the paper sheets was proposed. Fibre-fibre bond areas were located in binarized phase contrast XµCT images (Figure 2.13) by identifying the lumen voxels of each fibre and checking if two lumens could be connected without touching any non-fibre voxel, see Figure 2.14. Only fibres with intact lumen
can be considered with this method. The strength in paper sheets was found to be mainly determined by the fibre-fibre bonds, whereas no correlation between fibre bonds and strength was found in the paper-reinforced plastics.

2.5 Other approaches

Strömbro et al. [16] performed a mechano-sorptive creep study using a micromechanical model. Mechano-sorptive creep is the accelerated creep of paper by moisture cycling. In the simplified network model many structural parameters, including total fibre length, free fibre length, and fibre bond area were used to capture experimental observations. All parameters were obtained from experiments, literature or calculations and are shown in Table 2.2. Experiments performed at STFI Packforsk on flash-dried unbleached kraft pulp paper included hygroexpansivity tests, tensile tests, compressive tests, creep tests, and mechano-sorptive creep tests.

2.6 Conclusion

All methods discussed have drawbacks such as a limited image quality, complicated sample preparation or high cost. Although phase contrast X\(\mu\)CT has proved to provide high quality images of cellulosic fibre networks without elaborate preparation procedures, its main drawbacks are the high cost and small scanning volumes.

The continuously improving laboratory scale X\(\mu\)CT devices might reduce these drawbacks. In the second part of this study images are taken using a laboratory scale absorption contrast X\(\mu\)CT device. Image processing should demonstrate the quality of the images compared to phase contrast X\(\mu\)CT images.
Figure 2.13: Three-dimensional phase contrast X$\mu$CT reconstruction of a softwood kraft pulp hand sheet. Source [15].

Figure 2.14: A fibre bond cross-section. A bond is positively identified if gray areas (lumen) can be connected via only white areas (fibre material). Source [15].
Table 2.2: Parameters used in the network model. Source [16].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_{tot}$</td>
<td>3.5 mm</td>
<td>Length of fibres [17].</td>
</tr>
<tr>
<td>$B$</td>
<td>35 µm</td>
<td>Width of fibres [17].</td>
</tr>
<tr>
<td>$H$</td>
<td>5 µm</td>
<td>Height of fibres [17].</td>
</tr>
<tr>
<td>$\rho_f$</td>
<td>1500 kg/m³</td>
<td>Fibre density [17].</td>
</tr>
<tr>
<td>$\rho_p$</td>
<td>826 kg/m³</td>
<td>Paper density, from experiments.</td>
</tr>
<tr>
<td>$V_f$</td>
<td>$\approx 0.55$</td>
<td>Volume fraction of fibres.</td>
</tr>
<tr>
<td>$n$</td>
<td>$\frac{V_f L_{tot}}{\pi B}$</td>
<td>Number of fibre bonds. The number of fibre segments used here is $n - 1$.</td>
</tr>
<tr>
<td>$L$</td>
<td>50 µm</td>
<td>Total length of fibre segment, calculated from $L_{tot}$.</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>$\frac{L_f}{L} = \frac{L - B}{L} = 0.30$</td>
<td>Length of free fibre segment divided by total length of fibre segment.</td>
</tr>
<tr>
<td>$L_f$</td>
<td>$\lambda L = 15\mu m$</td>
<td>Length of free fibre segment.</td>
</tr>
<tr>
<td>$A$</td>
<td>$BH \approx 1.75 \cdot 10^{-10} m^2$</td>
<td>Fibre cross-section area; a rectangular cross-section has been assumed.</td>
</tr>
<tr>
<td>$I$</td>
<td>$\frac{BH^3}{12} \approx 3.65 \cdot 10^{-22} m^4$</td>
<td>Moment of inertia; a rectangular cross-section has been assumed.</td>
</tr>
<tr>
<td>$\eta$</td>
<td>6</td>
<td>Anisotropy constant (Schulgasser and Page [18]).</td>
</tr>
<tr>
<td>$E_L$</td>
<td>44 GPa</td>
<td>Modulus of elasticity along the fibre, estimated from experimental stress-strain curves in tension and creep curves at $t = 0$.</td>
</tr>
<tr>
<td>$E_T$</td>
<td>$E_L/g \approx 7.3$ GPa</td>
<td>Modulus of elasticity transverse to the fibre.</td>
</tr>
</tbody>
</table>
Chapter 3

Experimental procedures

3.1 Sample preparation

The paper samples used in this research are taken from a 0.9 mm thick paper-board consisting of three layers. The thin outer layers of chemical pulp contain a mixture of recycled and virgin fibres. The thick inner layer is made out of virgin fibre mechanical pulp. The thin outer layers were removed by tearing them off after immersing the sample in water. This procedure was done for all samples used in this study.

Other samples in this research were obtained from a market pulp sheet. This is a sheet of dried pulp with a microstructure of a fibrous network, but it lacks the mechanical properties of paper.

3.2 Optical microscopy

The Zeiss SteREO Discovery.V12 used in this study is a computer controlled stereo microscope with episcopic illumination. A Zeiss AxioCam HR camera is attached to capture high quality images.

The optical microscope is able to view the sample in colour, which is an advantage when compared to scanning electron microscopy or X µCT. Both materials were imaged on the surface and in the plane of the sample.

The stripped sample was cut to a size of 5 x 20 x 0.9 mm^3. In order to image individual fibres the sample was torn in machine direction. After tearing the sample, individual fibres and bundles became visible.

Visualization of the fracture process has been investigated using the optical microscope. The fracture process might provide insight into the location of actual fibre bonds, whereas static images only provide information on the location of possible fibre bonds. A paper sample was bent while being visualized by an optical microscope. The optical microscope was focused on the initial surface.

3.3 Environmental scanning electron microscopy

The Quanta 600F ESEM by FEI Company was used to obtain images of the paper sample. This ESEM is capable of operating in SE- and BSE-mode at the
same time, resulting in some depth perception in the images. An additional feature of the microscope is its micro tweezers with a load cell. This allows for micro tensile tests while the sample is imaged by the ESEM.

The paper samples were cut to a size of approximately 5 x 5 x 0.9 mm$^3$. Tearing the samples in machine direction resulted in a fracture with individual fibres sticking out. The micro tweezers were used to try to pull a single fibre from the network. However, the gripping force proved to be too low to pull out a single fibre. All images were obtained with a 10 kV electron beam and a working distance (WD) of 7.5 mm.

### 3.4 Confocal laser scanning microscopy

Confocal laser scanning microscopy is an imaging technique capable of optical sectioning. This allows for a three-dimensional image of a sample without the elaborate preparation procedures required for SEM and OM. The possibilities of CLSM were explored using profiling mode and fluorescence mode.

Profiling CLSM was done using the Sensofar PLµ 2300 with a 20x objective lens for magnification. The paper sample was cut to a size of 5 x 20 x 0.9 mm$^3$ without further preparation. Since a fibre width of 5 to 30 µm was found in literature, the scan was performed over 50 µm depth with measuring increments of 5 µm.

The Zeiss lsm 510 meta was used to visualize the microstructure with fluorescence mode CLSM. The sample was not dyed as described in literature, since only finished paper sheets were available. Images with dimensions of 450 x 450 µm$^2$ were captured every 2 µm, resulting in a stack of images over 78 µm in thickness direction. These images were reconstructed into a three-dimensional image using Volume Graphics MAX 1.2.1® (VG).

### 3.5 X-ray computed microtomography

Phase contrast XµCT seems to be the most preferable microscopy technique to characterize the microstructure of paper, since little sample preparation is needed while high quality three-dimensional images can be obtained. The main drawback is the limited availability of a phase contrast XµCT scanner, since only fifteen phase contrast XµCT scanners are operational in Europe. Moreover, new laboratory scale absorption contrast XµCT scanners are capable of high resolution scanning, making absorption contrast XµCT an appealing alternative for paper research.

#### 3.5.1 Image acquisition

The X-ray images were taken with a Phoenix X-ray Nanotom® at Eindhoven University of Technology. The scanner is capable of reaching a voxel size of 0.5 µm. The photon energy is adjusted to obtain optimized scanning conditions, which is vital for high quality images.

A tube voltage of 60 keV and a tube current of 180µA together with a molybdenum target resulted in an optimum X-ray beam for this purpose. The 5 megapixel digital detector captured the images with a 1000 ms imaging time. The physical pixel size of the detector is 50µm and an optical magnification
factor $m$ defined by the distance of the object to the target divided by the distance of the detector to the target $m = d_o/d_d = 33.3$ resulted in an effective pixel size of $50/33.3 = 1.5\mu m$. In order to obtain this magnification factor the sample should be placed very close to the target; therefore the sample was cut with a scalpel to a size of $3.5 \times 1.8 \times 0.9 \text{ mm}^3$. In order to reconstruct a three-dimensional object the sample was imaged 1200 times over a $360^\circ$ rotation.

### 3.5.2 Object reconstruction

The two-dimensional X-ray images were reconstructed into a single three-dimensional object using the Datosrec software. Object shifts were accounted for by comparing the $0^\circ$ and $360^\circ$ image. Due to computational limitations three sub-volumes of $1350 \times 470 \times 800$ voxels each were reconstructed. They were later stitched together to form a single object.

Image processing was performed in VG. The first step of noise removal was done by classifying the main grey scale values in order to cancel out all grey scale values of minor significance. This classification was used in a $3 \times 3 \times 3$ Gaussian blur filter, a widely used low-pass filter that has excellent smoothing properties. Other filters in VG such as median or gradient filters were tested without success. A small area of $3 \times 3 \times 3$ voxels was chosen because of the high density of fibres and inter-fibre material.

The segmentation tool in VG was used to separate individual fibres from the network. The contrast proved to be to low for this tool to distinguish individual fibres; therefore this post-processing was not pursued any further.
Chapter 4

Results and discussion

4.1 Optical microscopy

Optical microscopy provides two-dimensional images of an object with very little sample preparation. It is the only technique used in this study which allows one to obtain full colour images of the sample.

Cross-sectional OM images of both market pulp and paper given in Figure 4.1 show a layered structure in both fibre networks. This observation corresponds with data found using XµCT and observations found in literature [11].

Tearing the sample in machine direction makes it possible to visualize individual fibres and bundles (Figure 4.2). Initially the bundle was not identified as such. However, the grid structure in the bundle is also seen in XµCT cross-sectional images, see Figure 4.3, where the bundle structure is positively identified using various cross-sections.

Visualization of the bending experiment using OM to provide information about fibre bonds resulted in blurred images as soon as the surface layer fractured. The small depth of field in OM made it impossible to keep the fracture in focus.

Figure 4.1: Optical microscopy images of the cross section of market pulp (left) and paper (right).
4.2 Environmental scanning electron microscopy

Environmental scanning electron microscopy produced high resolution images with good contrast. The depth perception due to the use of multiple detectors facilitates the interpretation of the images.

The ESEM image in Figure 4.4 shows the fracture of a paper sample. Since ESEM does not allow one to see through an object, bundles and individual fibres are difficult to distinguish. Only the width of an object can be an indication of the difference.

As shown in Figure 4.5 no lumens are visible in the ESEM images, whereas all literature describes lumens to be present. It is not well understood why no lumens are visible in ESEM. A possible explanation for the lack of lumens is the edge deformation as described in [9].

ESEM is not suitable for complete fibre network analysis, since this would require extensive sample preparation. However, useful information about individual fibre dimensions can be obtained accurately.

4.3 Confocal laser scanning microscopy

In Figure 4.6 the result of profiling CLSM is shown. Very little information of the fibre network is visible. Although high and low regions show the surface roughness of the paper, profiling CLSM is not able to obtain images below the surface. Therefore, profiling CLSM is not suitable for fibre network research.
Figure 4.4: ESEM image of a fracture in paper.

Figure 4.5: **Left:** ESEM image of paper cut in the cross-machine directional plane. **Right:** Magnification of a single fibre.
X-ray Figure 4.7 shows fluorescence CLSM images at 20 µm and at 60 µm below the sample surface, respectively. The images clearly show deterioration of image quality with depth into the sample due to beam interference of layers above the focal plane, as was described in [4]. Individual fibres are visible in high quality images in the surface layer of the sample, whereas deeper images are too blurred to distinguish single fibre details. Another drawback of fluorescence CLSM is the difficulty to distinguish fibres from bundles, since no internal information is visible. Fibres and bundles appear to be solid bars in the three-dimensional representation whereas XµCT images and literature clearly indicate the presence of lumens. CLSM thus only allows for fibre network analyses of thin paper samples or only a thin surface layer of a sample.

Figure 4.6: CLSM height profile image of the surface of a paper sample. Colours represent areas of equal height.

Figure 4.7: Fluorescence CLSM images of paper at a depth of 20 µm (left) and 60 µm (right).
4.4 X-ray computed microtomography

Post-processing the XµCT images of paper resulted in a three-dimensional object, shown in Figure 4.8, consisting of three separate sub-volumes. It can be seen that the upper and middle sub-volumes show a ring-shape artefact, which resulted from the reconstructing algorithm. In Figure 4.9 individual fibres, bundles of fibres and fibre lumens can be identified. Two fibre bundles have been sectioned in axial direction showing the internal structure. The existence of fibre bundles is only mentioned in [11] which is the only study to investigate a mechanically pulped fibre network. This suggests that existence of fibre bundles depends on the paper production process.

![Three-dimensional XµCT reconstruction of a paper sample.](image)

The contrast of the image is too low to separate individual fibres or fibre bundles using the segmentation tool in VG. More advanced post-processing algorithms or procedures might provide sufficient contrast to identify fibres. Since developing a fibre segmentation or identification algorithm was outside the scope of this project, obtaining structural parameters was a tedious task performed manually.

Determining the length of fibres and bundles requires more volume to be analysed since most fibres were cut off at an edge of the sample. The longest stretch of fibre was found in a bundle shown in Figure 4.10. This fibre bundle spans 2.4 mm within the volume and, although not visible in the image, continues at both ends. This length is not uncommon in virgin fibre paper as [16] reported a fibre length of 3.5 mm.

A characteristic inter fibre bond distance is difficult to determine based on the XµCT images since fibre bonds are hard to detect manually due to noise. A large number of bonds is required to obtain a statistically accurate inter fibre bond distance. After this complexity is solved, a characteristic inter fibre bond
Figure 4.9: Three-dimensional image showing through a large bundle. Individual fibres and fibre lumens are visible as well.

Figure 4.10: Three-dimensional image of a paper sample. The largest bundle found in this volume is clearly visible.
distance can be determined by dividing the length of the fibre or bundle in the reconstructed volume by the number of bonds. In this study a few inter fibre bond distances have been determined to obtain some preliminary data for this parameter. From a population of eight fibre bond distances an average of 375 $\mu m$ was found. The longest inter fibre bond distance found measured 530 $\mu m$. These numbers are 20 times higher than the results presented in [16] which is probably a result of different pulp and paper production processes.

The fibre thickness is determined in cross-section images as shown in Figure 4.11. Only individual fibres were measured since individual fibre walls are indistinguishable in a bundle. A small population of fibres resulted in a mean fibre thickness of 30 $\mu m$. This is in agreement with dimensions found in [9]. Most fibres found had a circular cross-section which is in agreement with some literature while others reported an elliptic shape.

The fibre orientation distribution was determined with respect to the machine direction by selecting fibres in a layer and measuring the angle using the built-in measurement tool. This was done for every fiftieth voxel layer to prevent measuring a fibre twice. The results are shown in Figure 4.12 as a bar diagram. Four categories of angles are distinguished around respectively 0°, -45°, 45°, and 90° with respect to the machine direction. The categories $-90^\circ < \theta < -67.5^\circ$ and $67.5^\circ < \theta < 90^\circ$ have been combined and are shown on both ends of the histogram to visualize the symmetry. As can be expected from the production method most fibres are oriented in machine direction. The distribution is asymmetric with respect to the machine direction. This is a commonly observed phenomena resulting from dropping pulp onto the moving wire. Few fibres are oriented out of the surface plane of the paper, indicating a layered structure of the fibre network.

Figure 4.11: X$\mu$CT cross-section in machine direction of the three-dimensional reconstruction.
Figure 4.12: Fibre orientation in a paper sample. $\theta$ is the angle between fibre direction and machine direction.
Chapter 5

Conclusions and recommendations

A literature study was done to obtain insight in the current status of various imaging techniques in cellulosic fibre network research. XµCT and CLSM are frequently used to study fibre networks, while ESEM and OM are less used techniques. Image processing methods for XµCT are still being developed and differ widely depending on the type of information to be obtained from the images. The latest studies present methods to separate fibres individually and to detect fibre bonds. Structural parameters found in literature vary widely in magnitude due to differences in production processes and raw material. Structural parameters obtained in this study are in the same range of magnitudes.

All four imaging techniques were used in this study to explore their capabilities in cellulosic fibre network research. Absorption contrast XµCT proved to be the most promising technique since little sample preparation is needed while three-dimensional images are obtained. The image quality is not as good as for phase contrast XµCT, but commonly available image processing results in clear images in which fibres, bundles of fibres and lumen are discernable.

ESEM has promising features to obtain information about fibre networks on the individual fibre level. ESEM was not elaborately studied in this project but it is capable of capturing useful images. The absence of lumens when imaging with ESEM is a mystery that is still to be solved.

The semi-three-dimensional CLSM and two-dimensional OM are not capable of providing as much information as XµCT or ESEM while an equal amount of or even more sample preparation is required. Therefore, these techniques are less favourable for research in cellulosic fibre network.

Future research should primarily focus on image processing methods. Noise reduction and fibre segmentation methods provide a solid basis for accurate and detailed fibre network analysis. The methods presented by Walther et al. [11] provide the best results to obtain structural parameters.

Furthermore, information about fibre bonds should be obtained to positively identify two fibres or bundles crossing close to each other as an actual bond. A tensile or bending test visualized with ESEM could provide this information.
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