EXPERIMENTAL STUDY OF
MICRO-FIBRILLATED CELLULOSE
REINFORCED EPOXY COMPOSITES

A THESIS SUBMITTED TO THE UNIVERSITY OF MANCHESTER
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SCHOOL OF MATERIALS
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<tbody>
<tr>
<td>A</td>
<td>Aspect ratio</td>
<td></td>
</tr>
<tr>
<td>Å</td>
<td>Angstrom</td>
<td>m</td>
</tr>
<tr>
<td>α</td>
<td>Degree of cure</td>
<td>%</td>
</tr>
<tr>
<td>b</td>
<td>Critical percolation exponent</td>
<td></td>
</tr>
<tr>
<td>C_v</td>
<td>Critical volumetric concentration or percolation threshold</td>
<td>%</td>
</tr>
<tr>
<td>C_{v_{max}}</td>
<td>Maximum volumetric concentration</td>
<td>%</td>
</tr>
<tr>
<td>C_l</td>
<td>Chain length</td>
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<td>C_d</td>
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<tr>
<td>d</td>
<td>Fibre width</td>
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<tr>
<td>df</td>
<td>Degrees of freedom</td>
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<tr>
<td>dQ/dt</td>
<td>Rate of heat generation</td>
<td>J/minute</td>
</tr>
<tr>
<td>δ</td>
<td>Phase lag between stress and strain</td>
<td></td>
</tr>
<tr>
<td>E'</td>
<td>Storage modulus</td>
<td>GPa</td>
</tr>
<tr>
<td>E''</td>
<td>Loss modulus</td>
<td>GPa</td>
</tr>
<tr>
<td>E_c</td>
<td>Young’s modulus of a composite</td>
<td>GPa</td>
</tr>
<tr>
<td>E'_c</td>
<td>Storage modulus of a composite</td>
<td>GPa</td>
</tr>
<tr>
<td>E_f</td>
<td>Young’s modulus of a reinforcement phase</td>
<td>GPa</td>
</tr>
<tr>
<td>E'_f</td>
<td>Storage modulus of a reinforcement phase</td>
<td>GPa</td>
</tr>
<tr>
<td>E_m</td>
<td>Young’s modulus of a matrix</td>
<td>GPa</td>
</tr>
<tr>
<td>E'_m</td>
<td>Storage modulus of a matrix</td>
<td>GPa</td>
</tr>
<tr>
<td>F_{tl}</td>
<td>Total fracture edge length per unit fracture area</td>
<td>μm</td>
</tr>
<tr>
<td>f</td>
<td>Frequency</td>
<td>Hz</td>
</tr>
<tr>
<td>γ</td>
<td>Strain</td>
<td></td>
</tr>
<tr>
<td>γ_o</td>
<td>Resultant strain</td>
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</tr>
<tr>
<td>H</td>
<td>Heat released</td>
<td>J/g</td>
</tr>
<tr>
<td>H_R</td>
<td>Heat of reaction</td>
<td>J/g</td>
</tr>
<tr>
<td>η_f</td>
<td>Orientation efficiency factor of reinforcement</td>
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<td>η_l</td>
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<tr>
<td>η_s</td>
<td>Solvent viscosity</td>
<td>mPa·s</td>
</tr>
<tr>
<td>k_B</td>
<td>Boltzmann constant</td>
<td>J/K</td>
</tr>
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</table>
\( \varphi \)  Area ratio
\( l \)  Fibre length  \( \text{m} \)
\( l_c \)  Critical length  \( \text{m} \)
\( N \)  Number of fibres that are in contact
\( n \)  Repeat units
\( n_C \)  Total number of data points in control group
\( n_T \)  Total number of data points in treatment group
\( r^2 \)  Coefficient of determination
\( \rho_f \)  Density of reinforcement phase  \( \text{g/cm}^3 \)
\( \rho_m \)  Density of matrix phase  \( \text{g/cm}^3 \)
\( \sigma_f \)  Tensile strength  \( \text{Pa} \)
\( T \)  Absolute temperature  \( \text{K} \)
\( T_R \)  Relaxation time  \( \text{seconds} \)
\( T_g \)  Glass transition temperature  \( ^\circ \text{C} \)
\( t \)  Time  \( \text{minutes} \)
\( t_p \)  Thickness of a plate-like reinforcement phase  \( \text{m} \)
\( t_1 \)  Starting time of a reaction  \( \text{minutes} \)
\( t_2 \)  Ending time of a reaction  \( \text{minutes} \)
\( t_{\alpha} \)  Critical value at alpha level
\( \tau \)  Stress  \( \text{Pa} \)
\( \tau_i \)  Shear strength  \( \text{Pa} \)
\( \tau_o \)  Applied stress  \( \text{Pa} \)
\( \text{Var}_C \)  Variance of control group
\( \text{Var}_T \)  Variance of treatment group
\( V_f \)  Volume fraction of a reinforcement phase  \( \% \)
\( W_F \)  Work of fracture  \( \text{kJ/m}^2 \)
\( W_f \)  Weight fraction of a reinforcement phase  \( \% \)
\( w \)  Width of a plate-like reinforcement phase  \( \text{m} \)
\( \omega \)  Strain oscillation  \( \text{Hz} \)
\( x \)  Total number of data points
\( x_C \)  Total number of data points in control group
\( x_T \)  Total number of data points in treatment group
\( \overline{X_T} \)  Mean value of treatment group
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>$X_C$</td>
<td>Mean value of control group</td>
</tr>
<tr>
<td>$\psi$</td>
<td>Volume fraction of percolating reinforcement phase</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>Shape factor</td>
</tr>
<tr>
<td>$$</td>
<td>US dollar</td>
</tr>
<tr>
<td>$^{\circ}$</td>
<td>Degree</td>
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**LIST OF ABBREVIATIONS**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic force microscope</td>
</tr>
<tr>
<td>CI</td>
<td>Confidence interval</td>
</tr>
<tr>
<td>CP-MAS</td>
<td>Cross-polarisation magic angle spinning</td>
</tr>
<tr>
<td>DDS</td>
<td>4, 4’-Diaminodiphenylsulfone</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-Dimethylformamide</td>
</tr>
<tr>
<td>DMTA</td>
<td>Dynamic mechanical thermal analysis</td>
</tr>
<tr>
<td>DP</td>
<td>Degree of polymerisation</td>
</tr>
<tr>
<td>DP&lt;sub&gt;v&lt;/sub&gt;</td>
<td>Viscosity average degree of polymerisation</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>FE-SEM</td>
<td>Field emission scanning electron microscope</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>L</td>
<td>Lumen</td>
</tr>
<tr>
<td>MFC</td>
<td>Microfibrillated cellulose</td>
</tr>
<tr>
<td>ML</td>
<td>Middle lamella</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>P</td>
<td>Primary wall</td>
</tr>
<tr>
<td>PAN</td>
<td>Polyacrylonitrile</td>
</tr>
<tr>
<td>PF</td>
<td>Phenol formaldehyde</td>
</tr>
<tr>
<td>PLA</td>
<td>Polylactic acid</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>PVA</td>
<td>Polyvinyl alcohol</td>
</tr>
<tr>
<td>RCF</td>
<td>Recycled fibres</td>
</tr>
<tr>
<td>RH</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>rpm</td>
<td>Revolutions per minute</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>S1</td>
<td>Outer layer</td>
</tr>
<tr>
<td>S2</td>
<td>Middle layer</td>
</tr>
<tr>
<td>S3</td>
<td>Tertiary wall</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
</tr>
<tr>
<td>TEMPO</td>
<td>2,2,6,6-Tetramethyl-1-piperidinyloxy</td>
</tr>
<tr>
<td>TGpAP</td>
<td>Triglycidyl ρ-aminophenol</td>
</tr>
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ABSTRACT

Microfibrillated cellulose (MFC) is produced from naturally occurring, abundant and sustainable fibres of cellulose through mechanical treatments. It has been studied as a possible replacement for synthetic fibres in engineering composites, since it has many advantages that can enhance their mechanical properties.

MFC and epoxy resin composites were prepared with varying weight fractions for three different sources of cellulose fibre (softwood Kraft pulp, hardwood Kraft pulp and recycled newsprint). The nature of the MFC fibres was altered by solvent exchange using acetone and re-dispersed in N,N-dimethylformamide to make them more compatible with the hydrophobic matrix, as well as to aid interfacial adhesion between the fibres and matrix. Their mechanical properties and fracture surfaces were characterised using tensile testing and scanning electron microscope, respectively. Dynamic mechanical thermal analysis (DMTA) was also conducted for the composites made using softwood Kraft pulp MFC only.

The static tensile tests showed that significant enhancements were achieved by using MFC to reinforce epoxy resin. Improvements were found for tensile strength, Young’s modulus, strain-at-failure and work of fracture for all weight fractions and sources studied. Mechanical properties improved until a reinforcement level of 2 to 3 wt. %, after which the mechanical properties plateaued and showed no further improvement. This was true for all sources and agreed with the calculated maximum critical volume concentration value. SEM images of the fracture surfaces showed that good interfacial adhesion between the MFC and matrix and toughening effect were achieved. Fibre fracture was determined to be the main failure mechanism from studying the SEM micrographs. The estimated modulus of a single fibril was 65 to 95 GPa, which is consistent with the modulus of cellulose II and MFC reported in the literature.

Statistical analyses were carried out which showed that the results obtained from each source were comparable and repeatable. An assumption was made that as the static mechanical properties were similar, this would also be true for dynamic mechanical properties; and as such DMTA analysis was only carried out on the softwood MFC composites. A decrease in glass transition temperature was seen, whereas the storage modulus was found to increase. This confirmed that an observed toughening effect was achieved due to strong fibril-fibril interaction, despite the glass transition temperature being reduced. The storage modulus correlated well with the Young’s modulus obtained from static mechanical properties.

The results obtained indicated that MFC reinforcement could achieve a significant increase in mechanical properties of epoxy resin composites, regardless of the source of fibres. This effect was achieved by the good interfacial adhesion, which allowed for the efficient transfer of stress from the lower modulus matrix to the strong and stiff MFC.
DECLARATION

I declare that no portion of the work referred to in this thesis has been submitted in support of an application for another degree of qualification of this or any other university or other institute of learning.

Chun- Heng Huang

4th October 2015
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Finally, I am very appreciative and thankful for the assistance and support of everyone in the National Composites Certification and Evaluation Facility.
CHAPTER 1

INTRODUCTION

This chapter provides a brief background on the subject of this research, cellulose and microfibrillated cellulose (MFC), as well as information on recent findings and its uses in composites. An outline of the scope and structure of this thesis is also included.

1.1 BACKGROUND

Cellulose is the most abundant natural polymer on the planet; it is biodegradable and a renewable resource [1, 2]. It is most commonly found in plants where it forms their outer cell walls. Plant sources, in particular wood, are the most common sources of cellulose fibres for use in industry and research [3].

Cellulose is characterised as a hydrophilic material as it contains a high density of hydroxyl groups [2]. The formation of hydrogen bonds from these hydroxyl groups
plays a major role in its physical properties [4], such as its highly cohesive nature, multi-scale microfibrillated structure and hierarchical structure [5, 6]. In its crystalline form, cellulose has a modulus double that of aluminium and with a much lower density.

Compared to synthetic fibres, natural fibres, such as cellulose, have a lower cost and energy consumption, as well as a high specific modulus; they are renewable, biodegradable and sustainable, also being widely availability across the globe [7]. The benefits of natural fibres are well known, and cellulose is already used in many industries, such as paper and textile materials, pharmaceuticals, cosmetics and as additives in the optical industry, since it provides high transmittance compared to other reinforcing materials that could be used [1].

The advantages of natural and synthetic fibres mean that they are already used in a variety of composite materials. Composite materials consist of two or more components that display modified properties; when combined, the properties of the composite material are greatly enhanced compared to the individual components [8]. In fibre reinforced composites, the fibres are used to provide the strength and stiffness in the material and are a reinforcement to a polymer matrix. The matrix constrains the fibres and holds them in place, as well as facilitating stress transfer within the composite [8].

In engineering applications, composite materials have seen a rapid growth by showing the ability to replace traditional materials, such as metals [8]. Compared to conventional materials, the reduction in weight of using composites results in greater energy saving and efficiency, particularly sought after in the aerospace industry [8]. The use of cellulose fibres could be an alternative to conventional composites using man-made fibres, such as glass fibre and carbon fibre [9]. Compared to cellulose, the fabrication of synthetic fibres requires much more energy input and produces more carbon emissions.
Therefore, the use of cellulose fibres as an alternative to synthetics should help to reduce greenhouse gas emissions.

Although natural fibres have high stiffness, one drawback is the variation in the stability of their mechanical properties, caused by their high variation in fibre geometry and numerous defects, such as kink bands, that initiate brittle fracture in composites [7, 11]. These variations can be reduced by disintegrating cellulose fibres into a smaller form [12]; microfibrillated cellulose (MFC). MFC is a micro-nano sized cellulose broken down from the larger cellulose fibres; it consists of elementary fibrils or microfibrils formed into a larger unit. Microfibrils are formed when several cellulose chains are self-assembled and biosynthesised, they are composed of crystalline and amorphous regions [1, 6]. Cellulose chains that are located in the crystalline (or ordered) regions are packed together in crystallites, which are stabilised by a strong and complex intra- and inter-molecular hydrogen-bonded networks [13]. The physical properties of cellulose are strongly influenced by its crystallinity and crystalline orientation [1].

MFC can be defibrillated from cellulose fibres with simple mechanical processing. MFC is composed of large units of 5 nm diameter microfibrils, which each microfibril consisting of approximately 36 individual cellulose molecules [6]. The amorphous and crystalline regions of MFC form a web-like structure. Generally, the dimensions of MFC are 10 to 100 nm in diameter and several micrometres in length [3, 7, 14-16]. Due to their high aspect ratio, strength, stiffness and flexibility the use of MFC as reinforcement in composite applications has become the focus of significant attention in research [17].
However, there are issues when working with MFC that need to be overcome. Cellulose-based composites are generally reinforced plastics, such as the thermoset epoxy resin. The lack of compatibility between hydrophilic cellulose fibres and the hydrophobic polymer matrix [7, 18] results in poor interfacial adhesion, where stress cannot be efficiently transferred [8]. Thus, the mechanical properties, such as strength and stiffness of the composites, are negatively affected. This issue can be overcome by making cellulose less hydrophilic, for example by using surface modification or simple solvent exchange methods that replace water-hydrogen bonds from cellulose with hydrogen bonds from the solvent, stabilising the cellulose and making it more easy accessible to the polymer matrix [7, 18-20].

Sustainable green-composites of MFC have been produced using the thermoplastic PLA as a polymer matrix [21, 22]. The tensile strength and Young’s modulus were enhanced by 25 % and 40 %, respectively [21]. From the work reported by Lu et al. [7], where MFC and epoxy resin were used, the reinforcing effect can also be seen in the dynamic mechanical properties of the composites; with the storage modulus being increased up to 7-fold below the glass transition temperature, $T_g$.

Using MFC as reinforcement in a hydrophobic character matrix exhibits an improvement of mechanical properties (dynamic and static). This also shows that there should be no limitation of using MFC as a reinforcement for hydrophilic or hydrophobic characters of matrices. The improvement shown in other studies shows that MFC has great potential to be used as an alternative material for replacing synthetic fibres and could find uses and applications in industry. The systematic study of the interactions between MFC and polymer matrices will be valuable in the next generation of composite applications.
1.2 SCOPE OF THIS THESIS

Due to the particular characteristics of MFC, it has been increasingly used as reinforcement in composite materials [14, 23]. However there are still some areas that can be studied or re-examined.

Due to the strong hydrophilic nature of MFC, matrices have mainly been used in water soluble polymers that are also hydrophilic e.g. polyvinyl alcohol (PVA) [7, 24]. Hence, there is a need to further investigate the use of MFC in a matrix with a hydrophobic character. In advanced materials, the most commonly used thermosetting polymer with a hydrophobic character is epoxy resin [7]; therefore MFC is used as reinforcement to this matrix in the work described here.

The mechanical properties of the composites could be significantly negatively affected by surface modifications, as they can change the interaction between fibres [25, 26]. In order to avoid this situation and improve the compatibility between reinforcement and matrix, a simple solvent exchange method and re-dispersion in a strong polar solvent is carried out [18].

For example, in several studies MFC was treated with an organic solvent and then reinforced to a thermoplastic, such as polylactic acid (PLA) [21, 22]; only static mechanical testing of these composites was reported. In other studies where MFC was dispersed in thermoset epoxy resin [7], only dynamic mechanical testing was fully studied. Since the dynamic and static mechanical properties of MFC-based composites were not fully explored, or directly compared, this thesis compares the dynamic and static mechanical properties of MFC dispersed in an epoxy matrix. The reinforcing effect of MFC reinforced epoxy resin is analysed using tensile testing and dynamic mechanical thermal analysis (DMTA).
The toughening effect of MFC can also be examined by studying the roughness of fracture surfaces [27]. Previously, this was only evaluated by atomic force microscope (AFM) [27]. In order to develop an alternative method, simple image processing software is used to examine the micrographs obtained from scanning electron microscope (SEM).

Furthermore, a virgin fibre source is normally used for MFC production, *i.e.* bleached Kraft pulp [6]. However, waste materials, such as recycled paper and newsprint, could also be used as alternative sources of MFC [28]. Considering environmental issues, the use of waste materials that could potentially replace virgin sources of MFC is an area that is explored. Comparisons between the mechanical properties of composites using MFC obtained from virgin source and recycled sources are made.
1.3 OBJECTIVES

The main objectives of this research are as follows,

- To achieve a good compatibility between MFC and an epoxy resin, obtaining a strong interfacial adhesion, so that a significant reinforcing effect can be achieved.
- To compare the findings and establish the upper-limit and the most effective MFC content that can be used in the polymer matrix.
- To identify a technique for measuring the roughness of fracture surfaces.
- To compare the differences between MFC obtained from virgin sources and recycled sources in the reinforced composites.
- To determine the difference between static and dynamic mechanical properties of MFC/epoxy composites, *i.e.* the typical tensile tests and dynamic mechanical thermal analysis.
1.4 STRUCTURE OF THESIS

This chapter has provided an introduction to the thesis and a brief background of the subject matter, including justifications for this research, contemporary studies of cellulose and MFC and the objectives of this work. An outline for the structure of the rest of this thesis can be found below.

Chapter 2 provides a comprehensive background on cellulose and MFC, in particular MFC and its preparation procedure, as well as the characterisation of its morphology. In addition, a review of existing research into composite materials using MFC as a reinforcement phase, and research into different methods for preparation of fibres and composites is reported. Different techniques for testing, studying and analysing MFC composites are also addressed as well as the possible applications of these composites.

Chapter 3 details the methodology of this research, including the preparation of materials, composite fabrication and the testing methods used to analyse and characterise the MFC composites produced.

Chapter 4 focuses on analysing the results and data obtained from testing. It looks specifically at the characterisation of pulps and the morphology of MFC, before going on to discuss the findings from tensile testing, analysis of the fracture surfaces and the results of DMTA testing.

Chapter 5 provides conclusions and suggestions for future work.
A review of cellulose, specifically microfibrillated cellulose (MFC), its preparation methods and its morphology characterisation are provided in this chapter. The uses of MFC as reinforcement within a polymer matrix and its influence on the mechanical properties of nanocomposites, including applications, are also discussed.

2.1 CELLULOSE

Renewable and environmentally benign materials have received significant attention in recent years due to ‘green’ issues. Cellulose is the most abundant natural polymer on the planet; it is also biodegradable and a renewable resource [1, 2]. Cellulose has been used as a chemical raw material for over 150 years since it was identified by the French chemist, Anselme Payen in 1838 [29].
Table 2.1. Moduli of cellulose compared to some other engineering materials [30].

<table>
<thead>
<tr>
<th>Material</th>
<th>Modulus (GPa)</th>
<th>Density (g/cm$^3$)</th>
<th>Specific Modulus ($\times 10^{10}$ kNm/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel</td>
<td>200</td>
<td>7.8</td>
<td>2.6</td>
</tr>
<tr>
<td>Aluminium</td>
<td>69</td>
<td>2.7</td>
<td>2.6</td>
</tr>
<tr>
<td>Glass</td>
<td>69</td>
<td>2.5</td>
<td>2.8</td>
</tr>
<tr>
<td>Crystalline Cellulose</td>
<td>138</td>
<td>1.5</td>
<td>9.2</td>
</tr>
</tbody>
</table>

Table 2.1 compares cellulose to some commonly used engineering materials. Crystalline cellulose is shown to have a modulus double that of aluminium and with a much lower density. Crystalline cellulose also exhibits a high specific modulus, which is obtained from the ratio of modulus and density. Cellulose is used in many industries already, such as paper, textile materials, pharmaceuticals, cosmetics and as an additive in the optical industry [1].

Cellulose can be found in both plants and animals, but it is most prevalent in plants. The protective cell walls of plants contain a large amount of cellulose and the most abundant sources are wood, cotton, flax, hemp, jute, and ramie [30, 31]. Cellulose can be found in non-plant sources as well, such as sea creatures, with tunicates being a common example [30, 32]; it is also synthesized by a variety of bacteria, which belong to the genera Acetobacter, Agrobacterium, Pseudomonas, Rhizobium or Sacrina [30, 33]. Plant sources, in particular wood, are the most common sources of cellulose fibres for use in industry and research [3]. The information and details provided in this thesis will, therefore, focus on cellulose obtained from wood sources.
2.1.1 STRUCTURE OF CELLULOSE

Cellulose \((C_6H_{10}O_5)_n\) is classified as a complex polymeric carbohydrate [30, 34, 35]. The structure of cellulose, also known as cellobiose, is composed of repeating \(\beta\)-D-glucopyranosyl units connected by \(\beta\)-1,4-glycosidic linkages through oxygen, covalently bonded between C1 of one glucose ring and C4 of an adjoining ring-rotated by 180°, as shown in Figure 2.1 [1, 17, 36]. Each repeat unit constitutes of six hydroxyl groups and two glycosidic bonds.

Cellulose is characterised as a hydrophilic material as it contains a high density of hydroxyl groups [2]. The formation of hydrogen bonds from these hydroxyl groups plays a major role in its physical properties [4] such as its highly cohesive nature, multi-scale microfibrillated structure and hierarchical structure [5, 6].

![Figure 2.1](image)
The number of repeat units (n) represents the chain length of cellulose and is also described in terms of the degree of polymerisation (DP), which relates to the properties of cellulose materials [4]. Different sources of cellulose, treatment methods and acquired processes vary the value of DP [34, 35]. For example, the typical average DP values of cellulose in wood and pulp are approximately 3,500 and 1,050, respectively [34]. The DP value decreases during pulping, resulting in shorter chains of cellulose and a weaker pulp. Hence, it is important to ensure that the DP value remains as high as possible [34].

2.1.2 THE MORPHOLOGICAL STRUCTURE

Wood consists of cellulose as well as other components, namely hemicellulose, lignin and extractives. Each component is briefly discussed, respectively, below. A typical composition of wood and wood pulp are referred to in Table 2.2.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>42 ± 2</td>
<td>45 ± 2</td>
<td>73</td>
<td>64</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>27 ± 2</td>
<td>30 ± 5</td>
<td>20</td>
<td>32</td>
</tr>
<tr>
<td>Lignin</td>
<td>28 ± 3</td>
<td>20 ± 4</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>Extractives</td>
<td>3 ± 2</td>
<td>5 ± 3</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 2.2. The average composition of wood and wood pulp.
**Hemicellulose**

Hemicellulose is a branched polymer containing five different types of sugar units: glucose, mannose, galactose, xylose and arabinose [4, 34]. The composition or type of hemicellulose varies with different sources of wood and the location in the wood structure [34]. In contrast to cellulose, the chain length of hemicellulose is shorter and therefore has a lower value of $DP$ [34].

**Lignin**

Lignin is a highly branched (3-dimensional aromatic) polymer with a basic molecular unit, namely phenyl propane, with a high value of $DP$ [34]. However, lignin is removed for paper-making applications, since the addition of lignin causes paper to become brittle as well as causing yellowing and discoloration [37].

**Extractives**

Extractives are found in small amounts in wood. They consist of fatty acids, terpenes, resin acids, waxes and phenolic compounds. Extractives are soluble in water or neutral solvents meaning they are easily removed during processing [4, 34].

The origin of plant fibres or wood varies their structural morphology, but the main parts of cell walls of wood and plant fibres are similar. The typical morphological structure of cellulose from softwood is shown in Figure 2.2, which illustrates the cell wall organisation. The cell wall is composed of four groups of lamellae: the middle lamella, primary wall, secondary wall and lumen [4, 37, 38].
A tracheid consists of a primary wall and three secondary walls, where the primary wall is a thin impermeable covering layer and the secondary wall is the main part of the cell wall [4]. The middle lamella combines two contiguous tracheids together. It contains hemicellulose, but predominantly contains lignin [4].

The secondary wall has three layers, namely the outer layer ($S1$), middle layer ($S2$) and inner layer or tertiary wall ($S3$) [4, 37, 38]. The thicknesses of $S1$ and $S3$ are of order 100 to 200 $\mu$m and 100 $\mu$m, respectively, which are relatively thin layers compared to the $S2$ layer which has a thickness of 2 to 10 $\mu$m [4, 34]. The $S2$ layer forms the main body of the fibre as it contains approximately 80 to 90 % of fibre-wall materials [4, 37].
The modulus of elasticity is highly dependent on the $S2$ layer as well as the orientation of the cellulose microfibrils [4, 37]. Page et al. [40] reported that the strength of individual fibres in the longitudinal direction depends on the $S2$ fibril orientation. The tensile strength significantly decreases as the $S2$ fibril angle increases, which is illustrated in Figure 2.3 [40]. The orientation of cellulose microfibrils differs in each layer as shown in Figure 2.2. Fibrils are randomly oriented in the $P$ layer while $S1$ and $S2$ layers are both positioned spirally along the fibre axis. The $S1$ layer consists of intersecting fibrillar layers and the $S3$ layer contains tightly entwined fibrils [4, 37, 38]. The lumen is the void located in the centre of fibre [4, 37].

Softwoods consist of 90 to 95% of longitudinal fibre tracheids with length and width of order 2.5 to 7 mm and 25 to 60 μm [41]. In contrast, hardwoods consist of 35 to 70% fibre cells with an average fibre length of 1 to 1.5 mm. Hardwoods have a more complex structure than softwoods due the presence of a vessel element in their structure [41].

![Figure 2.3](image.png)

**Figure 2.3.** Fibre strength against $S2$ fibril angle [40].
2.1.3 CRYSTALLINE STRUCTURE OF CELLULOSE

Microfibrils are formed when several cellulose chains are self-assembled and biosynthesised. They are composed of crystalline and amorphous regions, as shown in Figure 2.4 [1, 6]. Cellulose chains that are located in the crystalline, or ordered regions, are packed together in crystallites and are stabilised by a strong and complex intra- and intermolecular hydrogen-bonded networks [13]. The physical properties of cellulose are strongly influenced by its crystallinity and crystalline orientation [1]. Cellulose comprises four different crystalline forms: Cellulose-I, II, III and IV.

Cellulose-I, native cellulose, is comprised two polymorphs, termed I\textsubscript{α} and I\textsubscript{β}. The composition of these polymorphs in native cellulose is dependent on the origin of the cellulose [42-44]. The presence of I\textsubscript{α} and I\textsubscript{β} was first established in 1984 by cross-polarisation magic angle spinning (CP-MAS) [42, 43]; it can be also characterised by other techniques, such as FTIR [1, 44], Carbon-13 NMR [45, 46] and synchrotron radiated X-ray diffraction [47].

![Microfibrils](image)

**Figure 2.4.** Crystalline (ordered) region and amorphous (less ordered) region in microfibrils.
I\(_{\alpha}\) is generally found in algae and bacteria, and has a triclinic unit cell structure with one polysaccharide chain [44, 48]; in contrast, I\(_{\beta}\) is typically found in cotton, ramie and tunicate, which has a monoclinic unit cell structure with two polysaccharide chains [44, 49, 50].

The polysaccharide chains in I\(_{\alpha}\) and I\(_{\beta}\) are both the same in their structural arrangement, but the pattern of their hydrogen bonds is different. This suggests that each polymorph adopts a different crystalline structure, as shown in Figure 2.5 and, with different unit cell parameters, Table 2.3 [51-53]. Comparing their stabilities, I\(_{\alpha}\) is a meta-stable form and can be converted into I\(_{\beta}\) by high temperature annealing in various media. This process is irreversible since I\(_{\beta}\) is a thermo-dynamically stable form, meaning it is more stable than I\(_{\alpha}\) [31, 45, 54].

(a) Triclinic structure  
(b) Monoclinic structure

\[\begin{array}{c}
\text{(a) Triclinic structure} \\
\text{(b) Monoclinic structure}
\end{array}\]

**Figure 2.5.** Crystalline structure of (a) I\(_{\alpha}\) and (b) I\(_{\beta}\) [1, 13].
Mercerisation or Chemical Regeneration

<table>
<thead>
<tr>
<th></th>
<th>( I_a )</th>
<th>( I_\beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a )</td>
<td>6.72 Å</td>
<td>7.78 Å</td>
</tr>
<tr>
<td>( b )</td>
<td>5.96 Å</td>
<td>8.20 Å</td>
</tr>
<tr>
<td>( c )</td>
<td>10.4 Å</td>
<td>10.38 Å</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>118.1°</td>
<td>90°</td>
</tr>
<tr>
<td>( \beta )</td>
<td>114.8°</td>
<td>90°</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>80.4°</td>
<td>96.5°</td>
</tr>
</tbody>
</table>

**Table 2.3.** The unit cell parameters of \( I_a \) and \( I_\beta \) [1, 13].

**Figure 2.6.** The main steps to obtain cellulose polymorphic forms [6].

Cellulose-I can be converted to cellulose-II (known as regenerated cellulose) by two different methods as shown in Figure 2.6: a mercerisation process with aqueous sodium hydroxide (NaOH) treatment or a chemical regeneration-dissolving cellulose, followed by precipitation [13, 31, 35, 36]. The crystalline structure of cellulose-II is different to cellulose-I [55]; the structural arrangement is determined by the anti-parallel chains [13]. Cellulose-II is a more thermodynamically stable form than cellulose-I, since its structural arrangement allows the establishment of a larger number of intermolecular hydrogen bonds. It has been manufactured extensively for commercial uses, such as Rayon fibres and Cellophane film [35, 36].
Cellulose-III is produced from cellulose-I and II by ammonia treatment and forms two individual polymorphs, respectively-III_I and III_II [6, 13]. The last cellulose crystalline form, cellulose-IV, has been found in primary cell walls from several plants [56, 57] and consists of two polymorphs, termed IV_I and IV_II. These forms are prepared from the modification of cellulose-III_I and III_II, respectively, [58, 59]. Both cellulose-III and IV are reversible to cellulose-I and -II; cellulose-III can be simply converted back by warming in water, whereas cellulose-IV can only be reversed to cellulose-I and II by boiling in acid [59, 60]. Cellulose-I and II are the most stable forms of cellulose, in fact cellulose-II is the most stable of these forms as the conversion of cellulose-I to II is irreversible [17, 36].

2.1.4 CELLULOSE SUSTAINABILITY

Cellulose and cellulose fibres are renewable and environmentally friendly resources. The use of cellulose stimulates environmental sustainability as it is the most abundant natural material on earth [1, 2]. Cellulose is already used in many aspects of everyday life. It is estimated that as much as 50 kg per day is used for each person on the planet [10]. As discussed in Section 2.1, cellulose can be obtained from various sources, with the most common being plants, such as wood.

The use of cellulose fibres could be an alternative to conventional composites using man-made fibres, such as glass fibre and carbon fibre [9]. Compared to cellulose, the fabrication of synthetic fibres requires much more energy input and produces more carbon emissions [10]. Therefore, the use of cellulose fibres as an alternative to synthetics will help to reduce greenhouse gas emissions.
In order to produce the raw materials for cellulose, namely wood, a large amount of land is needed. This can result in land competition with other uses, for example housing or food production [61]. A consequence of this is higher land costs or an increase in the distance that the raw materials need to be transported – pushing up the price of land, the cost of transport and the cost of the raw material itself. This can in turn have an impact on the financial viability of production of pulp and, subsequently, the production of cellulose fibres [61].

Furthermore, when producing cellulose fibres from wood, chemical treatment is typically required for pulp preparation; for example, Kraft pulp is prepared by using mixture of sodium hydroxide and sodium sulfide [23]. Consideration of the chemicals used, water consumption and waste during the pulp fabrication is needed. Therefore, the use of recycled material has become an important theme for environmental issues in pulp and paper making – as shown in Table 2.4. There has been a steady increase in the percentage of recycled material used over the past decades [62].

<table>
<thead>
<tr>
<th>Year</th>
<th>Pulp and paper production ($\times 10^6$ tonnes)</th>
<th>Waste consumption ($\times 10^6$ tonnes)</th>
<th>Apparent reutilisation rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1986</td>
<td>202</td>
<td>63</td>
<td>30</td>
</tr>
<tr>
<td>1990</td>
<td>237</td>
<td>85</td>
<td>35</td>
</tr>
<tr>
<td>1991</td>
<td>239</td>
<td>91</td>
<td>40</td>
</tr>
<tr>
<td>1992</td>
<td>246</td>
<td>96</td>
<td>40</td>
</tr>
<tr>
<td>2000</td>
<td>307</td>
<td>138</td>
<td>45</td>
</tr>
</tbody>
</table>

*Table 2.4. Global wastepaper use [62].*
2.2 MICROFIBRILLATED CELLULOSE

Microfibrillated cellulose (MFC) consists of elementary fibrils, or microfibrils, formed into a large unit. It can be defibrillated from cellulose fibres with simple mechanical processing and without the use of acid hydrolysis [6]. Microfibrils are composed of approximately 36 individual cellulose molecules and have a diameter of 5 to 20 nm [6, 63]. MFC has amorphous and crystalline regions and displays a web-like structure. Generally, the dimensions of MFC are 10 to 100 nm in diameter and several micrometres in length [3, 7, 14-16].

MFC was first obtained from wood pulp in the early 1980’s [15, 64]. Wood is the most significant industrial source of cellulose fibre and is also the main raw material for MFC production. Bleached sulfite pulp [65-67] and bleached Kraft pulp [28, 68-71] are normally used to produce MFC, with the latter being the most common starting material [6]. Due to the high demand for wood, it is widely used across many sectors i.e. building, paper, furniture, etc., alternative sources for producing MFC should be given significant attention [6].

MFC can also be extracted from non-wood sources such as sisal [72], bagasse [73] and sugar beet pulp [74, 75]. MFC obtained from agricultural fibres is located in their primary wall, which is easier to deconstruct [74], thus consuming less energy. In contrast, MFC obtained from wood demands more energy as the fibres are located in the secondary wall [6]. MFC is manufactured commercially by several companies e.g. Innventia (Sweden) and Daicel (Japan) [14]. It can be produced by two methods: mechanical treatment or chemical treatment.
Several applications of MFC were outlined by Turbak *et al.* [64] and Herrick *et al.* [15] and include uses such as rheology modifiers in foods, cosmetics, paints, paper, nonwoven textiles and pharmaceutical products. However, due to their high aspect ratio, strength, flexibility and the modulus of cellulose crystals (around 140 GPa), the use of MFC as a reinforcement in composite materials has become the focus of significant attention in research [17]. Different preparation methods, relative to the morphology of MFC, are discussed in more detail in the following sections.

2.2.1 PREPARATION OF MICROFIBRILLATED CELLULOSE

Mechanical treatment can be used to disintegrate fibres, however it requires a high amount of energy, *e.g.* 20 to 30 MWh per tonne [14, 23]. In order to scale-up MFC production in the industrial sector the development of disintegration methods with lower energy consumption has become an important concept in research.

The use of chemical treatments reduces the overall energy consumption to a fraction of that used in mechanical treatment, somewhere in the region of 1 MWh per tonne [14]. Chemical treatment is not a stand-alone method and is applied prior to or in between the separate stages of mechanical treatment processes [67, 74, 76, 77]. Typical energy inputs for the preparation of MFC using different pulps are compared in Table 2.5.
<table>
<thead>
<tr>
<th>Raw Material</th>
<th>Chemical Treatment</th>
<th>Energy Requirement per Tonne (MWh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kraft pulp</td>
<td>None</td>
<td>46</td>
</tr>
<tr>
<td>Sulfite pulp</td>
<td>None</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>Enzymatic</td>
<td>1.5</td>
</tr>
<tr>
<td>Kraft/Sulfite pulp</td>
<td>Carboxymethylation</td>
<td>0.5</td>
</tr>
</tbody>
</table>

*Table 2.5.* Approximated energy requirement for MFC preparation [23].

Kraft and sulfite pulp differ as they are produced from wood by using different chemical treatments [23]. The Kraft pulp contains the most pure cellulose fibres, whereas sulfite pulp contains additional products within the cellulose fibres, such as hemicellulose [23]. However, the degree of polymerisation value of hemicellulose in sulfite pulp is 50 % less than in Kraft pulp; therefore less energy is required for MFC preparation, as illustrated in Table 2.5 [78].

However, different sources of cellulose and the preparation methods used vary the morphology of MFC, such as the degree of polymerisation and aspect ratio [14]. Several techniques used for mechanical and chemical treatments are discussed in the following section.

---

### 2.2.2 MICROFIBRILLATED CELLULOSE PREPARATION USING MECHANICAL TREATMENTS

Several methods can be used for MFC preparation, including: refining and high-pressure homogenisation [28, 68, 69] or microfluidising [71, 72], grinding [3, 79] and high-speed blending [80].
Extracting MFC from pulp by using mechanical treatments, such as high pressure homogenisation, were first introduced in the 1980s [15, 64]. However, when processing pulp in this way the fibres can obstruct the homogeniser during the process, \textit{i.e.} fibre agglomeration, making it less efficient. Therefore, more energy is required to fully fibrillate the cellulose into MFC [23, 81]. In order to enhance the efficiency of this process, refining or beating is introduced prior to homogenisation [28, 68, 69].

The terms ‘refining’ or ‘beating’ are used interchangeably to describe the same function – the repeated passages of pulp through zones of compression and shearing in water. It is a common process in the paper industry, inducing controlled fibre damage by producing external fibrillation, the peeling off of the external cell wall layers of the fibres, \textit{i.e.} removing the primary wall and outer layer of the secondary wall [68]. The subsequent homogenisation process then fibrillates the internal fibre wall and provides a high level of fibrillated cellulose fibres [68].

Mechanical treatment by beating involves forcing the dilute fibre suspension through the gap between a roll and bedplate assembly. The fibres are subjected to cyclic stresses by the notches and grooves on the roll and bedplate, as seen in Figure 2.7 [68].

\textbf{Figure 2.7.} A schematic of a roll and bedplate in the refining process, such as a Medway beater.
After deconstructing fibres by beating, the diluted slurries are pumped into a high-pressure homogeniser. The slurry is forced through a spring loaded valve assembly which subjects fibres to shearing and impact forces, generated from the movement of the valve opening and closing [68]. These shear forces result in a high degree of fibrillation of the cellulose fibres [14, 68].

The number of times for a suspension to pass through the refiner and homogeniser before reaching an optimum degree of fibrillation is outlined by Nakagaito and Yano [68]. It was found that after passing the suspension through a refiner 16 times the fibres split into smaller bundles. These bundles did not disintegrate further for up to 30 passes, but the number of smaller bundles present in the suspension increased. Following this, the suspension underwent homogenisation in order to further disintegrate the fibres [68]. Fully established fibrillation was found to be occur after 14 cycles in the homogeniser, samples were taken up to 30 cycles, but it was noted that the fibrillation was not improved beyond 14 cycles of homogenisation [68, 69]. It was concluded that 30 passes through a refiner, followed by 14 cycles in a homogeniser, was the optimum method to achieve the best fibre fibrillation [68]. The viscosity of a suspension also indicates the amount of energy consumed during processing as their relationship is directly proportionally [69, 81].

Siqueira et al. [72] and Taipale et al. [71] discuss an alternate process for mechanical treatment using a microfluidiser. They fabricated MFC from sisal pulp and bleached hardwood Kraft pulp, respectively. Microfluidisers and homogenisers use the same method to defibrillate fibres, but have different structures in their chambers – these differences are outlined in Figure 2.8. Compared to the high-pressure homogeniser (e.g. around 550 bar), the fibre suspension was passed through thin z-shaped chambers; usually with a channel dimension of 200 to 400 μm under high pressure of
approximately 2,000 bar [17]. This provides a higher shear rate, producing more uniform and finer individualised fibres [6]. A homogeneous aqueous suspension of individual microfibrils was obtained after 10 passes through the microfluidiser [71, 72].

Figure 2.8. Schematic structure of the high-pressure a) homogeniser [82] and b) microfluidiser [6].
Iwamoto et al. [3] developed a different process for obtaining fibrillated cellulose fibres using a grinder. This method requires a lower number of passes to obtain fibrillated cellulose fibres. The fibres obtained through the grinder also have a higher degree of polymerisation than with the microfluidiser [83]. The grinder’s mechanism uses shearing forces to degrade the fibres whilst simultaneously fibrillating them. This is achieved by passing the pulp between two rotating grinding stones [3, 14].

Iwamoto et al. [3] studied different numbers of passes through the grinder at 1,500 rpm and the effect on fibre morphology. At one pass through the grinder, the fibres were found to have a variety of widths, such as micro, sub-micro and nano-sized. Sub-micro-sized and nano-sized fibres were observed at 3 passes, whereas the morphology of fibres remained unchanged after 5 passes through the grinder; this was determined to be the optimum condition for this method. In contrast, Taniguchi and Okamura [79] achieved the same outcome from preparing MFC from processing the wood slurry through a super-grinder 10 times, with less time needed for each pass.

The $DP$ of treated fibres reduces as the number of passes increases during fibrillation. For example, as reported by Iwamoto et al. [3], $DP$ was reduced by approximately 15% and 20% of for one and three passes through a grinder respectively. The degree of crystallinity of fibrillated pulp was also measured, concluding that the number of passes and degree of crystallinity show an inversely proportional relationship. The $DP$ value and degree of crystallinity of fibrillated pulp was approximated as a linear relationship, the coefficient of determination value, $r^2$, is 0.85 and is illustrated in Figure 2.9.
Uetani and Yano [80] used a high-speed blender to produce MFC from wood pulp, fibrillating the pulp by agitation. In order to draw a comparison with a grinder based method, in terms of damage to the fibres, the degree of crystallinity was measured [80]. The optimum operating conditions of a blender were found to be agitation of 30 minutes with a speed of 37,000 rpm. It was found that the degree of fibrillation was equal to that obtained from a single pass through a grinder operating at 1,500 rpm. The impact of the high-speed blender process on crystallinity of fibrillated pulp was significantly reduced during 0 to 5 minutes of agitation time; around a 5% reduction. Subsequently, the crystallinity was found to be unchanged up to 30 minutes [80]. Compared to passing through the grinder once, the degree of crystallinity decreased by approximately 8% and, overall, the high-speed blender achieved the same results with less of an impact on the cellulosic’s crystallinity [80].

Figure 2.9. The relationship between $DP$ and degree of crystallinity of fibrillated fibre pulp using a grinder [3].
A complete fibre disintegration, or fibrillation, enhances the mechanical and physical properties of MFC [68]. The degree of fibrillation obtained from the mechanical treatment influences the DP value and crystallinity of fibrillated fibres. The physical properties of composites based on fibrillated fibres are, therefore, affected.

2.2.3 MICROFIBRILLATED CELLULOSE PREPARATION USING CHEMICAL TREATMENTS

Chemical treatments are used to obtain less stiff and cohesive fibres prior to mechanical treatment. This can be achieved by limiting the hydrogen bonds, the addition of a repulsive charge or decreasing the DP amorphous links between individual MFC fibres [6]. Chemical treatments have been successfully introduced into several pre-treatment methods. They are enzymatic [67, 84]; TEMPO mediated oxidation [66, 70]; carboxymethylation [71, 85] or alkaline [74, 86, 87]. Each pre-treatment method is discussed, respectively, below.

**Enzymatic pre-treatment**

In nature, cellulose degrades by a set of enzymes known as cellulases [14]. In enzymatic pre-treatment, isolated cellulases are used to modify cellulose, without causing degradation during MFC preparation [88]. Enzymatic pre-treatment is a promising method resulting in less energy being required for MFC production [67, 88]. This method has been developed into a large scale industrial application and was made commercially available by Innventia (Sweden) in 2011[6, 88].
The interaction between hydrogen bonds from the microfibrils is limited by using the cellulases, which are classified into two groups - cellobiohydrolases and endoglucanases [14, 88]. Both cellobiohydrolases and endoglucanases exhibit strong synergistic effects [81]. The cellobiohydrolases consist of A- and B- types that are active on highly crystalline cellulose, whereas endoglucanases are active in the amorphous regions of the structure in order to degrade cellulose and comprises C- and D- types [89, 90]. The endoglucanase pre-treatment can be used to facilitate disintegration when obtaining MFC from wood.

Endoglucanase pre-treatment is used to increase fibre swelling in water and facilitate disintegration. This is a relatively environmentally friendly method compared to the acid hydrolysis technique discussed later [67]. In order to reduce the energy consumption during processing, several authors discuss a combination of endoglucanase pre-treatment and mechanical treatments. This combination helps to prevent the fibres from blocking or clogging parts of the machines used, such as the thin z-chambers in the microfluidiser. It also reduces the yield loss during preparation [67, 81, 84].

**TEMPO mediated oxidation pre-treatment**

TEMPO-mediated oxidation is the most commonly used pre-treatment. The cellulose surface modification takes place under aqueous and mild conditions [88]. Again, it is normally applied prior to mechanical treatment using simple equipment [66, 70], such as a blender. The oxidation of cellulose fibres is achieved by the addition of a primary oxidant, sodium hypochlorite (NaClO) in the presence of catalytic 2,2,6,6- tetramethyl-1-piperidinyloxy (TEMPO) and sodium bromide (NaBr) [14, 88, 91]. A schematic diagram in terms of chemical structure of the oxidation process is
shown in Figure 2.10. The primary hydroxyl group from C6 is converted to carboxylate groups via aldehyde functional groups and also consumes NaClO and NaOH [88]. As a result, the surface of the microfibrils become negative charged, which results in repulsive forces of ionised carboxylate groups overcoming the hydrogen bonds and easing fibrillation [14, 88]. In order to increase the carboxylate groups formed at the surface of microfibrils, the addition of more NaClO is required, but this significantly decreases the DP value [88]. The addition of a primary oxidant, NaClO, and catalyst, NaBr, are used, respectively, at pH 9 and 11 [14]. These alkaline conditions, caused by the presence of aldehyde group residuals, cause undesirable side reactions of oxidised cellulose, *i.e.* discoloration or significant depolymerisation [14]. To overcome this issue, Saito *et al.* [92] applied another oxidation system, under neutral conditions at pH 7, which used the primary oxidant, sodium chlorite (NaClO$_2$) as an alternative of NaClO and also replaced the catalyst, NaBr with NaClO. The DP value was maintained and a uniform distribution of fibres, without aldehyde group residuals, was obtained [92].

![Figure 2.10. Scheme of TEMPO-mediated oxidation mechanism of cellulose [88].](image-url)
TEMPO electro-mediated oxidation is an alternative sustainable method and it could well replace the previous two systems discussed. Isogai *et al.* [93] applied electro-mediated oxidation to softwood bleached Kraft pulp with TEMPO at pH 10 and 4-acetamido-TEMPO at 6.8 in a buffer solution. It required an increased oxidation time, but obtained a higher yield – of at least 80 % – and also preserved the main characteristic of TEMPO-oxidised MFC [93]. However, the oxidation yield is dependent on the starting material [14, 91]. The highest yield of oxidant product was obtained by using regenerated and mercerised cellulose, Cellulose-II [91]. On the other hand, the initial fibrous morphology of MFC was better preserved when Cellulose-I, native cellulose, was used with a lower yield of oxidant products [14, 94].

**Carboxymethylation pre-treatment**

Another chemical pre-treatment is carboxymethylation, which has a similar mechanism to TEMPO oxidation pre-treatment [66]. During this pre-treatment, carboxyl groups are produced in a sodium form by increasing the anionic charge on the surface of the MFC, resulting in repulsive forces to overcome the hydrogen bonds, as shown in Figure 2.11 [6, 77].

This pre-treatment is applied prior to mechanical treatment and greatly enhances the fibrillation efficiency and reduces the total energy consumption [71]. Taipale *et al.* [71] compared the net specific energy consumption needed between mechanical and chemical-mechanical methods during the MFC preparation. It was found that the use of carboxymethylation pre-treatment reduced the energy consumption of one pass through a microfluidiser by a factor of 2.5 [71].
However, the chemical modification of cellulose negatively affects its crystallinity and reinforcement potential. For example, Eyholzer et al. [85] reported how different methods for preparing MFC affect the crystallinity, shown in Table 2.6.

![Scheme of carboxymethylation pre-treatment mechanism of cellulose](image)

**Figure 2.11.** Scheme of carboxymethylation pre-treatment mechanism of cellulose [85].

<table>
<thead>
<tr>
<th>Methods</th>
<th>Reduction of crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical disintegration</td>
<td>4</td>
</tr>
<tr>
<td>Mechanical disintegration followed by</td>
<td></td>
</tr>
<tr>
<td>carboxymethylation</td>
<td>8</td>
</tr>
<tr>
<td>Carboxymethylation</td>
<td>10</td>
</tr>
<tr>
<td>Carboxymethylation followed by mechanical</td>
<td></td>
</tr>
<tr>
<td>disintegration</td>
<td>30</td>
</tr>
</tbody>
</table>

**Table 2.6.** The different methods applied by using refined, bleached beech pulp and their crystallinities [85].
Alkaline pre-treatment

In order to facilitate fibre defibrillation, an alkaline pre-treatment can be used prior to the mechanical treatment, such as using a grinder [86, 87] or by homogenisation [74]. Removal of lignin, hemicellulose, pectin and extractives in the fibres is achieved by this treatment – but without deconstructing the fibres [86].

Abe and Yano [86] and Okahisa et al. [87] applied the same chemical-mechanical treatment to obtain MFC from sources of wood and rice straw. Several chemicals were applied in their pre-treatment; a Soxhlet extraction was first used in order to remove extractives. The lignin, remaining hemicellulose and extractives were solubilised by the mild alkaline treatment for purification; careful alkaline extraction was needed to avoid causing the cellulose to degrade. Duferesne et al. [74] used a similar method, but with different raw materials. The Soxhlet extraction was not applied since the sugar beet they used did not contain extractives [74].

The purification of wood cellulose using this method is efficient as the lignin content is decreased to 0.1 wt. %, whereas it forms a minimum 85 % content of α-cellulose [87]. Therefore, less energy is consumed and fewer passes are required during the mechanical treatment to isolate MFC – this method also prevents damage to the MFC [86].
2.2.4 MORPHOLOGY OF MICROFIBRILLATED CELLULOSE

Morphology is a term used to describe the form and structure of the fibres. To study and characterise the morphology of MFC several techniques can be used, such as transmission electron microscope (TEM) [67, 71, 92, 93, 95], field emission scanning electron microscope (FE-SEM) [3, 80, 81, 85, 86] and atomic force microscope (AFM) [67, 71, 95].

Several studies compare the different techniques for determining fibre dimensions. Taipale et al. [71] estimated the dimensions of MFC from bleached hardwood Kraft pulp. Different widths were obtained using AFM and TEM. The same observation on bleached sulfite softwood pulp was also reported by Pääkkö et al. [67], where smaller widths of MFC were obtained using TEM. However, Fukuzumi et al. [95] reported that the fibre widths found had a good agreement with the results obtained from TEM and AFM. Dependent on the characterisation technique applied, sample preparation techniques are different; this in turn influences the accuracy for fibre dimension measurements. For example, the sample preparation for AFM does not require coating, whereas FE-SEM requires a layer of metallic coating to be applied to the sample surface, which may overestimate the fibre dimension [95]. In contrast, TEM requires much more delicate steps for sample preparation. This involves negative staining, which uses high atomic number elements, such as heavy metals, as the staining medium to give better contrast to the images. However, techniques such as FE-SEM are more commonly used for determining the morphology of MFC for fibre dimensions.

The fibre dimensions are studied in terms of the aspect ratio. It is an important factor to estimate a percolation threshold and maximum volumetric concentration of MFC,
especially when used as reinforcement in a polymer matrix. These are further discussed in Section 2.4.3.

The measurement of fibre dimensions can be determined by using image processing software [72]. As the aspect ratio of MFC is high, the width of a fibre is normally measured, but the fibre length can be hard to obtain [23].

Ishii et al. [96] estimated the average length of their MFC to be 2.2 μm; this was TEMPO-oxidised and obtained from bleached hardwood Kraft pulp. The storage, $E'$ and loss moduli, $E''$ of TEMPO-oxidised MFC were measured by using a stress-controlled rheometer [96]. They concluded that the nanofibres behaved as semi-flexible rod-like polymers in a dilute solution, which was applicable to the theory of linear viscoelasticity and the fibre length was calculated using Equation 2.1 [96].

$$T_R = \frac{\pi \eta_s C_l^3}{18 k_B T \ln\left(\frac{C_l}{C_d}\right)}$$

(2.1)

where $C_l$ and $C_d$ are the chain length (μm) and chain width (μm), respectively; $T$ and $\eta_s$ are of the order absolute temperature (K) and solvent viscosity (mPa s); $k_B$ is the Boltzmann constant (J/K) and $T_R$ is the longest relaxation time (s) of a semi-flexible polymer chain [96].

Although the morphology of MFC is affected by the various sources of cellulose and the preparation methods used, in general, they demonstrate a similar web-like structure [6]. Abe and Yano [86] used different sources of raw material to produce MFC using the same preparation method. They carried out an alkaline pre-treatment and followed by a single pass in a grinder. Different sizes of fibre were obtained from softwood and
rice straw, the average width was approximately 12 to 20 nm and 12 to 35 nm, respectively [86]. This was caused by a composition difference from the materials used.

Isogai et al. [93] produced MFC by applying electro-mediated oxidations with TEMPO pre-treatment under two conditions prior homogenisation, using bleached softwood Kraft pulp. The morphology of MFC obtained from these conditions was presented differently, related to the value of viscosity average degree of polymerisation ($DP_v$) [93], where $DP$ value is inferred from $DP_v$ [97]. Comparing electro-mediated oxidations with TEMPO at pH 10, 4-acetamido-TEMPO in a buffer at pH 6.8 was a preferable pre-treatment method to oxidise the fibres. This resulted in individual fibres with less damage or kinks observed after the fibre was disintegrated in water, resulting in a higher value of $DP_v$ [93]. Nevertheless, the average fibre widths from both conditions were measured as 5 to 7 nm [93].

Battista [98] reported a strong correlation between the $DP$ value and aspect ratio of fibres, meaning longer fibres had a higher $DP$ value. The reinforcement efficiency of MFC in a polymer matrix is affected by its $DP$ value, which translates into improved mechanical properties [98].

Depending on sources, the method for producing MFC and the morphology characterisation techniques that were used, there is some variation in the results for morphology that are obtained. As shown by the methods above, it is very hard to compare and investigate the most suitable method and techniques to characterise the morphology of MFC as all demonstrate benefits and limitations.
2.3 COMPOSITE MATERIALS

Composite materials demonstrate specific properties by combining the characteristics of two or more different materials [8]. Composites aim to achieve better mechanical properties than those of their individual components. Engineering composites usually feature stiff fibre reinforcements, designed to carry the applied load, with a polymer matrix that binds the fibres and helps to facilitate stress transfer. Wood is a typical natural composite material, consisting of cellulose fibres that are held together in a matrix of lignin and hemicellulose. Other natural composites can also be found in animals or other plants, i.e. bone, muscle and bamboo [8].

The use of fibre-reinforced composites in engineering applications has seen a rapid growth in recent years. Composites offer excellent specific modulus and strength and they have been used as replacements for some conventional materials, i.e. metals such as quenched and tempered low alloy steel [8]. Greater efficiency and energy savings are offered by composites, making them desirable for applications in aerospace, automotive, marine and sports industries [8].

The mechanical properties of composites can be enhanced through the improvement of their interlaminar properties [99], the relationship between the two components of the composite. Several parameters can affect the properties of fibre-reinforced composites. They are interfacial adhesion between the fibre and matrix; the volume-weight fraction of fibres, fibre orientation and aspect ratio of the fibres [14]. The use of man-made and natural fibre reinforced composites is further discussed below in respect to their mechanical properties, i.e. tensile properties.
2.3.1 MAN-MADE FIBRE-REINFORCED COMPOSITES

There are several examples of man-made fibres being used in composites materials, such as carbon fibre, glass fibre, aramid fibre and carbon nanotubes. These can be classified into continuous and discontinuous, or short fibres. An overview of their appearance and the arrangements that can be used in composites are shown in Figure 2.12.

![Diagram of fibre reinforcement types]

**Figure 2.12.** Types of reinforcement in fibre-reinforced plastic composites [100].
Conventional reinforcement based composites are normally presented as laminated materials, *i.e.* carbon fibre and glass fibre within layers of a matrix. The orientation of the individual laminae or layers of fibres has a significant effect on the mechanical properties of the composite. For example, unidirectional (0°) laminates are most stiff in the 0° direction, as the load is carried by the fibres. In contrast, the load would be carried more by the lower modulus polymer matrix in the 90° direction, when the force is applied across instead of along the fibres [100]. A balanced load-carrying capability, accounting for the number of different directions loading could be applied from, is required in order to gain the best enhancement of the mechanical properties in a composite.

Campbell and Flake [100] describe how the most effective orientation using multiple layers of fibres should be arranged. Orientating the majority of layers in the same direction is best if a uniaxial load is applied in a known direction [100]. However, if the structure could be loaded in many directions, layers orientated in the 0°, 90°, and ± 45° directions are most effective, since this ensures balanced mechanical strength is achieved, regardless of the load direction [100].

The properties of short fibre-reinforced composites are strongly influenced by the fibre length [101]. Several studies used reduced fibre lengths as reinforcement by chopping them into lengths of a few centimetres [101, 102]. Joesph *et al.* [101] used chopped E-glass roving fibre reinforced to phenol formaldehyde (PF). The tensile strength and Young’s modulus was greatly enhanced; five-fold and two-fold, respectively, as the fibre length increased up to 40 mm. This indicated the minimum fibre length for the stress to be effectively transferred between the fibre and matrix. In other words, the fibre length must be at least equivalent to this critical length, $l_c$, to reach the maximum
level of stress in the fibre. The critical length and its relation to composite fracture mechanisms are further discussed in Section 2.3.4.

In advanced engineering applications, the use of nanocomposites shows a lot of promise. Nanocomposites are defined as composites where one of the phases used has nanoscale dimensions, \textit{i.e.} 1 to 100 nm [14]. Compared to conventional composites, nanocomposites have better performance for mechanical, thermal and barrier properties, providing a higher specific modulus, whilst requiring a lower reinforcement level, \textit{i.e.} \( \leq 5 \) wt. % [14].

Nano-scale reinforcements are classified as discontinuous fibres/particles, such as carbon nanotubes. Carbon nanotubes can be considered the ultimate carbon fibres due to their high aspect ratio, strength and modulus [103]. Schadler \textit{et al.} [103] reported that the Young’s modulus of pure epoxy was increased 20 \% with the addition of just 5 wt. \% of multi-walled carbon nanotubes. Similar work was carried out by Allaoui \textit{et al.} [104], where the stiffness of 4 wt. \% multi-walled carbon nanotubes/epoxy composites was enhanced by factor of 3.

Several factors influence the improvement of mechanical properties in composites: the laminate orientation, and number of laminate layers, fibre content and fibre length [101]. From the studies outlined above, the level of enhancement provided by nano-scale reinforcements in composites has great potential for advanced engineering applications in the future.
2.3.2 NATURAL FIBRE-REINFORCED COMPOSITES

Compared to conventional materials, synthetic fibre composites offer equivalent mechanical properties with higher efficiency in their applications. However, improvements in the mechanical properties of composites can be made using natural fibres that are widely abundant and generally lower cost than synthetic materials. A comparison of natural and man-made fibres, in terms of their cost and energy required for manufacture are discussed in more detail in Section 2.4.4.

Increasingly, natural fibres are being studied as replacements for synthetic fibres such as glass fibres in composite applications [101, 105]. Wambua et al. [105] compared the tensile properties of hemp/polypropylene (PP) composites to glass fibre/PP composites, shown in Table 2.7. At a 30 vol. % fibre content, hemp reinforced PP exhibited higher tensile strength of around 50 % and obtained a similar Young’s modulus. The higher specific modulus of hemp/PP composites occurs as the fibre density is 30 % lower than glass fibre. This phenomenon was also reported by Joseph et al. [101]. They compared the tensile properties of banana fibre and glass fibre reinforced composites at different fibre loadings. The specific strength and modulus of banana fibre composites were comparable to glass fibre composites [101]. Since the natural fibres offer a lower density as well as excellent mechanical properties, this suggests that natural fibre composites have the potential to substitute synthetic fibres in composites.
<table>
<thead>
<tr>
<th>Composite</th>
<th>Tensile strength (MPa)</th>
<th>Young’s modulus (GPa)</th>
<th>Fibre density (g/cm³)</th>
<th>Specific modulus ($\times 10^9$ kNm/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hemp (mat)/PP</td>
<td>52</td>
<td>6.8</td>
<td>1.5</td>
<td>4.6</td>
</tr>
<tr>
<td>Glass fibre (mat)/PP</td>
<td>34</td>
<td>6.9</td>
<td>2.6</td>
<td>2.7</td>
</tr>
</tbody>
</table>

**Table 2.7.** Comparison of hemp and glass fibre reinforced polypropylene at 30 vol. % fibre content [105, 106].

Several studies have also investigated the mechanical properties of natural fibre reinforced composites, including fibres from bamboo [107], sisal [108] and sugar palm [109]. Due to the hydrophilic character of natural fibres, an improvement of the interfacial adhesion between the fibre and matrix is required when a matrix that is hydrophobic in nature is used. This is necessary to ensure that the stress transfer within the composite is effective and the mechanical properties are enhanced.

Bachtiar *et al.* [109] used an alkaline treated fibre to improve the tensile properties of sugar palm/epoxy composites. This treatment purified the cellulose by reducing the content of hemicellulose, lignin and extractives within the fibres, as mentioned in Section 2.2.3. The treatment improved the rougher surface that is created by those impurities, and thus the quality of the fibre-matrix interface was improved [109]. The tensile strength and Young’s modulus were reported to increase by 15 %.

In contrast, Rong *et al.* [108] compared alkaline treated and untreated unidirectional sisal fibre/epoxy composites. They found that the tensile strength was increased by 20 % using an alkaline treatment, but that the modulus demonstrated a 40 % reduction. This can be attributed to the cellulose being degraded by the treatment as a 2 %
reduction of cellulose crystallinity was found [108]. The conditions and parameters such as temperature, duration of treatment, concentration and type of alkaline solution used during alkaline treatment of natural fibres do influence the reinforcing effect of composites [109].

Jain et al. [107] investigated different forms of reinforcements and the effect they had on tensile properties. The tensile strength of bamboo fibre and orthogonal bamboo mat reinforced epoxy resin were studied. The average volume fraction of fibre and the orthogonal mat were 35 % and 60 %. Although different volume fractions of reinforcement were used, the same parameters were compared, such as the number of reinforcement layers and their orientations. The tensile strength of the multidirectional bamboo fibre composites decreased as the number of layers increased, whereas the mat reinforced composites exhibited the opposite trend [107]. The negative effect on strength was determined to be due to the poor cross-linking of the polymer [107], which was not uniform through the laminate layers, meaning that the shear stresses were not carried by the potential reinforcing strength of the composite.

In summary, natural fibres can be used as an effective reinforcement in composite materials and they can demonstrate similar improvements to synthetic fibres. However, care must be taken to ensure that the optimum conditions are applied during pre-treatments, the philicity of the fibres and matrix are compatible and that fibre orientation is also considered when producing the composites.
2.3.3 PREDICTION OF COMPOSITE PROPERTIES

The Young’s modulus of particulate composites can be predicted by using micro-mechanical models [30]. Using the Halpin-Tsai model, the overall elastic modulus of a unidirectional short fibre composite material can be estimated, in respect of the aspect ratio of the fibre. In this condition, fibre-fibre interaction was not taken into account as a perfect interface of fibre and matrix is assumed [30]. It can also be used for a variety of reinforcement geometries [110]. The Halpin-Tsai equation [110] is shown in Equation 2.2 and Equation 2.3.

\[
\frac{E_c}{E_m} = \frac{1 + \zeta \eta V_f}{1 - \eta V_f} \quad (2.2)
\]

with

\[
\eta = \left( \frac{E_f}{E_m} - 1 \right) \left( \frac{E_f}{E_m} + \zeta \right) \quad (2.3)
\]

where the \(E_c\), \(E_m\) and \(E_f\) are Young’s modulus of the composite, matrix and fibre, respectively; \(V_f\) represents the volume fraction of fibre and \(\zeta\) is the shape factor of the fibre.

The value of \(\zeta\) varies and depends on the shape and aspect ratio of the reinforcement [111]. An example is shown in Figure 2.13, which represents two types of aspect ratio for short or discontinuous reinforcements.
Ashton et al. [112] estimated the Young’s modulus of in-plane oriented plate-like composites using Equations 2.2 and 2.3 with the shape factor, $\zeta = 2 \frac{w}{t_p}$. However, Xanthos [113] discovered that the Young’s modulus was overestimated by using shape factor, $\zeta = 2 \frac{w}{t_p}$. Van Es [111] compared the Halpin-Tsai theory with several theories for plate-like reinforcements, i.e. Mori-Tanaka, Padaver and Riley. The shape factor was found to be as $\zeta = \frac{2}{3} \frac{w}{t_p}$ for plate-like reinforcements. Also, Van Es [111] concluded that the value of the shape factor for the plate-like and fibre reinforcements in a unidirectional composite are $\zeta = 2/3 \frac{w}{t_p}$ and $(1/2 \frac{l}{d})^{1.8}$, respectively.

The Young’s modulus of unidirectional composites, as a function of the aspect ratio for fibre and plate-like reinforcement, is shown in Figure 2.14 by applying the Halpin-Tsai model. Note that a significant difference of modulus in respect to the reinforcement geometries is exhibited when the aspect ratio of the reinforcements is between 10 and 1000.

Figure 2.13. Short/discontinuous reinforcement representing a fibre (left) and a plate-like filler (right) [111].
Figure 2.14. Young’s modulus of unidirectional composites reinforced with 20 vol. % of fibre and with plate-like reinforcement as a function of reinforcement aspect ratio. The shape factor, $\zeta = (1/2 \ l/d)^{1.8}$ and $2/3 \ w/t_p$ are used for fibre and plate-like reinforcements, respectively. The parameters of $E_m$ and $E_f$ were 3GPa and 172 GPa respectively [111].

On the other hand, when the shape factor becomes infinite, the Halpin–Tsai equations become equivalent to the rule of mixtures [110]. The elastic modulus, $E_c$ of unidirectional composites can also simply calculated by using rule of mixtures equations, as shown in Equation 2.4 [8].

$$E_c = V_f E_f + (1-V_f) E_m$$  \hspace{1cm} (2.4)

where $E_f$ and $E_m$ are the modulus of fibre and matrix and $V_f$ is fibre volume fraction.
The elastic modulus, $E_c$ of short fibre reinforced composites can be calculated by using Equation 2.5 [8]:

$$E_c = \eta_f \eta_l V_f E_f + (1 - V_f) E_m$$  \hspace{1cm} (2.5)

where $E_f$ and $E_m$ are the modulus of the fibre and matrix, respectively; efficiency factor of the fibre orientation and fibre length are of order $\eta_f$ and $\eta_l$. $V_f$ is the fibre volume fraction.

### 2.3.4 FRACUTURE BEHAVIOUR

The performance of composites can be further analysed by their fracture behaviour. The failure of fibre-reinforced composites is dominated by the fibre, matrix and fibre-matrix interface, as well as the arrangement and form of the fibres [114, 115]. Their properties play a major role in how the initial failure occurs.

The fracture of continuous or short fibre-reinforced composites has been categorised into several energy dissipation mechanisms. These include fibre fracture, fibre pull-out, de-bonding or crack bridging and matrix fracture and plastic deformation. Examples are shown in Figure 2.15 [114]. These mechanisms operate at a crack tip; the individual failure modes are illustrated in the micrographs below [114].
Figure 2.15. Mechanisms of energy dissipation in the fracture of short or continuous fibre-reinforced composites [114].

The failure mechanisms of fibre pull-out and de-bonding or crack bridging are associated with the weakness of the fibre-matrix interface [114]. The resulting stress concentration in the matrix is induced by the fibre end when the composite undergoes sustained loading [114]. The efficiency in load transfer to fibre-matrix interface depends on the fibre length, which is relative to its critical length. The critical length of fibres can be estimated using Equation 2.6 [115].

\[ l_c = \frac{1}{2} d \frac{\sigma_f}{\tau_i} \]  

(2.6)

Where \( l_c \) is the critical length (m); \( d \) is fibre width (m); \( \sigma_f \) is the tensile strength (Pa) of fibre and \( \tau_i \) is the shear strength (Pa) of the fibre-matrix interface.

When the fibre length is less than its critical length, the energy absorption mechanisms lead to composite failure, i.e. fibre pull-out and matrix fracture [114, 115]. On the other hand, if the fibre length is longer than its critical length, fibres will break in between
times or be pulled-out [114, 115]. The crack itself is related to the location and orientation of the fibres which is an important factor in determining the type of failure mechanism.

2.4 CELLULOSE NANOCOMPOSITES

Cellulose nanocomposites are prepared by using cellulose fibres with at least one nano-scale dimension, such as MFC, to reinforce a thermoset or thermoplastic polymer matrix, such as a polyurethane [116], polyvinyl alcohol [24, 117], polylactic acid (PLA) [21] or an epoxy resin [7]. Following MFC preparation described in Section 2.2.1, a polymer matrix is typically reinforced with MFC using one of several methods. The most commonly used methods are solution or solvent casting [24, 117], film stacking [116] and impregnation with resin [68].

This section provides a discussion of applications for MFC-based nanocomposites, as well as an explanation of how the improvements of mechanical properties are achieved in comparison to the neat polymer matrix.

MFC-based nanocomposites, consisting of microfibrillated cellulose in a variety of polymer matrices, will be discussed. Issues in manufacturing samples and how they can be overcome, namely the dispersion of fibres in the polymer matrix, will also be discussed in more detail.
2.4.1 MICROFIBRILLATED CELLULOSE BASED NANOCOMPOSITES AND THEIR APPLICATIONS

MFC is widely used as a reinforcement with hydrophilic/polar polymer matrices [7]. However, the fabrication of MFC-based nanocomposites using hydrophobic/non-polar polymer matrices is limited. This is due to the hydrophilic nature of cellulose fibres [7]. This incompatibility results in a weak interface between the fibre and matrix, which in turn affects the mechanical properties of composites [7], as the stress does not transfer efficiently from the low modulus matrix to the stiff fibres. Methods of dispersing MFC in hydrophobic polymer matrices, in order to improve their performance, are further discussed in Section 2.4.2. Hydrophilic and hydrophobic polymer matrices used in MFC-based nanocomposites are discussed, respectively, below.

MFC-based nanocomposites with hydrophilic polymers

Adding MFC reinforcement to a hydrophilic polymer matrix produces nanocomposites with excellent interfacial adhesion between the fibre and matrix [24, 116, 117]. For example, Seydibeyoğlu and Oksman [116] achieved significant advantages using polyurethane-MFC nanocomposites. In comparison to neat resin, the MFC nanocomposites demonstrated superior mechanical properties; specifically tensile strength and Young’s modulus, which increased by factors of 5 and 30, respectively [116].

Zimmermann et al. [117] and Lu et al. [24] also reported that the mechanical properties, such as Young’s modulus, obtained from tensile testing were greatly improved with the addition of MFC to a PVA polymer matrix. Compared to the neat polymer,
Zimmermann et al. [117] reported that the Young’s modulus of 10 wt. % MFC nanocomposites increased up to a factor of 2.5. In contrast, Lu et al. [24] obtained a 40 % enhancement of the Young’s modulus at the same MFC content. Zimmermann et al. [117] and Lu et al. [24] both found that the Young’s modulus reached a maximum value at a fibre fraction of 10 wt. %. It then remained unchanged with further addition of MFC. This is a typical phenomenon seen in nanocomposites with aspect ratio of reinforcement greater than 100, i.e. MFC [24, 30]. According to the composite properties predicted by using the Halpin-Tsai model (referred to Section 2.3.3), the composites modulus reaches a plateau when the aspect ratio of the fibres is greater than 100, which corresponds to the upper-limit of reinforcement used in these studies [30], shown in Figure 2.14.

**MFC-based nanocomposites with hydrophobic polymers**

The use of hydrophobic polymers for fabricating MFC-based nanocomposites is inhibited by the lack of compatibility between the two phases. The lack of compatibility results in poor interfacial adhesion between the fibre and matrix, as well as aggregation of the fibres [7]. In order to overcome this issue the fibres need to be treated before being combined with the matrix. This ensures a uniform distribution of fibres and avoids aggregation.

Techniques for fibre dispersion in a hydrophobic polymer are discussed further in Section 2.4.2. However, following treatment, the fibres can be well dispersed in the matrix and an improvement in mechanical properties can still be achieved [21, 22].
Iwatake et al. [21] and Suryanegara et al. [22] used similar preparation methods to fabricate PLA-MFC nanocomposites, with the mechanical properties being characterised by tensile testing. Iwatake et al. [21] reported that the tensile strength and Young’s modulus were significantly improved in comparison to the neat polymer – by 25 % and 40 %, respectively, at 10 wt. % MFC content. Different grades of PLA were used by Suryanegara et al. [22], who observed smaller increases of the mechanical properties. However, at the same content of MFC the tensile strength and Young’s modulus increased by approximately 10 % and 35 %, respectively.

Other testing methods have also been used. For example, hydrophobic epoxy-MFC composites were prepared by Lu et al. [7]. The thermal properties were characterised by using dynamic mechanical thermal analysis (DMTA) [7], although this cannot be directly compared with the studies using tensile testing. Seydibeyoğlu and Oksman [116] used a hydrophilic polymer matrix, polyurethane, and also characterised the thermal properties using the DMTA method.

Compared with the neat polymer matrix values from both studies [7, 116], the addition of MFC showed an improvement of the storage modulus, \( E' \), at a temperature above or below of their glass transition temperatures. This revealed that the mobility of polymer chains is reduced by the rigid MFC network and the formation of a good interfacial adhesion between fibril and matrix.

However, the glass transition temperature obtained from the hydrophilic polymer matrix remained the same throughout, meaning no significant changes of fibril-matrix interaction took place [116]. Other studies, such as Lu et al. [7], investigated a hydrophobic matrix with several coupling agents to modify MFC’s nature from hydrophilic to hydrophobic. It is worth mentioning from one coupling agent used, a 15
% decrease of glass transition temperature was observed when compared to the polymer matrix [7]. This suggests that the mobility of polymer chains at the fibre interface was increased, possibly due to the chemically inert and bulky features of the coupling agent used. However, the storage modulus was enhanced around 30% [7].

There are several applications for exploiting the enhancement of mechanical properties gained by using MFC as a reinforcement. Due to its low density, natural source and sustainability, it can be used as an alternative material to replace other fibres used in conventional composites, such as aramid fibres and glass fibre [9]. It can also be formed into a transparent and flexible composites film when used with a transparent polymer matrix, such as acrylic resin [3, 69] and epoxy resin [118]. The thinness of MFC also means it is suitable for applications in the optoelectronics industry [69].

2.4.2 MICROFIBRILLATED CELLULOSE DISPERSION IN A POLYMER MATRIX

The majority of polymer matrices used in composites have a hydrophobic character. The lack compatibility with hydrophilic MFC can result in the fibre aggregating, caused by poor dispersion within the matrix [119], which has a negative effect on the mechanical properties of the composite. This means that the full benefit of the reinforcement is not realised. In order to improve the reinforcing properties of the cellulose fibre, achieving a uniform dispersion and a good adhesion of cellulose fibre is critical.

The cellulose surface can be modified in order to improve dispersion [7]. Kim et al. [119] used a non-ionic surfactant as a dispersant to stabilise the dispersed
phase, improving the fibre adhesion to the surrounding polymer matrix. However, Van den Berg et al. [120] identified that the mechanical properties of the composites could be significantly affected by surface modifications as they can change the interactions between the fibres.

A stable cellulose fibre dispersion is only achieved in water or strong polar organic solvents, *i.e.* N, N-dimethylformamide (DMF). Several studies [7, 18-20, 119] have used polar organic solvents to improve cellulose fibre dispersion in a hydrophobic polymer matrix. This avoided modification of the cellulose surface, allowing greater potential to be realised for the enhancement of the mechanical properties [18].

In contrast, Gopalan Nair et al. [25] and Ljungberg et al. [26] obtained a stable cellulose suspension by using non-polar solvents for surface modification. Although, this resulted in a negative impact on the mechanical performance of the composites as the crystal structure of cellulose was damaged [25, 26].

However, Lu et al. [7] reported that the crystalline structure of cellulose was well maintained after surface modification using coupling agents. Furthermore, the mechanical properties of these modified MFC reinforced composites were greatly enhanced. MFC was obtained from Kraft wood, which had previously been homogenised and undergone a solvent exchange process with organic water-miscible solvents, *i.e.* acetone and ethanol. Another successful method, a sol-gel producing method was applied by Capadona et al. [20]. The dispersion of cellulose was improved and stabilised in the polymer matrix. Similarly, a solvent exchange method, was also used [19], but was then followed by re-dispersing using a strong polar organic solvent [18, 20].
The polymer matrix can be made easily accessible with the use of an organic solvent-based reinforcement [18]. The solvent exchange method replaces an entire water-hydrogen bond from the cellulose suspension with a hydrogen bond from an organic solvent [19]. A polar aprotic organic solvent such as DMF is likely to accept a hydrogen bond, stabilising the hydrogen bond from the cellulose and improving its dispersion.

2.4.3 PERCOLATION MODEL

It is noted in several studies that the mechanical properties of nanocomposites are greatly enhanced with the addition of MFC. This enhancement can be related to the formation of a percolating network in the composites, where the stress transfer is facilitated by hydrogen bonding between the fibrils [30].

Since MFC are finite in length, when the fibre content reaches a certain percentage within the material they can join together to form reinforcement chains throughout the composite – a percolated network. Percolation, in terms of specimen geometry, is a statistical theory that can be applied to any system containing a large number of substances that are liable to be in contact with each other [2]. In this case, it is used to describe the connectivity between fibres to create a system, or percolated network.

The Halpin-Kardos model [121] is a classic method for predicting the mechanical behaviour of semi-crystalline polymers and short-fibres that are homogenously dispersed in a continuous matrix [17]. The modulus and geometry of the fibres are included in this approach, but a strong interaction between fibres was not assumed. This
assumption results in much lower values of mechanical properties compared with experimental values [17].

However, the mechanical properties of MFC based nanocomposites can be predicted by a percolation model. An approach was introduced by Takayanaz et al. [122] and modified by Quali et al. [123] to include percolation related to the formation of infinite aggregates of fibrils [17], which corresponds to Equation 2.8. The percolation model is shown in Equation 2.7 and is expressed as the elastic modulus, $E'_c$.

\[
E'_c = \left(1 - 2\psi + 4V_f\right)E'_m + (1 - V_f)\psi E'_f + (1 - \psi)E'_f
\]

\[
(1 - V_f)E'_f + (V_f - \psi)E'_m
\]

(2.7)

where $E'_m$ and $E'_f$ represent the elastic moduli of the polymeric matrix and cellulose filler, respectively. $V_f$ and $\psi$ are the volume fractions of cellulose filler and percolating cellulose filler, respectively.

$\psi = 0$ for $V_f \leq C_v; \quad \psi = V_f \left(\frac{V_f - C_v}{1 - C_v}\right)^b$ for $V_f > C_v$

(2.8)

where $C_v$ is defined as the percolation threshold or critical volumetric concentration; $b$ is the critical percolation exponent and is acknowledged as 0.4 in a three dimensional network [124, 125].

Short-fibres, such as MFC, are numerous enough to make contact with one another and form a percolation network with the critical volumetric concentration – the percolation threshold. Favier et al. [126] and Dodson [127] estimated the critical volumetric concentration, $C_v$, using different numerators with the aspect ratio of fibre, shown in Equations 2.9 and 2.10, respectively. For rod-like particles, the critical volumetric concentration, $C_v$ is estimated by Equation 2.9:
\[ C_v = \frac{0.7}{A} \]  
(2.9)

where \( A \) is the aspect ratio of fibre.

However, Dodson [127] states “the contact number”, \( C_v \) by using Equation 2.10. This is the expected number of fibre contacts per fibre that can predict the critical volumetric concentration.

\[ C_v = \frac{N}{2A} \]  
(2.10)

where \( N \) is the number of contacts per fibre and assumed to be 2; \( A \) is the aspect ratio of fibre.

On the other hand, Parkhouse and Kelly [128] established a maximum volumetric concentration, \( C_v^{\text{max}} \) in a three dimensional fibre network, which can be calculated by using Equation 2.11.

\[ C_v^{\text{max}} = \frac{2 \ln A}{A} \]  
(2.11)

where the \( C_v^{\text{max}} \) is the maximum volumetric concentration and \( A \) is the aspect ratio.

Comparing findings with the Halpin-Kardos model [121], an excellent correlation was observed between the experimental data and predicted mechanical behaviours of cellulose-based nanocomposites by using a percolation model, reported by Samir et al. [2] and Capadona et al. [32].
2.4.4 THE MARKET PRICES OF PULP

Wood is widely used across many sectors and is the most commonly used source for producing cellulose fibres. The market prices of pulp are compared and discussed below. The market prices for 2014 and predicted prices up to the end of 2015 are provided in Figure 2.16 [129, 130].

Several examples of virgin and recycled pulps were compared. The average price for bleached softwood Kraft pulp is $970 per tonne, which is 15% higher than hardwood, at $830. The trends shown in their market prices were similar. In contrast, obtaining recycled pulp, such as from old newsprint, represents a significant cost saving. At $70 per tonne it is less than a tenth of the price of bleached softwood or hardwood Kraft pulp. Several researchers reported that using cellulose fibres or natural fibres obtained from pulp give an effective improvement in the mechanical properties of composites, but recycled sources have received little attention [21, 22, 24, 116, 117].

![Figure 2.16. The market prices of pulp for 2014 and 2015 delivered to USA [129, 130].](image-url)
As composite materials start to replace many conventional materials, there is a great potential to manufacture them on a larger scale [8]. Thus, the cost of manufacturing composites is being considered more closely, in particular the prices of raw materials and the production processes.

One of the most popular man-made reinforcements used in composites, carbon fibre, has an extremely high price caused by its raw material, a polyacrylonitrile (PAN) precursor [131]. The most up-to-date price for carbon fibre and PAN are approximately $15/kg and $20/kg, respectively [131, 132]. In contrast, softwood Kraft pulp that can be used for producing cellulose fibres has a much lower price of $1 per kg [129].

In order to reduce the raw cost, the use of recycled material has also increased. Spence et al. [28] used bleached Kraft pulp for MFC production and compared the properties of MFC from hornified and un-hornified fibre. They concluded that recycled paper can be used as the starting material for MFC production, since the physical and optical properties of the film produced were as good as the virgin fibres’ [28].

Looking at sustainability, forestry and wood is a naturally renewable source and is present across the globe. In contrast, man-made fibres are dependent on raw material manufacturing and, of course, the associated high energy costs. By comparing the embodied energy of each product – total energy that is required to produce 1 kg of the product – comparisons for manufacturing energy can be made [133]. The embodied energy for fibre-reinforced plastic is calculated as the sum of fibre and matrix. A table of embodied energy for individual materials is illustrated in Table 2.8.
The energy required to produce MFC from Kraft pulp is approximately 166 MJ/kg, which is 30% less than the energy for 1 kg of carbon fibres. As mentioned in Section 2.2.1, chemical treatment in MFC preparation results in a significant reduction in the energy required to disintegrate the fibres. Compared to carbon fibre (235 MJ/kg), only a fraction of the energy is required for MFC preparation from sulfite pulp when a chemical treatment is used (5 MJ/kg).

Overall, although the use of man-made fibre reinforced composites is increasing, the material, process costs and the energy required have become the focus of significant attention. Using alternative materials with lower cost and energy requirements, as well as recycled materials, should be explored further. Recycled materials more so, as the need for reducing landfill disposal is becoming a serious issue [133].

<table>
<thead>
<tr>
<th>Material</th>
<th>Embodied energy (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFC produced from sulfite pulp [23]</td>
<td>97</td>
</tr>
<tr>
<td>MFC produced from sulfite pulp using chemical treatment [23]</td>
<td>5</td>
</tr>
<tr>
<td>MFC produced from Kraft pulp [23]</td>
<td>166</td>
</tr>
<tr>
<td>Carbon fibre [134]</td>
<td>235</td>
</tr>
<tr>
<td>Glass fibre [134]</td>
<td>23</td>
</tr>
<tr>
<td>Epoxy resin [134]</td>
<td>78</td>
</tr>
<tr>
<td>Polyester resin [134]</td>
<td>71</td>
</tr>
</tbody>
</table>

Table 2.8. Estimated embodied energy for each constituent material used in composites.
CHAPTER 3

EXPERIMENTAL METHODOLOGY

The preparation of microfibrillated cellulose (MFC) composites and the process of composite characterisation are presented in this chapter. The details of material preparation, composite fabrication, preparation for physical properties examination and mechanical characterisation are provided.

3.1 PREPARATION OF MATERIALS

The MFC was prepared from three different sources; bleached Kraft pine pulp (Metsä, Finland), bleached Kraft birch pulp (Södra Gold Birch, Sweden) and a commercial source of recycled fibres - white newsprint offcuts (Globe Packaging, United Kingdom). Hereafter, these are classified as softwood, hardwood and recycled fibre (RCF), respectively.
Figure 3.1. The chemical structure of epoxy resin system; a) epoxy resin and b) hardener.

A thermoset plastic, epoxy resin, triglycidyl $\rho$-aminophenol (TGpAP) (Araldite® MY0500, Huntsman) and the curing agent, 4, 4$'$-diaminodiphenylsulfone (DDS) (Aradur® 976-1, Huntsman) were used as the polymer matrix for all composites prepared. The chemical structures of the epoxy resin and curing agent are shown in Figure 3.1.
3.1.1 PREPARATION FOR PULP CHARACTERISATION

The fibre dimensions and coarseness of pulps were measured by using a fibre image analyser (Metso FS5, Finland). Firstly, 3 grams of dry pulp sheet was soaked in a small volume of tap water overnight. The soaked sample was torn into approximately 1 cm × 1 cm squares. These pieces were then placed in a graduated cylinder and tap water added into a volume of 100 mL. The sample was disintegrated by using a perforated stirrer by hand for 30 seconds. The resulting slurry was then transferred directly into a sample cup for analysis to begin. Analysis was repeated five times for each type of pulp.

3.1.2 PREPARATION OF MICROFIBRILLATED CELLULOSE

The preparation of MFC involves three steps: refining, screening and homogenization.

**Step 1: Refining**

A Medway beater was used to beat the pulp, as shown in Figure 3.2. Before use, 120 grams of pulp was soaked overnight in 3.5 litres of tap water, such that the solid content of the dispersed fibre suspension was at the recommended ratio for the beater to operate.

The soaked pulp was then carefully added into the beating chamber, maintaining an approximate 15 mm gap between the roll and bedplate. The pulp was disintegrated for 5 minutes. This allowed the beater to fully disperse the pulp. Subsequently, a 5 kg load was applied on the bedplate arm for 25 minutes. This reduced the gap between the roll and bedplate in the beater. A schematic diagram of the roll and bedplate is presented in Section 2.2.1, Figure 2.7.
Finally, the beaten pulp was emptied into a bucket. To gather any remaining pulp from the beater, another 3.5 litres of tap water was added to circulate the remaining pulp in the beating chamber for one minute. This mixture was then emptied into the same bucket, resulting in a concentration of pulp of approximately 1.7 wt. %.

**Step 2: Screening**

The screening process used followed the TAPPI standard method T261cm-00 for fibre screening and was performed using a Somerville Fractionator (Reed Paper Group Ltd). Carrying out fibre screening ensured that the fibrils collected from the refining step were consistent with the papermaking definition of fines, *i.e.* the particles are able to pass through a 200 mesh screen with 76 μm opening dimensions [71].

The beaten pulp was transferred into the Somerville Fractionator, which was fitted with a standard 200 mesh screen. The material that passed through the mesh was collected on
a muslin cloth with the residual water being allowed to pass through the cloth and drain away. Any fibres caught on the mesh were discarded.

**Step 3: Homogenisation**

During homogenisation, a high-pressure homogeniser (ultra-turrax TP18/2k, Janke & Kunkel, Staufen) was used to fibrillate the cellulose particulates into microfibrils through mechanical shear forces. The material that was collected on the muslin cloth after the screening step was fibrillated using this homogeniser at a speed of 20,000 rpm for 60 minutes per 200 mL of a 1 wt. % cellulose suspension.

After following this three step process, the diameter of MFC was in the range of 10 to 100 nm [7, 15, 16] as shown in Figure 3.3.
Figure 3.3. The SEM images of microfibrillated cellulose obtained from a) softwood; b) hardwood and c) RCF.
3.1.3 DISPERSION OF MFC IN EPOXY RESIN

In preliminary experiments, composites were prepared by adding MFC suspensions directly into the epoxy matrix, using a simple stirring method to combine them. Obtaining a homogeneous mixture was difficult and aggregation was immediately observed. As discussed in Section 2.4.2, poor dispersion of fibres has a negative effect on the mechanical properties of composites. Accordingly, satisfactory composites could not be produced using this method and a new process needed to be developed.

One of the main difficulties affecting the production of the composites is the lack of compatibility between the hydrophilic MFC and the hydrophobic polymer. The solvent exchange method outlined by Tang and Weder [18] was followed to improve the compatibility of matrix and MFC. Acetone (Fisher Scientific), potassium carbonate (Fisher Scientific) and N,N-dimethylformamide (DMF) (Sigma-Aldrich) were used in this process.

To start the solvent exchange process, a separation funnel was used to transfer 150 mL of acetone carefully into a 50 mL of 1 wt. % MFC. The MFC suspension then naturally separated into two layers over a short period of time – where the top layer was the organic (acetone) layer and the bottom layer was an aqueous MFC-acetone gel (Figure 3.4). The top layer of acetone was replaced 1-2 times per day to accelerate the solvent exchange process. This step was repeated until the index refraction of liquid and gel interface no longer existed, i.e. until the bottom layer became an MFC-acetone gel. The top layer was replaced once more with dry acetone to concentrate the aqueous MFC-acetone gel. The entire solvent exchange process took approximately 4 days to complete. Dry acetone was used to dehydrate the water content from the acetone. Dry acetone was prepared using potassium carbonate as a desiccant.
After the solvent exchange process, the MFC-acetone gel was collected and transferred into a glass bottle. In order to improve MFC dispersion in the hydrophobic epoxy matrix, a strong polar organic solvent, DMF, was then added and gentle shaking was used to re-disperse the gel. The residual acetone was evaporated using a rotary evaporator at 35 °C; a lower temperature than the boiling point of acetone (57 °C) was used as the solvent was being evaporated in a vacuumed state.

Finally, the dispersed MFC in DMF was combined with the epoxy matrix by using mechanical stirring in an oil bath at 60 °C to maintain a lower viscosity.

The introduction of the solvent exchange method into the composite preparation process resulted in a significant improvement. The resulting mixture was easily worked with and was homogeneous with no perceptible aggregation of the mixture.
3.1.4 DEGREE OF CURE

The resin and composites needed to be fully cured to accurately demonstrate their mechanical properties [135]. To ensure that the epoxy resin and MFC composites used in this study were fully cured a thermal analysis technique, differential scanning calorimetry (DSC), was used.

The DSC technique is a non-equilibrium calorimetry. It measures the heat flow into, or from, the reference and sample as a function of time or temperature [135]. The heat flux DSC (Perkin-Elmer, DSC 8500) was used to determine the degree of cure. The method and process used are discussed below.

To prepare the DSC sample, 3 to 4 mg of uncured samples were encapsulated in a standard aluminium sample pan and positioned in the DSC sample holder. An empty aluminium reference pan with lid was placed in the adjacent holder as a baseline calibration prior to the test.

The degree of cure was calculated by using Equation 3.1 [136]:

$$\alpha = \frac{H(t)}{H_R}$$  \hspace{1cm} (3.1)

where $\alpha$ is the degree of cure; $H_R$ is the heat of reaction (J/g); $H$ is the heat released to a time, $t$ (J/g).

The degree of cure was established by using two DSC tests: a dynamic scan that steadily increases temperature up to a specified point; and an isothermal scan which maintains a specific temperature for the duration of the test. Figure 3.5 illustrates the technique with an example using data acquired from the analysis of MFC composites reinforced with 1wt. % of softwood. The degree of cure is calculated by using the area
within the trough from the isothermal scan divided by the area within the trough from the dynamic scan [13].

**Figure 3.5.** The rate of heat generation vs. time for 1wt. % softwood composite with a) dynamic scan and b) isothermal scan at 180°C.
Dynamic Scan:

The heat of reaction, $H_R$ is defined by Equation 3.2 [136] as determined by the area of the trough and was obtained by using a dynamic scan with a program setting of 30 °C to 340 °C at 10 °C/minute in a nitrogen atmosphere.

$$H_R = \int_{t_1}^{t_2} \left( \frac{dQ}{dt} \right) dt$$

(3.2)

where $H_R$ is the heat of reaction (J/g); $dQ/dt$ is the rate of heat generation; $t_1$ and $t_2$ are the starting and ending time for the reaction, respectively.

Isothermal Scan:

The heat released, $H$ up to time, $t$ is defined by Equation 3.3 [136] and was obtained by using a isothermal scan with a program setting of 30 °C to 180 °C with a shortest time and hold the temperature at 180 °C for 3 hours in a nitrogen atmosphere.

$$H(t) = \int_{0}^{t} \left( \frac{dQ}{dt} \right) dt$$

(3.3)

where $H$ is the heat released (J/g) up to time, $t$; $dQ/dt$ is the rate of heat generation.

The value of the degree of cure represents the percentage of the resin, or composite, that was cured. The desired value is at least 85 % cured, as at this point the resin, or composite, has the potential to reach its maximum mechanical properties.
3.2 FABRICATION OF COMPOSITES

When producing the composite specimens, three main points were considered: the amount of materials available; the time required to produce MFC; and the time needed for fabricating the composites themselves. Some materials used were purchased – such as solvents, the epoxy resin and the raw materials for the fibres – but the processed MFC, suspensions and dispersed MFC were all manufactured as part of this study.

Thin film composites with eight weight fractions were produced: 0.5 wt. %, 0.75 wt. %, 1 wt. %, 1.25 wt. %, 1.5 wt. %, 2 wt. %, 3 wt. % and 5 wt. %. The target thickness of the composites was 250 μm, with an area of 15 mm × 15 mm. A thin film was chosen as it can be scaled up into a thicker composite if the results from this study are favourable. A thin film also assisted with efficiency, as the procedures for processing and preparing dispersed MFC needed for the specimens were time consuming.

However, there are also disadvantages to fabricating thin films. It is challenging to de-mould a film with a thickness of less than 1 mm and cutting thin samples for testing is also more difficult. The method for cutting thin film specimens is addressed in Section 3.3.1.

The stoichiometric ratio of the epoxy resin and the curing agent, DDS, was 0.71 [137]. To begin the composite fabrication process, 4 grams of epoxy resin was preheated in a silicone oil bath at 60 °C for 30 minutes to lower its viscosity and make mixing easier; a schematic diagram of the experimental arrangement is shown in Figure 3.6. The epoxy resin was mixed together with a specified weight ratio of MFC for 30 minutes using mechanical stirring at a speed of 480 rpm. Following this, 1.75 grams of DDS was added into the mixture and stirred for a further 30 minutes at the same speed and conditions.
In order to remove air bubbles formed during the stirring process (air bubbles are detrimental to the strength of the composites), the mixture was placed in a lower mould with a release fabric at 60 °C for 30 minutes (Figure 3.7). The mild temperature condition and amount of time allowed air bubbles to flow from the bottom of the mixture to the top surface. A vacuum oven (Thermo-Scientific Heraeus®) was then used to remove air bubbles and solvent (i.e. DMF) from the mixture at 60 °C for 16 hours under vacuum. This was found to be an efficient method for removing all of the air bubbles from the mixture.

![Figure 3.6. Apparatus arrangement for sample mixing.](image)

![Figure 3.7. Schematic of composite film fabrication by using a hot press.](image)
Following this, the upper mould was then covered with a release fabric (Figure 3.7) and placed over the degassed mixture. The mixture was pressed into a thin film using a hot press (Dr Collin Platen Press). The hot press operating condition was 130 °C for 1 hour at 14 Pa pressure. The sample was then transferred into a programmable oven (Thermo Scientific Heraeus®), which was pre-heated to 130 °C and was followed by a 6 hour curing cycle. The curing cycle for MFC composites was 2 hours at three temperature increments of 130 °C, 160 °C and 200 °C. The MFC composites films produced had a thickness of between 0.25 and 0.33 mm.
3.3 TENSILE TESTING

The mechanical properties of the composites were characterised through static tensile testing. The process for tensile testing and treatment of results are discussed below.

3.3.1 SAMPLE PREPARATION AND TESTING CONDITIONS

The MFC composite films were tested using a universal testing machine, an Instron 5564 model, operated with BlueHill® software. The British standard, ISO 527-3, was adopted for sample preparation and testing conditions. The shape and dimensions of the specimens also followed this standard. However, specimen length was reduced from 150 mm to 100 mm to increase the number of specimens produced within each panel. Specimens were machined into 100 mm × 10 mm strips using a laser cutting machine (FB-1500, CadCam Technology).

The epoxy-based composites were brittle and it was challenging to machine the thin film specimens without causing damage during a mechanical cutting process. A computer controlled laser cutter was used as an accurate method of cutting the specimens and reducing any damage caused. The power of the laser, specimen shape and dimensions were all controllable variables, meaning the entire edge of the specimens was smooth and free from damage. The process also reduced wastage compared to mechanical cutting and allowed more specimens to be produced from a single manufactured panel.
Wedge action grips were used to hold the specimen in place during tensile testing. The deformation rate was set at 5 mm/min and the distance between the grips was 50 mm. Five specimens were tested for each weight fraction per MFC source. Prior to testing, the samples were pre-conditioned at 23 °C and 50 % RH for at least 48 hours.

The modulus of elasticity, or Young’s modulus, is calculated using measured values of strain. Typically a strain gauge, or an extensometer, is attached to the specimen to measure the strain. However, due to the delicate film thickness used in this work, gauges, or an extensometer, could not be attached without damaging the specimens. Strain was instead measured by using the crosshead displacement of the machine. Because of this, the machine compliance had to be corrected before tensile testing took place so that true values of strain were obtained.

The machine compliance correction can easily be done by running the same testing conditions – with the same gauge length and load cell – as the real test, but with a piece of steel replacing the thin composite film. After the test, compliance data were applied automatically in the BlueHill® analysing software. The tensile strain was subsequently calibrated and then applied to the testing results for the specimens, as shown in Figure 3.8. It can, therefore, be assumed that the results obtained from the following tests have a true value for all strain related results.
3.3.2 MECHANICAL PROPERTY CHARACTERISATIONS

The primary mechanical properties to be characterised are tensile strength, strain-at-failure, Young’s modulus and work of fracture. Tensile strength and strain-at-failure can both be determined from the maximum value in the stress-strain curve. The Young’s modulus of the specimens was obtained by calculating the greatest slope of the stress–strain curve. The work of fracture ($W_F$) is defined as ‘the total energy required per unit area for the specimen to reach failure’. The work of fracture was calculated by using the area under the force-elongation (or force-displacement) curve, divided by the crack area of the failure specimen. The unit for work of fracture is J/m$^2$ [138].

Figure 3.8. Typical stress-strain curves for the epoxy resin, before and after the tensile strain calibration.
3.4 DYNAMIC MECHANICAL THERMAL ANALYSIS

Another method used to analyse and characterise the mechanical behaviour of MFC/epoxy composites was dynamic mechanical thermal analysis (DMTA). The DMTA equipment (Perkin Elmer, DMA 8000) was used in a tension mode. This is a dynamic test that differs from the static tensile test (Section 3.3). The comparison of mechanical properties (i.e. elastic modulus) between these two tensile testing systems will be discussed further in Chapter 4. The preparation and outline of the DMTA analysis are discussed in more detail below.

3.4.1 SAMPLE PREPARATION AND TESTING CONDITIONS

The specimens were prepared using a laser cutting machine (FB-1500, CadCam Technology) with sample dimensions of 22 mm × 10 mm.

The specimens were heated from 30 °C to 250 °C at a rate of 5 °C/minute with 1 Hz frequency and 0.02 mm of dynamic displacement. The ratio tension was set as 150 %, which is the ratio of static force to the amount of dynamic force required from the specimen to obtain the set amplitude. A minimum of three specimens were tested for each weight fraction of each MFC source.
3.4.2 THERMAL ANALYSIS CHARACTERISATION

DMTA is a technique to determine the viscoelastic properties of a material. It consists of both solid and liquid material, which exhibits elastic and viscous responses to an applied oscillatory force (stress), respectively; the resulting displacement (strain) is measured.

The phase lag between stress and strain is between 0° and 90° as presented in Figure 3.9. The expressions of stress, \( \tau \), and strain, \( \gamma \), of a viscoelastic material are shown, respectively, as:

\[
\tau = \tau_0 \sin (t\omega + \delta) \\
\gamma = \gamma_0 \sin (t\omega)
\]  

(3.4)  

(3.5)

where \( \omega = 2\pi f \) and \( f \) is the frequency of strain oscillation; \( \delta \) is the phase lag between stress and strain; \( \tau_0 \) and \( \gamma_0 \) are the amplitudes of stress and strain; \( t \) is the time.

**Figure 3.9.** Schematic diagram of a phase lag between applied oscillatory stress and its resulting strain [139].
The mechanical behaviour of the epoxy resin characterised by dynamic tensile test in DMTA.

The elastic and viscous behaviour of a material can be measured in terms of modulus, namely the storage, $E'$, and loss, $E''$, moduli, respectively, which are referred to in Equations 3.6 and 3.7 [140].

$$E' = \frac{\tau_0 \cos \delta}{\gamma_0}$$  \hspace{1cm} (3.6)

$$E'' = \frac{\tau_0 \sin \delta}{\gamma_0}$$  \hspace{1cm} (3.7)

$$\tan \delta = \frac{E''}{E'}$$  \hspace{1cm} (3.8)

where $E'$ and $E''$ are the storage and loss modulus, respectively; $\tau_0$ is the amplitude stress; $\gamma_0$ is the resultant strain; $\delta$ is the phase angle between stress and strain.

The ratio of the two moduli is calculated as the tangent of the phase angle, $\delta$ (Equation 3.8). The glass transition temperature of a material is characterised from the
highest value of tan $\delta$ with respect to the temperature [140]. For example, the glass transition temperature of epoxy resin is approximately 220 °C as shown in Figure 3.10. DMTA was used to determine the value of elastic modulus below and above the glass transition temperature of MFC composites in a dynamic system.

3.5 EXAMINATION OF STRUCTURAL PROPERTIES

The physical properties of MFC composites were examined by using the scanning electron microscope (SEM) technique. The method used and preparations of samples for physical property examinations using this technique are discussed below.

3.5.1 SCANNING ELECTRON MICROSCOPE

The scanning electron microscope technique (Phillips FEG-SEM XL-30) was used to obtain images of the MFC morphology and the fracture surfaces resulting from tensile testing. The SEM operates under high vacuum conditions. The primary beam transmits electrons to the specimen surface and scans rapidly over the specimen surface simultaneously, either using backscattered or secondary electrons.

Backscattered electrons are the electrons from the primary beam that have been scattered by specimen atoms, whereas the secondary electrons are emitted from the surface of specimen. The specimens will then become either negatively or positively charged.
These charging effects may cause beam distortion, image brightness or resolution loss, which are undesirable situations. To minimise charging effects, the surface of the specimen must be electrically conductive or coated with a conducting film (*i.e.* platinum, gold or carbon) [141]. The backscattered electrons are normally used to analyse specimen information, such as composition and element investigation [141]. For high resolution specimen surface images or three-dimensional surface topography, the secondary electrons are generally used [141]. Accordingly, secondary electrons were used to image the morphology of MFC and fracture surface of specimens.

To reduce charging effects, sample preparation was required prior to imaging the MFC morphology and fracture surface. The specimens were prepared by using a laser cutting machine (FB-1500, CadCam Technology) and cut at a distance of 5 to 6 mm away from the fracture surface and positioned vertically, to present the fracture surface, on an SEM aluminium pin stub by using a double-sided adhesive copper tape (Agar Scientific). A

**Figure 3.11.** SEM sample preparation.
platinum conducting film was then applied to the specimen by using a precision etching coating system (Model 682 PECS, Gatan Inc.).

In order to have direct contact between the SEM aluminium pin stub and the specimen, silver paint (Agar Scientific) was applied to the specimen (Figure 3.11). The apparatus was fixed within a high vacuum column. The operating voltage of the electron beam was set to 6 kV. The images were then taken by scanning rapidly over the specimen surface, i.e. the fracture region.

3.5.2 MICROGRAPH CHARACTERISATION

The SEM technique was used to capture images of MFC and measure their dimensions. The fracture surfaces of the composites were also studied to determine the roughness for each weight fraction and each of the sources of MFC used. The images obtained from the SEM were analysed to obtain the average fibre width and to characterise the fracture surface of the specimens.

Image J software were used to process and analyse the SEM images. The scale bar within Image J was calibrated before analysing the images in the software.

Data for individual fibre widths were obtained from the MFC morphology images with 20 measurements being taken. The measured fibre widths of the three types of MFC used are presented in Chapter 4. The fracture surfaces of epoxy resin and MFC-based composites are noticeably different in their structure, as seen in Figure 3.12. In order to evaluate the effect of the addition of reinforcement in composites on their fracture structure, the fracture surfaces (Figure 3.11) were analysed. Five images per weight fraction for each source of MFC were processed.
Figure 3.12. Fractured surface of a) epoxy resin and b) 0.5 wt. % hardwood composites.

The sample with the closest value to the average value of the tensile properties was selected for comparison. The edges from the fracture surfaces were calculated by following five steps, which are shown in Figure 3.13. The method used to perform this analysis in Image J, is discussed in detail below.
Step 1: Smoothen Image

In order to reduce the ‘noise’ from the image, a mean filter was applied with “two pixels” to smooth the image. This replaces two pixels with the neighbourhood mean in the image.

Step 2: Edge Detection

To determine the fracture edges in the image, the convolve filter was used. This technique blurs an image, whilst at the same time making it more defined. It calculates the average of the number values of the pixels around the centre of a $3 \times 3$ grid and changes the centre value to this average. This has the effect of making grey pixels bordering white pixels more white and grey pixels bordering black pixels more black [142, 143].

Step 3: Thresholding

The image was adjusted by using “threshold”, an automatic function, to select the created edges from the previous steps. [143]

Step 4: Binarise

To present the fractured edges more clearly, and calculate their number, a binary filter was applied to the image. The binary filter converts the image to black and white, which represents the
fractured edges and the rest of the sample area as black colour and white colour respectively. Thus, the calculation of fracture length is easy to determine. [143]

**Step 5: Skeletonise**

The fractured edges were then skeletonised, which reduces them to 1 pixel size. The generated fracture edge length was measured by the total number of ‘white’ pixels.

A comparison is made by overlapping the original and processed images, shown in Figure 3.14.
Figure 3.13. A method for analysing the fractured surface of the 5 wt. % softwood composite using Image J software.
Figure 3.14. a) The original image and overlapped comparison of the original and b) processed image from Image J software; 5 wt. % softwood composite.
CHAPTER 4

RESULTS AND DISCUSSION

Following the procedure described in the previous chapter, three different cellulose fibre sources were used to produce MFC. Each of these was dispersed in an epoxy matrix via a simple solvent exchange method. The mechanical and thermal mechanical properties of MFC composites and the morphology of its reinforcements were characterised. The details of this characterisation and interpretation of the resulting data are provided in this chapter.

4.1 PULP CHARACTERISATION

The pulps from each of the raw materials – softwood, hardwood and recycled fibres (RCF) – were characterised using the fibre image analyser (Metso FS5, Finland). Five measurements were taken for each type of pulp. The fibre dimension measurements, including the length and width, were obtained and displayed as distribution histograms, shown in Figure 4.1 and Figure 4.2, respectively.
Figure 4.1. The fibre length distribution of a) softwood; b) hardwood and c) RCF.
As expected, the dimensions of fibres exhibit a distribution with maximum frequency close to the mean. From the shape of the distribution histogram, the length and width of the softwood fibres are more likely to have a symmetrical distribution. Looking at the fibre dimensions of hardwood and RCF, most of the data values are towards the left side of the histogram, such that there is a positively skewed distribution. In this case, the mode values tend to be more effective for determining an impression of fibre
dimensions as outlier values have less of an impact than they do on the mean value. Overall, the fibre dimensions obtained from hardwood exhibited narrower distributions compared to softwood and RCF, Figure 4.3. Softwood showed the highest variability in length, whereas RCF exhibited the largest difference in width measurement.

Figure 4.3. The fibre width and length of a) softwood; b) hardwood and c) RCF.
The aspect ratios of each of the individual fibre sources were calculated, and shown in Figure 4.4. Compared to the positively skewed distribution of RCF, softwood and hardwood have more evenly distributed histograms. The fibre aspect ratio of hardwood has a narrower distribution with a higher probability of mode values in comparison to softwood.

**Figure 4.4.** The fibre aspect ratios of a) softwood; b) hardwood and c) RCF.
The mode and mean values of the dimension specifications are shown in Table 4.1 and Table 4.2, respectively. Although the mode values are close to the mean, the mode value was used in this context. The skewness of distribution can be further analysed using the values of mean, mode and median. However, this level of analysis is beyond the scope of this thesis as the pulp material was further processed, as discussed in Chapter 3.

The dimensions obtained for softwood and hardwood were in line with the expected values from the literature [34, 37]. The aspect ratio of softwood was found to be higher than hardwood, as shown in Table 4.1. Compared to virgin fibres, a much smaller fibre length was observed for RCF; however RCF represented the largest width of all the sources used. As discussed in Section 3.1.2, MFC was obtained by screening the refined fibres through a mesh of 0.08 mm opening dimensions. Therefore, the obtained fibre length value of RCF, 0.1 mm, implies the presence of fines [71], i.e. the precursor to MFC. The term ‘fines’ in papermaking is qualified as particles which are able to pass
through a 200 mesh (0.08 mm) wire cloth aperture in a solid-liquid separation process [71].

The fibre width of RCF was similar and comparable with the work reported by Huda et al. [144, 145]. The aspect ratio of recycled fibre in Huda et al. [144, 145] was found to be 43. This fibre type was reclaimed from newsprint and magazine paper of unknown sources. In contrast, the aspect ratio of RCF reported in this thesis was smaller, at 25. This reveals that the amount of fines obtained was larger, as the fibre lengths were much shorter when compared to the literature. In addition, the fibre geometry for RCF was non-uniform and as it was obtained from an unknown blend of species, where different pulping methods could have been used in their initial processing.

Whilst evaluating the fibre dimensions, fibre coarseness was also investigated. Coarseness is defined as the mass of fibre wall material per unit length [4]. A summary of the fibre coarseness is provided in Table 4.3. The coarseness of RCF was the highest of the three sources used, whereas hardwood exhibited a much lower value. As RCF had the largest dimension in width, i.e. high fibre coarseness, as well as a large amount of fines, this suggests that a significant component of the RCF was mechanical pulp. Also, the colour of the fibre suspension was seen to be yellow; this colouration was due to the presence of lignin in the pulp.

In contrast, the origin of softwood and hardwood are both known to be bleached Kraft pulps and as such lower coarseness values were expected. The lignin in each of these sources was removed by bleach processing in the chemical pulp, which results in an obvious white colour. Moreover, a lower coarseness value for hardwood was anticipated as the fibre width and fibre wall were smaller than softwood [146]. Although the
information delivers some insight into the nature of fibre geometry, a further investigation on the morphology of fibrillated fibre-MFC is provided in the next section.

<table>
<thead>
<tr>
<th>Pulp material</th>
<th>Coarseness (mg/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softwood</td>
<td>12.2 – 12.7</td>
</tr>
<tr>
<td>Hardwood</td>
<td>5.2 – 5.3</td>
</tr>
<tr>
<td>RCF</td>
<td>16.3 – 17.8</td>
</tr>
</tbody>
</table>

**Table 4.3.** A summary of the fibre coarseness.
4.2 MORPHOLOGY OF MICROFIBRILLATED CELLULOSE

The dimensions of MFC were characterised by investigating a drop of MFC suspension using the SEM, the results of which are shown in Figure 4.5. The average fibre widths were measured by image analysis, by using calibrated image processing software – Image J. As seen in Figure 4.5, several areas in the micrograph show aggregate fibrils. Since some hemicellulose and most of the lignin are normally removed from the bleached Kraft pulp, a high content of cellulose is expected [69, 147].

In total, 20 measurements on a rod-like fibril were taken for each type of MFC. The average widths of softwood and hardwood were 102 nm and 90 nm, respectively, whereas the average width of RCF was measured as 146 nm. The width of softwood and hardwood MFC obtained agreed with the typical reported width of fibrils, of between 10 and 100 nm [3, 7, 14-16]. This shows that the fibrillation of the fibres achieved a good level. The width of RCF fibrils was affected by the presence of lignin, which could have filled voids and gaps between the fibrils making them appear larger, discussed in more detail below.

Prior to the mechanical treatment, the softwood and RCF pulp materials were found to have similar widths (19 μm and 22 μm, respectively). However, although the same fibrillation process was used, the width of fibrils obtained was different after homogenisation took place. This reveals that fibrillation did not take place to the same extent in RCF since lignin was present in the mechanical pulp; chemical pulp (softwood and hardwood) is often lignin-free. This can be further explained by comparing the micrographs in Figure 4.5. There are fewer rod-like fibrils present and more plane surfaces in comparison to those seen in softwood and hardwood. This may be due to the presence of lignin, which is sticky in nature, and could have filled the voids between
constituent fibrils and acted as a binder [148]. This would then form a plane surface in the dried condition [148].

A length measurement could not be obtained using the SEM or optical microscopes. Due to the nature of MFC, the fibrils were tangled in a web-like structure and the full length of fibril could not be clearly observed [23]. However, the length was known to be less than 76 μm, as the MFC was screened using a 200 mesh (Section 3.1.2) and the fibril length was further reduced after homogenisation [28]. The fibre image analyser used was unable to measure the length of the MFC, as the width dimension was below the minimum measurement range of the instrument, \(i.e.\) 10 μm. The greatest length of MFC used can be assumed as 50 μm. This estimation was consistent with the general fibril length from wood, which is within 20 to 100 μm [63]. It is dependent on the characterisation techniques used, preparation methods and naturally occurring differences within the species of the cellulose sources [14]. Using this information, the aspect ratio of MFC based on the measured width can be estimated, as shown in Table 4.4.

<table>
<thead>
<tr>
<th>MFC</th>
<th>Fibre width (nm)</th>
<th>Aspect ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softwood</td>
<td>102</td>
<td>490</td>
</tr>
<tr>
<td>Hardwood</td>
<td>90</td>
<td>560</td>
</tr>
<tr>
<td>RCF</td>
<td>146</td>
<td>340</td>
</tr>
</tbody>
</table>

*Table 4.4.* The estimation of aspect ratio of MFC using the assumed length of 50 μm.
Figure 4.5. Micrographs of MFC. Top: softwood; middle: hardwood; bottom: RCF.

In order to improve the dispersion and lack of compatibility with epoxy resin, MFC was solvent treated during composite preparation. The micrographs obtained for untreated and solvent treated MFC are compared in Figure 4.6.
Figure 4.6. Micrographs of MFC. Top: softwood; middle: hardwood; bottom: RCF. Left and right column are untreated and solvent treated MFC, respectively.

Although the morphology of MFC shows no easily discernible difference after solvent treatment, the use of the solvent exchange method and dispersion in a polar aprotic organic solvent helps to preserve the main characteristics of MFC. In addition, the
structure of solvent treated MFC was more likely to form a three-dimensional network, \textit{i.e.} tending to separate the tangled network of fibrils, compared to MFC in its untreated state. The fibrils were tended towards the z-direction, whereas untreated fibrils formed as a two-dimensional network. This can be attributed to the hydrogen bonds from cellulose being stabilised when a polar aprotic organic solvent was used.

4.3 MECHANICAL PROPERTIES

The mechanical properties of cellulose-based composites were characterised using constant rate of elongation tensile testing. The major mechanical properties of composites formed from the three sources of MFC, with eight different weight fractions each, are reported. Comparisons between the different sources and weight fractions are discussed.

Each source of reinforcement in the epoxy resin (ER) is discussed, respectively, as softwood, hardwood and RCF based composites. All plots show error bars, which represent the 95\% confidence interval (CI); meaning that 95 \% of the time, the true value will lie within the confidence interval when the measurements are repeated.
4.3.1 TENSILE TESTS

Tensile strength, Young’s modulus, strain-at-failure and work of fracture ($W_F$) were all determined from the tensile tests. Each mechanical property is discussed, respectively, below where appropriate. Typical stress-strain curves for MFC based composites with various fractions are shown in Figure 4.7. MFC based composites show non-linear curves, which have been previously observed [21, 22].

![Figure 4.7](image-url)  
*Figure 4.7.* Typical stress-strain curves of a) softwood; b) hardwood and c) RCF- based composites.
**Tensile strength**

The results for tensile strength are shown in Figure 4.8. The MFC composites show an excellent reinforcing effect when compared to the epoxy resin (ER). The strength of pure epoxy was almost doubled by the addition of MFC for each of the different sources tested. For example, the tensile strength of the softwood composite was more than double that of pure epoxy at 1 wt. % of MFC content. At high concentrations, the strength reaches a plateau after which no significant additional reinforcing effect was observed. A similar phenomenon was also found for the hardwood and RCF composites, demonstrated as illustrated curves in Figure 4.8.

![Figure 4.8](image_url)

**Figure 4.8.** Tensile strength of a) softwood composites; b) hardwood composites; c) RCF composites and d) all MFC composites.
The plateau was reached at a different point for each source of MFC used in the composites. It was reached when MFC content was just below 2 wt. % in softwood, whereas it occurs at around 2.5 wt. % in the hardwood composites. The tensile strength of the hardwood composites was found to be similar to the RCF composite in this case, i.e. approximately 80 MPa. The plateau seems to occur between 2 to 3 wt. % of MFC content in the RCF composites. However, a slightly less enhanced tensile strength was observed in the softwood composites, just below 80 MPa, on the illustrated curve. Overall, the tensile strength of the pure epoxy was improved by the addition of MFC, regardless of the source of the fibres. This reinforcing effect was consistent with a typical composite mechanism, where stress is transferred from the epoxy matrix to the high modulus fibrils, demonstrating good interfacial adhesion between MFC and matrix [14].

**Young’s modulus**

The Young’s modulus, or stiffness, of MFC composites was also calculated, shown in Figure 4.9. As with tensile strength, it can also be seen that using different sources of MFC provided similar improvements in the modulus values obtained, presented in Figure 4.9d.

According to the illustrated curves, the presence of the plateau with respect to MFC content was similar to the phenomenon discussed for tensile strength. The Young’s modulus of softwood composite exhibited an increase of 30 % at 1.5 wt. % of MFC content. However, after this point the modulus of the composites showed no significant improvement with further addition of MFC, up to around 3 wt. %. The increase observed at an MFC content of 5 wt. % was likely to be anomalous. Hardwood and
RCF composites displayed a similar trend, with their plateaus being reached at 2 wt. % of MFC content, with their moduli being improved by 50 % and 40 %, respectively. As with the softwood composites, once the modulus reached a plateau no significant improvement was observed as the MFC content was increased.

The virgin and recycled sources of MFC displayed similar reinforcing effects in relation to stiffness. Overall, the addition of stiff MFC increased the Young’s modulus compared to pure epoxy, suggesting that good interfacial adhesion between fibrils and matrix was obtained [14].

**Figure 4.9.** Young’s modulus of a) softwood composites; b) hardwood composites; c) RCF composites and d) all MFC composites.
Tensile strength and Young’s modulus relationship

It can be clearly seen that the addition of MFC to pure epoxy greatly enhanced the properties of the composites, i.e. the tensile strength and Young’s modulus. The tensile strength value of each individual weight fraction was plotted against their Young’s modulus values, as shown in Figure 4.10.

![Figure 4.10. Tensile strength and Young’s modulus relationship of all the MFC composites.](image-url)
In order to explore the addition of MFC to pure epoxy and its influence on tensile strength and Young's modulus, the properties of pure epoxy were included for evaluating this relationship. Several points were aligned against the regression line from pure epoxy, meaning that the addition of MFC increased the tensile strength, as well as the Young’s modulus of composites gradually. The remaining data points are represented as a cluster. The effectiveness at these data points was equivalent to the plateau observed in Figure 4.7 and Figure 4.8.

The gradient of the regression lines from hardwood and RCF composites were found to be similar (i.e. around 0.06). Both were also greater than the softwood composites (approximately 0.05). However, if the 5 wt. % value of softwood composite was considered anomalous and discounted, then the slope increases to 0.07, were in line with hardwood and RCF. This means that using different sources of MFC resulted in similar improvements to the mechanical properties.

The coefficients of determination, $r^2$, were greater than 0.8 in all cases. This suggests that there was a strong association between these mechanical properties of the MFC composites, meaning that the addition of MFC made pure epoxy stronger as well as stiffer. However, when the data point for pure epoxy was excluded in these plots, the reduced values of $r^2$ are as expected (between 0.6 to 0.8). This relationship could only be based on the effect of the addition of reinforcement in the composites.
**Strain-at-failure**

The data for strain-at-failure of the MFC composites are shown in Figure 4.11. MFC composites exhibit an improvement of strain-at-failure compared to pure epoxy. The reinforcing effect was achieved by both virgin and recycled fibre sources, which were found to have similar impact on mechanical properties, as seen in Figure 4.11d.

![Figure 4.11](image)

**Figure 4.11.** Strain-at-failure of a) softwood composites; b) hardwood composites; c) RCF composites and d) all MFC composites.
In contrast to the tensile strength and Young’s modulus of the composites, the strain-at-failure reduced as the MFC content increased, after an initial maximum value was reached. As seen from the illustrated curve, a steady improvement of strain-at-failure was observed up to around 2 wt. % of MFC content in softwood composites, an increase of 25 %. However, as the MFC content was increased further, the strain decreased slightly or performed at an equivalent level to the pure epoxy resin, *i.e.* from 1.25 to 5 wt. %. This can be clearly seen as the error bars of 5 wt. % composite overlap with those of the pure epoxy resin.

This peak value can be considered as the point at which the amount of MFC reached the upper-limit that can be uniformly distributed in the matrix. In other words, the MFC was reinforced into a finite space containing epoxy resin. As the MFC content increased beyond the upper-limit (*e.g.* up to 5 wt. %), the available space for fibre distribution was reduced. This caused an increased amount of fibre-fibre contact, or aggregation. Aggregation results in a reduced interface between the fibres and matrix, crucial for efficient stress transfer in the composites, leading to a reduction in the mechanical properties.

Although the reduction was not exhibited significantly in tensile strength and Young’s modulus values, discussed previously, the hardwood and RCF composites also demonstrated similar performance for strain-at-failure. The upper-limit was observed when the MFC content reached to 2 wt. % and 2.5 wt. % for hardwood and RCF composites, respectively. Following this, the reinforcing effect steadily reduced as MFC content increased.

However, a slightly different view was observed from the illustrated line (dashed). The strain-at-failure of MFC composites was likely to remain constant (around 4.5 %) with
the addition of MFC. A constant strain value was maintained as the fibre content increased; nonetheless the strain-at-failure value of pure epoxy was improved with the addition of MFC.

Work of fracture

The overview of work of fracture, \( W_F \) for the MFC composites is shown in Figure 4.12. MFC composites required more energy to reach the failure state compared to the pure epoxy. The reinforcing effect was observed up to the upper-limit of MFC present in the composites [30], \( i.e. \) where no significant improvement was found with further addition of MFC. For example, the \( W_F \) of softwood composites was more than tripled at 1 wt. \% of MFC content. Subsequently, the \( W_F \) value remained almost unchanged, with no significant increase found in the higher MFC content composites, shown in Figure 4.12a.

From the illustrated curve (without considering 1 wt. \%), a plateau occurred at 2 wt. \% in the softwood composites. In contrast, a plateau was reached at 2 wt. \% and 3 wt. \% for hardwood and RCF composites, respectively.

According to the illustrated line (dashed), the \( W_F \) for MFC composites maintained a constant value for each concentration of MFC used, approximately 80 to 120 kJ/m\(^2\). Regardless, the \( W_F \) value was still enhanced when compared to pure epoxy. The pure epoxy was enhanced in a similar way with the addition of each of the different sources of MFC, as seen in Figure 4.12d.
Figure 4.12. Work of fracture of a) softwood composites; b) hardwood composites; c) RCF composites and d) all MFC composites.

Summary of mechanical properties

The weak compatibility of the hydrophilic-MFC and the hydrophobic-epoxy matrix was overcome by improving MFC dispersion in the epoxy matrix, as discussed in Section 3.1.3 [18]. MFC reinforced epoxy composites exhibited a significant improvement of mechanical properties compared to pure epoxy. The composites exhibited a high resistance to deformation before reaching their failure state, indicating a good interfacial adhesion between the MFC and matrix [14]. The well dispersed MFC and the formation of a rigid network played a major role in establishing the reinforcing effect in the matrix. A strong MFC-matrix interface was formed where the stresses acting on the matrix transferred to the microfibrils, resulting in a stronger composite [8]. The mechanical
properties of the MFC composites showed no significant difference between the
different sources of reinforcement used; the results from virgin and recycled fibres are
comparable.

The reinforcement effect observed mirrored similar phenomena seen in other MFC
reinforced polymers. The maximum extent that the composites’ mechanical properties
were enhanced was at around 2 to 3 wt. %. Following this, the mechanical properties
remain unchanged with further addition of MFC, i.e. a saturation point or upper-limit of
reinforcement was reached.

It is also worth investigating the maximum MFC content that can be randomly
orientated and distributed in the pure epoxy. This is useful for confirming if the
variations of MFC content for the composites covered a full range of suitable
concentrations. Also, it can help to show the MFC content reached the observed plateau
in mechanical properties. As discussed in Section 2.4.3, the maximum volumetric
concentration, $C_v^{\text{max}}$ of MFC composites can be calculated using Equation 2.11 [128].

An overview of $C_v^{\text{max}}$ can be seen in Figure 4.13, representing $C_v^{\text{max}}$ as a function of the
aspect ratio. According to Section 4.2, the estimated aspect ratio of softwood was 490;
hardwood and RCF were of the order, 560 and 340. Therefore the $C_v^{\text{max}}$ of MFC
composites should fall between around 2 to 3 vol. %.

\[
C_v^{\text{max}} = \frac{2 \ln A}{A} \tag{2.11}
\]

where $A$ is the aspect ratio of MFC.
The relationship between the maximum volumetric MFC concentration, $C_{v_{\text{max}}}$, in pure epoxy and the aspect ratio of MFC. The shaded area represents the range of $C_{v_{\text{max}}}$ values obtained from the estimated aspect ratio of MFC.

Since various weight fractions ($W_f$) of MFC were used, the volume fractions ($V_f$) can be calculated for the weight fraction by using Equation 4.1 [149], represented in Figure 4.14. In terms of weight fractions, the maximum amount of MFC that can be fully distributed in the epoxy matrix was calculated to be in the region of 2.5 to 4.0 wt. %.

$$V_f = \frac{1}{1 + \frac{\rho_f}{\rho_m} \times \left( \frac{1}{W_f} - 1 \right)}$$  \hspace{1cm} \text{(4.1)}

where $\rho$ is the density and subscripts $f$ and $m$ is fibre and matrix, respectively. The values of $\rho_f$ and $\rho_m$ used are of order 1.5 g/cm$^3$ [30] and 1.37 g/cm$^3$. 

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As the highest loading of MFC used was 5 wt. %, the above estimation of $C_v^{\text{max}}$ verifies that the mechanical properties of MFC composites were fully evaluated in this thesis, *i.e.* the improvement in the mechanical properties reached the maximum achievable value. From the experimental results, this can be speculated to be in the range of 2 to 3 wt. % of MFC content. This range was consistent with the predicted $C_v^{\text{max}}$ values, although the aspect ratio of MFC was based on an approximation of fibril length.

On the other hand, when the MFC content exceeds $C_v^{\text{max}}$, the mechanical properties of the MFC composites remained unchanged. This can be attributed to the fibril distribution in the epoxy matrix, *i.e.* aggregation occurs. MFC begins to aggregate at higher fibre loadings and this in turn inhibits the further enhancement of mechanical properties. With any further addition of reinforcement, *i.e.* more than 5 wt. %, a significant reduction in mechanical properties can be assumed as the volume of MFC
becomes over loaded, resulting in the composites’ embrittlement and where the surface of the composites becomes uneven and cracked. An example of this is shown in Figure 4.15.

As discussed, the Young’s modulus of pure epoxy was greatly improved by using stiff microfibrils, which offer a high modulus. The modulus of a single fibril can be estimated using Equation 2.5 [8], a modified rule of mixture equation, which is discussed in Section 2.3.3.

\[
E_c = \eta_f \eta_v E_f + (1 - V_f) E_m
\]  
(2.5)

where \(E_f\) and \(E_m\) are the Young’s modulus of a single fibril and the epoxy resin, respectively. \(V_f\) and \(\eta_f\) are of the order the MFC volume fraction and orientation efficiency factor of reinforcement and \(\eta_l\) is the reinforcement length efficiency factor.

**Figure 4.15.** 10 wt. % of softwood MFC composite.
The efficiency factor is described as the orientation distribution of MFC. The value of \( \eta_f \) was used as 3/8 [8, 150], since the MFC network was exhibited as an in-plane random network, seen in the micrographs provided from Section 4.2. Referring to the micrographs in Section 4.2, MFC’s network was a fully percolated network with an estimated aspect ratio of more than 100. Thus, an MFC network can be treated like a continuous phase and the value of \( \eta_f \) set as 1 [150].

Using this information and the maximum modulus of MFC composites of 2.2 GPa, \( E_c \) where it reached a plateau (i.e. around 2 to 3 wt. % of MFC content), the modulus of a single fibril from each source of MFC can be obtained by substituting these parameters with the modulus of the pure epoxy, \( E_m \) (1.6 GPa) in Equation 2.5. Although Equation 2.5 shows a linear relationship between \( E_c \) and \( V_f \), which does not fit well with the data obtained from modulus of MFC composites represented as linear and following a constant value once the plateau was reached, with respect to \( V_f \). However, the modulus of MFC composites was assumed to be applicable to Equation 2.5, and using the range of plateau values that was reached. The modulus of single fibrils, with respect to the volume fraction of MFC, can then be calculated using Equation 4.2 that is re-arranged from Equation 2.5 and summarised, as shown in Figure 4.16.

\[
E_f = \frac{E_c - E_m (1 + V_f)}{\eta_f \eta_f V_f}
\]

(4.2)
Figure 4.16. The modulus of a single fibril estimation with respect to the volume fraction of MFC in the composites. The shaded area represents the estimated range of moduli of the individual fibrils of MFC.

The estimated moduli of the individual fibrils of MFC were between 65 to 95 GPa approximately; obtained from the maximum modulus of MFC composites at a concentration of around 2 to 3 wt. % (or vol.%). Using this method to back calculate the modulus of fibrils, the values found were comparable to the practical measurements reported in the literature [150].

As the produced MFC was further subdivided by the mechanical treatment, the modulus of pulp fibres was expected to increase since the aspect ratio had increased [151]. The estimated moduli of individual fibrils are as expected, similar to Bledzki and Gassan [151] who reported modulus of microfibrils produced by mechanical disintegration (70 GPa). In addition, the modulus of MFC was similar to the reported
modulus value of Cellulose-II (90 GPa), which was as expected since regenerated sources (pulp) were used [152].

The modulus of pure epoxy was greatly improved by using the stiff fibrils as reinforcement, indicating the formation of a good interface between the microfibrils and the matrix. This allows for effective stress transfer from the matrix to the microfibrils.
4.3.2 FRACTURE SURFACES OF COMPOSITES

An SEM was used to characterise the fractured surfaces of composites by analysing the images taken. MFC composites using different sources of reinforcement are discussed, respectively, as softwood, hardwood and RCF composites.

**Softwood composite**

![Fracture surfaces of softwood composites](image)

**Figure 4.17.** Fracture surfaces of a) pure epoxy resin and softwood composites with MFC contents of b) 0.5 wt.%; c) 0.75 wt.%; d) 1 wt.% and e) 1.25 wt.%. 

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Figure 4.18. Fracture surfaces of softwood composites with MFC contents of a) 1.5 wt.%; b) 2 wt.%; c) 3 wt.% and d) 5 wt.%.

The fracture surfaces of pure epoxy resin could be clearly observed and were presented as directional and uniform, as shown in Figure 4.17a. However, with the addition of MFC the fracture surfaces formed randomly and irregularly, shown in Figure 4.17 and Figure 4.18.

Clear and complex fracture surfaces are observed with the addition of MFC in the composites. This implies that a toughening contribution was achieved by the reinforcement as the roughness of the fractured sample surface had increased [27]. In contrast, the surface of the pure epoxy resin was smooth and glossy, typical of a brittle thermosetting polymer [153]. This surface type indicates that during the fracture process, little plastic energy dissipation occurred [153].
On the other hand, feather effect markings were observed in the pure epoxy resin and the softwood composites. These markings are caused by crack forking, an excess of energy associated with relatively fast crack growth [27]. The amount of repeated forking on the surface increased with MFC content, showing that the excess energy was being absorbed in a very brittle material. The feathering results from the matrix yield, a toughening mechanism present where there was a strong interface between the reinforcement and matrix. These markings confirm that there was a strong bond within the composites and justify using MFC as reinforcement to the pure epoxy resin.
**Hardwood composite**

The fracture surfaces of the hardwood composites with increasing fractions of MFC content are shown in Figure 4.19 and Figure 4.20 below.

![Fracture surfaces](image)

**Figure 4.19.** Fracture surfaces of a) epoxy resin and hardwood composites with MFC contents of b) 0.5 wt.%; c) 0.75 wt.%; d) 1 wt.% and e) 1.25 wt.%.
Figure 4.20. Fracture surfaces of hardwood composites with MFC contents of a) 1.5 wt.%; b) 2 wt.%; c) 3 wt.% and d) 5 wt.

Compared to the softwood composites, a similar appearance of the fracture surfaces can be observed. A toughening mechanism, the feather effect, was also clearly seen in the composites with the addition of MFC obtained from hardwood. The fracture surfaces are formed in a more complex and irregular manner with additional reinforcement, whereas the pure epoxy exhibits regular and uniform surfaces. The roughness of the fracture surface increased with additional MFC content compared to the pure epoxy.
Recycled fibre (RCF) composites

RCF composites, with MFC from non-virgin sources, are shown in Figure 4.21 and Figure 4.22 below.

Figure 4.21. Fracture surfaces of a) epoxy resin and RCF composites with MFC contents of b) 0.5 wt.%; c) 0.75 wt.%; d) 1 wt.% and e) 1.25 wt.%.
Figure 4.22. Fracture surfaces of RCF composites with MFC contents of a) 1.5 wt.%; b) 2 wt.%; c) 3 wt.% and d) 5 wt.%.

In contrast to the virgin fibre composites, there was a difference in the outline of the fracture surfaces obtained from RCF composites. The roughness of the fracture surface was expected to be much less than for the virgin fibres, since the morphology of MFC from RCF was slightly different.

As discussed in Section 4.2, the morphology of the virgin fibres is a web-like structure, composed of a large number of rod-like fibrils. In contrast, RCF has no significant web-like structures. Due to the presence of lignin, it was composed of a lesser amount of fibrils with plane surfaces and the interface between the reinforcement and matrix was reduced, i.e. a lower surface contact area was formed in the fracture surface region. This phenomenon was in line with the reported work from Rojo et al. [148], who
observed nanocellulose films with different lignin content. Rojo et al. [148] concluded that the nanocellulose films were smoother with the presence of lignin, as lignin acts as cementing material between fibrils.

The difference between the pure epoxy and MFC composites can still be easily seen. The roughness of the surface was increased, with more complex fracture surfaces present. In addition, the feather effect was also clearly observed from these fracture surfaces, indicating that the toughening mechanism occurred and formed during the mechanical test.

The phenomenon observed in the SEM images was further analysed. The length of fracture edges was measured using calibrated Image J software. A summary of total fracture edge length per unit fracture area, $F_{tl}$, is exhibited in Figure 4.23.

**Figure 4.23.** Total fracture edge length per unit area, $F_{tl}$, of a) softwood composites; b) hardwood composites; c) RCF composites and d) all MFC composites.
Compared to the pure epoxy resin, the $F_d$ values for the MFC composites was significantly increased, around two-fold, before reaching a plateau where further addition of reinforcement shows no changes, as seen in Figure 4.23. This phenomenon seems to agree with the mechanical properties observed in Section 4.3.1, *i.e.* tensile strength. The fibre concentrations where the plateau in $F_d$ values begin was similar to that observed previously, around 2 to 3 wt. % for virgin composites and approximate 3 to 4 wt. % for the RCF composites. In addition, this was congruent with the calculated $C_v^{\text{max}}$ value of maximum fibre content (2.5 to 4.0 wt. %).

Despite the overall mechanical properties of RCF composites being similar in softwood and hardwood composites, a less effective of $F_d$ value was observed when RCF composites were used. This can be attributed to the presence of lignin, verified by the previous observations from the SEM images. It also indicates that the mechanical properties of RCF composites were not negatively affected by the lignin content. The relationship between $F_d$ and mechanical properties is discussed further below.

**Relationship between fracture surfaces and the properties of composites**

As discussed in Section 4.3.1, the mechanical properties of the epoxy resin were greatly enhanced by the addition of MFC. In order to further analyse the relationship of the fracture surfaces of the composites, created from the tensile testing, the tensile strength and work of fracture ($W_F$) data were used.

A strong correlation between the tensile strength and $F_d$ obtained from softwood and hardwood composites was found. The coefficients of determination, $r^2$, were both greater than 0.8, as shown in Figure 4.24. In contrast, the association between $F_d$ and
tensile strength for RCF composites was not as strong, and a lower value of $r^2$ was obtained, 0.7. The gradient of the regression lines for all of the MFC composites was found to be around $2 \times 10^4$.

![Figure 4.24](image)

**Figure 4.24.** The relationship between tensile strength and $F_{tl}$ of all the MFC composites.
The $F_{dl}$ from a fracture surface was created by the amount of tensile strength needed for the composites to reach their failure state. When the data points were presented as a cluster, which shows that a plateau was reached, a similar amount of tensile strength was needed for composites to reach failure; this resulted in similar $F_{dl}$ values for total fracture length being found. In this case, the cluster observed from the softwood and hardwood composites were similar and occurred when the MFC content reached 1 wt. %. In contrast, a broader range was presented by the RCF composites with a plateau beginning after 0.5 wt. % of MFC content; although their tensile strength values were found to be similar.

The morphology of the reinforcement used is one of the factors that can affect the amount of $F_{dl}$ produced. As discussed in Section 4.2, the morphology observed from virgin MFC was slightly different from that of the recycled source. Despite this, the tensile strengths of RCF composites were comparable to the virgin MFC composites at the same MFC content. This implies that the surface contact area between fibrils and matrix play a major role that dominated the amount of $F_{dl}$ under stress. It suggests that the $F_{dl}$ value was influenced by two factors, the tensile strength of the composites and the morphology of the reinforcement, such as the shape and aspect ratio.
Figure 4.25. The relationship between work of fracture and $F_{tl}$ of all the MFC composites.

The relationship between $W_F$ and $F_{tl}$ obtained from MFC composites is shown in Figure 4.25. Although, the gradients of the regression lines were all found to be around $4 \times 10^4$ for all MFC composites, the $r^2$ of softwood, hardwood and RCF composites were calculated to be 0.65, 0.70 and 0.45, respectively. Softwood and RCF composites exhibited a weak relationship between $W_F$ and $F_{tl}$, whereas a moderate association was
observed from hardwood composites. However, this indicates that the correlation between $W_F$ and $F_{tl}$ was less strong overall.

This was due to $W_F$ being dominated by the stress and strain of a specimen under testing, *i.e.* the total amount of energy required per unit fractured area to reach the failure state [138]. $W_F$ was obtained from the entire tensile test, whilst the failure point reached created a small amount of the fracture length. In contrast, the tensile strength of the composites was dominated by the maximum stress tolerance of a specimen, showing a strong correlation between tensile strength and $F_{tl}$.

**Statistical analyses using t-tests**

In order to analyse the effect that using different sources of MFC had on the mechanical properties of composites, t-test statistical analysis was used. The independent group t-test was constructed by using confidence intervals. Full details of the method can be found in Appendix A.

It can be summarised that using various sources of MFC reinforcement had a similar impact on the composites’ mechanical properties, as no significant differences between them were found. Virgin sources of reinforcement of the pure epoxy have similar $F_{tl}$ values. However, the formation of $F_{tl}$ from using RCF as reinforcement in such composites was found to be different from the virgin sources. The t-test evaluation agrees with the results discussed previously.
4.3.3 THE SHAPE OF THE STRESS-STRAIN CURVES OF MFC COMPOSITES

As discussed in Section 4.3.1, non-linear stress-strain curves for the MFC composites were obtained from the tensile test data. Overall, the shape of the curves all exhibited similar forms, as seen in Figure 4.7. Other studies report comparable shapes of stress-strain curves when testing paper [154]. These stress-strain curves were represented as a master curve, with the endpoint of the weaker composites earlier on the curve than the stronger composites [154]. This suggests that even though the gradient of the curve, \textit{i.e.} Young’s modulus, varied the overall shape of the curves remained the same.

Since the stress and strain values of each individual sample have different data points, the stress-strain curves for each weight fraction of MFC composites were normalised to the maximum stress and strain values. The stress values of a curve were divided by the maximum stress and similarly for the strain values. This resulted in the endpoint of stress and strain both being exhibited as 1. Thus, this provides a clear comparison between the individual curves.

The normalised stress-strain curves for pure epoxy resin and softwood composites are shown in Figure 4.26 and indicate that the shape of the curves was equal or almost repeatable with respect to MFC content. As expected, this phenomenon was also observed in hardwood and RCF composites, in Figure 4.27 and Figure 4.28, respectively.
Figure 4.26. The normalised stress-strain curves for a) pure epoxy resin and the softwood composites with MFC contents of b) 0.5 wt. %; c) 0.75 wt. %; d) 1 wt. %; e) 1.25 wt. %; f) 1.5 wt. %; g) 2 wt. %; h) 3 wt. % and i) 5 wt. %
Figure 4.27. The normalised stress-strain curves for the hardwood composites with MFC contents of a) 0.5 wt. %; b) 0.75 wt. %; c) 1wt. %; d) 1.25 wt. %; e) 1.5wt. %; f) 2 wt. %; g) 3wt. % and h) 5 wt. %.
Figure 4.28. The normalised stress-strain curves for the RCF composites with MFC contents of a) 0.5 wt.%; b) 0.75 wt.%; c) 1wt.%; d) 1.25 wt.%; e) 1.5wt.%; f) 2 wt.%; g) 3wt. % and h) 5 wt. %.
Regardless of the source of MFC used to reinforce the epoxy resin, it can be speculated that the ratio of the area under the curve and total area of data points remained constant, known as the area ratio, $\phi$.

In a linear stress-strain curve, the area under the curve is 50% of the total area of the data points. In contrast, the curves for MFC composites were nonlinear stress-strain curves and are represented as an arc, rather than as a straight line. When the curvature is presented in a perfect state, the area under the curve is equivalent to a quarter circle. Thus, the value of $\phi$ for the nonlinear stress-strain curve is more than 0.5 and less than $\pi/4 \approx 0.79$. As the highest modulus was near to the origin, the modulus of the testing sample becomes less stiff as the stress and strain increased during the test. The gradient decreased gradually towards the fracture point, decreasing in one direction. In this condition, a monotonic decreasing gradient can be assumed.

In this case, instead of evaluating the stress-strain curves, load and displacement curves were used to determine the value of $\phi$. Firstly, the area under the curve (described as work) was computed and plotted against the total area of the data points. These were obtained by multiplying the maximum load and displacement values. The summary of this relationship with respect to all the MFC composites is shown in Figure 4.29.

The gradient of this relationship is defined as the area ratio, which was estimated as 0.6 for MFC composites. This means that the area under the load and displacement (or stress-strain) curve was 60% of the total area of the data points. Furthermore, as they were strongly related, the coefficients of determination, $r^2$, were equal to 1 in all cases, as expected. On the other hand, when the error bars of the computed results were considered, the area ratio can be affected and possibly shifted to a higher or lower value. Although the value of the error bars was not great, it still reveals that the area ratio of
nonlinear stress-strain curves are within the range discussed in the hypothesis, i.e. $0.5 < \phi < 0.79$.

Figure 4.29. The relationship between work and $(\text{load}^{\text{max}} \times \text{displacement}^{\text{max}})$ for the MFC composites.
Therefore, it can be summarised that the stress-strain curves of MFC composites with stronger or weaker mechanical properties can be normalised into a master curve. This indicates that the area ratio and the shape of curves remain unchanged. The shape of curves obtained is independent of the performance in respect of mechanical properties.

4.3.4 DYNAMIC MECHANICAL THERMAL ANALYSIS

The addition of MFC has been shown to greatly improve the static mechanical properties of pure epoxy, as discussed in Section 4.3.1. Since the mechanical properties of MFC composites exhibited no significant changes when different sources of fibres were used (referred to in the statistical analysis), the dynamic mechanical properties of the composites from only one source – softwood – are studied further. Comparisons between different weight fractions will be made and discussed.

The evolution of the storage modulus, $E'$, and loss factor, $\tan \delta$, as a function of temperature are calculated and discussed, respectively. The typical storage modulus of softwood composites, as a function of temperature, with varying MFC content is illustrated in Figure 4.30. For pure epoxy, the storage modulus decreased gradually as the temperature was increased from 30 °C up to 220 °C, subsequently followed by a rapid decrease.
The ‘onset drop point’ can be used as a method for determining the glass transition temperature, $T_g$, shown in Figure 4.30. This is the point of transition of a material from a rigid glassy solid into a flexible rubbery state. In this case, the $T_g$ value of the pure epoxy was approximately 220°C. However, the value of $T_g$ can also be easily defined from the peak of the tan $\delta$ curve. Tan $\delta$ is a measure of the damping of a material. Following this method, the pure epoxy shows a peak at approximately 230°C, slightly higher than when using the onset measurement.

Since the highest curing temperature used for preparing the composite was 200°C, the $T_g$ value obtained was, as expected, for the pure epoxy resin. In order to observe the $T_g$ value more clearly and precisely, the method using the peak value from the tan $\delta$ is preferable. A typical tan $\delta$ versus temperature of softwood composites, with varying MFC content, is shown in Figure 4.31.
According to Figure 4.32, the intensity (or peak height) of tan δ of softwood composites was reduced compared to the pure epoxy, excluding data for the 0.5 wt. % of MFC content. The reduced tan δ value indicated that there was the good interfacial adhesion between fibril and matrix; poor interfacial adhesion would have caused more energy to be dissipated [155, 156]. However, the tan δ value for the 0.5 wt. % softwood composite was slightly higher compared to the pure epoxy. This can be attributed to the low content of MFC in the composite, where the intensity of tan δ value was not affected by its addition [155]. Further work would be required to investigate whether this was a genuine dependence.

**Figure 4.31.** DMTA tan δ as a function of temperature for the softwood composites.
Figure 4.32. The intensity of tan δ with respect to MFC content of softwood composite.

Moreover, as discussed in Section 3.4.2, the tan δ value is defined as the ratio of the loss modulus, \( E'' \), to the storage modulus, \( E' \). A reduction of peak height implies that the storage modulus values of the softwood composites were higher than the pure epoxy at an increasing temperature [157]. This can be attributed to the addition of reinforcement reducing the mobility of the polymer segments, which resulted in the storage modulus increasing as the viscoelastic lag between the stress and strain was being reduced [157]. Therefore, the tan δ values should reduce as the reinforcement level increases, as a lesser fraction of the epoxy matrix was present to dissipate the vibration energy [7, 24, 158].

In this case, the tan δ values exhibited no significant trend in relation to the reinforcement level; a constant value of tan δ (i.e. 0.3 seen as the dashed line in Figure 4.32) was maintained from 0.75 to 5 wt. % of MFC content. This suggests that the storage modulus of softwood composites maintains a constant value.
The broadening of the transition region, or the width of the peak, can also be analysed. It indicates the amount of temperature span and volume of the fibre-matrix interface needed for the transition to take place [156, 158]. The peak width was estimated as a half peak, summarised with respect to MFC content in Figure 4.33.

Looking at the mean values of the peak width, the softwood composites with lower MFC content exhibited no significant difference when compared to the pure epoxy, shown as the dashed line in Figure 4.33. On the contrary, significant differences were exhibited at a higher reinforcement level, displayed as the solid line.

![Graph showing the half of peak width of tan δ with respect to MFC content of softwood composite.](image)

**Figure 4.33.** The half of peak width of tan δ with respect to MFC content of softwood composite.
Considering the error bars along the scatter points, the peak width value remained unchanged with addition of MFC to the pure epoxy. This can be attributed to the number of specimens tested for each weight fraction being limited, whereas the variance of peak width value obtained from the softwood composites was high. Although, in every individual measurement, the values presented were higher than pure epoxy. Also, the peak width became noticeably broader when MFC was added to the pure epoxy resin. This suggests that the effect of molecular relaxations increased as the volume of the interface increased, since there was no MFC present in the pure epoxy matrix [156]. The majority of the damping can be assumed to take place in the interfacial regions rather than within the fibres or matrix [156].

The width of peak values for the tan curve did not follow the suggested phenomena, i.e. the width of peak did not increase as the height of peak decreased, with increasing MFC content. Instead both values remained similar for each weight fraction of MFC used. However, the addition of MFC to pure epoxy did indicate that a good level of interfacial adhesion between the fibres and matrix had been achieved.

A summary of $T_g$ and storage modulus, $E'$ of softwood composites, compared to pure epoxy, is provided in Figure 4.34. The $T_g$ value represents a measure of the interaction between fibre and matrix. At a higher $T_g$ value, the addition of the reinforcement to the matrix constrains the movement of polymer segments due to a strong fibre-matrix interaction.
Also, the mobility of the polymer segments can be limited by incorporating the reinforcement, which forms a rigid cross-linked network. This network enhances the stress transfer at the fibre interface and increases the modulus of the composite [155]. In addition, composite stiffness could be increased by the interference of neighbouring polymer chains, as the relaxation process cannot occur without greater interaction [155].

The storage modulus of the softwood composites was enhanced up to 40% in the glassy state (i.e. 30 °C), which exhibits a plateau until the MFC content reaches 2 wt. % (shown in Figure 4.34d). In another view, when the 95% confidence level was considered from Figure 4.34b, the storage modulus remained at a constant value (3 GPa)
with increasing content of MFC content. A similar phenomenon was observed from the of tan δ value. This suggests a good interfacial adhesion between fibril and matrix. Since, the storage modulus was enhanced and also reduced the intensity of the tan δ value, as expected.

As the $T_g$ value obtained from the pure epoxy resin was found to be significantly different to the softwood composites, a comparison of their storage modulus in the rubbery state, above $T_g$, could not be determined.

Nevertheless, the storage modulus of softwood composites in their rubbery state (i.e. 200 °C) increased as MFC content increased, up to 3 wt. % (Figure 4.34c). Following this, a dramatic decline was found at 5 wt. % of MFC content, which was likely to be anomalous. Compared to the glassy state of the softwood composite, a lower variance of the storage modulus in the rubbery state shows a more obvious improvement with respect to the MFC content. This implies that at higher temperatures, the stress transfer from the matrix to fibrils at higher MFC content was significantly facilitated by hydrogen-bonding between fibrils [18].

On the other hand, an unexpected decrease (around 50 %) can be seen in the value of $T_g$, shown in Figure 4.34d. This phenomenon has been reported elsewhere, with a similar composites demonstrating an enhanced storage modulus as well as rapidly decreasing values for of $T_g$ [159]. Several studies also reported a reduction of $T_g$ values, although the decrease was much smaller, around 10 % [7, 24].

The rapid decrease in $T_g$ can be verified by investigating the cross-link density of the composites [160, 161]. The degree of cure of a softwood composite (1 wt. %) and pure epoxy were compared using DSC. The outcome is relevant as the measurement of the $T_g$ value gives an indication of the segments mobility, which is dependent on the degree of
cure [160]. A low $T_g$ value suggests, the molecular mobility of the polymer was increased and thus a lower degree of cure. The degree of cure at a constant temperature is shown as a percentage of reaction and as a function of time in Figure 4.35.

From the result shown, the degree of cure of softwood composites is 10 % lower than the pure epoxy at two hours. This means that the cross-link density of the softwood composite was lower than pure epoxy resin, which is consistent with the obtained results from DMTA. The $T_g$ value of pure epoxy was significantly affected by the addition of MFC, which exhibits a reduction in cross-link density.

![Figure 4.35. Degree of cure at isothermal temperature, 180 °C, of the epoxy resin and the softwood composite at 1 wt. % MFC content as a function to of time.](image)
It can be concluded that with the addition of MFC to epoxy, the glass transition temperature was significantly reduced, although the storage modulus was enhanced. López-Manchado and Arroyo [159] identify one possible reason for this phenomenon. They speculated that the energy dissipation of fibril-fibril interaction was greater than the interaction between fibril and matrix. A reduced $T_g$ value, suggests that the mobility of polymer segments was increased due to weak fibril-matrix interaction. The enhanced modulus can be attributed to strong fibril-fibril interaction and a good interfacial adhesion between fibril and matrix.

The interfacial adhesion between fibril and matrix can be observed from the fracture surfaces illustrated in the micrographs, Figure 4.36. Fibre pull-out mechanisms cannot be observed, i.e. no voids can be seen in the micrographs. This indicates that fibril-matrix interfacial adhesion was good as the fibrils are trapped by the matrix, shown in Figure 4.36. The fracture mechanism can be speculated to be fibre fracture, revealing that the fibril length was much longer than the critical length [114, 115] and that, the fibrils carried the majority of load in the composites [162].

In this case, the measured storage modulus correlates well with the Young’s modulus values obtained from the static tensile tests, as stated previously in Section 4.3.1. Following the rule of mixtures, the weaker polymer matrix was greatly enhanced by the addition of stiff reinforcement, resulting in a stronger composite [8]. The enhanced mechanical properties were confirmed due to two factors: the good interfacial adhesion between fibril and matrix; and the strong fibril-fibril interaction facilitated by hydrogen bonding.
Figure 4.36. Fracture surfaces of softwood composites with a) 0.75 wt. % and b) 1 wt. % of MFC content. Arrows indicate fibrils.

**Applying the percolation model to the dynamic mechanical properties**

As discussed, the storage modulus (i.e. glassy state) of the pure epoxy was enhanced with the addition of MFC. This suggests that hydrogen bonding between fibrils facilitated stress transfer, enhancing the reinforcement effect. This can be attributed to the formation of a percolated system [18]. As discussed in Section 2.4.3, the mechanical properties of composites, such as storage modulus, $E'$, can be predicted by using the percolation model, as expressed in Equation 2.7 [122] and with Equation 2.8 [123].
\[ E'_c = \left( \frac{1 - 2\psi + 4V_f}{1 - V_f} \right) \frac{E'_f E'_m + (1 - V_f)\psi E'_f^2}{(1 - V_f)E'_f + (V_f - \psi)E'_m} \]  

(2.7)

where \( E'_m \) and \( E'_f \) are represent the storage moduli of the pure epoxy and MFC, respectively. \( V_f \) and \( \psi \) are the volume fractions of randomly oriented MFC and the volume fraction of percolated MFC in the stress transfer, respectively.

\[
\psi = 0 \text{ for } V_f \leq C_v; \quad \psi = V_f \left( \frac{V_f - C_v}{1 - C_v} \right)^b \text{ for } V_f > C_v
\]  

(2.8)

where \( C_v \) is the critical volumetric concentration; \( b \) is the critical percolation exponent and is acknowledged as 0.4 in a three dimensional network [124].

To compute the percolation model, the value of \( E'_f \), 9.70 GPa (at 30 °C) was acquired from Lu et al. [7], obtained from softwood Kraft pulp. The \( E'_m \) value was experimentally determined as 2.20 GPa at the same temperature. As discussed in Section 2.4.3, different numerators can be used to estimate the value of the critical volumetric concentration, \( C_v \), and divided by the aspect ratio of the fibrils. The estimated aspect ratio of MFC obtained from softwood was 490, reported in Table 4.4. The numerators used (0.7 [126] and 1 [127]) resulted in similar \( C_v \) values, as shown in Figure 4.37. The \( C_v \) values for softwood composite were estimated between 0.1 vol. % to 0.2 vol. %, using numerators of 0.7 and 1, respectively. In this case, the \( C_v \) value of 0.2 vol. % was used to evaluate the percolation model.
The percolation threshold is defined as the point where separate fibres become connected in a system [2]. It occurs at a specific volumetric concentration, in this case between 0.1 wt. % and 0.2 wt. % of MFC in the pure epoxy. In contrast, the minimum MFC content of 0.5 wt. % was used in this thesis, which was higher than the estimated $C_v$ values. MFC’s high aspect ratio results in a low percolation threshold in the matrix.

According to Figure 4.5 in Section 4.2, fibril percolation needs to be treated with caution as it can be seen that the fibres are not truly separate. This shows that MFC has the potential to form a true percolated system and it may be appropriate to further investigate the percolation of irregular flakes. However, this investigation is beyond the scope of this thesis. The MFC network is expected to be reinforced by the fibrillar nature of the constituents of these flakes. Also, this suggests that the observed significant reinforcement effect can be explained by the percolated MFC, facilitating the stress transfer by hydrogen bonding between fibrils [18].
The predicated storage modulus of softwood composites, $E'_c$, is illustrated in Figure 4.38 and compared with experimentally determined data at 30 °C. The experimental data did not fit precisely with the predicted values. A similar phenomena of the percolation model underestimating $E'_c$ was reported by Tang and Weder [18]. They suggest that the strong interaction between the fibres and matrix play a major role. A fibril-bound matrix layer forms around each fibril, and, therefore, the volume fraction of fibre is increased, that in turn increases the $E'_c$ value [18]. As discussed, the enhanced $E'_c$ was due to strong fibril-fibril interaction that facilitated the stress transfer via hydrogen bonds. Hence, the difference in storage modulus values was possibly due to the value of $E'_f$ not being obtained experimentally. It could also be partially attributed to different fibre preparation methods, materials and equipment being used. However, the predicted and experimental mean values of $E'_c$ show a similar trend, with the storage modulus values increasing as MFC content increases.

![Figure 4.38](image)

**Figure 4.38.** Storage modulus, $E'_c$ of softwood composites at 30 °C as a function of volume fraction of MFC. The dashed line represents $E'_c$ values predicted by the percolation model.
As discussed in Section 4.3.2, the mechanical properties (static test) showed similar results when different species of MFC were used. The enhanced storage modulus of hardwood and RCF composites can be assumed when compared to pure epoxy.
5.1 CONCLUSIONS

The primary objective of this thesis was to investigate the mechanical properties of MFC reinforced polymer composites. The analysed mechanical properties were: tensile strength, Young’s modulus, strain-at-failure and work of fracture. As discussed in Chapter 4, the addition of MFC to pure epoxy significantly improved its mechanical properties.

Compared to pure epoxy, the tensile strength of softwood, hardwood and RCF composites were increased by around 75 %. Smaller increases were seen in the Young’s modulus and strain-at-failure values, although work of fracture showed a two-fold increase. The mechanical properties remained unchanged with further addition of MFC as an ‘upper-limit’ of reinforcement was reached.

The stress-strain curves of MFC composites were normalised into a master curve. The shapes of curves remain unchanged and the area ratios of the nonlinear stress-strain
curves were found to be constant and around 0.6. These values fall within the hypothesised range of $0.5 < \varphi < 0.79$ and show that the stress and strain values obtained are all consistent and repeatable.

The greatest enhancement of mechanical properties was reached at a reinforcement level of between 2 to 3 wt. % in MFC composites. However, an improvement was seen at all weight fractions and with each of the different sources used. The upper-limit of MFC content in pure epoxy was consistent with the estimated maximum fibre packing volume that can fully distribute within the matrix, $C_{v}^{\text{max}}$. This was calculated from the aspect ratio of MFC, estimated from the assumed fibril length, 50 μm, for all MFC sources, and the measured widths taken from the SEM images. The aspect ratios of the fibres were estimated to be 490, 560 and 340, respectively.

One of the challenges that needed to be overcome in this thesis was the compatibility between hydrophilic MFC and the hydrophobic epoxy resin matrix. Using the solvent exchange method outlined in Section 3.1.3, followed by re-dispersion in a strong polar solvent, adjusted the philicity of the MFC fibrils and ensured that they were compatible with the matrix. The composites showed good values for strength and stiffness, indicating that good interfacial adhesion between the fibrils and matrix was achieved. This allowed stress to be efficiently transferred from the lower modulus of the matrix to the stiff reinforcing microfibrils.

Further evidence of the good adhesion between the fibres and matrix was observed in the micrographs (Section 4.3.4). From studying the fracture surfaces, the primary failure mechanism was determined to be fibre fracture; if there was poor adhesion between the fibres and matrix, fibre pull-out would be evident as the major failure mechanism. Since fibre fracture was observed, a fibril length longer than the critical length can be also
assumed [114, 115], this means that the fibrils carried the majority of the load in the composite.

The modulus of a single fibril was estimated between 65 to 95 GPa. This value was comparable to the reported modulus values of MFC produced by mechanical treatment (70GPa) [151] and cellulose-II (90 GPa) [152].

The SEM images also allowed the roughness of the fracture surfaces to be studied. The increased roughness of the fracture surface indicated that significant toughening and reinforcing effects were provided by the reinforcement. The association between $F_{tl}$ and tensile strength for virgin MFC composites was stronger than for RCF composites. Since their morphology was different, fewer rod-like fibrils were seen in RCF, possibly due to the presence of lignin. Nevertheless, the tensile strength of RCF composites was comparable to the virgin MFC composites at the same reinforcement level. Therefore, the total fracture length per unit area, $F_{tl}$, can be related to the tensile strength of the composites and the morphology of their reinforcement, such as the shape and aspect ratio. On the other hand, a weak correlation between $F_{tl}$ and $W_F$ was obtained. This can be accounted for by the $W_F$ being obtained from the duration of the tensile test, whilst the failure point reached created an increase of the total fracture length. As the tensile strength of the composites was dominated by the maximum stress tolerance of a specimen, a strong correlation between tensile strength and $F_{tl}$ was obtained.

One of the aims of this study was to compare the differences between virgin and recycled fibre sources. The values obtained from the RCF composites were comparable to the virgin sources. In order to analyse the effects on the static mechanical properties of composites and $F_{tl}$ more closely, t-test statistical analysis was used. The results of the t-tests concluded that RCF reinforcement performs to the same level as virgin MFC in
composites, with respect to their mechanical properties. However, the formation of $F_d$ using RCF was found to be different to the virgin sources. This can be assumed to be due to differences in their morphology, namely the presence of lignin in the raw material used for RCF.

DMTA was also carried out to determine the dynamic mechanical properties of the MFC composites. As discussed in Section 4.3.4, only softwood composites were put through DMTA. It was assumed that the outcome of DMTA would be consistent for each source of MFC, since the improvements in all of the analysed static mechanical properties were also consistent. The addition of MFC resulted in a 50 % reduction in the glass transition temperature compared to neat epoxy resin. Although the storage modulus of the composites was enhanced, this correlates well with the Young’s modulus values obtained from the static tensile test.

The reduced $T_g$ value, suggests that the mobility of polymer segments was increased, due to weak fibril-matrix interaction. The enhanced modulus can be attributed to strong fibril-fibril interaction and the formation of good interfacial adhesion between fibril and matrix; this agrees with the micrographs of the fracture surfaces.

In summary, using MFC as reinforcement for epoxy resin significantly enhanced the mechanical properties of composites, with an upper-limit of reinforcement found between 2 to 3 wt. %. The solvent exchange method used did have the desired effect on the compatibility of the fibres and matrix, as evidenced by the micrographs and observed failure mechanism. The fracture surfaces also showed that the desired toughening effect had been achieved.
Using recycled sources of MFC as reinforcement achieved a similar improvement in mechanical properties when compared to the virgin sources. Their morphology and fracture surface was slightly different due to the presence of lignin, although this did not have a negative impact on their reinforcement potential.

Dynamic mechanical properties were also enhanced with the addition of MFC, although the glass transition was significantly reduced. This indicated that the strong and stiff MFC composites are most applicable at temperatures below 100 °C, as this is the point at which they change to a rubbery state.

### 5.2 FUTURE WORK

Whilst significant improvements were seen by using MFC as reinforcement for a polymer matrix, there is still scope for future work in this area.

- Firstly, a more in-depth analysis using DMTA could be carried out to verify the assumption that the outcome for each of the three sources used would be equal. Specimens from each of the sources would need to be tested and compared.

- A practical measurement of fibril length would also be useful as it would allow for a more accurate aspect ratio of MFC to be determined. The values used in this thesis were estimated from an assumed length of 50 μm. As discussed in Section 2.2.4, the length of fibrils can be investigated using the theory of linear viscoelasticity.
The upper-limit of MFC content in the epoxy resin matrix was found to be in the range of 2 to 3 wt. %. Despite this being an acceptable range, consistent with computed values, further investigation could be carried out on weight fractions within this range. For example, producing additional composites with increments of 0.1, starting from 2 wt. %. This would allow for a more accurate experimental value for the upper-limit of mechanical property enhancements to be established.

The high-pressure homogenisation technique used to fibrillate the fibres is also a possible area for future study. Although good fibrillation was achieved, several examples of different techniques have been reported [3, 71, 72, 79, 80]. A microfluidiser technique was described by Siqueira et al. [72] and Taipale et al. [71] as the most effective way to produce highly fibrillated fibres, but due to the resources available for this thesis a homogeniser was the only option available. Hence, one more possible avenue for future work could be to explore the reinforcing effect of more highly fibrillated cellulose fibres. Chemical treatment could also be applied prior to the mechanical treatment to reduce the energy consumption during the process and ensure that the highest possible level of fibrillation is achieved.

As discussed in Section 3.2, the thin films used in this thesis were selected as they could be scaled up if the results were favourable. The logical next step is to repeat the testing and analysis methods that were developed here to test samples with increased dimensions. This would determine if the reinforcing effect is maintained on a larger scale, similar to any real world applications for MFC/epoxy composites. Other testing methods could also be considered, such as the compact tension test, which investigates the plain strain fracture toughness of the composites.
Section 2.1.4 highlighted the importance of finding low energy, sustainable and waste-reducing sources for composite materials. Therefore, it would also be prudent to explore the use of recycled fibres in polymer matrices, such as an MFC reinforced biodegradable polylactic acid matrix. Providing favourable results using RCF would provide evidence that MFC composites can be produced from widely available ‘waste’ materials, thus reducing the raw cost, energy consumption and amount of chemical treatment needed in fabrication.

Other sources of MFC could also be explored, such as widely available plant sources, other waste materials or even smaller scale cellulose nano-whiskers, although the production of cellulose nano-whiskers requires more time and a higher cost.
APPENDIX A

T-Tests for statistical significance of data

The three sources of reinforcement were compared to pure epoxy at each weight fraction, in terms of their mechanical properties and $F_t$ using the t-test. The mechanical properties compared include tensile strength, Young’s modulus, strain-at-failure and work of fracture.

The t-test is defined as the mean of two groups of data that are statistically different to each other and are described as a probability. There are three types of t-test: a t-test between a population and a sample mean; a t-test for independent groups; and a t-test for dependent groups [163].

The independent groups of t-test was used and the 95 % confidence intervals are constructed to estimate the how large the mean differences were. This can be calculated using Equation A.1 [163]. The degrees of freedom, $df$ are calculated by using Equation A.2 [163].

$$\bar{X}_T - \bar{X}_C \pm t_{a/2} \times \sqrt{\frac{Var_T}{x_T} + \frac{Var_C}{x_C}}$$  \tag{A.1}

$$df = x - 1$$  \tag{A.2}

where subscripted $T$ and $C$ are the treatment and control group, $\bar{X}$ is the mean, $Var$ is the variance of the group , $x$ is the total number of data points, $t_{a}$ is the critical value at alpha level. The alpha level is obtained using 1-CI, whereas CI is the confidence interval, $i.e. 95 \%$. According to Table A9, using $\alpha$ equal to 0.05 for two tailed test and degree of freedom of 4, the critical value is obtained as 2.78.
<table>
<thead>
<tr>
<th>MFC sources</th>
<th>Tensile strength (MPa)</th>
<th>Young’s modulus (GPa)</th>
<th>Strain-at-failure (%)</th>
<th>Work of fracture (kJ/m²)</th>
<th>$F_{tl}$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softwood</td>
<td>mean differences 14</td>
<td>0.3</td>
<td>0.2</td>
<td>15</td>
<td>1019</td>
</tr>
<tr>
<td></td>
<td>CI 7</td>
<td>0.2</td>
<td>0.7</td>
<td>16</td>
<td>242</td>
</tr>
<tr>
<td>Hardwood</td>
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<td>0.7</td>
<td>31</td>
<td>597</td>
</tr>
<tr>
<td></td>
<td>CI 10</td>
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<td>1.0</td>
<td>26</td>
<td>241</td>
</tr>
<tr>
<td>RCF</td>
<td>mean differences 20</td>
<td>0.2</td>
<td>1.1</td>
<td>41</td>
<td>236</td>
</tr>
<tr>
<td></td>
<td>CI 9</td>
<td>0.2</td>
<td>1.3</td>
<td>39</td>
<td>226</td>
</tr>
</tbody>
</table>

**Table A1.** T-test at 95 % confidence level for differences between 0.5 wt. % MFC composites and pure epoxy in mechanical properties and $F_{tl}$.

<table>
<thead>
<tr>
<th>MFC sources</th>
<th>Tensile strength (MPa)</th>
<th>Young’s modulus (GPa)</th>
<th>Strain-at-failure (%)</th>
<th>Work of fracture (kJ/m²)</th>
<th>$F_{tl}$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softwood</td>
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</tr>
<tr>
<td></td>
<td>CI 7</td>
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<td>0.7</td>
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<td>301</td>
</tr>
<tr>
<td>Hardwood</td>
<td>mean differences 35</td>
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<td>1.4</td>
<td>62</td>
<td>1062</td>
</tr>
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<td></td>
<td>CI 12</td>
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<td>1.1</td>
<td>41</td>
<td>221</td>
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<tr>
<td>RCF</td>
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<td>87</td>
<td>635</td>
</tr>
<tr>
<td></td>
<td>CI 5</td>
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<td>0.5</td>
<td>19</td>
<td>245</td>
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</tbody>
</table>

**Table A2.** T-test at 95 % confidence level for differences between 0.75 wt. % MFC composites and pure epoxy in mechanical properties and $F_{tl}$. 
<table>
<thead>
<tr>
<th>MFC sources</th>
<th>Tensile strength (MPa)</th>
<th>Young’s modulus (GPa)</th>
<th>Strain-at-failure (%)</th>
<th>Work of fracture (kJ/m²)</th>
<th>$F_{fl}$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Softwood</strong></td>
<td>mean differences</td>
<td>44</td>
<td>0.5</td>
<td>2.2</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>CI</td>
<td>10</td>
<td>0.2</td>
<td>1.0</td>
<td>41</td>
</tr>
<tr>
<td><strong>Hardwood</strong></td>
<td>mean differences</td>
<td>38</td>
<td>0.6</td>
<td>1.5</td>
<td>67</td>
</tr>
<tr>
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<td>CI</td>
<td>5</td>
<td>0.2</td>
<td>0.6</td>
<td>17</td>
</tr>
<tr>
<td><strong>RCF</strong></td>
<td>mean differences</td>
<td>30</td>
<td>0.4</td>
<td>1.2</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>CI</td>
<td>9</td>
<td>0.2</td>
<td>0.7</td>
<td>24</td>
</tr>
</tbody>
</table>

Table A3. T-test at 95 % confidence level for differences between 1 wt. % MFC composites and pure epoxy in mechanical properties and $F_{fl}$.

<table>
<thead>
<tr>
<th>MFC sources</th>
<th>Tensile strength (MPa)</th>
<th>Young’s modulus (GPa)</th>
<th>Strain-at-failure (%)</th>
<th>Work of fracture (kJ/m²)</th>
<th>$F_{fl}$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Softwood</strong></td>
<td>mean differences</td>
<td>31</td>
<td>0.6</td>
<td>0.9</td>
<td>48</td>
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<td></td>
<td>CI</td>
<td>8</td>
<td>0.3</td>
<td>0.8</td>
<td>27</td>
</tr>
<tr>
<td><strong>Hardwood</strong></td>
<td>mean differences</td>
<td>32</td>
<td>0.4</td>
<td>1.6</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>CI</td>
<td>12</td>
<td>0.2</td>
<td>0.9</td>
<td>33</td>
</tr>
<tr>
<td><strong>RCF</strong></td>
<td>mean differences</td>
<td>35</td>
<td>0.5</td>
<td>1.4</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>CI</td>
<td>9</td>
<td>0.2</td>
<td>0.9</td>
<td>36</td>
</tr>
</tbody>
</table>

Table A4. T-test at 95 % confidence level for differences between 1.25 wt. % MFC composites and pure epoxy in mechanical properties and $F_{fl}$. 
<table>
<thead>
<tr>
<th>MFC sources</th>
<th>Tensile strength (MPa)</th>
<th>Young's modulus (GPa)</th>
<th>Strain-at-failure (%)</th>
<th>Work of fracture (kJ/m²)</th>
<th>$F_t$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softwood</td>
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<td>1.4</td>
<td>63</td>
<td>1635</td>
</tr>
<tr>
<td></td>
<td>CI</td>
<td>9</td>
<td>0.2</td>
<td>42</td>
<td>416</td>
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<tr>
<td>Hardwood</td>
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<td>0.4</td>
<td>2.4</td>
<td>97</td>
<td>1773</td>
</tr>
<tr>
<td></td>
<td>CI</td>
<td>7</td>
<td>0.2</td>
<td>43</td>
<td>233</td>
</tr>
<tr>
<td>RCF</td>
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<td>0.6</td>
<td>1.4</td>
<td>69</td>
<td>1084</td>
</tr>
<tr>
<td></td>
<td>CI</td>
<td>10</td>
<td>0.2</td>
<td>40</td>
<td>285</td>
</tr>
</tbody>
</table>

Table A5. T-test at 95 % confidence level for differences between 1.5 wt. % MFC composites and pure epoxy in mechanical properties and $F_t$.

<table>
<thead>
<tr>
<th>MFC sources</th>
<th>Tensile strength (MPa)</th>
<th>Young's modulus (GPa)</th>
<th>Strain-at-failure (%)</th>
<th>Work of fracture (kJ/m²)</th>
<th>$F_t$ (μm)</th>
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<tbody>
<tr>
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<td>0.8</td>
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<tr>
<td></td>
<td>CI</td>
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<td>0.2</td>
<td>25</td>
<td>353</td>
</tr>
<tr>
<td>Hardwood</td>
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<td>1.9</td>
<td>93</td>
<td>2038</td>
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Table A6. T-test at 95 % confidence level for differences between 2 wt. % MFC composites and pure epoxy in mechanical properties and $F_t$. 
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<th>Strain-at-failure (%)</th>
<th>Work of fracture (kJ/m²)</th>
<th>$F_{tl}$ (μm)</th>
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Table A7. T-test at 95 % confidence level for differences between 3 wt. % MFC composites and pure epoxy in mechanical properties and $F_{tl}$.

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Table A8. T-test at 95 % confidence level for differences between 5 wt. % MFC composites and pure epoxy in mechanical properties and $F_{tl}$. 
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**Table A9.** Critical values [163].
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52. Nishiyama, Y., Langan, P., and Chanzy, H., Crystal structure and hydrogen-bonding system in cellulose $\beta$ from synchrotron x-ray and neutron fiber


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