Micromechanics of Microfibrillated Cellulose Reinforced Poly(lactic acid) Composites Using Raman Spectroscopy

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<td>$a$</td>
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<td>$q_0$</td>
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<td>$r$</td>
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<td>Raman band shift rate</td>
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<td>Raman band shift rate for a sample aligned at the angle $\theta$</td>
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<td>$S_{VV}(\phi)$</td>
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<td>Time</td>
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<td>$V_m$</td>
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<td>$Z$</td>
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<td>Polarisability of a molecule</td>
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<tr>
<td>$\alpha_0$</td>
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<tr>
<td>$\varepsilon_f$</td>
<td>Strain of a reinforcement phase</td>
</tr>
<tr>
<td>$\varepsilon_m$</td>
<td>Strain of a matrix</td>
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<td>$\varepsilon_p$</td>
<td>Porosity</td>
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<td>$\theta$</td>
<td>Angle between the strain direction and the fibril axis</td>
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<tr>
<td>$\lambda$</td>
<td>Wavelength</td>
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<td>Frequency of the laser light</td>
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<tr>
<td>$\nu_m$</td>
<td>Frequency of the scattered light</td>
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<tr>
<td>$\rho$</td>
<td>Radius of a matrix</td>
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<td>$\rho_c$</td>
<td>Density of cellulose</td>
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<tr>
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<td>Stress</td>
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<td>$\sigma_f$</td>
<td>Stress of a fibre</td>
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<td>Maximum stress</td>
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<td>Specific stress</td>
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<tr>
<td>$\tau$</td>
<td>Shear stress</td>
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<td>Interfacial shear stress of a matrix</td>
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<tr>
<td>$\chi_c$</td>
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</tr>
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<td>$\bar{\omega}$</td>
<td>Average width of MFC fibrils within a network</td>
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<tr>
<td>$\phi$</td>
<td>Angle between the strain direction and the laser polarisation axis</td>
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<tr>
<td>$\Delta \nu$</td>
<td>Raman wavenumber</td>
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<table>
<thead>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>BC</td>
<td>Bacterial cellulose</td>
</tr>
<tr>
<td>BNC</td>
<td>Bacterial nanocellulose</td>
</tr>
<tr>
<td>CCD</td>
<td>Charged-coupled device</td>
</tr>
<tr>
<td>CNWs</td>
<td>Cellulose nanowhiskers</td>
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<tr>
<td>COO</td>
<td>Carboxyl group</td>
</tr>
<tr>
<td>Cu</td>
<td>Copper</td>
</tr>
<tr>
<td>cm</td>
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<td>cm⁻¹</td>
<td>Wavenumber</td>
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<td>cm³</td>
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<td>DP</td>
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<td>DSC</td>
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<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
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<td>GPa</td>
<td>Gigapascal</td>
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<tr>
<td>g</td>
<td>Gramme</td>
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<tr>
<td>HIUS</td>
<td>High intensity ultrasonicator</td>
</tr>
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<td>h</td>
<td>Hour</td>
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<td>IR</td>
<td>Infrared spectroscopy</td>
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<td>J</td>
<td>Joule</td>
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<td>Kilonewton</td>
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<td>kWh</td>
<td>Kilowatt-hour</td>
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<td>kg</td>
<td>Kilogramme</td>
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<tr>
<td>L</td>
<td>Lumen</td>
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<tr>
<td>l</td>
<td>Litre</td>
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<tr>
<td>M</td>
<td>Molar</td>
</tr>
<tr>
<td>MAPP</td>
<td>Maleic anhydride grafted polypropylene</td>
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<td>MCC</td>
<td>Microcrystalline cellulose</td>
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<td>MFC</td>
<td>Microfibrillated cellulose</td>
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<tr>
<td>ML</td>
<td>Middle lamella</td>
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<td>Megapascal</td>
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<td>Metre</td>
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<td>P</td>
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<td>Pa</td>
<td>Pascal</td>
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</tr>
<tr>
<td>PET</td>
<td>Poly(ethylene terephthalate)</td>
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<td>PLA</td>
<td>Poly(lactic acid)</td>
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<td>Poly(L-lactic acid)</td>
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<td>Poly(vinyl alcohol)</td>
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<td>Polarisation configuration in which incident and scattering lights are perpendicular to each other</td>
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<td>$\Delta H_m$</td>
<td>Enthalpy of melting</td>
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ABSTRACT

Micromechanics of Microfibrillated Cellulose Reinforced Poly(lactic acid) Composites Using Raman Spectroscopy

The University of Manchester
Supachok Tanpichai
Doctor of Philosophy
25 April 2012

Microfibrillated cellulose (MFC) is an alternative material that has been widely studied to enhance the mechanical properties of a polymer matrix due to a number of perceived advantages over traditional plant fibre forms.

Mechanical properties of MFC networks were found to depend on parameters such as the modulus of fibrils, bonding strength, porosity, degree of crystallinity, contact area of fibrils and possibly the modulus of the cellulose crystals of the raw materials (cellulose I or II). Even though the longer processing time used to produce MFC was found to yield networks with fewer fibre aggregates, finer fibrils and higher density, some properties, for instance thermal stability and degree of crystallinity, decreased due to the degradation of fibrils caused by the harsh treatment. The aims of this thesis were to assess the mechanical properties and interfaces of composites produced using a range of MFC materials, prepared using different treatments and from different sources.

Raman spectroscopy has been used to detect the molecular orientation of cellulose chains within an MFC network, and to monitor the deformation micromechanics of MFC networks. The Raman band initially located at ~1095 cm\(^{-1}\) obtained from MFC networks was observed to shift towards a lower wavenumber position upon the application of tensile deformation. The intensity of this band as a function of rotation angle of MFC networks was similar, indicating randomly oriented networks of fibrils. From the Raman band shift rate data, the effective moduli of MFC single fibrils produced from pulp were estimated to be in the range of 29 - 41 GPa.

Poly(lactic acid) (PLA) composites reinforced with MFC networks were prepared using compression moulding. Enhanced mechanical properties of MFC reinforced composites were reported, compared to neat PLA films. The mechanical properties of these composites were found to mainly depend on the interaction of the PLA matrix and the reinforcement phase. The mechanical properties of the composites reinforced with dense networks were shown to be dominated by the network properties (fibril-fibril interactions), while matrix-fibril interactions played a major role where more open networks were used to reinforce a polymer matrix. The penetration of the matrix into the network was found to depend on the pore sizes, fibre width and porosity within the network. It was found that the matrix easily penetrates into the network with a range of mean fibril dimensions, rather than for networks with only fine fibrils present.

The stress-transfer process in MFC reinforced PLA composites was monitored using Raman spectroscopy. Greater Raman band shift rates with respect to tensile deformation for the composites were observed compared to pure MFC networks. This indicates that stress is transferred from the PLA matrix to MFC fibrils, supporting the enhancement of the mechanical properties of the composites.
DECLARATION

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

Supachok Tanpichai

25 April 2012
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To my family, Natthaya and friends
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CHAPTER 1

INTRODUCTION

This chapter gives the background of this research. The objectives of this research and the structure of the thesis are provided also.

1.1 BACKGROUND

Cellulose is the most abundant natural biopolymer, and can be found in plants, animals and bacteria (Atalla and Van der Hart, 1984; Yamamoto and Horii, 1994; Klemm et al., 2005; Cheng et al., 2009; Eichhorn et al., 2010; Tingaut et al., 2010). Due to its advantages such as low density, low cost and renewability, cellulose in the form of fibres has been widely used as alternative reinforcements in composite materials to replace inorganic fillers such as glass fibres and synthetic polymer fibres (Mohanty et al., 2002; Oksman et al., 2003; Lu et al., 2008; Tingaut et al., 2010; Mukherjee and Kao, 2011). An important issue concerned with the use of natural fibres, however, is the variation in their mechanical properties (Oksman et al., 2003). Natural fibres contain a large number of defects called kink bands and voids which have a detrimental effect on their mechanical properties, initiating brittle fracture (Eichhorn et al., 2000; Baley,
The kink bands are produced when isolating fibres from plants (Eichhorn et al., 2000; Hughes et al., 2000; Baley, 2004). However, it is generally thought that these defects can be removed by disintegrating fibres into nano or micro fibrils (Dufresne, 2008). Also, nanoscale cellulose fibres have attracted considerable interest as possible reinforcements in composite materials due to their attractive properties such as high strength, high aspect ratio, low density, biodegradability and renewability (Lu et al., 2008; Nakagaito et al., 2009; Siqueira et al., 2009; Siro and Plackett, 2010; Klemm et al., 2011).

Microfibrillated cellulose (MFC) is a web-like structure of interconnected cellulose microfibrils with widths ranging from 10 to 100 nm and lengths of several µm (Iwamoto et al., 2007; Henriksson et al., 2008; Siro and Plackett, 2010; Tingaut et al., 2010). Even though many terms are used to explain MFC such as microfibril aggregates, nanofibrillated cellulose (NFC), nanofibres, to name but a few examples (Siro and Plackett, 2010; Klemm et al., 2011), the term “microfibrillated cellulose (MFC)” was selected to be used in this thesis due to this term coined by the original investigators (Herrick et al., 1983; Turbak et al., 1983).

MFC was first introduced by Herrick et al. (1983) and Turbak et al. (1983); a dilute wood pulp suspension was passed through a homogeniser for several times in order to make MFC (Herrick et al., 1983; Turbak et al., 1983). Recently, many different techniques have been introduced to produce MFC, such as microfluidisation (Siqueira et al., 2009), refining (Iwamoto et al., 2005; Iwamoto et al., 2008), grinding (Iwamoto et al., 2007), high intensity ultrasonication (Wang and Cheng, 2009; Yoo and Hsieh, 2010; Chen et al., 2011) or a combination of two mechanical treatment methods such as
refining and homogenisation (Nakagaito and Yano, 2004; Stelte and Sanadi, 2009). These mechanical treatments, however, require a large number of passes through highly energy consumptive machinery (Plackett et al., 2010; Siro et al., 2010; Spence et al., 2011). The degradation of MFC fibrils, therefore, may occur during this processing, as has been confirmed by a decrease in the degree of polymerisation and crystallinity of the resultant materials (Henriksson et al., 2007; Iwamoto et al., 2007; Siro et al., 2010).

To lower the energy consumption and damage to MFC, the use of pretreatments prior to mechanical treatment has been proposed such as enzymatic modification (Henriksson et al., 2007; Pääkko et al., 2007), TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) oxidation (Iwamoto et al., 2008; Johnson et al., 2009; Isogai et al., 2011) and carboxymethylation (Wågberg et al., 2008; Eyholzer et al., 2010; Siro et al., 2010). It is worth noting that using the combination of both pretreatment and mechanical treatment to produce MFC can reduce energy consumption from 30 MWh tonne\(^{-1}\) to only 1 MWh tonne\(^{-1}\) (Siro and Plackett, 2010; Klemm et al., 2011). The use of mechanical treatment and both pretreatment and mechanical treatment to prepare MFC is discussed in more detail in Chapter 2.2.1.

The Young’s modulus of MFC produced from a cellulose I source is expected to be high because the value for the cellulose crystal of the cellulose I polymorph measured by X-ray diffraction has been found to be as high as 138 GPa (Sakurada et al., 1962). Similarly, a value of 143 GPa for tunicate whiskers has been reported using Raman spectroscopy (Sturcova et al., 2005). However, a measurement of the modulus of single filaments of MFC prepared from a cellulose I source has not been reported. The
investigation of the modulus of single fibrils of MFC using Raman spectroscopy, therefore, could have a major impact on the informed use of this material.

In addition, bio-based polymers have become more interesting as replacements for petroleum-based polymers such as polypropylene and polyethylene because of major concerns about the environment and petroleum availability (Oksman et al., 2006; Mukherjee and Kao, 2011; Sawpan et al., 2011). Poly(lactic acid) (PLA), a biodegradable versatile polymer, has been used in a wide variety of applications such as food packaging, fibres and composites (Garlotta, 2001; Graupner et al., 2009) owing to its mechanical properties, biodegradability and processing route similar to polypropylene and polyethylene (Suryanegara et al., 2010).

MFC has been used to reinforce PLA in order to make green composites (Siro and Plackett, 2010; Tingaut et al., 2010; Suryanegara et al., 2011). However, it is difficult to fully disperse MFC in PLA because MFC is hydrophilic, and PLA is a hydrophobic polymer (Siro and Plackett, 2010; Klemm et al., 2011). Hence, the modification of MFC to reduce the hydrophilicity or the use of different techniques to prepare composites with fully dispersed MFC are of great interest to solve this issue (Jonoobi et al., 2010; Tingaut et al., 2010). In this work, MFC networks (two dimensional random networks) were firstly prepared, and were subsequently used to prepare MFC reinforced PLA composites using compression moulding. This technique can reduce the problem of MFC aggregates during the fabrication of composites. In order to study the stress-transfer process in MFC reinforced PLA composites, Raman spectroscopy is proposed.
1.2 PROBLEM STATEMENTS

MFC has been increasingly used as a reinforcement to produce composite materials (Siro and Plackett, 2010; Klemm et al., 2011), there are, however, some questions that remain unanswered:

I. Is an MFC single filament prepared from a cellulose I source as stiff as a cellulose nanowhisker or cellulose I crystal?

II. Do the physical and mechanical properties of MFC networks prepared from enzymatic and carboxymethylation pretreatments differ?

III. Is an MFC network an effective reinforcement in a composite material and if so, what is the mechanism of reinforcement?

IV. Is a Raman spectroscopic method able to monitor the stress transfer process within MFC reinforced composites as a function of tensile deformation?

1.3 OBJECTIVES

The aims of this research were to determine the Young’s modulus of MFC single filaments produced from a cellulose I source using Raman spectroscopy, and understand the physical and mechanical properties of MFC networks prepared by different methods and from different sources (wood pulp and Lyocell fibres). The effect of MFC networks on the physical and mechanical properties of MFC reinforced composites, and the stress-transfer mechanisms in these composites were investigated also.
1.4 STRUCTURE OF THESIS

This chapter has provided an introduction to the thesis including problem statements, objectives and the structure of the thesis. The subsequent chapters are as follows:

- Chapter 2 reviews the literature on cellulose, MFC, cellulose nanocomposites and the use of Raman spectroscopy to study the stress-transfer process in cellulose materials and cellulose reinforced composite materials.

- Chapter 3 describes the experimental methodology used in this study including the preparation of MFC networks and MFC reinforced composites and techniques used to characterise the physical and mechanical properties of MFC networks and composites.

- Chapter 4 describes an investigation of the physical and mechanical properties of MFC networks prepared from Lyocell fibres. The MFC network possessing the optimum mechanical properties was selected to prepare composites with PLA using compression moulding.

- Chapter 5 reports the effective Young’s modulus of single fibrils of MFC produced from pulp estimated using Raman spectroscopy. The effects of polarisation configurations (VV and VH) and the angles between the incident light direction and MFC network axis on the molecular deformation of MFC within the networks are reported.

- Chapter 6 details the physical and mechanical properties of MFC networks prepared from wood pulp and Lyocell fibres.
Chapter 7 details the physical and mechanical properties of composites reinforced with four types of MFC networks (MFC-A, MFC-B, MFC-C and MFC-D). Micromechanics of MFC reinforced composites using Raman spectroscopy are reported also.

Chapter 8 provides conclusions and suggestions for future work.

1.5 REFERENCES


CHAPTER 2

LITERATURE REVIEW

An overview of cellulose and cellulose nanocomposite materials including microfibrillated cellulose used as a reinforcement for composite materials is reviewed in this chapter. The use of Raman spectroscopy to monitor the stress-transfer mechanisms in cellulose materials and cellulose reinforced composite materials is introduced also.

2.1 INTRODUCTION TO CELLULOSE

Cellulose is one of the most ubiquitous materials in nature, and has been widely used in the form of intact wood, paper, board and fibres such as cotton and flax (Klemm et al., 2006; Eichhorn et al., 2010; Moon et al., 2011). Also, cellulose is a raw material used to make regenerated cellulose products such as fibres and films (Klemm et al., 1998; Klemm et al., 2005). Plants, for instance pulp, cotton, hemp, flax and sisal fibres, are the main raw material sources of cellulose (Klemm et al., 2005; Iwamoto et al., 2007). Cellulose can be produced also by several species of bacteria belonging to the genera Acetobacter, Agrobacterium, Pseudomonas, Rhizobium or Sacrina (Smook, 1992;
Nakagaito et al., 2005; Soykeabkaew et al., 2009; Eichhorn et al., 2010) and sea creatures e.g. tunicates (Eichhorn et al., 2010).

2.1.1 Morphological Structure of Natural Fibres

The main components of wood and natural fibres are cellulose, hemicelluloses and lignin (Smook, 1992). There are also other substances which can be found such as fatty acid, pectin and alcohol, depending on the source of plants (Smook, 1992).

Even though the structural morphology of wood and plant fibres depends on their origin, the main parts of cell walls of wood and plant fibres are similar (Klemm et al., 1998; Klemm et al., 2005). Figure 2.1 shows the cell wall structure of a spruce wood fibre comprising four parts: namely the middle lamella, primary wall, secondary wall and lumen. The middle lamella, containing mostly lignin, bonds adjacent cells together (Smook, 1992). In both the primary and secondary walls, there are bundles of microfibrils consisting of cellulose molecules, and their orientation plays a major role in the mechanical properties of fibres (Smook, 1992). The microfibrils of cellulose in the primary wall are randomly arranged. The secondary wall consists of three layers: the outer layer (S1), middle layer (S2) and inner layer (S3) (Smook, 1992; Klemm et al., 1998). The S2 layer is the main component of wood and cellulose fibres because this layer contains approximately 80 - 90 % by weight of the fibres (Smook, 1992). The mechanical properties of fibres, therefore, are dominated by the structural morphology of the S2 layer (Smook, 1992). The arrangement of microfibrils in the S2 layer is helically oriented, and is more longitudinally directed compared to the S1 and S3 layers (Smook, 1992; Klemm et al., 1998). The S1 layer, on the other hand, is a cross fibrillar
network, and the orientation of the S3 layer is transverse (Smook, 1992; Klemm et al., 1998). The lumen is the central channel of wood fibres (Smook, 1992; Klemm et al., 1998).

**Figure 2.1** Schematic representation of the structural morphology of a spruce wood fibre; ML - middle lamella, P - primary wall, S1 - the outer layer of the secondary wall, S2 - the main body of the fibre, S3 - the inner layer of the secondary wall, and L is lumen, the central canal of the fibre. Reproduced with modification from from Klemm et al. (1998) and Smook (1992).

### 2.1.2 Structure of Cellulose

Cellulose is classified as a carbohydrate *i.e.* containing carbon, hydrogen and oxygen (Smook, 1992; Klemm *et al.*, 2005; Eichhorn *et al.*, 2010). Cellulose is a series of repeating anhydroglucose units \((\text{C}_6\text{H}_{10}\text{O}_5)_n\) joined through an oxygen covalently bonded between C1 of one glucose ring and C4 of the neighbouring ring (\(\beta\)-1,4 glycosidic bonds) (Smook, 1992; Klemm *et al.*, 2005; Eichhorn *et al.*, 2010; Moon *et al.*, 2011), as
illustrated in Figure 2.2. This cellulose unit is called a cellobiose unit (Smook, 1992; Eichhorn et al., 2010). As a result, cellulose is a linear chain polymer with a large number of hydroxyl groups (OH) (three hydroxyl groups per anhydroglucose unit) (Klemm et al., 2005; Moon et al., 2011). At both ends of cellulose chains the hydroxyl groups exhibit two different behaviours: non-reducing end and reducing end. The non-reducing end is the glucose unit end group with an original hydroxyl group at C4; on the other hand, the hydroxyl group at C1 is in equilibrium with the aldehyde structure, called the reducing end (Klemm et al., 1998; Klemm et al., 2005).

The molecular size of cellulose can be defined by the average degree of polymerisation, which depends on the origin of cellulose materials and treatment used to prepare cellulose (Smook, 1992; Klemm et al., 1998; Klemm et al., 2005; Moon et al., 2011). Typical values of the degree of polymerisation for a number of cellulose materials are reported in Table 2.1 (Smook, 1992; Klemm et al., 1998).

![Molecular structure of cellulose](image)

**Figure 2.2** Molecular structure of cellulose. Reproduced with modification from Klemm et al. (1998) and Smook (1992).
### Table 2.1 Degree of polymerisation of cellulose materials (Smook, 1992; Klemm et al., 1998)

<table>
<thead>
<tr>
<th>Material</th>
<th>Degree of polymerisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ramie</td>
<td>6,000 - 7,000</td>
</tr>
<tr>
<td>Flax</td>
<td>7,000 - 9,000</td>
</tr>
<tr>
<td>Purified cotton linters</td>
<td>1,000 - 3,000</td>
</tr>
<tr>
<td>Commercial wood pulps</td>
<td>600 - 1,500</td>
</tr>
<tr>
<td>Viscous rayon</td>
<td>200 - 600</td>
</tr>
<tr>
<td>Cellulose powders (prepared by partial hydrolysis and mechanical disintegration)</td>
<td>100 - 200</td>
</tr>
</tbody>
</table>

#### 2.1.3 Crystalline Structure of Cellulose

There are six different polymorphic forms of cellulose: cellulose I, II, III\(_{\alpha}\), III\(_{\beta}\), IV\(_{I}\) and IV\(_{II}\), as determined by X-ray diffraction (O'Sullivan, 1997; Eichhorn et al., 2005; Klemm et al., 2005). Cellulose I, sometimes known as natural cellulose, is the main form found in nature such as plants, animals and algae, and is produced also by bacteria (Moon et al., 2011). The chains in Cellulose I are packed in a parallel conformation (Kong and Eichhorn, 2005; Klemm et al., 2005). It is known that the cellulose I crystal form has two allomorphs: namely cellulose I\(_{\alpha}\) and I\(_{\beta}\) (Atalla and Van der Hart, 1984; Van der Hart and Atalla, 1984; Debzi et al., 1991; Nishiyama et al., 2002; Nishiyama et al., 2003; Klemm et al., 2005; Eichhorn et al., 2010; Moon et al., 2011). The ratio of these allomorphs (I\(_{\alpha}/I_{\beta}\)) has been reported to depend on the origin of cellulose sources (Atalla and Van der Hart, 1984; Van der Hart and Atalla, 1984; Sugiyama et al., 1991). For example, algae and bacterial cellulose are I\(_{\alpha}\) rich, while plants, such as cotton and
ramie, and tunicate are rich in the I$_\beta$ form (Atalla and Van der Hart, 1984; Van der Hart and Atalla, 1984; Sugiyama et al., 1991).

Cellulose I$_\alpha$ and I$_\beta$ have the same conformation of the heavy atom skeleton, but their hydrogen bonding patterns are different (Nishiyama et al., 2002; Nishiyama et al., 2003; Festucci-Buselli et al., 2007), as shown in Figure 2.3.

![Figure 2.3](image)

**Figure 2.3** Hydrogen bonding patterns in cellulose (a) I$_\alpha$ and (b) I$_\beta$. Hydrogen bonds are indicated by dotted lines. Carbon, oxygen and hydrogen are represented by large opened circles, large closed circles and small opened circles respectively. Reproduced with modification from Nishiyama et al. (2002) and Festucci-Buselli et al. (2007).

The crystal structure and hydrogen bonding system in cellulose I$_\alpha$ and I$_\beta$ obtained from oriented fibrous samples of an alga *Glaucocystis nostochinearum* and tunicin have been determined using a combination of synchrotron and neutron diffractions (Nishiyama et al., 2002; Nishiyama et al., 2003). The cellulose structure of I$_\alpha$ is a triclinic containing
one cellulose chain, and the unit cell parameters are $a = 0.672 \, \text{nm}$, $b = 0.596 \, \text{nm}$, $c = 0.104 \, \text{nm}$, $\alpha = 118.08^\circ$, $\beta = 114.8^\circ$ and $\gamma = 80.37^\circ$ (Nishiyama et al., 2002; Nishiyama et al., 2003; Moon et al., 2011). Cellulose I$_\beta$, on the other hand, is a monoclinic structure, containing two cellulose chains with dimensions of $a = 0.778 \, \text{nm}$, $b = 0.820 \, \text{nm}$, $c = 1.038 \, \text{nm}$ and $\gamma = 96.5^\circ$ (Nishiyama et al., 2002; Nishiyama et al., 2003; Moon et al., 2011). Cellulose I$_\alpha$ is a metastable structure which can be converted to cellulose I$_\beta$, which is more stable, by annealing at high temperature (Debzi et al., 1991; Yamamoto and Horii, 1993; O'Sullivan, 1997; Moon et al., 2011).

Cellulose I can be converted to cellulose II by treatment with sodium hydroxide (NaOH) called a mercerisation process or by dissolution of cellulose and then regeneration (Ishikawa et al., 1997; O'Sullivan, 1997; Klemm et al., 2005; Moon et al., 2011). There are many commercially available products manufactured from cellulose II such as regenerated fibres, cellophane films (transparent films), to name a few (Ishikawa et al., 1997; O'Sullivan, 1997; Klemm et al., 2005; Moon et al., 2011). Cellulose III and IV are reversibly produced from cellulose I and II (Gardiner and Sarko, 1985; Ishikawa et al., 1997; Moon et al., 2011). Cellulose III can be obtained from Cellulose I or II by chemical treatment such as liquid ammonia or amines (Ishikawa et al., 1997; O'Sullivan, 1997; Moon et al., 2011). Heat treatment is used to convert Cellulose III to Cellulose IV (Gardiner and Sarko, 1985; O'Sullivan, 1997; Kong and Eichhorn, 2005; Moran et al., 2008). The transformation of these allomorphs is shown in Figure 2.4.
In the cellulose structure, hydroxyl (OH) groups have a large influence on its properties (Smook, 1992). The OH groups interact with other OH groups within the same cellulose chain or neighbouring cellulose chains to form hydrogen bonding (Smook, 1992; Moon et al., 2011), as shown in Figure 2.3. The hydrogen bonding between cellulose chains, therefore, renders the cellulose crystal more stable, making the so-called “melting temperature” of cellulose much higher than the temperature of decomposition (cellulose does not melt) (Eichhorn et al., 2010). For the same reason, cellulose is insoluble in water and common aqueous chemical solvents (Klemm et al., 2005; Zugenmaier, 2008; Eichhorn et al., 2010). Cellulose, nevertheless, can be converted into a cellulose derivative, which then can be dissolved using specific cellulose solvents such as sodium hydroxide (NaOH), N-methyl morpholine N-oxide (NMMO), lithium chloride/N,N-dimethylacetamide (LiCl/DMAc), to name a few examples (Klemm et al., 2005). The OH groups in the cellulose ring structure can be fully or partly converted to other groups by these solvents. This reduces the strength of the hydrogen bonds, and modifies
the structure of cellulose, making it possible to dissolve in a solvent (Klemm et al., 2005).

Lyocell fibres, for example, are one such regenerated cellulose product that can be produced from wood pulp (White, 2001; Klemm et al., 2005). The wood pulp is dissolved in a hot solution of \( N \)-methyl morpholine \( N \)-oxide (NMMO). This cellulose solution passes through a spinneret, a device used to extrude fibres, and then a washing process is used to extract the solvent, while fibres are formed (White, 2001; Kong and Eichhorn, 2005).

2.2 MICROFIBRILLATED CELLULOSE

Currently, the use of cellulose nanofibres as reinforcements in composites is attracting a large amount of interest (Eichhorn et al., 2010; Klemm et al., 2011; Moon et al., 2011). This is partly due to the fact that the crystal modulus of cellulose has been reported to be \( \sim 138 \) GPa (Sakurada et al., 1962; Nishino et al., 1995). If the density of cellulose (\( \sim 1.5 \) g cm\(^{-3}\)) is taken into the account, the specific modulus (Young’s modulus divided by density) of crystalline cellulose is much higher than other materials used in composites such as glass fibres, steel and aluminium, as shown in Table 2.2 (Eichhorn et al., 2010). The high aspect ratio of nanofibres is another reason why these nanofibres could be useful for composites. In addition, the mechanical properties of plant fibres are intently variable due to the variable cross section area, voids in the form of lumen inside fibres, cell wall pores, defects such as kink bands, to name a few (Hughes et al., 2000; Eichhorn et al., 2010). The preparation of nanofibres from plant cell walls, therefore, can potentially eradicate the variable properties and defects, and provide high stiffness...
and aspect ratio, which are suitable to be used as a reinforcement for composite materials (Eichhorn et al., 2010; Klemm et al., 2011).

**Table 2.2** Moduli of engineering materials compared to crystalline cellulose (Bledzki and Gassan, 1999; Eichhorn et al., 2001; Eichhorn et al., 2010).

<table>
<thead>
<tr>
<th>Material</th>
<th>Modulus (GPa)</th>
<th>Density (g cm⁻³)</th>
<th>Specific modulus (GPa g⁻¹ cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>69</td>
<td>2.7</td>
<td>26</td>
</tr>
<tr>
<td>Steel</td>
<td>200</td>
<td>7.8</td>
<td>26</td>
</tr>
<tr>
<td>E-glass fibre</td>
<td>69</td>
<td>2.5</td>
<td>28</td>
</tr>
<tr>
<td>Crystalline cellulose</td>
<td>138</td>
<td>1.5</td>
<td>92</td>
</tr>
<tr>
<td>Carbon fibres</td>
<td>230 - 240</td>
<td>1.4</td>
<td>164 - 171</td>
</tr>
</tbody>
</table>

Nanocelluloses can be separated into three main categories: namely cellulose nanowhiskers (CNWs), bacterial cellulose (BC) and microfibrillated cellulose (MFC) (Eichhorn et al., 2010; Klemm et al., 2011). Table 2.3 summarises the different forms of nanocellulose materials.

Cellulose nanowhiskers (CNWs), also called nanocrystalline cellulosics (NCC), are generated by acid hydrolysis to remove the amorphous regions from cellulose sources such as wood, cotton, hemp, flax, wheat straw, ramie, tunicin, algae and bacteria, followed by the ultrasonic treatment (Eichhorn et al., 2010; Klemm et al., 2011). These treatments provide rod-like shaped cellulose nanofibres with up to 90% of crystallinity (Eichhorn et al., 2010; Klemm et al., 2011). The size (width and length) of these
materials depends on the raw materials. Due to fewer amorphous regions, their flexibility is limited (Klemm et al., 2011).

Bacterial cellulose (BC), also known as bacterial nanocellulose (BNC), is produced by several genera of bacteria: namely Acetobacter, Rhizobium, Agrobacterinum and Sarcina, fermented in the low molecular weight carbon sources such as glucose (Iguchi et al., 2000; Nakagaito et al., 2005; Soykeabkaew et al., 2009; Eichhorn et al., 2010). A nanofibre network with diameters ranging 20 - 100 nm is obtained. This material is found to have high crystallinity, high molecular weight and good mechanical properties (Iguchi et al., 2000; Eichhorn et al., 2010; Siro and Plackett, 2010).

Microfibrilated cellulose (MFC), also called nanofibrillated cellulose (NFC), is a network of interconnected nanofibrils and microfibrils with diameters in the range of 5 - 100 nm (Eichhorn et al., 2010; Siro and Plackett, 2010). These fibrils have a higher aspect ratio and are more flexible than cellulose whiskers (Eichhorn et al., 2010; Siro and Plackett, 2010).
Table 2.3 Summary of the different types of nanocellulose materials (Klemm et al., 2011).

<table>
<thead>
<tr>
<th>Type</th>
<th>Synonym</th>
<th>Original sources</th>
<th>Average size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose nanowhiskers (CNWs)</td>
<td>Nanocrystalline cellulose (NCC)</td>
<td>Wood, cotton, hemp, flax, wheat straw, ramie, tunicin, algae and bacteria</td>
<td>Diameter: 5 - 70 nm&lt;br&gt;Length: 100 - 250 nm from plant; 100 nm to several µm from tunicates, algae and bacteria</td>
</tr>
<tr>
<td>Bacterial cellulose (BC)</td>
<td>Bacterial nanocellulose (BNC)</td>
<td>Low molecular weight sugars and alcohols</td>
<td>Diameter: 20 - 100 nm&lt;br&gt;Length: depending on types of nanofibre networks</td>
</tr>
<tr>
<td>Microfibrillated cellulose (MFC)</td>
<td>Nanofibrillated cellulose (NFC)</td>
<td>Wood, sugar beet, potato, hemp and flax</td>
<td>Diameter: 5 - 100 nm&lt;br&gt;Length: several µm</td>
</tr>
</tbody>
</table>

2.2.1 Mechanical Treatments for MFC Preparation

MFC was first introduced in the 1980s by Herrick et al. (1983) and Turbak et al. (1983). Originally, dilute wood pulp suspensions were repeatedly passed through a high pressure homogeniser to make MFC. MFC is now a commercially available product manufactured by a number of companies e.g. Daicel (Japan) and Innventia (Sweden) (Siro and Plackett, 2010). The morphology, the aspect ratio and the degree of polymerisation of MFC fibrils depend on the source of cellulose and fibrillation techniques (Siro and Plackett, 2010).
MFC has been recently produced using different mechanical methods such refining (Nakagaito and Yano, 2004; Iwamoto et al., 2005), grinding (Iwamoto et al., 2008), microfluidising (Pääkko et al., 2007), high-speed blending (Uetani and Yano, 2011), high intensity ultrasonic sonication (Cheng et al., 2009; Chen et al., 2011a) or using a combination of two mechanical methods such as refining and high pressure homogenising (Nakagaito and Yano, 2004; Iwamoto et al., 2005; Stelte and Sanadi, 2009; Siro and Plackett, 2010). Some of these treatments are now discussed.

(a) Refining and high pressure homogenising

Even though a high pressure homogeniser has been used to prepare MFC since the 1980s (Herrick et al., 1983; Turbak et al., 1983), this technique is impractical industrially because of the high energy consumption and the clogging in a homogeniser caused by fibre agglomerates (Henriksson et al., 2007; Klemm et al., 2011). The combination of two mechanical techniques such as refining and high pressure homogenising, however, has been efficiently used to manufacture MFC (Nakagaito and Yano, 2004; Iwamoto et al., 2005; Stelte and Sanadi, 2009; Siro and Plackett, 2010). A dilute fibre suspension is firstly passed through a gap between rotor and stator disks, which have surfaces fitted with bars and grooves, in a refiner (Nakagaito and Yano, 2004; Siro and Plackett, 2010). The dilute suspension is subsequently treated by a high pressure homogeniser. The solution is forced through spring loaded valves at high pressure, where the shearing and impact forces occur, as shown in Figure 2.5. Fibrils with a high degree of microfibrillation can be obtained from this process (Nakagaito and Yano, 2004; Siro and Plackett, 2010).
Nakagaito and Yano (2004) and Iwamoto et al. (2005) used a combination of a refiner and a high pressure homogeniser to produce MFC. It was found that after passing the suspension through the refiner for 16 times, the fibres were split into small bundles. Then, these small bundles were found to be separated into thinner bundles after 30 passes through the refiner. Refiner treated MFC was subsequently passed through a high pressure homogeniser. Fibre aggregates were found to be disintegrated by the additional passes through a high pressure homogeniser.

It has been reported that as the number of passes through the high pressure homogeniser increase, the viscosity of the treated suspension is found to be gradually higher, indicating the higher degree of fibrillation (Iwamoto et al., 2005; Henriksson et al., 2007). This combination, however, seems to damage the structure of fibrils, confirmed by a decrease in the degree of polymerisation of the resulting materials compared to the raw materials (Henriksson et al., 2007; Siro and Plackett, 2010).

**Figure 2.5** Schematic illustration of a high pressure homogeniser. Reproduced with modification from Klemm et al. (2011).
(b) Grinding

Iwamoto et al. (2007) used a grinder to fibrillate pulp suspensions at fibre contents of 1 wt.% at 1500 rpm. These suspensions were passed through the grinder for 1, 3, 5, 9, 15 and 30 times respectively, producing MFC. During the grinding treatment, the cell wall structure was broken by shear force generated by a static grind stone and a rotating grind stone, and then MFC were formed. It was found that as the number of passes through the grinder increased, the size of MFC was smaller. No significant change in the size of the MFC, however, was observed after the number of passes through the grinder was greater than five. The lateral size of MFC was in the range of 20 - 50 nm, and the length was longer than 1 µm. Compared to that for 1 pass (1.04 g cm\(^{-3}\)), the densities of networks prepared by passing the suspensions through the grinder for 3, 5, 9, 15 and 30 times were found to be approximately constant with a value of ~1.3 g cm\(^{-3}\). This was attributed to the fact that the fibres at one pass were micron sized and larger than those prepared with a higher number of passes (Iwamoto et al., 2007).

The mechanical properties of the fibrillated pulp networks were then investigated (Iwamoto et al., 2007). The results showed as the number of passes through the grinder increased, the failure stress, failure strain and Young’s modulus of the MFC networks were found to decrease. This was thought to be due to degradation of MFC, confirmed by the increase of thermal expansion and the decrease in the degree of polymerisation and the degree of crystallinity of the MFC (Iwamoto et al., 2007). Even though uniform MFC can be produced by this method, this method is a batch process, and does not allow users to observe fibrillated fibres during the processing due to the closed system (Uetani and Yano, 2011). Hence, methods which allow users to observe fibrillated
fibres during the treatment, run continuously and less damage the resulting fibrils, using an as efficient process as grinding, have been introduced, such as high speed blending and high intensity ultrasonication.

(c) High intensity ultrasonication

High intensity ultrasonication is an alternative method for isolating MFC (Wang and Cheng, 2009; Cheng et al., 2010; Chen et al., 2011a). Ultrasonic waves generated by converting the mechanical energy into high frequency acoustical energy can produce a very strong mechanical oscillating power via a cavitation mechanism (Wang and Cheng, 2009; Cheng et al., 2010; Chen et al., 2011a). This mechanism consists of three processes: the formation, growth and implosion of microbubbles (Wang and Cheng, 2009; Cheng et al., 2010; Chen et al., 2011a). When the ultrasound energy is absorbed by cellulose molecules, hydrogen bonding between fibrils is broken. This results in individual MFC fibrils from original fibres (Wang and Cheng, 2009).

Lyocell fibres used as a raw material were treated by a high intensity ultrasonicator (HIUS) (Cheng et al., 2009; Wang and Cheng, 2009). As the treatment time increased, an increased water retention value for MFC was observed, indicating that the surface area of MFC fibrils was higher. After treatment for 30 min, the diameters of fibres and fibrils ranging from several µm to few nm were obtained. It was found that some of the MFC isolated from the Lyocell fibres had diameters in the range of 20 - 30 nm.
(d) High speed blending

The use of a high speed blender to disintegrate fibres into uniform MFC has been recently introduced (Uetani and Yano, 2011). MFC with a uniform width of ~15 nm, similar to MFC passed through a grinder for one time studied by Iwamoto et al. (2007), can be obtained from wood pulp using this technique with a speed of 37,000 rpm for 30 min. The fraction of MFC increased with an increase of blending time. During the fibrillation, a balloon-like structure was observed to form along a fibre. This balloon-like structure continued to the edges of the fibre, and then MFC were disintegrated individually. This behaviour was thought to occur due to the strike of sharp blender blades. Moreover, the degree of crystallinity was investigated to evaluate the damage to MFC prepared by the high speed blender, compared to the grinding method. It was found that the degree of crystallinity of MFC gradually decreased by ~3% to 69%, when the blender was used for 1 to 5 min. No significant change of the degree of crystallinity of MFC was observed for going from 5 to 30 min treatment time, whereas passing the pulp suspension through the grinder for one time decreased the degree of crystallinity of MFC by ~10% compared to that of the original fibres. These results revealed that by using a high speed blender less damage was done to the structure of MFC than a grinder (Uetani and Yano, 2011).

2.2.2 Pretreatments and Mechanical Treatments for MFC Preparation

All mechanical treatments seem to damage fibres, and energy consumption as high as 20 - 30 MWh tonne\(^{-1}\) is required (Siro and Plackett, 2010; Klemm et al., 2011). Pretreatments, such as enzymatic, acetylation, carboxymethylation and TEMPO-
mediated oxidation prior to mechanical treatment have been introduced to overcome these problems (Henriksson et al., 2007; Pääkko et al., 2007; Wågberg et al., 2008; Siro and Plackett, 2010; Tingaut et al., 2010; Isogai et al., 2011). The use of pretreatments has been found to considerably reduce the energy consumption to only 1 MWh tonne\(^{-1}\) to produce MFC (Siro and Plackett, 2010). Table 2.4 reports typical energy consumption values for MFC preparation. Some of these pretreatments are now discussed.

### Table 2.4 Typical energy consumptions for the preparation of MFC (Klemm et al., 2011).

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>Raw material</th>
<th>Energy requirement (MWh tonne(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>Kraft pulp</td>
<td>12 - 70</td>
</tr>
<tr>
<td>None</td>
<td>Sulphite pulp</td>
<td>27</td>
</tr>
<tr>
<td>Carboxymethylation</td>
<td>Kraft/ sulphite pulp</td>
<td>0.5</td>
</tr>
<tr>
<td>Enzymatic</td>
<td>Sulphite pulp</td>
<td>1.5</td>
</tr>
</tbody>
</table>

(a) Alkaline pretreatment

Alkaline pretreatment has been applied prior to mechanical treatment in order to remove lignin, hemicelluloses, pectin and extractives from fibres (Abe and Yano, 2009; Siqueira et al., 2009; Chen et al., 2011b). This pretreatment is to be used with care, to avoid the degradation of cellulose (Siro and Plackett, 2010). The cellulose suspension is then further mechanically processed by techniques such as grinding (Abe and Yano,
2011; Okahisa et al., 2011), microfluidising (Siqueira et al., 2009) and high intensity ultrasonication (Chen et al., 2011a).

It was found that after the alkaline pretreatment was used to extract purified nanofibres from three different sources- softwood, rice straw and potato tuber pulp- the resultant suspensions required only one pass through a grinder to achieve MFC (Abe and Yano, 2009). Uniform MFC with diameters in the range of 12 - 20 nm for wood were obtained, whereas the diameters of MFC prepared from rice straw and potato tuber were in the ranges of 12 - 35 and 12 - 55 nm respectively. The degree of crystallinity of MFC obtained from these three sources was found to be higher compared to the original sources. This was thought to be due to the removal of amorphous polymers, such as lignin and hemicelluloses, during the alkali pretreatment, and due to the fact that only one cycle of passing through the grinder was required, limiting damage to MFC fibrils (Abe and Yano, 2009).

(b) Enzymatic pretreatment

Enzymatic pretreatment has been introduced as an environmentally friendly method to prepare MFC (Yoo and Hsieh, 2010). The number of passes through the mechanical treatment equipment have been reported to decrease after using this approach (Yoo and Hsieh, 2010). Cellulase enzymes can be classified into 3 groups: namely endocellulases, exocellulases and cellobiases (Siqueira et al., 2010; Yoo and Hsieh, 2010). Figure 2.6 shows the enzymatic reactions of the three types of cellulosases. Endocellulases ($\beta$-1,4-endoglucanases) randomly break intermolecular hydrogen bonds between cellulose chains to expose individual cellulose chains. Then, the termini of cellulose chains are
attacked by exocellulases, sometimes called cellobiohydrolases, to release cellobioses or glucose as products. Cellobioses, known as $\beta$-glucosidases, hydrolyse cellobioses into glucoses (Siqueira et al., 2010; Yoo and Hsieh, 2010).

Mild enzymatic hydrolysis and mechanical treatment have been combined together to prepare MFC from wood pulp (Henriksson et al., 2007; Pääkko et al., 2007). This combination has been used widely for preparing MFC with high aspect ratios and high molar mass.

**Figure 2.6** Enzymatic processes by three types of cellulase enzymes. Reproduced with modification from Yoo and Hsieh (2010).
(c) Carboxymethylation pretreatment

In order to increase the isolation rate and reduce the energy consumption, the carboxymethylation pretreatment is one of the most successful approaches combined with mechanical treatment (Eyholzer et al., 2010b). Carboxymethylation functionalises hydroxyl groups of celluloses to carboxymethyl groups in their sodium form, as shown in Figure 2.7 (Eyholzer et al., 2010b). Wågberg et al. (2008) prepared MFC by the following methods. Pulp was first pretreated using the carboxymethylation process, followed by a high pressure homogenisation step. This resulted in MFC fibrils with diameters in the range of 5 - 15 nm, and lengths of up to 1 µm.

![Figure 2.7 Carboxymethylation pretreatment of cellulose. Reproduced from Eyholzer et al. (2010b).](image)

Later, Eyholzer et al. (2010a) prepared carboxymethylated MFC by the comparison of two different approaches. Firstly, pulp was mechanically treated by a microfluidiser, followed by carboxymethylation treatment. The second route was a reversed step: carboxymethylation pretreatment and subsequently mechanical disintegration. The degree of crystallinity of MFC was found to be lower for the second route (49 %),
compared to values of 65% and 71% for carboxymethylated pulp using the first route and the original pulp respectively.

Thermal properties of carboxymethylation pretreated MFC from both two routes were found to be lower compared to the original pulp and only mechanically treated pulp. In addition, the MFC suspension prepared by the initial carboxymethylation pretreatment and subsequently mechanical disintegration were found to be more transparent and less agglomerated (with the overall diameters below 100 nm) than that produced using the reverse step (first mechanical treatment followed by carboxymethylation treatment). These results confirmed that applying the carboxymethylation pretreatment prior to the mechanical treatment can improve the efficiency of mechanical isolation (Eyholzer et al., 2010a).

**d) TEMPO-oxidation pretreatment**

A new pretreatment approach has been developed to prepare MFC from wood using 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation followed by mechanical treatment (Isogai et al., 2011). TEMPO-mediated oxidation is an efficient method to oxidise polysaccharides under a mild condition such as cotton linters, pulp and bacterial cellulose (Johnson et al., 2009; Isogai et al., 2011). TEMPO is used with sodium hypochlorite (NaOCl) and sodium bromide (NaBr) as a catalyst and primary oxidant in water at pH 8-11. The primary hydroxyl at the C6 position of cellulose is converted to a carboxylate group by this pretreatment. No changes of the degree of crystallinity and crystal sizes of the cellulose I allomorph have been observed (Hirota et al., 2009; Isogai et al., 2011). Figure 2.8 reports the mechanisms of TEMPO-mediated
oxidation. Pulp fibres with lengths and widths of 262 ± 156 and 24.2 ± 7 µm respectively were pretreated using TEMPO oxidation, a sonication was subsequently used for only 10 min to almost completely fibrillate the pulp fibres to MFC with widths in the range of 2.5 - 4 nm (Johnson et al., 2009).

**Figure 2.8** TEMPO-mediated oxidation of primary hydroxyls at the C6 position of cellulose to carboxylate groups in aqueous at pH 8-11. Reproduced with modification from Isogai et al. (2011).

### 2.2.3 Stress-strain Curves of Networks

This section contains information that has been used to explain the mechanical properties of paper, which can be applied for networks of MFC. The elastic modulus of
paper is controlled by three main factors (Page et al., 1979; Page and Seth, 1980; Seth and Page, 1983):

1. It is assumed that when the stress and strain distribution in paper is homogeneous, the elastic modulus of paper is equal to one third of the elastic modulus of fibres.

2. The degree of bonding between fibres dominates the stress distribution in paper caused by the transfer of load from a fibre to its neighbours in the regions of fibre ends, as shown in Figure 2.9. It is assumed that a fibre is bonded to fibres crossing it, which can be considered as a fibre embedded in a matrix. Then, when paper is deformed, the stress distribution along the length of this fibre, $L$, is considered. The stress is a maximum at the centre and zero at the fibre ends. When the degree of bonding of paper is higher, the stress can reach the maximum value with the shorter length along the fibre $L$.

3. The presence of defects in a fibre, such as curl, voids and kink bands, is found to reduce the modulus of paper.
The influences on the stress-strain curves of paper have been investigated (Seth and Page, 1983). They are a plenty of factors experimentally tested to follow the change of the stress-strain curves of paper. Examples of the influences on the stress-strain curves of paper are introduced as follows:

- The tensile strength and strain at failure of paper are found to be higher when the wet pressure and/or the beating level applied in the system to prepare paper are increased.

- If a large number of defects such as crimps and kinks are introduced to fibres by the treatment, the tensile strength of paper is found to decrease, with longer treatment times.

Figure 2.9 Tensile stress distributions along the length L of a fibre at (a) low and (b) high degrees of bonding. Reproduced from Seth and Page (1983).
• The molecular mobility of the matrix phase in fibres, such as hemicelluloses, is found to be more mobile with increasing the humidity or decreasing the rate of deformation. These result in the lower tensile strength and higher elongation at break of paper.

2.3 COMPOSITE MATERIALS

The term “composite” is a material processed by dispersing a reinforcement phase in a matrix phase, in order to enhance the mechanical and physical properties of the latter (Hull and Clyne, 1996; Young and Lovell, 2011). For example, embedding glass fibres in thermosetting polymers, such as polyester and epoxy resins, exhibits superior mechanical properties to those of the resin alone (Young and Lovell, 2011). Due to the superior mechanical properties of the composite materials, there are a large number of commercial composite material products or parts of products available on the market for instance aircraft, automobiles, boats and furniture (Hull and Clyne, 1996).

Even though composite materials show outstanding mechanical properties, in some cases the mechanical or physical properties of these materials can be lower than expected (Hull and Clyne, 1996). It has been reported that the addition of natural fibres in a hydrophobic polymer, such as polypropylene (Bledzki and Gassan, 1999; Ganster et al., 2006; Ganster et al., 2008; Johnson et al., 2008; Miyazaki et al., 2009) and polyethylene (Freire et al., 2008), can reduce tensile strength and transparency of these composites, if the poor interaction between the matrix and natural fibres occurs in the composite materials. This interaction, therefore, is one of the most important factors for enhancing the mechanical properties of composites. Also, the mechanical properties of
composites can be affected by the size, alignment and volume fraction of the reinforcement phase (Siro and Plackett, 2010).

### 2.3.1 Types of Interactions in Composites

Interactions in composites can be categorised into five main mechanisms: wetting, interdiffusion, electrostatic attraction, chemical bonding and mechanical adhesion (Hull and Clyne, 1996), as shown in Figure 2.10.

- **Wetting** is the ability of a solid surface to absorb liquid in order to form physical bonding. It is an important to consider the wetting behaviour when selecting a type of a resin for interaction with a particular reinforcement surface. Contamination such as voids or air on the solid surface can affect the mechanical properties of composite materials (Hull and Clyne, 1996).

- **Interdiffusion** occurs when the polymer molecules of one component surface disperse through polymer chains of another polymer surface. Then, their chains entangle with each other to form a bond, as shown in Figure 2.10b. The strength of the bond is controlled by the volume of chain entanglements and the number of chains (Hull and Clyne, 1996).
Electrostatic attraction occurs when the surfaces have electrical charges of an opposite sign, as shown in Figure 2.10c. Each surface has a different charge, consisting of positive and/or negative charges. The positive charge is attracted by the negative charge on another surface and vice versa to form a bond. The density of the charges on the surface controls the strength of interaction between the two surfaces (Hull and Clyne, 1996).

Chemical bonding can improve the interaction between two phases which have different polarity (hydrophobic and hydrophilic) using a coupling agent such as maleic anhydride grafted polypropylene (MAPP) (Zhang et al., 2002; Ibrahim et al., 2010), silane (Lu and Drzal, 2010), to name a few. For example, polypropylene and cellulose have a limited interaction with each other because polypropylene consists of only carbon and hydrogen atoms in molecular chains, whereas a cellulose fibre is a
hydrophilic material containing hydroxyl groups (-OH) (Smook, 1992; Beckermann and Pickering, 2008). The use of MAPP, therefore, is one of the most efficient ways to improve the interaction between a matrix and reinforcement phase since MAPP has both hydrophilic and hydrophobic properties on the same molecular chain. Whilst the hydrophobic part of MAPP is connected with a molecular chain of polypropylene, another part of MAPP, a polar part, interacts with a hydroxyl group of cellulose fibres (Beckermann and Pickering, 2008). Figure 2.11 illustrates the mechanism of MAPP interacting with OH groups on cellulose chains. Using this coupling agent to improve the interaction between two different components, however, is related to the volume fraction of MAPP. Applying a small amount of the coupling agent can increase the bonding along some parts of the chain. Using a large amount of the coupling agent, nevertheless, can actually weaken the mechanical properties of the composite (Ganster et al., 2008; Johnson et al., 2008; Miyazaki et al., 2009).

![Figure 2.11](image.png)

**Figure 2.11** Mechanism of MAPP chains coupled to cellulose. Reproduced with modification from Zhang et al. (2002).
**Mechanical adhesion** is the interlocking mechanism of two surfaces (Figure 2.10e). The strength of adhesion depends on the roughness of the two surfaces. If the surfaces of components are too smooth, it is difficult to interlock with each other (Hull and Clyne, 1996). Nevertheless, the rougher the surface, the stronger the adhesion because holes and valleys in each surface can stick together. For example, sodium hydroxide (NaOH) has been used to treat fibres and make the surface of cellulose fibres rougher. The treated fibres were blended with polypropylene to improve their bonding and mechanical properties (Vilaseca et al., 2008).

Another way to enhance the mechanical properties of cellulose fibre reinforced composite materials is to improve the bonding between a matrix and fibres by merging two processes together; pretreatment followed by using a coupling agent (Beckermann and Pickering, 2008). Beckermann and Pickering (2008) studied the effect of fibre treatment and the use of MAPP on the mechanical properties of hemp fibre reinforced polypropylene composites. Compared to composites with untreated hemp fibres, the mechanical properties of composites reinforced by treated fibres were found to improve significantly. In terms of thermal properties, the treated fibre reinforced composites began to degrade at ~240 °C, whereas the untreated fibre reinforced composites started to degrade at ~205 °C because of unstable components in the hemp fibres such as hemicelluloses and pectins.

**2.3.2 Elastic Deformation of Composites**

As mentioned before, the reinforcement is used to enhance the mechanical properties of the matrix (Hull and Clyne, 1996). Therefore, to study the elastic deformation of
composites, a composite reinforced by unidirectionally aligned continuous fibres is selected as a simple model (Figure 2.12a) (Hull and Clyne, 1996; Young and Lovell, 2011). It is assumed that the aligned fibres and matrix are equivalent to two slabs of materials perfectly bonded together, and the area fractions are equal to the volume fractions, as shown in Figure 2.12b (Hull and Clyne, 1996; Young and Lovell, 2011).

\[\text{Figure 2.12 Schematics of (a) an aligned continuous fibres reinforced composite and (b) a slab model of the matrix and fibre composite. Reproduced with modification from Hull and Clyne (1996).}\]

In order to estimate the Young’s modulus of a composite and to understand the way a composite behaves when it is deformed in different directions, two simple models: Voigt (axial deformation) and Reuss (transverse deformation), have been used (Gibson, 1994; Hull and Clyne, 1996; Daniel and Ishai, 2006; Young and Eichhorn, 2007; Young and Lovell, 2011), as shown in Figure 2.13.
When a composite is deformed in the axial direction, the two slabs, fibre and matrix phases, are constrained to be under the same strain (Figure 2.13a). The Young’s modulus of the composite $E_c$ for a uniform strain is written as (Gibson, 1994; Hull and Clyne, 1996; Daniel and Ishai, 2006; Young and Lovell, 2011)

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

This equation is sometimes called “Rule of Mixtures” (Young and Lovell, 2011).

On the other hand, when the composite is deformed in a transverse direction to the fibre axis the stress is constant, while the matrix and fibre strains in the transverse direction are different (Figure 2.13b). Hence, the composite modulus $E_c$ is given by (Gibson, 1994; Hull and Clyne, 1996; Daniel and Ishai, 2006; Young and Lovell, 2011)

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

where $E$ and $V$ are the Young’s modulus and the volume fraction and subscripts $f$, $m$ and $c$ refer to fibre, matrix and composite respectively.
2.3.3 Stress Transfer in Composites

This section contains information from Piggott (1980), Gibson (1994), McCrum et al. (1997) and Young and Lovell (2011). In the case of discontinuous fibre reinforced composites, stress transfer between the matrix and fibre occurs through interfacial shear, which is the highest near the fibre ends (Figure 2.14). The axial stress in the fibre, however, is zero at the fibre ends, and reaches the maximum in the middle of the fibre.

![Schematic illustration of a discontinuous fibre composite before and after deformation](image)

Figure 2.14 Schematic illustration of a discontinuous fibre composite before and after deformation. Reproduced with modification from Piggott (1980) and Gibson (1994).

The behaviour of the short fibre reinforced composite can be explained using shear lag theory originally developed by Cox (1952). In this theory it is assumed that the fibre is a uniform cylinder, a fibre and matrix are elastically deformed, and the interface between a fibre and a matrix is perfectly bonded, as shown in Figure 2.15a. This results in stress being transferred from the matrix to the fibre without yielding and slippage.
According to Figure 2.15b, owing to the force balance acting on the element on the fibre in the length of $dx$, the force due to the tensile stress $\sigma_t$ in the fibre is equal to the force due to the shear stress $\tau_i$ at the interface (Piggott, 1980; Gibson, 1994; Hull and Clyne, 1996; Young and Lovell, 2011). So that

$$2\pi \tau_i dx = -\pi \tau_i^2 d\sigma_t$$  \hspace{1cm} (2.3)$$

Rearranging Equation 2.3 this becomes

$$\frac{d\sigma_t}{dx} = -\frac{2\tau_i}{r}$$  \hspace{1cm} (2.4)$$
The stress distribution in a discontinuous fibre $\sigma_i$ in a matrix can be determined using the shear lag analysis by Cox (1952). In the model the fibre of a diameter of $2r$ is surrounded by a cylinder of a matrix of a radius of $\rho$ shown in Figure 2.15a. It is assumed that the shear force per unit length carried by the matrix cylinder surface is transmitted to the surface of the fibre. The shear stress $\tau$ at radius $\rho$, therefore, is given by

$$2\pi \rho \tau = 2\pi r \tau_i$$ \hspace{1cm} (2.5)

and so

$$\tau = \left( \frac{r}{\rho} \right) \tau_i$$ \hspace{1cm} (2.6)

If the matrix displacement in the fibre direction at a radius of $\rho$ is $u$, the shear strain $\gamma$ in the cylinder of matrix yields

$$\gamma = \frac{du}{d\rho}$$ \hspace{1cm} (2.7)

The shear modulus of the matrix, $G_m$, is $\tau / \gamma$. Therefore,

$$\frac{du}{d\rho} = \frac{\tau}{G_m}$$ \hspace{1cm} (2.8)

Substituting Equation 2.6, this becomes

$$\frac{du}{d\rho} = \frac{\tau_i \left( \frac{r}{\rho} \right)}{G_m}$$ \hspace{1cm} (2.9)
This equation is integrated as a function of \( \rho \) from the fibre surface at \( \rho = r \) where \( u = u_f \) to the surface of the cylinder of the matrix at \( \rho = R \) where \( u = u_R \)

\[
 u_R - u_f = \left( \frac{r \tau_i}{G_m} \right) \ln \left( \frac{R}{r} \right) \tag{2.10}
\]

This can be rewritten as

\[
 \tau_i = \frac{G_m (u_R - u_f)}{r \ln \left( \frac{R}{r} \right)} \tag{2.11}
\]

Substituting Equation 2.4 and rearranging provides

\[
 \frac{d \sigma_i}{dx} = - \frac{2G_m (u_R - u_f)}{r^2 \ln \left( \frac{R}{r} \right)} \tag{2.12}
\]

The displacements \((u_R \text{ and } u_f)\) can be converted into strain because the fibre strain \( \varepsilon_f \) and matrix strain \( \varepsilon_m \) are \( du_f/dx \) and \( du_R/dx \) respectively. Then, Equation 2.12 is differentiated with respect to \( x \), and is substituted by \( du_f/dx \) and \( du_R/dx \), which leads to

\[
 \frac{d^2 \sigma_i}{dx^2} = - \frac{2G_m (\varepsilon_f - \varepsilon_m)}{r^2 \ln \left( \frac{R}{r} \right)} \tag{2.13}
\]

\( E_i \) is multiplied through

\[
 \frac{d^2 \sigma_i}{dx^2} = - \frac{2G_m (E_i \varepsilon_f - E_i \varepsilon_m)}{r^2 E_i \ln \left( \frac{R}{r} \right)} \tag{2.14}
\]
This can be rewritten

$$\frac{d^2 \sigma_t}{dx^2} = -\frac{n^2}{r^2} \left( \sigma_t - E_f \varepsilon_m \right)$$  \hspace{1cm} (2.15)$$

where $n$ is a dimensionless constant given by

$$n = \sqrt{\frac{2G_m}{E_f \ln(R/r)}}$$  \hspace{1cm} (2.16)$$

Equation 2.15 has the solution

$$\sigma_t = E_f \varepsilon_m + C \sinh\left( \frac{nx}{r} \right) + D \cosh\left( \frac{nx}{r} \right)$$  \hspace{1cm} (2.17)$$

where $C$ and $D$ are constants of integration. It is assumed that no stress is transferred to the fibre across fibre ends. Therefore, $\sigma_t = 0$ at the fibre ends ($x = \pm L/2$) where $L$ is the length of the fibre. The constants $C$ and $D$ using the boundary conditions can be determined to provide the final equation of the stress distribution along the length of the fibre

$$\sigma_t = E_f \varepsilon_m \left[ 1 - \frac{\cosh(nx/r)}{\cosh(nL/2r)} \right]$$  \hspace{1cm} (2.18)$$

The equation can be rewritten as

$$\sigma_t = E_f \varepsilon_m \left[ 1 - \frac{\cosh(ns2x/L)}{\cosh(ns)} \right]$$  \hspace{1cm} (2.19)$$

where $E_f$ is the Young’s modulus of the fibre, $\varepsilon_m$ is the strain of the matrix, $x$ is the distance along the fibre, $r$ is fibre radius and $s$ is the aspect ratio, $L/2r$. 

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The interfacial shear stress $\tau_i$ determined using Equations 2.4 and 2.19 is given as

$$\tau_i = \frac{nE_i\varepsilon_m}{2} \left[ \frac{\sinh \left( \frac{nsL}{L} \right)}{\cosh(ns)} \right]$$ (2.20)

Figure 2.16 shows the variations in the fibre stress and interfacial shear stress distributions along the length of the fibre with three different values of the product $ns$ using Equations 2.19 and 2.20.

It can be clearly seen that the tensile stress is zero at the fibre ends and a maximum in the centre, as shown in Figure 2.16a. The interfacial shear stress, on the other hand, is zero in the centre and at a maximum at the fibre ends (Figure 2.16b) (Gibson, 1994; Hull and Clyne, 1996; Young and Lovell, 2011). When the value of $ns$ increases the aspect ratio is higher, allowing the reinforcement to be more efficient. This is due to the fact that when the fibre is long enough, the stress is gradually increased, and reaches the maximum when the strain of the fibre is equal to that of the matrix. This is similar to the stress in continuous fibre reinforced composites (Hull and Clyne, 1996; Young and Lovell, 2011), as mentioned earlier in Chapter 2.3.2.
Figure 2.16 Distributions of the (a) fibre stress and (b) interfacial shear stress with respect to distance along the discontinuous fibre in the matrix calculated with the different values of $n_s$ (2, 5 and 20) indicated in each case using Equations 2.19 and 2.20. Reproduced from Young and Lovell (2011).

In discontinuous fibre reinforced composites the matrix transfers the external stress to the fibre. The fibre length, however, is a major impact on stress transfer. The dependence of the fibre length on the fibre stress and shear stress distributions was first studied by Kelly and Tyson (1965), as shown in Figure 2.17. According to the Kelly-Tyson model, the length of the fibre allowing the stress to reach the maximum $\sigma_f^*$, called the critical length $L_c$, is given as
where $r$ is a fibre radius, and $\tau_i$ is the interfacial shear stress of the matrix. When the fibre length $L$ is much larger than the critical length $L_c$, the majority of the load in the composite is carried by the fibre (Powell, 1983; Gibson, 1994).

2.3.4 Cellulose Nanocomposites

Nanocomposites are two-phase materials where one of these phases has at least one dimension on the nanometre scale ($10^{-9}$ m) (Young and Lovell, 2011). These composite materials tend to have superior physical and mechanical properties to typical composites (Oksman et al., 2006; Siro and Plackett, 2010). Cellulose nanocomposites can be prepared by many processing methods. Some of these methods are now introduced.
(a) Solution casting or solvent casting

Generally, for this processing route, cellulose nanofibres are dispersed in a medium such as water or organic solvents, and then this suspension is mixed with a polymer solution (Moon et al., 2011). The suspension is subsequently casted on a suitable place, and cellulose nanocomposite films are formed by evaporation of water or solvents.

(b) Melt compounding

This technique allows thermoplastic polymers to be used as a matrix such as poly(lactic acid), poly(vinyl alcohol), polyethylene, polypropylene, to name a few examples (Moon et al., 2011). Cellulose nanofibres are mixed with a thermoplastic polymer using compounding mixing, and then extrusion. Compression moulding or injection moulding are subsequently used to prepare specimens (Lee et al., 2011; Moon et al., 2011).

(c) Partial dissolution

Composites produced by this method are often called all-cellulose composites, or self-reinforced composites (Nishino et al., 2004; Gindl and Keckes, 2005; Soykeabkaew et al., 2009; Pullawan et al., 2010). Partial dissolution occurs by dispersing a cellulose source, such as cellulose fibres, microcrystalline cellulose or bacterial cellulose in a mixed solution of N,N-dimethylacetamide (DMAc) and lithium chloride (LiCl) for a specific time to dissolve the surface of cellulose to be a matrix phase reinforced by the remaining undissolved cellulose component (Nishino et al., 2004; Gindl and Keckes,
These composite materials show excellent interfacial compatibility because both matrix and reinforcing phases are cellulose (Gindl and Keckes, 2005; Soykeabkaew et al., 2009; Pullawan et al., 2010).

2.3.5 Microfibrillated Cellulose Nanocomposites

Due to the superior properties of MFC to natural fibres, as mentioned in Section 2.2, MFC has been used to prepare composite materials with a large number of polymers such as poly(vinyl alcohol) (PVA) (Cheng et al., 2007; Lu et al., 2008; Cheng et al., 2009), polyurethane (Seydibeyoglu and Oksman, 2008), phenol formaldehyde resin (Nakagaito and Yano, 2004), acrylic resin (Iwamoto et al., 2005; Iwamoto et al., 2007), to name a few examples. Specifically, the effect of MFC on the mechanical properties of thermoplastic polyurethane has been studied (Seydibeyoglu and Oksman, 2008). At a MFC content of 16.5 wt.%, the strength and stiffness of this composite were found to increase by ~500 % and 3,000 % respectively, compared to pure polyurethane. Also, Lu et al. (2008) found that MFC reinforced poly(vinyl alcohol) composites showed excellent mechanical properties and biodegradability. In addition, the bending strength of MFC reinforced phenol formaldehyde resin composites was found to increase by ~50 % compared to the pure resin (Nakagaito and Yano, 2004).

Lately, poly(lactic acid) (PLA), a biodegradable polymer, has attracted extensive attention due to problems over environmental waste. In this respect it has advantages over conventional oil-based polymers such as biodegradability. The mechanical properties and processing routes of PLA are similar to some conventional polyolefins (Oksman et al., 2006; Suryanegara et al., 2010). PLA is now commercially available by
many companies such as Mitsui Chemicals, Treofan, NatureWorks, Purac and Galactic (Avérous, 2008). For these reasons, PLA can be used as an alternative to produce green composites with MFC (Iwatake et al., 2008; Nakagaito et al., 2009; Siro and Plackett, 2010). Examples of MFC reinforced PLA composites prepared using different methods and their mechanical properties are reported in Table 2.5.

Table 2.5 Mechanical properties of PLA composites reinforced by MFC prepared by different techniques. Mechanical properties of neat PLA are provided in the brackets.

<table>
<thead>
<tr>
<th>Manufacturing process</th>
<th>MFC Content (wt.%)</th>
<th>σ (MPa)</th>
<th>ε (%)</th>
<th>E (GPa)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Premixing, kneading and compression moulding</td>
<td>10</td>
<td>75.0</td>
<td>2.2</td>
<td>4.7</td>
<td>(Iwatake et al., 2008)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(56.2)</td>
<td>(4.2)</td>
<td>(3.4)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>66.2</td>
<td>2.0</td>
<td>4.7</td>
<td>(Suryanegara et al., 2009)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(60.9)</td>
<td>(3.1)</td>
<td>(4.0)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>69.4</td>
<td>1.7</td>
<td>5.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(60.9)</td>
<td>(3.1)</td>
<td>(4.0)</td>
<td></td>
</tr>
</tbody>
</table>

MFC was premixed with PLA in a mixture of acetone and water. After PLA had been completely dissolved, this suspension was evaporated at 70 °C. The remaining part (MFC and PLA) was subsequently blended by a twin rotary roller mixer. The blend was cut into pieces, and compression moulding was applied to prepare composite sheets. PLA composites reinforced by 10 wt.% MFC were observed to show the highest mechanical properties. Young’s modulus and strength of this composite were found to
increase by 38 and 33 % respectively, compared to pure PLA. When adding more than 10 wt.%, the mechanical properties of the composites, however, decreased due to the agglomeration of MFC (Iwatake et al., 2008).

Later, Suryanegara et al. (2009) used a similar procedure to Iwatake et al. (2008) to prepare MFC reinforced PLA composites. MFC was first stirred in a mixture of water and acetone. The liquid phase was subsequently solvent exchanged from a mixture of water and acetone to acetone. Again, the acetone was removed, and subsequently replaced by dichloromethane. PLA was then gradually added to this suspension and stirred for 2 hr until the PLA had completely dissolved. After the solvent was totally evaporated, the mixture of PLA and MFC was blended using a twin rotary roller mixer. The compound was cut into pieces, and compression moulding was applied to prepare composite sheets. Subsequently, samples were annealed at 100 °C for 60 min to obtain highly crystallised materials. It was found that adding 20 wt.% MFC to the PLA matrix improved the Young’s modulus and tensile strength by 57 % and 20 % respectively, compared to annealed PLA. The strain at break, however, decreased from 7 % to 2 %. This improvement in the mechanical properties (Young’s modulus and tensile strength) of the composites was thought to be due to the stress transfer from the polymer matrix to the stiff fibrous reinforcement of MFC and the high degree of crystallinity of these composite materials.

No improvement of the mechanical properties of PLA composites reinforced by 10 wt.% MFC using directly compounding, however, was observed, compared to pure PLA matrix (Iwatake et al., 2008). This is due to the agglomeration of MFC in the composites.
2.4 INTRODUCTION TO RAMAN SPECTROSCOPY

When electromagnetic radiation interacts with a sample, changes in vibrational energy states can be detected by infrared spectroscopy (IR) or Raman spectroscopy (Campbell and White, 1989; Young and Lovell, 2011). These two techniques, however, detect different effects concerning the interaction of electromagnetic radiation with molecules. For IR spectroscopy, the energy absorption of infrared light by a sample is detected as a function of frequency. A change in an induced polarisability of the bond vibration, on the other hand, is required for Raman spectroscopy (Campbell and White, 1989; Young and Lovell, 2011).

2.4.1 Historical Background of Raman Spectroscopy

The Raman effect was first discovered in 1928 by Raman and Krishnan (1928). They discovered a new type of light scattering by using sunlight as a light source. A beam of sunlight was passed through filters, and focused on different kinds of liquids such as water, alcohol, ketone and acetaldehyde and vapours i.e. ether (Raman and Krishnan, 1928). Colour changes in the scattered light were observed by eyes (Raman and Krishnan, 1928). The long exposure time, however, was needed to be used in this case because the Raman effect is inherently weak (only 1 in $10^8$ of the intensity of the incident scattered radiation) (Campbell and White, 1989; Gardiner, 1989).

Even though the first Raman spectrum of a polymer, polystyrene, was obtained in 1932 (Signer and Weiler, 1932), Raman spectroscopy was not initially widely used, due to the lack of instrumental developments, which came later, such as laser sources. In the
early 1960s, powerful laser sources were invented, making Raman spectroscopy available to detect spectra from small samples. Later, a large number of instruments such as detectors, filters and microelectronics were developed. These allows the recording of Raman spectra in microseconds (Gardiner, 1989; Turrell, 1996).

Raman spectroscopy is now used in a wide variety of applications such as the characterisation of materials, the study of polymer structure and the monitor of deformation micromechanics of polymers and composites (Campbell and White, 1989; Young and Eichhorn, 2007)

### 2.4.2 Classical Theory of Raman Scattering

This section contains information taken from Gardiner (1989), Ferraro and Nakamoto (1994), Koenig (1999) and McCreery (2000). The classical description of Raman scattering illustrated in Figure 2.1, and can be explained as follows.

As a molecule is placed in an electric field of the incoming light, its electron orbits within the molecule are perturbed with the same frequency ($\nu_0$) as the electric field of the incident light, resulting in an induced dipole moment.
Figure 2.18 Polarisation induced in a molecule by an electric field. Scattering may occur in various directions (90° and 180° scatterings are only shown). Reproduced with modification from McCreery (2000).

This induced dipole moment radiates scattered light with or without exchanging energy with vibrations in the molecule. The strength of the induced polarisation $\vec{P}$ is given by the equation

$$\vec{P} = \alpha_m \vec{E}$$  \hspace{1cm} (2.22)

where $\alpha_m$ is the polarisability of the molecule, and $\vec{E}$ is the electric field strength of the electromagnetic wave (laser beam). The polarisability is a material property depending on the molecular structure and the nature of the bonds.

When the electric field of the electromagnetic wave interacts with the molecule, the electric field and the dipole moment in the molecule oscillate. This fluctuating dipole moment emits radiation in all directions. The electric field is an oscillating function,
which depends on the frequency of the laser light, $v_0$, and time, $t$, according to the equation

$$\tilde{E} = E_0 \cos(2\pi v_0 t) \quad (2.23)$$

where $E_0$ is the equilibrium field strength.

If the molecule vibrates with a frequency of $v_m$, the displacement of the atoms at their equilibrium position with vibrational mode, $q$, at time $t$ can be expressed as

$$q = q_0 \cos(2\pi v_m t) \quad (2.24)$$

where $q_0$ is the maximum displacement at the equilibrium position.

If the polarisability of electrons in the molecule, $\alpha_m$, changes during the vibration, for a small vibrational displacement its value can be written as

$$\alpha_m = \alpha_0 + \left( \frac{\partial \alpha_m}{\partial q} \right)_0 q \quad (2.25)$$

where $\alpha_0$ is the polarisability of the molecular mode at the equilibrium position, and $(\partial \alpha_m / \partial q)_0$ is the rate of change of polarisability as a function of the change in $q$, evaluated at the equilibrium position.

Substitution of Equation 2.24 into Equation 2.25 leads to

$$\alpha_m = \alpha_0 + \left( \frac{\partial \alpha_m}{\partial q} \right)_0 q_0 \cos(2\pi v_m t) \quad (2.26)$$
Substitution of Equations 2.23 and 2.26 into Equation 2.22 yields

\[ \tilde{P} = \alpha_0 E_0 \cos(2\pi v_0 t) + \left( \frac{\partial \alpha_m}{\partial q} \right)_0 q_0 E_0 \cos(2\pi v_0 t) \cos(2\pi v_m t) \] (2.27)

From basic trigonometry, \( \cos a \cos b = [\cos(a + b) + \cos(a - b)]/2 \), this equation can be rewritten as

\[ \tilde{P} = \alpha_0 E_0 \cos(2\pi v_0 t) + \frac{1}{2} \left( \frac{\partial \alpha_m}{\partial q} \right)_0 q_0 E_0 [\cos(2\pi(v_0 + v_m) t) + \cos(2\pi(v_0 - v_m) t)] \] (2.28)

This equation demonstrates that the light is scattered with three different components.

1) Rayleigh scattering has the same frequency as the incoming radiation, meaning the energy of the molecule before and after the collision remains constant.

2) Stokes Raman scattering can be found when the scattered light has a frequency of \( v_0 - v_m \).

3) Anti-stokes Raman scattering occurs when the scattered light has a higher frequency \( (v_0 + v_m) \) than the incident light.

It is worth noting that if a change of polarisability of a molecule occurs, \( (\frac{\partial \alpha_m}{\partial q})_0 \neq 0 \), Raman vibrations are shifted to a higher or lower frequency than \( v_0 \). If the rate of change of polarisability as a function of displacement \( (\frac{\partial \alpha_m}{\partial q})_0 \), however, is zero, no Raman vibrations are observed.
Figure 2.19 shows the electronic transitions required for Rayleigh, Stokes and anti-Stokes scattering, where \( v = 0 \) represents the ground state, and \( v = 1 \) and \( 2 \) are the excited vibrational states.

Figure 2.19  Electronic transitions for Rayleigh and Raman scattering events. Reproduced with modification from Gardiner (1989).

2.4.3 Polarised Raman Spectroscopy

Molecular orientation of polymer chains or cellulose molecular chains can be obtained from the intensity of Raman scattering (Bower, 1972; Sturcova et al., 2005; Tanaka and Young, 2006). The intensity of Raman scattering \( I \) is given by

\[
I \propto \cos^2 \phi
\]  

(2.29)

where \( \phi \) is the angle between the molecular chain axis and the direction of polarisation of the incident light.
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When the polarised incident light and Raman scattering light are parallel (the VV polarisation configuration is used), the dependence of intensity of Raman scattering is found to be (Gommans et al., 2000; Kannan et al., 2007; Rusli, 2011)

\[ I \propto \cos^4 \phi \]  

(2.30)

The strong intensity of a Raman band is obtained when the molecular chain axis within a sample is parallel to the incident light direction (Kong, 2007).

However, when the polarisation direction of Raman scattering is perpendicular to the polarised incident light axis (the VH polarisation configuration is applied), the intensity is given by (Gommans et al., 2000; Kannan et al., 2007)

\[ I \propto \cos^2 \phi \sin^2 \phi \]  

(2.31)

The use of Raman spectroscopy with the VV and VH polarisation configurations to investigate molecular orientation in cellulose and cellulose nanocomposites is discussed in the following section.

2.4.4 Application of Raman Spectroscopy to Cellulosic Materials

Wiley and Atalla (1987) investigated the relationship between intensities of the Raman bands of two different types of native cellulosics: namely Valonia and ramie fibres, as a function of the polarisation of the incident and scattering light using Raman spectroscopy. The band intensities were found to depend on the directions of the vibrational motions in the cellulose fibres. Band assignments for Raman spectra of Valonia and ramie fibres are shown in Table 2.6.
Table 2.6 Band assignments for Raman spectra obtained from Valonia and ramie fibres. Reproduced from Wiley and Atalla (1987).

<table>
<thead>
<tr>
<th>Raman band (cm^{-1})</th>
<th>Valonia</th>
<th>Ramie</th>
<th>Vibrational mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>331</td>
<td>331</td>
<td></td>
<td>Heavy atom bending</td>
</tr>
<tr>
<td>344</td>
<td>344</td>
<td></td>
<td>Heavy atom bending</td>
</tr>
<tr>
<td>381</td>
<td>380</td>
<td></td>
<td>Heavy atom bending</td>
</tr>
<tr>
<td>437</td>
<td>437</td>
<td></td>
<td>Heavy atom bending</td>
</tr>
<tr>
<td>459</td>
<td>458</td>
<td></td>
<td>Heavy atom bending</td>
</tr>
<tr>
<td>520</td>
<td>519</td>
<td></td>
<td>Heavy atom bending</td>
</tr>
<tr>
<td>913</td>
<td>910</td>
<td></td>
<td>HCC and HCO bending at C6</td>
</tr>
<tr>
<td>968</td>
<td>969</td>
<td></td>
<td>Heavy atom (CC and CO)</td>
</tr>
<tr>
<td>997</td>
<td>995</td>
<td></td>
<td>Stretching</td>
</tr>
<tr>
<td>1034</td>
<td>1037</td>
<td></td>
<td>Stretching</td>
</tr>
<tr>
<td>1057</td>
<td>1057</td>
<td></td>
<td>Stretching</td>
</tr>
<tr>
<td>1095</td>
<td>1095</td>
<td></td>
<td>Stretching</td>
</tr>
<tr>
<td>1118</td>
<td>1117</td>
<td></td>
<td>Stretching</td>
</tr>
<tr>
<td>1123</td>
<td>1121</td>
<td></td>
<td>Stretching</td>
</tr>
<tr>
<td>1152</td>
<td>1151</td>
<td></td>
<td>Heavy atom stretching and HCC and HCO bending</td>
</tr>
<tr>
<td>1279</td>
<td>1275</td>
<td></td>
<td>HCC and HCO bending</td>
</tr>
<tr>
<td>1292</td>
<td>1291</td>
<td></td>
<td>HCC and HCO bending</td>
</tr>
<tr>
<td>1334</td>
<td>1331</td>
<td></td>
<td>HCC and HCO bending</td>
</tr>
<tr>
<td>1337</td>
<td>1337</td>
<td></td>
<td>HCC, HCO and HOC bending</td>
</tr>
<tr>
<td>1378</td>
<td>1378</td>
<td></td>
<td>HCC, HCO and HOC bending</td>
</tr>
<tr>
<td>1406</td>
<td>1407</td>
<td></td>
<td>HCC, HCO and HOC bending</td>
</tr>
<tr>
<td>1455</td>
<td>1456</td>
<td></td>
<td>HCH and HOC bending</td>
</tr>
<tr>
<td>1477</td>
<td>1475</td>
<td></td>
<td>HCH and HOC bending</td>
</tr>
<tr>
<td>2868</td>
<td>2866</td>
<td></td>
<td>CH and CH\textsubscript{2} stretching</td>
</tr>
<tr>
<td>2885</td>
<td>2889</td>
<td></td>
<td>CH and CH\textsubscript{2} stretching</td>
</tr>
<tr>
<td>2941</td>
<td>2943</td>
<td></td>
<td>CH and CH\textsubscript{2} stretching</td>
</tr>
<tr>
<td>2965</td>
<td>2963</td>
<td></td>
<td>CH and CH\textsubscript{2} stretching</td>
</tr>
<tr>
<td>3291</td>
<td>3286</td>
<td></td>
<td>OH stretching</td>
</tr>
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<td>3334</td>
<td>3335</td>
<td></td>
<td>OH stretching</td>
</tr>
<tr>
<td>3361</td>
<td>3363</td>
<td></td>
<td>OH stretching</td>
</tr>
<tr>
<td>3395</td>
<td>3402</td>
<td></td>
<td>OH stretching</td>
</tr>
</tbody>
</table>
Raman spectroscopy has been used extensively to study the molecular deformation of different types of cellulose, such as natural and regenerated cellulose fibres, wood, paper and nanocellulose materials such as cellulose nanowhiskers and bacterial cellulose (Eichhorn et al., 2001; Eichhorn and Young, 2001; Kong and Eichhorn, 2005; Sturcova et al., 2005; Gierlinger et al., 2006; Hsieh et al., 2008; Bakri and Eichhorn, 2010). When cellulose materials are subjected to tensile deformation, the position of a Raman band initially located at ~1095 cm\(^{-1}\), corresponding to the C-O ring stretching mode within the backbone of cellulose structure (Eichhorn et al., 2001; Eichhorn and Young, 2003) and possibly the glycosidic C-O-C stretching mode (Gierlinger et al., 2006), is monitored. This Raman band has been reported to shift towards a lower wavenumber, which is thought to be due to molecular deformation (Eichhorn and Young, 2001; Eichhorn et al., 2001; Kong and Eichhorn, 2005; Sturcova et al., 2005).

The cause of Raman bands shifts upon the application of deformation on materials has been reviewed by Tashiro (1993) and Young et al. (1995). When a sample is subjected to tensile deformation, the interatomic separation distance is increased, resulting in the decrease of the force constant of the vibration. This results in a shift of the vibrational mode to a lower frequency, because the Raman wavenumber is proportional to the force constant of the vibration (Young et al., 1995).

Eichhorn et al. (2001) studied the deformation mechanisms of several types of natural and regenerated cellulose fibres using Raman spectroscopy. The Raman peak initially located at ~1095 cm\(^{-1}\) for all types of fibres shifted approximately linearly towards a lower wavenumber when fibres were deformed. The Raman band shifts with respect to strain for different types of cellulose fibres were found to vary. The stress sensitivity of
the Raman band for all types of fibres, however, was found to be similar with a value of \(-4.5 \pm 0.1 \text{ cm}^{-1} \text{ GPa}^{-1}\). This means that the Raman band shift as a function of stress for the fibres is invariant.

A study conducted by Gierlinger et al. (2006) investigated the molecular deformation of spruce latewood fibres during tensile deformation using Raman spectroscopy. Raman spectra of wood were found to be complex due to the multicomponent nature of the material, combining cellulose, lignin and hemicelluloses. The main Raman peaks normally come from cellulose and lignin, while hemicelluloses have a smaller contribution. The Raman spectra of spruce latewood fibres showed two dominant peaks located at \(~1097\) and \(~1602\) cm\(^{-1}\), corresponding to C-C and C-O stretching of cellulose and the aryl stretching of lignin respectively. During tensile deformation, the Raman band peak located at \(~1097\) cm\(^{-1}\) was found to shift towards a lower wavenumber, and return back to its original position after the fibres failed. This was an indication of the elastic nature of the deformation. In contrast, the band at \(~1602\) cm\(^{-1}\) was found to be constant in position with the application of deformation. This may be because lignin serves as a low modulus, non load-bearing amorphous polymer. Therefore, the position of the Raman band initially located at \(~1097\) cm\(^{-1}\) was chosen to monitor molecular changes in this cellulose fibre.

Recently, Quero et al. (2011) studied the influence of glyoxalisation treatment on the molecular deformation of bacterial cellulose (BC) networks. Glyoxalisation treatment was used to crosslink cellulose chains of BC with covalent bonds. The stress-transfer mechanisms of unmodified and glyoxalised BC networks in the dry and wet condition were revealed by Raman spectroscopy. The glyoxalised BC networks showed a higher
stress transfer efficiency in both the dry and wet states compared to unmodified BC networks. This is thought to be due to the effect of glyoxalisation treatment on the mechanical properties of BC networks.

Moreover, the molecular orientation of cellulose chains within fibres has been monitored by Raman spectroscopy. The intensity of Raman bands of celluloses has been shown to depend on the angle between the incident light direction and the molecular chain axis (Wiley and Atalla, 1987). This method has been used to investigate the orientation of cellulose chains within fibres such as flax, celery and coir fibres (Bakri and Eichhorn, 2010) by recording the intensity of the Raman band initially located at ~1095 cm\(^{-1}\), associated with the backbone structure of cellulose as a function of the angle between the incident light direction and the cellulose molecular chain axis. Also, the orientation of cellulose molecules within nanocellulose materials such as cellulose nanowhiskers (Sturcova et al., 2005; Rusli et al., 2010) and bacterial cellulose (Hsieh et al., 2008) and composite materials reinforced with nanocellulose materials has been studied using this method.

Likewise, Raman spectroscopy has been applied to obtain the stiffness of single fibrils of nanocellulose materials, for instance bacterial cellulose (Hsieh et al., 2008) and cellulose nanowhiskers prepared from tunicate and cotton sources (Sturcova et al., 2005; Rusli and Eichhorn, 2008). The effective Young’s modulus of single fibrils of these cellulose materials can be estimated using the Raman band shift in the peak position initially located at ~1095 cm\(^{-1}\) with the following method.

First, the modulus of a network of nanofibres \(E_{\text{network}}\) is determined from the equation (Eichhorn and Young, 2001; Sturcova et al., 2005)
\[ E_{\text{network}} = \frac{d\sigma}{d\epsilon} = \left( \frac{d\sigma}{d(\Delta \nu)} \right) \times \left( \frac{d(\Delta \nu)}{d\epsilon} \right) \]  

(2.32)

Therefore,

\[ E_{\text{network}} = \left( \frac{\frac{d(\Delta \nu)}{d\epsilon}}{\frac{d(\Delta \nu)}{d\sigma}} \right) \]  

(2.33)

where \( \frac{d(\Delta \nu)}{d\epsilon} \) is the Raman band shift rate with respect to strain obtained from cellulose samples. A value of -4.3 cm\(^{-1}\) GPa\(^{-1}\) for the Raman shift rate as a function of tensile strain, \( \frac{d(\Delta \nu)}{d\sigma} \), determined from a number of cellulose fibrils (Eichhorn et al., 2001), has been used.

In order to estimate the effective Young’s modulus of a single filament of bacterial cellulose and a single nanowhisker, \( E_{\text{fibril}} \), the equation is given as

\[ E_{\text{network}} = \eta_0 E_{\text{fibril}} \]  

(2.34)

where \( \eta_0 \) is an efficiency factor developed by Krenchel (1964). This factor has the values of 3/8 for a two-dimensional (2D) in-plane random network and 1/5 for a three-dimensional (3D) network.

According to these two equations, a value of \(~114\) GPa for the modulus of a single fibril of bacterial cellulose was obtained (Hsieh et al., 2008), and the modulus of a single whisker extracted from tunicates was found to be \(~143\) GPa (Sturcova et al., 2005). This value is close to a value of 138 GPa which has been reported for the crystal modulus of cellulose-I determined by an X-ray diffraction method (Sakurada et al.,...
A single whisker from cotton, however, showed a lower value of Young’s modulus of 57 GPa (Rusli and Eichhorn, 2008). This was thought to possibly be due to its lower aspect ratio (Rusli and Eichhorn, 2008).

2.4.5 Application of Raman Spectroscopy on Cellulose Reinforced Nanocomposites

Cellulose nanocomposites have attracted much attention due to their potentially high mechanical performance (Nakagaito and Yano, 2005; Nakagaito et al., 2009; Quero et al., 2010). In order to better understand the molecular deformation of cellulose based nanocomposites, and the interfacial behaviour between the matrix and reinforcement phases, Raman spectroscopy has been applied.

The use of Raman spectroscopy to understand the stress transfer mechanisms in bacterial cellulose (BC)/ poly(L-lactic acid) laminated composites was reported by Quero et al. (2010). In this work, BC networks with two different culturing times (3 and 6 days) were used as reinforcements for composites. Higher mechanical properties of BC networks cultured for 6 days were reported, compared to BC networks cultured for 3 days. However, the specific Young’s moduli (Young’s modulus divided by density) for both networks were found to be similar. The Raman band initially located at ~1095 cm\(^{-1}\) from cellulose within the BC/PLLA composites was detected, making it possible to follow the stress transfer process in the composites. Higher Raman band shifts as a function of strain and stress were observed from both PLLA composites reinforced with BC networks cultured for 3 and 6 days, compared to pure BC networks, indicating the stress transfer efficiency in these composites.
Raman spectroscopy has also been used to monitor the deformation of all-cellulose nanocomposites (Pullawan et al., 2010). All-cellulose nanocomposites were produced by dispersing cellulose nanowhiskers (CNWs) used as a reinforcement into dissolved microcrystalline cellulose matrix (MCC), as mentioned earlier in Chapter 2.3.4. Even though both reinforcement and matrix phases of these all-cellulose nanocomposites were derived from cellulose, it was possible to distinguish the stress transfer in this composite using Raman spectroscopy. CNWs only exhibited a dominant peak initially located at ~1095 cm\(^{-1}\); however, the pure matrix exhibited peaks located at both ~895 and ~1095 cm\(^{-1}\). As the volume fraction of CNWs in the composites increased, the shifts in the position of the Raman band initially located at ~1095 cm\(^{-1}\) as a function of tensile strain were found to be greater, indicating an increase in the stress-transfer efficiency from the matrix to the reinforcement phase. A value of the shift of the Raman band initially located at ~895 cm\(^{-1}\) with respect to strain for the pure matrix, on the other hand, was found to be similar for all nanocomposites with different volume fractions of CNWs. This proved that even though the stress-transfer process occurred within the matrix, the enhancement of the mechanical properties of these nanocomposites resulted from the addition of CNWs.

Subsequently, the molecular deformation of 0.7% volume fraction of cellulose nanowhiskers embedded in epoxy resin using Raman spectroscopy was reported (Rusli et al., 2011). Three types of cellulose nanowhiskers: tunicate nanowhiskers prepared by sulphuric acid hydrolysis and cotton nanowhiskers prepared by sulphuric acid hydrolysis or hydrochloric acid hydrolysis, were studied. A value of ~76 for the aspect ratio of tunicate nanowhiskers was found to be much greater compared to that of ~19 for cotton nanowhiskers. The Raman band initially located at ~1095 cm\(^{-1}\) can be
detected from all three types of cellulose nanowhiskers in the composites. This Raman band position obtained from composites reinforced by both tunicate and cotton nanowhiskers prepared by sulphuric acid hydrolysis was observed to shift towards a lower wavenumber during the tensile deformation. This was an indication of the direct deformation along the cellulose backbone structure. However, the shift of this Raman band obtained from the composites reinforced with cotton nanowhiskers produced by hydrochloric acid hydrolysis was not observable. This was thought to be because of their aggregation, as supported by AFM images.

2.5 REFERENCES


CHAPTER 3

EXPERIMENTAL METHODOLOGY

The details of materials used in this study and the methods used to prepare microfibrillated cellulose networks and composites are provided in this chapter. Also, the techniques used to characterise the physical and mechanical properties of MFC networks and composites are included.

3.1 MATERIALS

Commercial bleached sulfite softwood cellulose pulp (Domsjö ECO Bright, Domsjö Fabriker AB, Sweden) consisting of 40% pine (*Pinus sylvestris*) and 60% spruce (*Picea abies*) with a hemicellulose content of 14% and a lignin content of 1% was used as the source for a cellulose-I derived MFC to produce networks of MFC which are subsequently called MFC-A, MFC-B and MFC-C. These data were obtained from the pulp supplier.
Lyocell fibres, produced using a draw ratio (take-up speed/dope speed) of 8.9 (trade name Tencel®), were provided by Lenzing AG, Austria, and used as a raw material to produce a cellulose-II derived MFC.

Poly(lactic acid) (PLA), PLA 4042D, purchased from NatureWorks LLC., was used as a matrix to prepare MFC reinforced PLA composite materials. The density of this matrix material was 1.24 g cm$^{-3}$. Its glass transition temperature ($T_g$) was 52 - 58 °C, and its melting temperature ($T_m$) was 150 °C, as reported by the material supplier.

3.2 PREPARATION OF MICROFIBRILLATED CELLULOSE NETWORKS FROM PULP

Three different types of MFC networks were produced by Prof. Lindström’s group at Innventia AB (Stockholm, Sweden), which are subsequently labelled MFC-A, MFC-B and MFC-C. Before use, sulfite softwood cellulose pulp was thoroughly washed with deionised water. Figure 3.1 shows the diagrams of the preparation of MFC-A, MFC-B and MFC-C networks.
MFC-A networks were prepared using the following process, which has been described elsewhere (Pääkkö et al., 2007). MFC gel was prepared in four steps; a refining step, an enzymatic pretreatment, a second refining step and a high pressure homogeniser treatment, as shown schematically in Figure 3.1. Firstly, a 4 wt.% pulp suspension was passed through a refiner (Angle Refiner R1L, Escher-Wyss) with power/mass ratio of 33 kWh tonne\(^{-1}\), and this was followed by the enzymatic pretreatment. 100 g of the refined pulp was dispersed in 2.5 l of phosphate buffer with 0.17 μl of monocomponent endoglucanases per gram of fibre at 50 °C for 2 h. Then, the treated pulp suspension was washed with deionised water, and monocomponent endoglucanases were denatured.
at 80 °C for 30 min. After this, the enzyme-treated pulp was further washed with deionised water. The enzyme-treated pulp was subsequently refined with the Escher-Wyss refiner. To prevent bacterial growth in the slurry, 0.4 µl ml⁻¹ of microbicide (5-chloro-2-methyl-4-isothiazolin-3-one) was added to the suspension. Then, a 2 wt.% enzyme-treated pulp fibre slurry was passed through a high-pressure fluidiser (Microfluidiser M-110EH, Microfluidics Corp.) equipped with two chambers of different sizes connected in series, as shown in Figure 3.2. This slurry passed through the first chamber with a diameter of 400 µm, and then the second chamber with a diameter of 200 µm, three times. This was followed by five times through a chamber pair with diameters of 200 µm and 100 µm for the first and second chambers respectively. After this process, MFC networks were prepared. A 2 wt.% MFC suspension was prepared, and the suspension was then mixed using a propeller mixer and an ultrasound bath (Branson 5510, Branson Ultrasonics, USA). The suspension was then filtered on a Durapore membrane (0.65 micrometre Durapore DVPP, Millipore, USA). The filtered network was subsequently dried under restraint using drying frames at 50 °C in an oven.

MFC-B and MFC-C networks were manufactured using the same commercial sulfite softwood dissolving pulp as above, and produced using a similar process to MFC-A networks but using the carboxymethylation pretreatment (Figure 3.1b) according to the procedure which has been described in detail by Wågberg et al. (2008). 110 g of pulp was first washed with deionised water, and then followed by ethanol for four times. The pulp was dispersed in a solution of 10 g of monochloroacetic acid and 500 ml of isopropanol for 30 min, and transferred into a solution of 16.2 g of sodium hydroxide (NaOH) in 500 ml of methanol mixed with 2 l of isopropanol. This carboxymethylation
reaction was continued for 1 h. Then, the treated fibres were filtered, and washed in three steps: 20 l of deionised water, 2 l of acetic acid (0.1 M) and 10 l of deionised water respectively. After these steps, in order to convert the carboxyl groups to the sodium form, the fibres were washed with 2 l of sodium bicarbonate (NaHCO₃) solution (4 wt.% solution) for 60 min, followed by washing with 15 l of deionised water. After the pretreatment, the 2 wt.% treated fibres suspension were passed through a high-pressure fluidiser (Microfluidiser M-110EH, Microfluidics Corp.) equipped with two chambers with diameters of 200 µm and 100 µm connected in series for 1 time and 4 times to produce MFC-B and MFC-C respectively. Finally, MFC-B and MFC-C networks were prepared as the same as MFC-A networks. The densities of MFC-A, MFC-B and MFC-C networks were determined from their dimensions and weights.

![Figure 3.2](image.png)

**Figure 3.2** Schematic illustration of a microfluidiser equipped with two chambers connected in series. Reproduced with modification from Lee et al. (2009).
3.3 PREPARATION OF MICROFIBRILLATED CELLULOSE NETWORKS FROM LYOCELL FIBRES

The chopped Lyocell fibres of length of ~10 mm were soaked in distilled water to a fibre content of 1 wt.% for 24 h prior to mechanical treatment. These suspensions were treated using a homogeniser (ULTRA-TURRAX TP18/2K, Janke & Kunkel, Staufen) at 20,000 rpm for specified times of 10, 20, 30, 40, 50 and 60 min to produce MFC, and then were sonicated by a high intensity sonifier (BRANSON MODEL 250) at 200 W for another 30 min. The suspensions were poured into a Petri dish to a height of 1 cm, and kept in an environmentally controlled room at a temperature of 23 ± 2 °C and relative humidity of 50 ± 2 % for at least a week until MFC networks were formed on evaporation of the liquid phase. The networks were then dried in an oven at 70 °C for 12 h and compression moulded at a pressure of 5 MPa at 80 °C for 3 min. Then, the densities of these networks were subsequently determined as done for MFC-A, MFC-B and MFC-C networks. The networks possessing optimum mechanical properties, as discussed in chapter 4.5, were called MFC-D, and used to prepare composites later.

3.4 COMPOSITE PREPARATION

MFC-A, MFC-B, MFC-C and MFC-D networks with thicknesses of 110.6 ± 8.9, 82.8 ± 5.6, 63.5 ± 4.7 and 80.5 ± 5.3 µm respectively were cut into strips with dimensions of about 2 × 30 mm using a razor blade. PLA pellets (PLA 4042D) were dried in an oven at 50 °C for 24 h before PLA film preparation. PLA films were prepared using compression moulding. The pellets were melted at 180 °C for 3 min in a
thin metal mould, and then compressed at a pressure of 12 MPa for another 3 min. After that, the mould was cooled down for 6 min, yielding transparent films with a thickness of \( \sim 110 \) \( \mu \text{m} \). Strips of MFC were placed between two of these PLA films, and MFC reinforced PLA composites were prepared by compressing the laminate at 12 MPa and 180 °C for 3 min, as done previously. The thickness of the composites was \( \sim 200 \) \( \mu \text{m} \) and the weight fractions of the MFC-A, MFC-B, MFC-C and MFC-D networks in the composites determined by weighing the MFC strips before and after making composites were found to be 38.7 ± 0.1, 35.5 ± 4.0, 32.9 ± 2.5, 23.7 ± 1.7 wt.% respectively.

3.5 SCANNING ELECTRON MICROSCOPY

The surface of the MFC networks and composites and their fracture surfaces after tensile testing were investigated using scanning electron microscopy (SEM). Samples were placed onto adhesive carbon tabs on aluminium pin stubs. The samples were subsequently coated with carbon using an Edward coating system, E306A, to avoid electrical charging during imaging. Imaging in the scanning electron microscope (Phillips FEG-SEM XL-30) was carried out using a 5 kV accelerating voltage and a working distance of 10 mm. The resolution of images is poor when the accelerating voltage is low; however, using a high accelerating voltage can damage the sample. Before analysis of images, the scanning electron microscope was calibrated using a standard sample with 2,160 lines mm\(^{-1}\), supplied by Agar Scientific Ltd. (Figure 3.3). The difference between a number of lines on the reference grid and the true distance on the standard sample was measured using the Image J software package. The mean diameters of Lyocell fibres and MFC fibrils were subsequently determined.
3.6 FOURIER TRANSFORM INFRARED SPECTROSCOPY

Fourier transform infrared (FTIR) spectra of MFC networks were collected using a Nicolet 5700 FTIR spectrometer (Thermo Electron Co-operation) in order to determine the effect of pretreatments and mechanical treatment used to prepare MFC from pulp and Lyocell fibres on functional groups of cellulose molecules of MFC. All spectra were recorded between 400 and 4000 cm$^{-1}$ with a resolution of 4 cm$^{-1}$ and 32 scans. At least three points on each network were collected.

Figure 3.3 SEM micrograph of the standard sample used for calibration of SEM.
3.7 X-RAY DIFFRACTION

X-ray diffraction (XRD) patterns of Lyocell fibres and MFC networks produced from wood pulp and Lyocell fibres were obtained using an X-ray diffractometer (X’pert PW3710 MPD, Philips) using Cu Kα radiation ($\lambda = 0.154$ nm) with an accelerating voltage of 50 kV and a current of 40 mA. The range of the diffraction angle $2\theta$ was from 5 to 50° with 0.05° per step and an exposure time of 10 s per step. At least three samples of each material were investigated. A typical XRD pattern for an MFC network is shown in Figure 3.4, highlighting the key diffraction peaks required to determine the degree of crystallinity. The degree of crystallinity ($\chi_c$) was calculated using Segal’s method (Segal et al., 1959; Cheng et al., 2007; Lu et al., 2008; Eyholzer et al., 2010).

$$\chi_c (\%) = \frac{I_{200} - I_{AM}}{I_{200}} \times 100$$ (3.1)

where $I_{200}$ is the intensity of the 200 peak representing the crystalline packing of the cellulose structure, and $I_{AM}$ is the minimum intensity between the 200 and 110 peaks, representing only the amorphous region (Cheng et al., 2007; Lu et al., 2008; Siro et al., 2010).
3.8 THERMOGRAVIMETRIC ANALYSIS

In order to measure the change of mass as a function of temperature, a NETZSCH Simultaneous Thermogravimetric analysis (STA) 449C instrument was used to characterise the degradation temperature and weight loss as a function of temperature for Lyocell fibres, MFC networks and composites. Samples with a mass of $5.0 \pm 0.5$ mg were placed in an aluminium crucible, and then were heated in the range of 30 - 500 °C at 10 °C min$^{-1}$ under a 50 ml min$^{-1}$ nitrogen purge gas flow. The onset degradation temperature ($T_d \_\text{onset}$) was determined from the intersection of the two tangents at the start of the transition, as shown in Figure 3.5. At least three measurements were repeated to ensure reliability of the results.
Figure 3.5 Determination of the onset degradation temperature of an MFC-A network.

3.9 DIFFERENTIAL SCANNING CALORIMETRY

A TA Q100 heat-flux differential scanning calorimeter was used to investigate the thermal properties of neat PLA films and MFC reinforced composites. Samples were enclosed in hermetic aluminium pans. They were heated, cooled and then heated again in the temperature range of 30 - 200 °C at 10 °C min\(^{-1}\) under a 50 ml min\(^{-1}\) nitrogen purge gas flow. The glass transition temperature (\(T_g\)), cold crystallisation temperature (\(T_{cc}\)), melt temperature (\(T_m\)) and enthalpy of melting (\(\Delta H_m\)) were determined from the first heating scan of the samples using the same method as the degradation temperature in Section 3.8. Experiments were repeated at least three times to ensure that the results were reliable.
3.10 MECHANICAL TESTING

3.10.1 Sample Preparation

The methods used to prepare the samples of single Lyocell fibres and MFC networks, including composites for mechanical testing, were the same. The samples were fixed to cardboard windows using a two-part cold-curing epoxy resin (Araldite®, Huntsman, UK) in order to prevent the slippage of the samples during the test, as shown in Figure 3.6. The MFC network and composite samples were cut using a razor blade to a width of 2 mm. Prior to testing, all specimens were conditioned in an environmentally controlled room at a temperature of 23 ± 2 °C and relative humidity of 50 ± 2 % for 48 h.

Figure 3.6 Schematic illustration of mechanical test specimens of (A) a single Lyocell fibre and (B) MFC network or MFC reinforced composite.
3.10.2 Procedure for Mechanical Testing

An Instron 1121 universal testing machine equipped with a 5 N load cell for single Lyocell fibres and a 500 N load cell for MFC networks and composites was used to determine their mechanical properties. Before testing, the Instron universal testing machine was calibrated by hanging a standard weight of 0.1 N for the 5 N load cell and 20 N for the 500 N load cell.

Samples were placed between a fixed jaw and a movable jaw connected to the load cell. Both sides of the sample card were burnt away with a hot wire before applying strain. The force applied to deform a sample was measured using the load cell, and the extension was recorded. At least 10 samples for each material were prepared and tested at gauge lengths of 4, 10 and 20 mm. Mean values and standard deviations were calculated.

The cross-sectional area of Lyocell fibres was calculated from the mean diameter measured using a FEG-SEM (XL-30, Phillips). The width of MFC network and composite samples was measured using a light microscope (Olympus BH2-UMA) and an image analysis programme (Axiovision LE). A micrometer was used to measure the thickness of these samples taking care not to compress the samples. Young’s modulus, strength and strain of each sample were determined from the stress-strain curves.

In order to obtain the true value of Young’s modulus of the MFC networks, at an infinite gauge length, thereby taking into account end effects (Arridge et al., 1976). Samples were tested with a range of gauge lengths (4, 10 and 20 mm) at a constant strain rate of 0.05 s⁻¹. Graphs of the Young’s moduli of the MFC networks versus the reciprocal gauge length (1/gauge length) were plotted, and an extrapolation to the
ordinate was taken. The true stress and strain of the MFC networks can also be obtained from extrapolation to a zero gauge length.

3.10.3 Correcting for Machine Compliance

Machine compliance was taken into account before interpreting data of the mechanical properties obtained from samples. The machine compliance of the loading and gripping system was determined by deforming pieces of steel (10 × 0.1 mm) with a number of gauge lengths (4, 10 and 20 mm) at a strain rate of 0.05 s⁻¹. Then, the graph between the displacement with respect to force ($\delta/F$) and a gauge lengths ($l$) was plotted as shown in Figure 3.7, and the intercept of the graph to the ordinate, when the gauge length is equal to zero, was determined, which is equal to the machine compliance, $c$. The cross-head speed displacement during tensile testing is given as (Chawla et al., 2005; Silva et al., 2008)

$$\frac{\delta}{F} = ml + c$$  \hspace{1cm} (3.2)

where $m$ is the gradient of the fit, $1.4 \times 10^{-4}$ N⁻¹.
Figure 3.7 Displacement as a function of force versus gauge length fitted using a linear regression with slope for steel. The machine compliance was obtained from the intercept of this graph to the ordinate.

Measured data are then corrected for the machine compliance value, $6.7 \times 10^{-3}$ mm N$^{-1}$, using the equation

$$N = A - (F \times c)$$

(3.3)

where $N$ and $A$ are the corrected and measured elongation data (mm), and $F$ is force applied to deform samples (N). Figure 3.8 reports the measured and corrected stress-strain behaviour of a typical MFC network.
3.11 ZERO SPAN TESTING

Strips of MFC networks were cut for the zero span testing (5 mm × 15 mm) using a razor blade. Zero span strength index, determined according to TAPPI T 231-96, was measured using a Zero span testing machine (Pulmac Instruments Ltd). The strip was inserted between zero-span jaws, and the jaws were then firmly clamped on the sample. At least 7 samples of each network were tested. Values of the zero span strength index $Z$ (kNm kg$^{-1}$) were subsequently used with the tensile strength index $T$ (kNm kg$^{-1}$) to calculate the bond strength of networks $B$ (kNm kg$^{-1}$) using the equation

![Stress-strain curve](image-url)
\[ \frac{1}{T} = \frac{1}{Z} + \frac{1}{B} \]  

(3.4)

The tensile strength index \( T \) was obtained from MFC network samples with the width of 5 mm and the gauge length of 4, 10 and 20 mm using the same procedure and tested under the same condition as discussed in Section 3.10.1 and 3.10.2. The tensile strength index of MFC networks at the infinity gauge length was then obtained by plotting the tensile strength index of each network with the reciprocal gauge length (1/gauge length), and the ordinate was taken.

### 3.12 RAMAN SPECTROSCOPY

A Renishaw system 1000 Raman spectrometer coupled to a 25 mW 785 nm near-infrared laser was used to record spectra of Lyocell fibres, MFC networks and MFC reinforced composites. An Olympus BH-1 microscope with a 50× objective lens was employed to focus on the surface of samples with a spot size of \(~2 \mu m\) and an intensity of \(~1 \text{ mW}\). Figure 3.9 shows a schematic diagram of a Renishaw Raman spectrometer system.
The incident light (laser beam) passes through the monochromator (A) which enables only the monochromatic and polarised beam to enter the system. Then, this laser beam passes through an objective lens and a pinhole (B), rendering the beam circular. The beam is subsequently reflected by two mirrors (C and D) onto the holographic notch filter (E). The holographic notch filter serves as a beam diverter, which reflects the laser beam to the optical microscope (M), and the beam is then focussed on the sample surface (N).

Subsequently, the scattered light returns back the same way to the holographic notch filter (E). The Rayleigh scattered light is filtered out by this filter, whereas the scattered light having different vibrational frequencies (Raman scattering light) is allowed to pass through it. Inserting a 1/2 wave plate (F) and/or a polariser (G) in the system depends on which polarisation configuration is needed to be used. The scattered light then passes
through the slit (H), and reflects onto the isosceles triangle mirror (I) to the diffraction
grating assembly (J), which splits the scattered light into constituent frequencies. This
radiation then passes through a focusing lens (K), and individual frequencies are
detected by a charge-coupled device (CCD) detector (L), which transforms the optical
signals into electrical signals.

3.12.1 Calibration of Raman Spectrometer

Before the beginning of each experiment, the Raman spectrometer was calibrated using
a silicon standard, which produces a sharp peak at 520 cm\(^{-1}\) as shown in Figure 3.10. The Raman spectrum of the silicon standard was fitted to determine its peak position. If the peak position deviated from 520 cm\(^{-1}\), the Renishaw WIRE\(^{\text{TM}}\) software was used to reposition the silicon peak to be at 520 ± 0.1 cm\(^{-1}\) in order to ensure that consistent measurements were taken.


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EXPERIMENTAL METHODOLOGY

3.12.2 Deformation Micromechanics

Deformations micromechanics of single Lyocell fibres, MFC networks and composites were investigated using Raman spectroscopy. Single Lyocell fibres were mounted onto 20 mm gauge length cardboard windows, as shown in Figure 3.6. The single Lyocell fibre samples were secured on a tensile deformation rig equipped with a 2 N load cell (Figure 3.11), using cyanoacrylate adhesive, and fitted directly onto the microscope stage. The load cell was calibrated before the test. A series of known weights were hung from the load cell, and values from the transducer were recorded. These values were subsequently converted to stress. Figure 3.12 shows a calibration curve.

Figure 3.10 Raman peak located at ~520 cm$^{-1}$ for a silicon standard.
Figure 3.11 Schematic representation of a single fibre tensile deformation rig for Raman deformation studies.

Figure 3.12 Calibration curve of the load cell for the tensile deformation rig coupled with a 2 N load cell used for the single fibre testing.
However, the tensile deformation rig equipped with a 2 N load cell used to deform single Lyocell fibres is unable to deform cellulose networks and composites because of the limited load cell capacity. A 2 kN load cell customised deformation rig (Deben Microtest, Deben, Bury St Edmonds, UK), as shown in Figure 3.13, was used to deform network and composite samples.

![Figure 3.13 Schematic representation of a 2 kN load cell customised deformation rig for MFC network and composite micromechanics studies.](image)

Before testing, each side of the sample window was burnt away in order to enable the sample to be deformed. Raman spectra were obtained from the samples in the range of 1050 - 1150 cm⁻¹. Three Raman spectra were recorded from the same spot for each strain increment (0.1%) using an exposure time of 10 s and 5 accumulations, giving a total time of 50 s. At least three samples were tested for each material. The cross sectional areas of Lyocell fibres, cellulose networks and composites were calculated using the methods described in Chapter 3.10.2.
3.12.3 Molecular Orientation Determined by Raman Spectroscopy

The orientations of cellulose molecules within single Lyocell fibres and MFC networks were determined using Raman spectroscopy by measuring the intensity of the Raman peak initially located at ~1095 cm\(^{-1}\) as a function of the angle between the incident light and sample axis. Samples were placed on a rotation stage, and were rotated from 0 to 360° with 5° increments. A Raman spectrum at each angle increment was recorded using an exposure time of 10 s with 5 accumulations. The incident laser beam was polarised parallel to the sample axis. The intensities of the Raman band initially located at ~1095 cm\(^{-1}\) were plotted against the angle between the incident light and sample axis to give an indication of the orientation of cellulose molecular chains within networks of MFC and single Lyocell fibres.

3.12.4 Effect of Laser Polarisation and the Angle on Raman Band Shift Rates

The relationship between the Raman band shift as a function of strain obtained from MFC networks and composites and the angles between the axis of the fibrils, the strain axis, and the laser polarisation direction, was determined. Figure 3.14 reports the diagram of the laser direction of the polarisation configurations.

When the polarised laser beam interacts with samples, the direction of the scattered light obtained from samples has no specific polarisation, without inserting the 1/2 wave plate (part: F in Figure 3.9) and polariser analyser (part: G in Figure 3.9) in the system, which is called the VN configuration. If the polariser analyser is used in the system, it allows only the scattered light parallel to the electric vector of the incident light to pass.
through, then this configuration is called VV, which can be known as the parallel-parallel polarised configuration (Deng, 2010; Deng et al., 2011; Rusli, 2011). For the VH polarisation configuration, the 1/2 wave plate and the polariser analyser are inserted in the system. When the scattered light passes through the 1/2 wave plate, the scattered light direction is rotated by 90°, and then the scattered light, perpendicular to the incident light, can pass through the analyser. This configuration is sometimes called a crossed-polarised configuration (Deng, 2010; Deng et al., 2011; Rusli, 2011). The positions of the optical components for different polarisation configurations are reported in Table 3.1.

**Figure 3.14** Schematic illustration of the different polarisation configuration effects on the polarisation direction. Reproduced with modification from Rusli (2011).
Table 3.1 Directions of the incident laser and scattered light relative to the y-axis (shown in Figure 3.14) and the position of the optical components for different polarisation configurations in the Raman spectroscopic system (Deng, 2010; Rusli, 2011).

<table>
<thead>
<tr>
<th></th>
<th>VN</th>
<th>VV</th>
<th>VH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direction of incident beam</td>
<td>Parallel to y axis</td>
<td>Parallel to y axis</td>
<td>Parallel to y axis</td>
</tr>
<tr>
<td>Direction of scattered light</td>
<td>No preferential direction</td>
<td>Parallel to y axis</td>
<td>Perpendicular to y axis</td>
</tr>
<tr>
<td>The 1/2 wave plate</td>
<td>Out</td>
<td>Out</td>
<td>In</td>
</tr>
<tr>
<td>(part: F in Figure 3.9)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>The polariser analyser</td>
<td>Out</td>
<td>In</td>
<td>In</td>
</tr>
<tr>
<td>(part: G in Figure 3.9)</td>
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</table>

In order to study the effect of the angle between the strain direction and the fibril axis, $\theta$, and the angle between the strain direction and the laser polarisation axis, $\phi$, as shown in Figure 3.15, on the Raman band shifts for single Lyocell fibres and MFC networks (MFC-A, MFC-B and MFC-C) as a function of tensile deformation with two different polarisation configurations (VV and VH), MFC networks were deformed using a 2 kN load cell customised deformation rig (Deben Microtest, Deben, Bury St Edmonds, UK), and the tensile deformation rig equipped with a 2N load cell was used to deform single Lyocell fibres. During tensile deformation, the samples were rotated from 0 to 90$^\circ$ using 10$^\circ$ increments at each 0.1% strain increment from 0 up to 1%. Raman spectra were collected at each rotation angle increment. Subsequently, the effective Young’s modulus of single fibrils of MFC was estimated.
3.12.5 Repeatability of the Determination of Raman Band Positions

In order to estimate the accuracy of the Raman band initially located at \( \sim 1095 \text{ cm}^{-1} \), two different sets of 40 measurements were recorded for single Lyocell fibres, MFC networks and composites using VV and VH polarisation configurations. The first set involved recording 40 random points of the laser beam on the samples and the second set of 40 measurements were taken from the fixed position of the laser beam on the same samples.

3.12.6 Data Analysis

The recorded data for the Raman spectra were fitted to a combined Gaussian-Lorentzian function using a least-squares method. The mixed Gaussian-Lorentzian function was chosen to determine the central peak of spectra because this function was found to

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**Figure 3.15** Schematic illustration of the angles between the fibril direction and strain axis (\( \theta \)) and the strain direction and the laser polarisation direction (\( \phi \)) in a two-dimensional plane of a cellulose network. Reproduced with modification from Deng et al. (2011).
provide the best fit of the Raman peak. The mixed Gaussian-Lorentzian function, \( f(x) \), is as follows

\[
f(x) = (1 - M)G(x) + (M)F(x)
\]  

(3.5)

where \( M \) is the percentage of the Lorentzian part of the mixed function. \( G(x) \) (Gaussian function) and \( F(x) \) (Lorentzian function) are given as

\[
G(x) = He^{\frac{(X - X_0)^2}{w_f^2}}
\]  

(3.6)

\[
F(x) = \frac{H}{4\left(\frac{X - X_0}{w_f}\right)^2 + 1}
\]  

(3.7)

where \( X \) and \( X_0 \) are the positions of the peaks and their initial position, \( H \) is the height of the peak, and \( w_f \) is the full width of the peak at a half maximum height. Figure 3.16 shows an example of a Raman spectrum in the range 1050 to 1150 cm\(^{-1}\) for an MFC-A network containing the peak initially located at \( \sim 1095 \) cm\(^{-1}\). This particular Raman band has been used successfully to monitor the molecular deformation of a wide range of cellulosic materials (Eichhorn et al., 2001; Eichhorn and Young, 2001; Sturcova et al., 2005; Gierlinger et al., 2006; Hsieh et al., 2008; Rusli et al., 2010; Bakri and Eichhorn, 2010).
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Figure 3.16 Mixed Gaussian-Lorentzian function fitted to the Raman spectrum obtained from an MFC-A network.

3.13 REFERENCES


CHAPTER 4

PREPARATION AND CHARACTERISATION OF MICROFIBRILLATED CELLULOSE FROM LYOCELL FIBRES

Compared to natural fibres, Lyocell fibres show uniform physical properties such as diameters and mechanical properties, and can be more reliable source to produce MFC. In addition, it is assumed that MFC produced from Lyocell fibres consumes less energy than MFC prepared from natural fibres, even though some additional costs will be involved in making the Lyocell fibres.

MFC was produced from Lyocell fibres using the combination of two different mechanical methods; namely homogenisation and sonication, as discussed in Section 3.3. The physical and mechanical properties of MFC networks were then characterised. The MFC networks possessing optimum mechanical properties, subsequently called MFC-D, were selected to prepare composites.
4.1 CHARACTERISATION OF LYOCELL FIBRES

The physical and mechanical properties of the Lyocell fibres as a raw material to prepare MFC were characterised. Figure 4.1 shows a typical SEM micrograph of a single Lyocell fibre produced using a spinning process using a draw ratio (take-up speed/dope speed) of 8.9. As the geometry of Lyocell fibres has been reported to be cylindrical (Fink et al., 2001; Kong, 2007), the mean fibre diameter, taken from 30 measurements of the Lyocell fibres using a scanning electron microscope, was found to be 10.4 ± 0.5 µm. It has been reported also that the diameter of Lyocell fibres depends on the draw ratio (Kong and Eichhorn, 2005a). With the increase of the draw ratio, the average diameter of fibres and the variation in diameters of fibres decrease (Kong and Eichhorn, 2005a; Corsini et al., 2007).

The mean diameter of the Lyocell fibres in this work was found to be smaller than reported values of diameters for natural cellulose fibres (Eichhorn et al., 2001; Bakri and Eichhorn, 2010). Flax and hemp fibres have been reported to have the diameters of 17.1 and 31.2 µm respectively (Eichhorn et al., 2001; Bakri and Eichhorn, 2010).
A typical stress-strain curve obtained from a single Lyocell fibre is shown in Figure 4.2. It can be clearly seen that the Lyocell fibres exhibit non-linear behaviour. When the Lyocell fibre is deformed in tension, there is an initial linear region up to approximately 1 % strain, and then a yield point occurs (Kong and Eichhorn, 2005a; Kong and Eichhorn, 2005b). Similar non-linear behaviour has been observed also for natural fibres such as celery and coir (Bakri and Eichhorn, 2010). It has been reported that the Young’s modulus determined before the yield point of the stress-strain curve of regenerated cellulose fibres is found to increase with an increase of the draw ratio used to produce fibres (Kong and Eichhorn, 2005a; Kong and Eichhorn, 2005b). This is thought to be due to the increase in orientation of molecule chains of cellulose within a fibre (Kong and Eichhorn, 2005a; Kong and Eichhorn, 2005b). Highly aligned fibres such as flax and hemp exhibit near linear elastic behaviour (Eichhorn et al., 2001).
The summary of the mechanical properties of the Lyocell fibres is reported in Table 4.1. These properties of the Lyocell fibres are found to be similar to those which have been previously reported (Eichhorn et al., 2001; Kong and Eichhorn, 2005a; Kong and Eichhorn, 2005b).

![Stress-strain curve](image)

**Figure 4.2** Typical stress-strain curve for a single Lyocell fibre.

**Table 4.1** Summary of the mechanical properties of the Lyocell fibres. Errors reported are standard deviations from the mean.

<table>
<thead>
<tr>
<th>Material</th>
<th>E (GPa)</th>
<th>σ (GPa)</th>
<th>ε (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lyocell</td>
<td>27.6 ± 3.4</td>
<td>0.6 ± 0.04</td>
<td>5.8 ± 1.1</td>
</tr>
</tbody>
</table>
4.2 MORPHOLOGY OF MICROFIBRILLATED CELLULOSE

Figure 4.3 shows images of aqueous suspensions of the original Lyocell fibres and MFC after mechanical treatment used to fibrillate Lyocell fibres for 10, 20, 30, 40, 50 and 60 min. It can be clearly observed that the original Lyocell fibres sedimented to the bottom of the bottle immediately after initially dispersing them, as shown in Figure 4.3a. After the mechanical treatment was used to fibrillate the Lyocell fibres to produce MFC; no appreciable sedimentation occurred, even after 24 hours. This indicates an increase of the degree of fibrillation and the increased surface area of MFC fibrils (Chen et al., 2011a).

Figure 4.3 Aqueous suspensions of (a) Lyocell fibres and MFC fibrils after mechanical treatment for (b) 10 min, (c) 20 min, (d) 30 min, (e) 40 min (f) 50 min and (g) 60 min.
SEM micrographs of MFC prepared using mechanical treatment to fibrillate Lyocell fibres between 10 and 60 min are shown in Figure 4.4. These micrographs show the web-like structure of MFC. The average diameters of MFC after the mechanical treatment used for specified times are reported in Figure 4.5.

It has been reported that since Lyocell fibres consist of highly oriented crystalline regions along cellulose fibrils, when they are under mechanical stress in a wet condition, intra-hydrogen bonds between crystalline regions are easily broken. This allows fibrillation to occur (Lenz et al., 1993; Nicolai et al., 1996; Udomkichdecha et al., 2002; Chaudemanche and Navard, 2011). Therefore, as the treatment time used to fibrillate the Lyocell fibres increases, the amount of MFC generated from an original fibre increases (Cheng et al., 2010).

It was found that when Lyocell fibres were mechanically treated for 10 min, fibrils with the mean diameter of ~450 nm were generated from the intact fibres with diameters of ~10 µm. Finer fibrils with the mean diameter of ~365 nm were then produced after the 30 min treatment. After that, no significant change in the average diameter of MFC could be observed, suggesting that this is the ultimate fibrillar sub-structure that can be achieved by this mechanical treatment. It has been reported that during the mechanical treatment, two mechanisms of fibre fibrillation are observed: external and internal fibrillation. While shear forces release fine fibrils from the fibre surface, internal fibrillation occurs due to the disruption of bonding between fibrils (Ebeling, 1981; Kang, 2007; Stelte and Sanadi, 2009).
Figure 4.4 Typical SEM micrographs of MFC mechanically treated from Lyocell fibres for (a) 10 min, (b) 20 min, (c) 30 min, (d) 40 min, (e) 50 min and (f) 60 min.
Figure 4.5 Mean fibre diameters of MFC, taken from 100 measurements using a scanning electron microscope, after mechanical treatment used to prepare MFC as a function of the mechanical treatment time. Error bars are standard deviations from the mean, and the dashed line is a guide for the eye only.

Figure 4.6 shows the density of MFC networks. The density of MFC networks, determined from their dimensions and weights, was found to be higher with the increase of treatment time to fibrillate Lyocell fibres. This is due to the fact that more fibrils are disintegrated from the original fibres, increasing density of packing within networks (Iwamoto et al., 2007; Stelte and Sanadi, 2009; Spence et al., 2010; Yoo and Hsieh, 2010). After 30 min treatment, no significant change of the density of MFC networks can be observed, which was similar to the MFC diameters with treatment time, as shown in Figure 4.5. It has been reported previously that the density of a network is a function of the fibre diameter (Stelte and Sanadi, 2009; Spence et al., 2010).
Figure 4.6 Density of MFC networks as a function of treatment time. Error bars are standard deviations from the mean and the dashed line is a guide for the eye only.

4.3 X-RAY DIFFRACTION OF MICROFIBRILLATED CELLULOSE

Typical XRD patterns for the Lyocell fibres and MFC produced using times between 10 and 60 min are shown in Figure 4.7. Four peaks at the angular positions (2θ) of approximately 12, 20, 22 and 35°, corresponding to the 110, 1̅10, 200 and 400 diffraction planes of cellulose II are observed for all XRD spectra of MFC networks. These four peaks have been reported before for regenerated fibres (Ozturk et al., 2009; Cheng et al., 2010).
The degree of crystallinity of MFC prepared using different processing times is reported in Figure 4.8. The trend of the degree of crystallinity of MFC as a function of treatment time can be discussed in two ways.

First, as the mechanical treatment time used to fibrillate MFC increases to 20 min, the degree of crystallinity of MFC decreases to be 74.5 %, compared to a value of 80.6 % for the original source. This could be because MFC is degraded during mechanical disintegration (Iwamoto et al., 2007; Uetani and Yano, 2011). No significant difference in the degree of crystallinity is observed for MFC beyond 20 min of mechanical treatment (solid line in Figure 4.8).
Alternatively, no significantly change of the degree of crystallisation of MFC is observed during the first 10 min of treatment. Then, the degree of crystallisation of MFC decreases, and no change of the degree of crystallisation of MFC can be found after 20 min of mechanical treatment (dashed line in Figure 4.8). This indicates that the crystalline regions of fibrils may be damaged in the early stages of the mechanical treatment (Uetani and Yano, 2011).

![Figure 4.8](image)

**Figure 4.8** Degree of crystallinity of MFC as a function of time used to fibrillate Lyocell fibres compared to the original fibres. Error bars are standard deviations from the mean, and the solid and dashed lines are a guide for the eye only.

Similarly, a decrease in the degree of polymerisation of fibrillated fibres has been observed when the number of passes through a homogeniser increases (Iwamoto et al., 2007; Henriksson et al., 2007; Eyholzer et al., 2010). Also, this behaviour has been observed when microcrystalline cellulose and pulp were mechanically treated to prepare
MFC (Levis and Deasy, 2001; Suzuki et al., 2001; Cheng et al., 2010; Uetani and Yano, 2011). However, an increase of the degree of crystallinity of mechanically treated cellulose has been reported in some cases (Cheng et al., 2007; Abe and Yano, 2009; Cheng et al., 2010; Chen et al., 2011a). This is thought to be due to the removal of hemicelluloses, lignin and amorphous cellulose (Cheng et al., 2007; Abe and Yano, 2009; Cheng et al., 2010; Chen et al., 2011a).

4.4 THERMOGRAVIMETRIC ANALYSIS OF MICROFIBRILLATED CELLULOSE

The thermal properties of Lyocell fibres and MFC are shown in Figure 4.9. A decrease of the onset degradation temperature is observed due to the degradation of MFC, as confirmed by the results of the degree of crystallinity shown in Figure 4.8. Weight loss at 500 °C is observed to gradually increase from 92.2% to 95.8% as the treatment time increases from 10 to 30 min. Then, the weight loss of MFC fibrillated between 40 and 60 min remains unchanged at ~96%. The degradation rate (weight loss per unit rise in temperature) has been previously reported to increase with an increase of sonication time due to the high surface area of MFC fibrils (Johnson et al., 2009).
Onset degradation temperature and weight loss of MFC with respect to time to fibrillate Lyocell fibres between 10 and 60 min, compared to the original Lyocell fibres. Error bars are standard deviations from the mean, and the dashed lines are a guide for the eye only.

Figure 4.9

4.5 MECHANICAL PROPERTIES OF MICROFIBRILLATED CELLULOSE NETWORKS

Figure 4.10 shows typical stress-strain curves of MFC networks prepared using different processing times between 10 and 60 min and the mechanical properties of MFC networks prepared from mechanically-treated Lyocell fibres for a specified time are shown in Figure 4.11.
It can be seen that when an MFC network is subjected to tensile deformation, the stress-strain curve exhibits non-linear behaviour. After reaching the maximum stress, the failure occurs successively due to disentanglement of fibrils within the networks (Nishino and Arimoto, 2007). This will be discussed in detail in Chapter 6, and the fracture mechanism of MFC networks made from Lyocell fibres will be compared with other MFC networks i.e. MFC-A, MFC-B and MFC-C networks. Similar stress-strain curves have been observed for filter paper (Nishino and Arimoto, 2007) and pulp paper (Kotik et al., 2005).

It was noticed that as the treatment time used to prepare MFC increased to 30 min, the tensile strength and Young’s modulus (6.8 MPa and 0.6 GPa respectively) of the MFC

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**Figure 4.10** Typical stress-strain curves for MFC networks with different treatment times.
network were found to be higher than those networks produced using a treatment time of 10 and 20 min. This was thought to be due to a greater surface area and smaller diameters of MFC fibrils and the higher density of the network increasing the amount of hydrogen bonding between the MFC fibrils (Iwamoto et al., 2007; Stelte and Sanadi, 2009; Yoo and Hsieh, 2010). Similarly, with an additional passes through a homogeniser the tensile strength and Young’s modulus of MFC networks have found to increase (Iwamoto et al., 2007; Stelte and Sanadi, 2009; Yoo and Hsieh, 2010).

However, after 30 min treatment, the tensile strength, tensile strength index, Young’s modulus and strain of MFC networks gradually decreased. Specifically, the decrease in the strain at maximum stress has been related to the low aspect ratio of MFC fibrils, resulting from the long mechanical treatment because MFC with low aspect ratio are rigid, and can be more easily pulled out from the MFC aggregations when they are deformed in tension (Iwamoto et al., 2007).

The density of these MFC networks, however, was lower compared to a value of more than 1.2 g cm\(^{-3}\) for the density of typical MFC networks, which has been previously reported (Iwamoto et al., 2007; Henriksson et al., 2008) and typical paper (more than 0.7 g cm\(^{-3}\)) (Kotik et al., 2005; I'Anson et al., 2006; Almgren et al., 2009). This results in the low mechanical properties of the MFC networks in this study.
Figure 4.11 Tensile properties of MFC networks with different treatment times. Error bars represent the standard deviations from the mean.
4.6 CONCLUSIONS

The combination of homogenisation and sonication has been successfully used to prepare MFC from the raw material, Lyocell fibres. It was found that after the mechanical treatment for 10 min to prepare MFC. The mean diameter of fibrillated MFC was ~450 nm, compared to a diameter of ~10 µm for the original Lyocell fibres. The density of the MFC networks was found to be a function of fibre diameter. The values of the degree of crystallinity for the mechanically treated Lyocell fibres were lower than that of the original highly oriented Lyocell fibres. This decrease in the degree of the crystallinity was thought to be due to degradation of MFC fibrils. This decrease correlated with a change in the degradation temperature of MFC observed in thermogravimetric analysis (TGA) results. Mechanical properties of these MFC networks (tensile strength and Young’s modulus) were lower than expected because of the low density of the networks. As the time for mechanical treatment increased to 30 min, tensile strength and Young’s modulus of the MFC networks were found to increase. After this point, these values reduced gradually with increasing treatment time due to the low aspect ratio of MFC caused by the long mechanical treatment. MFC networks with 30 min treatment showed the highest tensile strength and Young’s modulus. Therefore, this network, subsequently called MFC-D, was selected to prepare composites using compression moulding. Physical and mechanical properties of these composites will be discussed in Chapter 7.
4.7 REFERENCES


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RESULTS AND DISCUSSIONS


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CHAPTER 5

EFFECTIVE YOUNG’S MODULUS OF SINGLE FIBRILS OF MICROFIBRILLATED CELLULOSE FROM PULP

In this chapter the orientation of cellulose molecular chains within MFC networks (MFC-A, MFC-B and MFC-C) determined using Raman spectroscopy with VV and VH polarisation configurations is reported, and is compared to that within Lyocell fibres. In addition, the effects of the angles between the fibril direction, the strain axis and the direction of laser polarisation on the Raman band shifts are reported as a function of tensile strain with two different polarisation configurations (VV and VH). From these studies, the effective modulus of a single filament of MFC prepared from pulp (MFC-A, MFC-B and MFC-C) was subsequently estimated. The modulus of single fibrils of MFC fibrillated from Lyocell fibres (MFC-D), on the other hand, will be determined in Chapter 6.10.

The modulus of single fibrils of MFC has rarely been reported. A value of ~98 GPa for the elastic modulus of individual filaments of MFC prepared from Lyocell fibres by
sonication method was determined using an AFM tip (Cheng et al., 2009). Iwamoto et al. (2009) reported a value of ~145 GPa for the modulus of single microfibrils of tunicate determined using the same technique. However, to date, no values have been reported on MFC fibrils prepared from pulp. Since the use of MFC for composites is considered desirable based on the premise that they have high modulus, such a study is timely.

5.1 RAMAN SPECTROSCOPY OF LYOCELL FIBRES AND MICROFIBRILLATED CELLULOSE NETWORKS

Typical VV polarisation configuration Raman spectra obtained from MFC-A, MFC-B and MFC-C networks compared to Lyocell fibres produced, with a high draw ratio of 8.9, are shown in Figure 5.1. All Raman spectra show a dominant peak initially located at ~1095 cm\(^{-1}\), corresponding to the C-O ring stretching mode within the cellulose backbone structure (Wiley and Atalla, 1987; Eichhorn et al., 2001; Hsieh et al., 2008; Bakri and Eichhorn, 2010), and possibly the C-O-C glycosidic stretching mode (Gierlinger et al., 2006; Qin et al., 2008). As discussed in Section 2.4.4, this Raman band has been used to monitor the deformation micromechanics of cellulose materials.
Figure 5.1 Typical Raman spectra for MFC networks compared to a single Lyocell fibre, highlighting the Raman peak initially located at ~1095 cm\(^{-1}\).

Figure 5.2 shows the Raman bands obtained from MFC networks and Lyocell fibres using two different polarisation configurations (VV and VH discussed in Section 3.12.4). It can be clearly seen that the intensity of the Raman peak initially located at ~1095 cm\(^{-1}\), for both Lyocell fibres and MFC networks, was found to depend on the polarisation configuration used. This is due to the direction and the magnitude of the Raman tensor components of molecular vibrations with respect to the laser polarisation direction (Tanaka and Young, 2006). This will be explained in more detail in Section 5.3.
Figure 5.2 Typical Raman spectra obtained from Lyocell fibres and MFC-A, MFC-B and MFC-C networks using the VV and VH polarisation configurations.

5.2 REPEATABILITY OF THE MEASUREMENT OF RAMAN BAND POSITIONS OF LYOCELL FIBRES AND MICROFIBRILLATED CELLULOSE NETWORKS

Figures 5.3 - 5.6 report the distributions of the peak position of the Raman band initially located at ~1095 cm\(^{-1}\) for the Lyocell fibres and MFC-A, MFC-B and MFC-C networks. It can be seen that the standard deviations obtained from the fixed position of the laser beam on the Lyocell fibres and MFC-A, MFC-B and MFC-C networks with the VV polarisation configuration were 0.09, 0.02, 0.03, 0.04 cm\(^{-1}\) respectively, and those taken from different positions of the laser beam on those samples with the same polarisation configuration were 0.12, 0.04, 0.09 and 0.04 cm\(^{-1}\) respectively. These results reveal that
the values of the standard deviations taken from the laser beam on the same and different positions of the samples with the VV polarisation configurations are found to be similar.

Using the VH polarisation configuration values of 0.14, 0.04, 0.06 and 0.05 cm$^{-1}$ for standard deviations were obtained from the same positions of the laser beam on the Lyocell fibre, MFC-A, MFC-B and MFC-C networks, compared to those taken from the different points of the laser beam on the Lyocell fibre, MFC-A, MFC-B and MFC-C networks of 0.16, 0.05, 0.09 and 0.06 cm$^{-1}$ respectively. No significant difference was found in the values for standard deviations obtained from the same and different positions of the laser beam on the samples with the VH polarisation configuration. These confirm that Raman results of these networks can be repeatable, which is important for monitoring the micromechanical deformation of these materials using Raman spectroscopy.
Figure 5.3 Distributions of the peak positions of the Raman band initially located at ~1095 cm\(^{-1}\) for 40 measurements taken from the same and different positions of the laser beam on Lyocell fibres using (a) VV and (b) VH polarisation configurations.

Figure 5.4 Distributions of the peak positions of the Raman band initially located at ~1095 cm\(^{-1}\) for 40 measurements taken from the same and different positions of the laser beam on MFC-A networks using (a) VV and (b) VH polarisation configurations.
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RESULTS AND DISCUSSIONS

Figure 5.5 Distributions of the peak positions of the Raman band initially located at ~1095 cm\(^{-1}\) for 40 measurements taken from the same and different positions of the laser beam on MFC-B networks using (a) VV and (b) VH polarisation configurations.

Figure 5.6 Distributions of the peak positions of the Raman band initially located at ~1095 cm\(^{-1}\) for 40 measurements taken from the same and different positions of the laser beam on MFC-C networks using (a) VV and (b) VH polarisation configurations.
5.3 MOLECULAR ORIENTATION OF LYOCELL FIBRES AND MICROFIBRILLATED CELLULOSE NETWORKS

Raman spectroscopy has been used to study the molecular orientation of cellulose materials, as mentioned in Section 2.4.4. The Raman band peak initially located at ~1095 cm\(^{-1}\), therefore, was selected to characterise the molecular orientation of cellulose chains within MFC networks, compared to highly-aligned Lyocell fibres. Figure 5.7 reports the Raman spectra obtained from Lyocell fibres and MFC-A networks using the VV and VH polarisation configurations at four different angles \(\phi\) between the laser polarisation axis and the strain direction; namely 0°, 30°, 60° and 90°. The decrease of the intensity of the Raman peak initially located at ~1095 cm\(^{-1}\) for the Lyocell fibres with increasing the angle between the strain direction and the laser polarisation axis, \(\phi\), is evident, whereas there is no significant change of the intensity of this Raman band for the MFC-A networks. Similar spectra to those for MFC-A networks are observed for networks of MFC-B and MFC-C. The effect of the angle on the intensity of this Raman band for the Lyocell fibres and MFC networks will be subsequently discussed.
Figure 5.7 Raman spectra of the (a) Lyocell fibres and (b) MFC-A networks at the angles \( \phi \) of 0\(^\circ\), 30\(^\circ\), 60\(^\circ\) and 90\(^\circ\) using VV and VH polarisation configurations.
Figure 5.8 shows the normalised intensities of the Raman band initially located at ~1095 cm\(^{-1}\) for the MFC-A, MFC-B and MFC-C networks as a function of the angle \(\phi\), in the VV and VH polarisation configurations, compared to those of single Lyocell fibres. It can be clearly seen that the intensity of this band for the Lyocell fibres using the VV polarisation configuration gradually decreases when the angle \(\phi\) increases from 0\(^\circ\) to 90\(^\circ\). The maximum intensity of this Raman band with the VV polarisation configuration occurs when the orientation of cellulose molecules within the microfibrils of the Lyocell fibres is parallel to the laser polarisation axis (\(\phi = 0^\circ\)), and at a minimum when the alignment of cellulose molecules is perpendicular to the laser polarisation axis (\(\phi = 90^\circ\)). This indicates a high degree of orientation of fibrils along the fibre axis, as has been found in highly aligned flax fibres (Sturcova et al., 2005; Bakri and Eichhorn, 2010). The intensity of this Raman band for the Lyocell fibres with the VH polarisation configuration, on the other hand, reaches a maximum at the angle \(\phi = 45^\circ\).

The intensity of the Raman band for a cellulose material has been reported to depend on the angle of the incident laser direction and fibre or fibril axis (Wiley and Atalla, 1987). The data for the Lyocell fibres in Figures 5.8a and 5.8c obtained with VV and VH polarisation configurations were fitted using (Wiley and Atalla, 1987; Gommans et al., 2000; Kannan et al., 2007)

\[
I_{\text{VV}} = a + (1-a)\cos^4(\phi) \tag{5.1}
\]

\[
I_{\text{VH}} = a' + 4(1-a')\cos^2(\phi)\sin^2(\phi) \tag{5.2}
\]

where \(a\) and \(a'\) are alignment constants, related to the derivatives of the polarisability tensors, with the VV and VH polarisation configurations respectively. \(I_{\text{VV}}\) and \(I_{\text{VH}}\) are
intensities of the Raman band initially located at ~1095 cm$^{-1}$ with the VV and VH polarisation configurations respectively. The least-squares fit to the experimental data for the VV polarisation configuration was found for $a = 0.32$, and $a' = 0.36$ for the VH polarisation configuration. The data and the curves fitted using Equations 5.1 and 5.2, shown in Figures 5.8a and 5.8c, are in good agreement, indicating high alignment of cellulose molecule chains along the Lyocell fibre axis (Wiley and Atalla, 1987; Kannan et al., 2007).

All MFC networks, on the other hand, exhibit similar intensities of this Raman band at all angles $\phi$ for both VV and VH polarisation configurations, as shown in Figures 5.9b and 5.9d. This indicates a uniformly random distribution of fibril orientation in a two-dimensional (2D) plane within the networks of MFC-A, MFC-B and MFC-C. Similar orientation of fibrils has been observed for bacterial cellulose networks (Hsieh et al., 2008) and carbon nanotube reinforced composites prepared by a solvent casting method (Deng et al., 2011). This result will be used to determine the effective Young’s modulus of a single filament of MFC prepared from pulp (MFC-A, MFC-B and MFC-C) in Section 5.5.
Figure 5.8 Normalised intensities of the Raman band initially located at \( \sim 1095 \text{ cm}^{-1} \) as a function of the angle \( \phi \) for (a) Lyocell fibres and (b) MFC-A, MFC-B and MFC-C networks using the VV polarisation configuration. The VH polarisation configuration was used to monitor the intensities of the (c) Lyocell fibres and (d) MFC-A, MFC-B and MFC-C networks at different angles \( \phi \). The solid lines in (a) and (c) are generated using Equations 5.1 and 5.2 respectively, while dashed lines in (b) and (d) are the average values of 0.94 and 0.93 obtained from all MFC networks using the VV and VH polarisation configurations respectively. Error bars are standard deviations from the mean.
5.4 ANGULAR-DEPENDENCE OF RAMAN BAND SHIFT RATES OF LYOCELL FIBRES AND MICROFIBRILLATED CELLULOSE NETWORKS

A typical Raman band shift of the peak initially located at \( \approx 1095 \text{ cm}^{-1} \), taken using the VV polarisation configuration, for the MFC-A network subjected to tensile deformation, is shown in Figure 5.9. Similar shifts of this Raman band can be observed for the Lyocell fibres, MFC-B and MFC-C networks in both VV and VH polarisation configurations. This shift has been thought to be due to the molecular deformation of the cellulose backbone, as already mentioned in Section 2.4.4.

![Figure 5.9](image)

**Figure 5.9** Typical shift in the Raman peak initially located at \( \approx 1095 \text{ cm}^{-1} \) with respect to tensile deformation, using the VV polarisation configuration, for the MFC-A network. Solid lines mark the position of the peaks, and are a guide for the eye only.
Figure 5.10 reports the dependence of the position of the Raman band initially located at ~1095 cm\(^{-1}\) as a function of tensile strain for different angles \(\phi\) recorded using the VV and VH polarisation configurations for the Lyocell fibres. The intensity of the Raman band initially located at ~1095 cm\(^{-1}\) for the Lyocell fibres, using the VV polarisation configuration, decreases at higher angles \(\phi\); therefore, it was difficult to obtain spectra at angles higher than 80\(^\circ\). The Raman band shifts with respect to strain of the Lyocell fibres at different angles \(\phi\) using the VV and VH polarisation configurations, are shown in Figure 5.11.

The Raman band shift as a function of tensile strain, sometimes called the Raman band shift rate \((d(\Delta v)/d\varepsilon)\), with respect to the angle \(\phi\) for the Lyocell fibres was found to be constant, and the average values for Raman band shift rates using the VV and VH polarisation configurations for the Lyocell fibres were -0.87 and -0.85 cm\(^{-1}\) \%\(^{-1}\) respectively. Therefore, the Raman shift rate of the highly aligned Lyocell fibres was independent of the laser polarisation direction and the angle \(\phi\) for both polarisation configurations, as has been previously reported for electrospun nanofibres containing carbon nanotubes (Deng et al., 2011).
Figure 5.10 Shifts of the position of the Raman band initially located at ~1095 cm\(^{-1}\) for the Lyocell fibres aligned at different angles \(\phi\) to the laser polarisation axis using the (a) VV and (b) VH polarisation configurations.
Figure 5.11 Dependence of the shifts of Raman peak initially located at ~1095 cm\(^{-1}\) as a function of the angle \(\phi\) to the laser polarisation direction for Lyocell fibres, obtained using the VV and VH polarisation configurations. Solid and dashed lines are the average values of -0.87 and -0.85 cm\(^{-1}\) %\(^{-1}\) of the Raman band shift rates for the Lyocell fibres, obtained using VV and VH polarisation configurations respectively. Error bars are standard deviations from the mean.

Shifts in the position of the Raman band initially located at ~1095 cm\(^{-1}\) with respect to tensile strain at different angles \(\phi\) recorded using the VV and VH polarisation configurations for the MFC-A networks are shown in Figure 5.12. Similar shift rates with VV and VH polarisation configurations can be found for the MFC-B and MFC-C networks. It was found that the Raman band shift rate using the VV polarisation configuration for MFC-A, MFC-B and MFC-C networks was sensitive to the angle \(\phi\). The rate of the Raman band shift for these MFC networks using a VH polarisation configuration was, however, independent of the angle \(\phi\) (Cooper et al., 2001).
Figure 5.12 Shifts of the Raman band position initially located at ~1095 cm\(^{-1}\) for the MFC-A networks aligned at the angles $\phi$ of 0°, 30°, 60° and 90° to the laser polarisation axis as a function of strain using the (a) VV and (b) VH polarisation configurations.
The relationship of the Raman band shift rate of a fibre in a composite aligned at an angle $\theta$ ($\phi = 0^\circ$), as shown in Figure 5.13, has been given as (Andrews et al., 1992; Cooper et al., 2001; Wood et al., 2001; Deng et al., 2011)

$$S(\theta) = S_0 (\cos^2 \theta - \nu \sin^2 \theta)$$  \hspace{1cm} (5.3)

where $S(\theta)$ is the Raman band shift rate for a fibre aligned in a composite at an angle $\theta$, $S_0$ is the band shift rate for a fibre aligned parallel to the strain direction, and $\nu$ is Poisson’s ratio of the composite.

![A fibre in a composite](image)

**Figure 5.13** Schematic illustration of a fibre lying in a composite at an angle $\theta$, to the tensile direction ($\phi = 0^\circ$). Reproduced with modification from Cooper et al. (2001) and Deng et al. (2011).

For two-dimensional and uniformly dispersed materials, the Raman intensity for the different polarisation configurations (VV and VH) can be considered as intensity weighted averages of the contributions of single fibrils oriented at different directions in a network. The Raman intensities at the angle $\phi$, obtained using the VV and VH polarisation configurations, are given as (Cooper et al., 2001; Deng et al., 2011)
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\[ I_{VV} = \frac{1}{\pi} \int_0^\pi I_o \cos^4(\theta + \phi) d\theta \]  
(5.4)

\[ I_{VH} = \frac{1}{\pi} \int_0^\pi I_o' \cos^2(\theta + \phi) \sin^2(\theta + \phi) d\theta \]  
(5.5)

where \( I_o \) and \( I_o' \) are the maximum intensities of the Raman band initially located at ~1095 cm\(^{-1}\) using the VV and VH polarisation configurations respectively.

Therefore, in a random network Raman band shift rates of MFC networks at the angle \( \phi \), \( S(\phi) \), obtained with the VV and VH polarisation configurations, using Equations 5.3, 5.4 and 5.5, can be given as (Deng et al., 2011)

\[ S_{VV}(\phi) = \frac{\int_0^\pi I_o \cos^4(\theta + \phi) S_o(\cos^2(\theta) - \nu \sin^2(\theta)) d\theta}{I_{VV}} \]  
(5.6)

\[ S_{VH}(\phi) = \frac{\int_0^\pi I_o' \left( \cos^2(\theta + \phi) \sin^2(\theta + \phi) \right) S_o' \left( \cos^2(\theta) - \nu \sin^2(\theta) \right) d\theta}{I_{VH}} \]  
(5.7)

Evaluation of the integrals in Equations 5.4 and 5.5 gives

\[ I_{VV} = \frac{3}{8} I_o \]  
(5.8)

\[ I_{VH} = \frac{I_o'}{8} \]  
(5.9)
Therefore, $S_{VV}(\phi)$ and $S_{VH}(\phi)$ can be written as

$$S_{VV}(\phi) = \frac{S_0}{2} (1 - \nu) + \frac{S_0}{3} (1 + \nu) \cos(2\phi)$$  \hspace{1cm} (5.10)

$$S_{VH}(\phi) = \frac{S'_0}{2} (1 - \nu)$$  \hspace{1cm} (5.11)

where $S_0$ and $S'_0$ are the shift rates of the Raman band initially located at ~1095 cm$^{-1}$ obtained from fibrils within a network parallel to the strain direction using VV and VH polarisation configurations respectively. $\nu$ is Poisson’s ratio of a network. Poisson’s ratio for cellulose is dependent on the source; for example $\nu = 0.38$ has been reported for single ramie fibres, and $\nu = 0.46$ for flax fibres (Peura et al., 2008; Nishiyama, 2009). Values of Poisson’s ratio have been reported to be between -0.26 and -1.17 for cellulose microfibrils forming a network (Peura et al., 2008).

It is worth noting that Raman band shift rates of MFC networks at the angle $\phi$, $S_{VV}(\phi)$, is dependent on the angle, as confirmed by Equation 5.10, whereas there is no relationship between the Raman band shift rate and the angle for the VH polarisation configuration $S_{VH}(\phi)$, as confirmed by Equation 5.11.

Figure 5.14 shows the theoretical dependence of the Raman band shift rates of an MFC network at different angles $\phi$ with a range of Poisson’s ratios between -0.3 and 0.3 with the VV polarisation configuration, as given by Equation 5.10.
Figure 5.14 Dependence of the Raman band shift rate on the orientation angle $\phi$ with the VV polarisation configuration generated by using theoretical Equation 5.10 with the different values of Poisson's ratio between 0.3 and -0.3.

Figures 5.15 and 5.16 show Raman band shift rates obtained from MFC-A, MFC-B and MFC-C networks with the VV and VH polarisation configurations. It was found that values of Poisson’s ratio with 95% confidence intervals, evaluated using a least squares fit of Equation 5.10, for MFC-A, MFC-B and MFC-C networks were -0.23 ± 0.11, -0.12 ± 0.11 and -0.21 ± 0.07 respectively. These values provided the best fit to the experimental data. It can be seen that the upper and lower values of Poisson’s ratio for MFC-A, MFC-B and MFC-C networks are negative. This indicates strong confident of the negative Poisson's ratio for MFC-A, MFC-B and MFC-C networks, even though no direct evident of the negative Poisson’s ratio for the MFC networks is shown.
Figure 5.15 Shift rates of the Raman band initially located at ~1095 cm\(^{-1}\) obtained with the VV polarisation configuration from the (a) MFC-A, (b) MFC-B and (c) MFC-C networks as a function of the angle \(\phi\) fitted using Equation 5.10. Solid and dashed lines represent fits to the data and 95% confidence intervals on the fitted curves respectively. Error bars are standard deviations from the mean.
Figure 5.16 Raman band shift rates with the VH polarisation configuration for the MFC-A, MFC-B and MFC-C networks as a function of the angle $\phi$ fitted using Equation 5.11. Solid and dashed lines represent fits to the average Raman band shift rate of MFC networks and 95% confidence intervals on the fitted curves respectively. Error bars are standard deviations from the mean.

The negative value of Poisson’s ratio suggests that MFC networks may expand in the “out of plane” or “in plane” direction when they are deformed, demonstrating what has been termed “auxetic” behaviour (Evans, 1991; Ravirala et al., 2005; Alderson and Alderson, 2007; Hall et al., 2008; Chen et al., 2009; Tatlier and Berhan, 2009; Jayanty et al., 2011; Kuznetsov et al., 2011). The mechanisms that might give rise to auxetic behaviour are not clear, but one possibility could be the presence of re-entrant networks of fibrils, or transverse strains arising in elements perpendicular to the deformation axis due to high levels of bonding within polygonal constructs of fibrils, as shown in Figure 5.17. This may be because during the MFC network preparation, as discussed in
Chapter 3.2, the fibrils deposited on each other without any preferable orientation to form dense networks. Then, the re-entrant structure may be formed, as has been previously reported for fibre networks (Tatlier and Berhan, 2009). This auxetic behaviour has been found in other materials such as foams and composites (Evans, 1991; Ravirala et al., 2005; Hall et al., 2008; Jayanty et al., 2011).

![Schematic representation of a re-entrant network of fibrils](image)

**Figure 5.17** Schematic representation of a re-entrant network of fibrils (a) without deformation and (b) with deformation. Reproduced with modification from Evans (1991).

### 5.5 STIFFNESS OF SINGLE FILAMENTS OF MICROFIBRILLATED CELLULOSE (MFC-A, MFC-B AND MFC-C)

The shift rates of the Raman peak initially located at ~1095 cm\(^{-1}\) obtained from fibrils parallel to the strain axis \((S_0)\) has been found to be proportional to the network modulus \((E_{\text{network}})\) according to the equation (Eichhorn and Young, 2001; Eichhorn et al., 2001; Sturcova et al., 2005; Rusli and Eichhorn, 2008)
Therefore,

\[ E_{\text{network}} \times \frac{d(\Delta \nu)}{d\sigma} = S_0 \]  

A value of -4.3 cm\(^{-1}\) GPa\(^{-1}\) for \(d(\Delta \nu)/d\sigma\) has been obtained from the micromechanical deformation of a variety of natural and regenerated cellulose fibres using Raman spectroscopy (Eichhorn \textit{et al.}, 2001). This value has been used previously to determine the modulus of single filament of cellulose materials such as a fragment of microcrystalline cellulose (Eichhorn and Young, 2001), bacterial cellulose (Hsieh \textit{et al.}, 2008) and nanowhiskers (Sturcova \textit{et al.}, 2005; Rusli and Eichhorn, 2008), as mentioned in Section 2.4.4.

\(S_0\) of MFC-A, MFC-B and MFC-C networks estimated by fitting the Raman shift data obtained at various angles \(\phi\) using the VV polarisation configuration with \textit{Mathematica} were found to be -0.50, -0.46 and -0.60 cm\(^{-1}\) %\(^{-1}\) respectively. Using the VH polarisation configuration MFC-A, MFC-B and MFC-C networks, on the other hand, yielded Raman shift rates \(S_0\) of -0.57, -0.57 and -0.67 cm\(^{-1}\) %\(^{-1}\) respectively. Values of \(S_0\) for each MFC network using the VV and VH polarisation configurations were found to be similar, indicating consistency in this method.

The Young’s moduli of MFC networks can be estimated from the Raman band shift rates using Equation 5.13, and are shown in Table 5.1. The higher value of Young’s modulus for MFC-C networks was estimated, compared to values for MFC-A and
MFC-B networks. This may be due to the lower porosity, less fibre aggregates and less coarse fibrils in MFC-C networks. The effect of pretreatments on the physical and mechanical properties of MFC networks will be discussed further in Chapter 6. The Young’s modulus of MFC networks obtained from Raman band shift rates will be compared to that taken from the stress-strain curves of MFC networks also.

In order to estimate the effective modulus of MFC single fibrils, \( E_{\text{fibril}} \), Krenchel’s analysis was used in a form of the equation (Krenchel, 1964)

\[
E_{\text{network}} = \eta_0 E_{\text{fibril}}
\]  

(5.14)

where \( \eta_0 \) is an efficiency factor, and \( E_{\text{network}} \) is the Young’s modulus of a two-dimensional random network. The efficiency factor for a two dimensional in-plane random network of fibrils can be found from the following integral (Krenchel, 1964).

\[
\eta_0 = \frac{1}{\pi} \int_{\pi/2}^{\pi/2} \cos^4 \theta d\theta = \frac{3}{8}
\]  

(5.15)

Equations 5.13 - 5.15 were used to determine the effective modulus of a single filament of MFC. The effective moduli of single filaments of MFC-A, MFC-B and MFC-C are reported in Table 5.1. It is worthwhile noting that similar values of the effective modulus of MFC fibrils obtained from the same type of networks determined using the VV and VH polarisation configurations can be observed.

The effective moduli of MFC fibrils prepared from pulp were found to be in the range of 29 - 41 GPa. These values of the effective moduli of single fibrils of MFC are much lower than the generally accepted value for the crystal modulus of cellulose I, 138 GPa.
(Sakurada et al., 1962; Nishino et al., 1995), tunicate whiskers (143 GPa) (Sturcova et al., 2005) and a value of 114 GPa for a single filament of bacterial cellulose (Hsieh et al., 2008). Also, the moduli of single fibrils of MFC prepared from a Cellulose II source, 98 GPa, (Cheng et al., 2009) and MFC prepared from tunicate, 145 GPa, (Iwamoto et al., 2009) determined using an AFM tip have been found to be higher than that of MFC fibrils in this work. These values (29 - 41 GPa), however, are found to be higher than a value obtained for a microcrystalline cellulose, 25 GPa (Eichhorn and Young, 2001).

This difference between the crystal modulus of cellulose and MFC could be because Raman spectroscopy records molecular deformation of both crystalline and amorphous regions (Hsieh et al., 2008). MFC is not completely crystalline, and the degree of crystallinity of MFC is lower than that of bacterial cellulose. Also, MFC preparation might damage and shorten the molecular chain length (or degree of polymerisation), reducing their stiffness (Henriksson et al., 2007; Siro and Plackett, 2010). In addition, coarse fibrils can be found in the networks (Figure 6.1), which affects the mechanical properties of the networks. It is important to add that after mechanical treatment using homogenisation, the degree of polymerisation of MFC has been reported to be reduced which has been shown to compromise the mechanical properties of the fibrils (Henriksson et al., 2007).

Importantly, the value of the effective modulus of a single filament of MFC obtained from this method does not take into account the voids and the bonding in networks, which may affect the stiffness of the whole material (Henriksson et al., 2008; Hsieh et al., 2008; Retegi et al., 2010). It is worth noting that according to Equation 5.14, it can be found that the modulus of a fibril is derived from network modulus only. The
underestimated value of the effective modulus for a single fibril, therefore, can be possibly obtained from a network with high porosity or low bonding strength. It has been previously reported that the mechanical properties of MFC networks is found to be lower when porosity of networks increases (Henriksson et al., 2008). This issue is needed to be considered before using this method to estimate the effective modulus of fibril filaments. The porosity and bond strength of networks of MFC-A, MFC-B and MFC-C will be discussed in Chapter 6.

Table 5.1 Estimated Poisson’s ratio, measured average Raman band shift rates, estimated network modulus and effective Young’s modulus of single MFC fibrils obtained from MFC networks (MFC-A, MFC-B and MFC-C). Errors reported are standard deviations from the mean.

<table>
<thead>
<tr>
<th>Polarisation Configuration</th>
<th>Material</th>
<th>Optimised fitting Poisson’s ratio, $\nu$</th>
<th>Raman band shift rate, $S_0$, (cm$^{-1}$%$^{-1}$)</th>
<th>Network modulus, $E_{\text{network}}$, (GPa)</th>
<th>Fibril modulus, $E_{\text{fibril}}$, (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VV</td>
<td>MFC-A</td>
<td>-0.23 ± 0.11</td>
<td>-0.50 ± 0.05</td>
<td>11.7 ± 1.2</td>
<td>31 ± 3.1</td>
</tr>
<tr>
<td></td>
<td>MFC-B</td>
<td>-0.12 ± 0.11</td>
<td>-0.46 ± 0.04</td>
<td>10.7 ± 0.9</td>
<td>29 ± 2.5</td>
</tr>
<tr>
<td></td>
<td>MFC-C</td>
<td>-0.21 ± 0.07</td>
<td>-0.60 ± 0.04</td>
<td>14.0 ± 0.9</td>
<td>37 ± 2.5</td>
</tr>
<tr>
<td>VH</td>
<td>MFC-A</td>
<td>-0.23 ± 0.11</td>
<td>-0.57 ± 0.04</td>
<td>13.0 ± 1.2</td>
<td>35 ± 2.6</td>
</tr>
<tr>
<td></td>
<td>MFC-B</td>
<td>-0.12 ± 0.11</td>
<td>-0.57 ± 0.05</td>
<td>13.3 ± 1.2</td>
<td>36 ± 3.3</td>
</tr>
<tr>
<td></td>
<td>MFC-C</td>
<td>-0.21 ± 0.07</td>
<td>-0.66 ± 0.04</td>
<td>15.3 ± 1.0</td>
<td>41 ± 2.7</td>
</tr>
</tbody>
</table>
Even though the estimated modulus of single fibrils of MFC is found to be similar to modulus of natural and regenerated fibres (Bisanda and Ansell, 1992; Bledzki et al., 1996; Eichhorn et al., 2001; Cheung et al., 2009; Bledzki and Jaszkiewicz, 2010; Mukherjee and Kao, 2011; Zini and Scandola, 2011), it would be better to use MFC to enhance the mechanical properties of the polymer matrix than natural fibres due to the longer aspect ratio and greater specific surface area.

5.6 CONCLUSIONS

Raman spectroscopy has been shown to be a useful technique for studying the orientation of MFC fibrils within networks, and for following their deformation micromechanics. The intensity of the Raman peak initially located at ~1095 cm\(^{-1}\) for the Lyocell fibres using the VV polarisation configuration decreased when the angle \(\phi\) between the fibre axis and laser polarisation direction increased from 0° to 90°, while the intensity of this Raman intensity for the Lyocell fibres with the VH polarisation configuration was highest at 45°, and lowest at 0° and 90°. The intensities of this Raman peak for MFC networks (MFC-A, MFC-B and MFC-C) with the VV and VH polarisation configurations as a function of the angle \(\phi\), on the other hand, were found to be constant.

The peak position of the Raman band initially located at ~1095 cm\(^{-1}\) for the Lyocell fibres and MFC networks was found to shift towards a lower wavenumber when Lyocell fibres and MFC networks were subjected to tensile deformation. The shift of this Raman band for the MFC networks with the VV polarisation configuration was dependent on the angle \(\phi\); however, the Raman band shift rate using the VH
polarisation configuration obtained from MFC networks was found to be independent of the angle $\phi$. The Raman band shift rate for Lyocell fibres, on the other hand, was found to be independent of both the angle $\phi$ and polarisation configurations used. In addition, values of Poisson’s ratio for the MFC networks were found to be negative. This may be due to the re-entrant structure of the MFC networks.

The Young’s moduli of single filaments of MFC prepared from pulp using the different polarisation configurations (VV and VH) estimated using the Raman band shift rates were found to be in the range of 29 - 41 GPa, which is much lower than values reported for tunicate nanowhiskers, single filaments of bacterial cellulose and the crystal modulus of cellulose I. This might be due to the fact that MFC is not completely crystalline, the degree of crystallinity of MFC is lower than that of bacterial cellulose, and Raman spectroscopy records molecular deformation of both crystalline and amorphous regions.

5.7 REFERENCES


CHAPTER 6

PHYSICAL AND MECHANICAL PROPERTIES OF MICROFIBRILLATED CELLULOSE NETWORKS

The physical and mechanical properties of MFC networks, namely MFC-A, MFC-B, MFC-C and MFC-D, were investigated. Paper is a sheet or a web of natural or synthetic fibres bonded together with or without other substances, while the term “MFC network” in this work is a network of MFC produced from wood pulp or Lyocell fibres using mechanical treatment or the combination of pretreatment (enzymatic or carboxymethylation) and mechanical treatment.

6.1 MORPHOLOGY OF MICROFIBRILLATED CELLULOSE NETWORKS

The in-plane surfaces and fracture surfaces of MFC networks were investigated. Typical SEM micrographs of the in-plane surfaces of MFC networks are shown in Figure 6.1. It is clear that individual fibrils within the networks of MFC-A, MFC-B and MFC-C could not be observed due to the densely packed networks, as has been previously reported for
dense nanofibre sheets (Nogi et al., 2009); however, coarse fibrils can be observed for all MFC-A, MFC-B and MFC-C networks. These coarse fibrils can be reduced with an additional number of passes through a microfluidiser (Plackett et al., 2010; Siro et al., 2010). The individual fibres in the range of 100 - 500 nm of the MFC-D networks, on the other hand, could be seen, as shown in Figure 6.1d.

Figure 6.1 Typical SEM micrographs of the surfaces of (a) MFC-A, (b) MFC-B, (c) MFC-C and (d) MFC-D networks.
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Compared to the MFC-D network, it was difficult to see voids inside the dense networks of MFC-A, MFC-B and MFC-C; however, the porosity of these MFC networks ($\varepsilon$) can be calculated using the equation

$$e\,\%(\%) = \left(1 - \frac{\rho_l}{\rho_c}\right) \times 100 \quad (6.1)$$

where $\rho_l$ is the density of an MFC network, and $\rho_c$ is the density of cellulose assumed to be 1.5 g cm$^{-3}$ (Mwaikambo and Ansell, 2001; Sampson, 2004; Svagan et al., 2007; Henriksson et al., 2008). This equation has been used widely to calculate the porosity of networks (Svagan et al., 2007; Henriksson et al., 2008; Retegi et al., 2010).

The density and porosity of the MFC networks is summarised in Table 6.1. It can be clearly seen that the porosity of the MFC-D networks was found to be ~68 %, which was considerably higher than that of MFC-A, MFC-B and MFC-C networks, 12.7, 12.0 and 1.3 % respectively. The structure of MFC-D networks, therefore, was more open than other MFC networks studied in this work, which may affect the stress transfer between MFC in the networks (Svagan et al., 2007).

The densities of MFC-A, MFC-B and MFC-C networks are similar to MFC networks prepared by others (Henriksson and Berglund, 2007; Iwamoto et al., 2007; Abe and Yano, 2009; Nogi et al., 2009). Compared to the MFC-B network (1.32 g cm$^{-1}$), the value of 1.48 g cm$^{-1}$ for the density of MFC-C networks was clearly higher. This is due to the finer MFC fibrils, less MFC aggregates and less coarse fibrils made by a higher number of passes through a microfluidiser (Iwamoto et al., 2007; Siro and Plackett, 2010; Siro et al., 2010; Spence et al., 2010). Moreover, when the density of a network
increases, porosity decreases and the contact area between neighbouring fibrils has been reported to be higher (Sampson, 2004; Stelte and Sanadi, 2009).

**Table 6.1** Density and calculated porosity of MFC networks. Errors represent standard deviations from the mean.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Density (g cm(^{-1}))</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFC-A</td>
<td>1.31 ± 0.03</td>
<td>12.7 ± 2.3</td>
</tr>
<tr>
<td>MFC-B</td>
<td>1.32 ± 0.05</td>
<td>12.0 ± 3.7</td>
</tr>
<tr>
<td>MFC-C</td>
<td>1.48 ± 0.05</td>
<td>1.3 ± 3.6</td>
</tr>
<tr>
<td>MFC-D</td>
<td>0.48 ± 0.02</td>
<td>68.1 ± 1.3</td>
</tr>
</tbody>
</table>

The fracture surfaces of MFC networks after tensile deformation are shown in Figure 6.2. SEM micrographs of the fracture surfaces of MFC-A, MFC-B and MFC-C networks after tensile testing reveal a laminated structure in the out-of-plane direction (Henriksson and Berglund, 2007; Svagan et al., 2007). This structure has been previously reported for MFC networks in the literature (Henriksson and Berglund, 2007; Svagan et al., 2007; Henriksson et al., 2008; Aulin et al., 2010; Plackett et al., 2010). Fibril pull-out, however, is observed for MFC-D networks, as has been found for low density handsheet paper (Imamoglu and Karademir, 2006). It has been reported that the failure mechanisms of paper, fibre breakage or fibre pull-out, depend on the strength of fibre-fibre bonds in a network relative to the strength of fibres (Page, 1969; Almgren et al., 2009).
Figure 6.2 Typical SEM micrographs of the fracture surfaces of the (a) MFC-A, (b) MFC-B, (c) MFC-C and (d) MFC-D networks after tensile testing with the same magnification.

The mean pore diameter is an important factor that should be considered for the penetration of the PLA matrix through voids within a network. It has been reported that parameters such as the porosity of a network, fibre density and fibre width can affect the mean diameter of pore size (Eichhorn and Sampson, 2005). The average pore diameter ($\bar{d}$) can be calculated using the equation (Sampson, 2009; Eichhorn and Sampson, 2010).
where $\bar{w}$ and $\varepsilon_p$ are the average width of MFC fibrils within a network, and porosity of a network. The mean diameter of MFC-D fibrils was \(\sim 365\) nm, as discussed in Chapter 4.2, while the mean diameters of enzymatic and carboxymethylation pretreated MFC have been reported to be in the range 5 - 20 nm (Henriksson et al., 2007; Pääkko et al., 2007; Wågberg et al., 2008; Siro and Plackett, 2010). Hence, the mean pore diameter of the MFC-D network can be determined to be \(\sim 1.9\) µm compared to a value of less than 0.02 µm (20 nm) for the mean pore diameter of MFC-A, MFC-B and MFC-C networks. Therefore, it could be difficult for the polymer matrix to penetrate within dense MFC networks with small pore sizes between fine fibrils (MFC-A, MFC-B and MFC-C); however, it was much more likely that the polymer matrix would penetrate through the, on average, larger pores between MFC-D fibrils. These will be explained in more detail in Chapter 7.1.

6.2 FOURIER TRANSFORM INFRARED SPECTROSCOPY OF MICROFIBRILLATED CELLULOSE NETWORKS

Figure 6.3 reports Fourier transform infrared (FTIR) spectra obtained from MFC-A, MFC-B, MFC-C and MFC-D networks in the range 400 - 4000 cm\(^{-1}\). The bands, located at \(\sim 1060, 2900\) and 3300 cm\(^{-1}\), correspond to C-O, C-H and O-H stretching of cellulose respectively, and can be observed for all types of MFC networks (Liang and Marchessault, 1959; Vasko et al., 1972; Ibrahim et al., 1997; El-Zaher and Osiris, 2005; Chen et al., 2009; Ibrahim et al., 2010; Jonoobi et al., 2010; Chen et al., 2011a; Tome et
In addition, the broad band located at ~1640 cm\(^{-1}\), observed for all networks, is associated with H-O-H stretching of water absorbed by networks (Ibrahim et al., 1997; El-Zaher and Osiris, 2005; Eyholzer et al., 2010; Chen et al., 2011a; Tome et al., 2011). The amount of moisture in networks, measured using the thermogravimetric analysis method, will be discussed in Section 6.4.

The peak located at ~1600 cm\(^{-1}\), attributed to C=O stretching of the carboxyl group (COO) within cellulose, is however observed only for MFC-B and MFC-C networks (El-Zaher and Osiris, 2005; Chen et al., 2009; Hashem et al., 2009; Eyholzer et al., 2010; Ibrahim et al., 2010; Jonoobi et al., 2010; Mohkami and Talaeipour, 2011; Tome et al., 2011). This carboxyl group resulted from the carboxymethylation pretreatment. Similar spectra have been found for other carboxymethylated cellulose materials (Chen et al., 2009; Hashem et al., 2009; Eyholzer et al., 2010; Mohkami and Talaeipour, 2011).

No difference of FTIR spectra obtained from MFC-B and MFC-C networks can be observed, revealing that the mechanical treatment does not affect the structure of cellulose. Similar results have been reported for cellulose treated by ultrasonication (Chen et al., 2011a; Chen et al., 2011b), microfluidising (Eyholzer et al., 2010) and the combination of refining and high pressure homogenisation (Jonoobi et al., 2010).
Figure 6.3 FTIR spectra for MFC networks, highlighting the peaks located at ~1060, 1600, 1640, 2900, 3300 cm\(^{-1}\).

6.3 X-RAY DIFFRACTION OF MICROFIBRILLATED CELLULOSE NETWORKS

Figure 6.4 reports typical X-ray diffraction (XRD) patterns obtained from MFC networks. The four peaks located at \(2\theta = 15.5^\circ, 16.5^\circ, 22.6^\circ\) and \(35^\circ\), corresponding to 110, 1\(\bar{1}\)0, 200 and 040 crystal planes respectively, are observed from the patterns of MFC-A, MFC-B and MFC-C networks. These peaks are representative of a cellulose I crystal structure (Lu et al., 2008; Qin et al., 2008; Abbott and Bismarck, 2010; Liu et al., 2010; Siro et al., 2010; Chen et al., 2011b; Cho and Park, 2011; Tome et al., 2011). The peaks located at ~12\(^\circ\), 20\(^\circ\), 22\(^\circ\) and 35\(^\circ\) corresponding to 110, 1\(\bar{1}\)0, 200 and 040 crystal planes respectively, on the other hand, are observed for the MFC-D network.
These peaks are representative of a typical cellulose II structure (Cheng et al., 2007; Qin et al., 2008; Isogai et al., 2009; Ozturk et al., 2009; Cheng et al., 2010). These results suggest that the pretreatment and mechanical treatment used to prepare MFC networks do not significantly alter the crystal structure of the cellulose.

The degree of crystallinity of MFC networks determined using Segal’s method is reported in Table 6.2. It is worth noting that when the number of passes through a microfluidiser were increased to four, the degree of crystallinity of the MFC-C network was found to be 74.3% compared to a value of 76% for the MFC-B network, which was only passed through a microfluidiser a single time. Even though these data show no significant effect of mechanical treatment on the degree of crystallisation, it should be noted that the degree of crystallinity can be affected by the additional number of passes through a mechanical machinery (Iwamoto et al., 2007; Eyholzer et al., 2010; Karande et al., 2011). This is due to the fact that the crystalline regions of cellulose are damaged by the shear and impact forces generated by the machine (Iwamoto et al., 2007; Cheng et al., 2010; Karande et al., 2011). This is similar to what happens with MFC prepared from Lyocell fibres as discussed in Section 4.3.
Figure 6.4 X-ray diffraction patterns for MFC-A, MFC-B, MFC-C and MFC-D networks in the 2θ range 5 to 50°.

Table 6.2 Summary of the degree of crystallinity for MFC networks. Errors are standard deviations from the mean.

<table>
<thead>
<tr>
<th>Materials</th>
<th>MFC-A</th>
<th>MFC-B</th>
<th>MFC-C</th>
<th>MFC-D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degree of crystallinity (%)</td>
<td>76.0 ± 0.8</td>
<td>76.0 ± 0.3</td>
<td>74.3 ± 0.2</td>
<td>75.5 ± 4.7</td>
</tr>
</tbody>
</table>
6.4 THERMOGRAVIMETRIC ANALYSIS OF MICROFIBRILLATED CELLULOSE NETWORKS

Thermogravimetric analysis (TGA) was used to investigate the effect of pretreatments and mechanical treatment on the degradation temperature and weight loss of MFC networks with respect to temperature, as shown in Figure 6.5. Values for the onset degradation temperature and maximum degradation temperature for MFC networks are reported in Table 6.3. The initial weight of MFC networks is found to gradually decrease up to temperature of ~100 °C; due to the loss of moisture, resulting in a weight loss of ~10 wt.% (Lu et al., 2008; Nystrom et al., 2010; Cho and Park, 2011; Frone et al., 2011). Subsequently, MFC-B, MFC-C and MFC-D networks begin to decompose at ~284, 283 and 298 °C respectively, while the onset degradation temperature of MFC-A samples is ~321 °C. This process is known as the decomposition process, where cellulose is depolymerised to low molecular weight oligosaccharides for instance carbon dioxide and D-glucopyranose (Saafan and Habib, 1987; Abbott and Bismarck, 2010; Nystrom et al., 2010). Char is formed by cross-linking and re-polymerisation of the pyrolysis products (Saafan and Habibi, 1987; Abbott and Bismarck, 2010; Nystrom et al., 2010).

The derivative of weight loss curves for MFC networks exhibit a sharp degradation trough at ~346, 319, 318 and 325 °C for MFC-A, MFC-B, MFC-C and MFC-D networks respectively. MFC-A networks show better thermal stability than networks MFC-B and MFC-C because the C6 primary hydroxyls of the MFC-B and MFC-C networks were converted into sodium carboxylate groups (Fukuzumi et al., 2009),
decreasing the hydrogen bonding in the networks, as mentioned in Section 2.1.2, while MFC-D networks were produced from regenerated cellulose fibres.

It has been reported that the thermal stability of cellulose pretreated by carboxymethylation is found to be lower than that of the original pulp (Eyholzer et al., 2010). This decrease has been reported for TEMPO-oxidised cellulose (Fukuzumi et al., 2009) and acetylated bacterial cellulose also (Tome et al., 2011). The number of passes through the mechanical machinery are another variable which affects the thermal stability of MFC (Iwamoto et al., 2007). The thermal stability of MFC-C networks was found to be lower than that of MFC-B networks due to the degradation of cellulose with an increase in the number of passes (Iwamoto et al., 2007; Uetani and Yano, 2011).
Figure 6.5 Thermogravimetric analysis curves representing (a) the weight loss and (b) derivative of weight loss with respect to temperature for MFC networks.
### Table 6.3 Summary of thermal properties of MFC-A, MFC-B, MFC-C and MFC-D networks, reporting the onset degradation temperature ($T_{d\text{ onset}}$) and maximum degradation temperature ($T_{d\text{ max}}$). Errors reported are standard deviations from the mean.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$T_{d\text{ onset}}$ ($°C$)</th>
<th>$T_{d\text{ max}}$ ($°C$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFC-A</td>
<td>$321.4 \pm 1.4$</td>
<td>$343.6 \pm 1.3$</td>
</tr>
<tr>
<td>MFC-B</td>
<td>$284.3 \pm 0.5$</td>
<td>$318.9 \pm 0.2$</td>
</tr>
<tr>
<td>MFC-C</td>
<td>$282.7 \pm 0.8$</td>
<td>$317.7 \pm 0.5$</td>
</tr>
<tr>
<td>MFC-D</td>
<td>$298.3 \pm 2.6$</td>
<td>$325.3 \pm 1.2$</td>
</tr>
</tbody>
</table>

### 6.5 MECHANICAL PROPERTIES OF MICROFIBRILLATED CELLULOSE NETWORKS

Typical stress-strain curves for MFC networks are shown in Figure 6.6a, and a summary of the mechanical properties for MFC networks is reported in Table 6.4. MFC networks show non-linear stress-strain curves, as has been previously observed (Nakagaito et al., 2005; Henriksson et al., 2008; Stelte and Sanadi, 2009; Plackett et al., 2010). MFC-D networks exhibited lower mechanical properties than the dense networks (MFC-A, MFC-B and MFC-C) because of lower density, larger fibrils and higher porosity. These combined factors result in less contact area of MFC fibrils and less hydrogen bonding between MFC fibrils in the network (Henriksson et al., 2008; Stelte and Sanadi, 2009; Spence et al., 2010). In addition, compared to the Young’s modulus of the cellulose I crystal (138 GPa), the lower modulus of the cellulose II crystals (88 GPa) is thought to be another effect on the low mechanical properties of networks of MFC-D (Sakurada et al., 1962; Nishino et al., 1995).
A value of 9.6 GPa for the Young’s modulus of the MFC-C networks was higher than values of 8.7 and 9.1 GPa obtained from the MFC-A and MFC-B networks respectively. These values were different to the estimated modulus of MFC networks obtained from the Raman band shift rates, as discussed in Chapter 5.5, because at least 50 s were needed to record one Raman spectrum, while tensile testing was greatly faster. The values of Young’s modulus of MFC networks obtained from the tensile testing and Raman band shift rates, however, showed that MFC-C networks were stiffer compared to MFC-A and MFC-B networks. This may be due to the smaller size of MFC-C fibrils, the presence of fewer MFC aggregates and less coarse fibrils, resulting from an increase in the number of passes through a microfluidiser (Siro et al., 2010). In addition, the porosity of the MFC-C network was found to be lower compared to that of MFC-A and MFC-B, as shown in Table 6.1.

The mechanical properties of MFC-A, MFC-B and MFC-C networks, nevertheless, are found to be similar to those of MFC networks reported in literature (Henriksson et al., 2008; Abe and Yano, 2009; Stelte and Sanadi, 2009; Plackett et al., 2010; Siro et al., 2010). The mechanical properties have been normalised in this case by dividing by the density of networks to determine specific properties. Figure 6.6b shows the specific stress-strain curves for MFC networks. It was found that the specific Young’s moduli of MFC-A, MFC-B and MFC-C networks were similar. This indicates that the mechanical properties of MFC networks depend on the porosity within the networks, the width of fibrils and the modulus of single fibrils.

Henriksson et al. (2008) have reported that the mechanical behaviour of MFC networks is different with a change in the porosity of networks. The strength (95 MPa) and
modulus (7.4 GPa) of an MFC network with 40 % porosity were found to be lower than an MFC network with 19 % porosity (205 MPa and 14.7 GPa for strength and modulus respectively). Strain to failure, however, was reported to not depend on the porosity of a network (Henriksson et al., 2008). Other factors such as the degree of polymerisation of MFC and the number of defects within MFC are thought to have a strong influence on the mechanical properties of MFC networks (Henriksson et al., 2008; Stelte and Sanadi, 2009).

In addition, defects such as cracks may be induced in MFC network samples during the sample preparation step, which could reduce their mechanical properties. This effect can be eliminated by considering the stress and strain at zero gauge length, which will be discussed subsequently.
Figure 6.6 (a) Typical stress-strain curves and (b) specific stress-strain curves for MFC-A, MFC-B, MFC-C and MFC-D networks.
Table 6.4 Mechanical properties of MFC-A, MFC-B, MFC-C and MFC-D networks. Errors reported are standard deviations from the mean.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$\sigma$ (MPa)</th>
<th>$\sigma_{\text{specific}}$ (kNm kg$^{-1}$)</th>
<th>$\varepsilon$ (%)</th>
<th>$E$ (GPa)</th>
<th>$E_{\text{specific}}$ (MNm kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFC-A</td>
<td>123.9 ± 16.3</td>
<td>94.6 ± 12.4</td>
<td>6.2 ± 1.5</td>
<td>8.7 ± 0.7</td>
<td>6.6 ± 0.5</td>
</tr>
<tr>
<td>MFC-B</td>
<td>118.5 ± 12.5</td>
<td>89.7 ± 9.5</td>
<td>4.6 ± 1.2</td>
<td>9.1 ± 0.7</td>
<td>6.9 ± 0.5</td>
</tr>
<tr>
<td>MFC-C</td>
<td>100.3 ± 19.8</td>
<td>67.8 ± 13.3</td>
<td>2.2 ± 1.5</td>
<td>9.6 ± 0.3</td>
<td>6.5 ± 02</td>
</tr>
<tr>
<td>MFC-D</td>
<td>6.8 ± 0.5</td>
<td>14.2 ± 1.0</td>
<td>4.1 ± 0.7</td>
<td>0.6 ± 0.1</td>
<td>1.3 ± 0.2</td>
</tr>
</tbody>
</table>

In order to eliminate the influence of end effects (Arridge et al., 1976), the true Young’s modulus can be determined from MFC networks with different gauge lengths using the same strain rate, and extrapolating to infinite gauge length, as shown in Figure 6.7. As the gauge length of MFC networks increases, the Young’s modulus increases due to a reduced influence of end effects (Arridge et al., 1976). Tensile stress and strain at failure of materials, however, have been observed to decrease with an increase of defects such as cracks, voids and coarse fibrils with the longer gauge length; so by extrapolation to zero gauge length the true strength of MFC networks can be found (Figure 6.8) (Pardinia and Manhanib, 2002; Thanikaivelan et al., 2006; Kong, 2007; Lim et al., 2011). The values of extrapolated true Young’s modulus, stress and strain of MFC networks are summarised in Table 6.5.

It was found that MFC-C networks were stiffer and stronger than MFC-A and MFC-B networks. This could be due to lower porosity of MFC-C networks compared to MFC-A
and MFC-B networks as shown in Table 6.1 and possibly less coarse fibrils in the networks acting as defects. The strain of MFC-C networks was, however, lower than MFC-B networks, possibly because of the shorter fibrils caused by the additional passes (Iwamoto et al., 2007; Stelte and Sanadi, 2009).

**Figure 6.7** Effect of the reciprocal gauge length on Young’s modulus of the MFC-A, MFC-B, MFC-C and MFC-D networks using the same strain rate. Error bars are standard deviations from the mean.
Figure 6.8 Effect of gauge length on (a) stress and (b) strain of the MFC-A, MFC-B, MFC-C and MFC-D networks using the same strain rate. Error bars are standard deviations from the mean.
Table 6.5 Summary of the extrapolated mechanical properties for MFC-A, MFC-B, MFC-C and MFC-D networks. Errors are standard deviations from the mean.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Extrapolated stress (MPa)</th>
<th>Extrapolated strain (%)</th>
<th>Extrapolated Young’s modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFC-A</td>
<td>187.2 ± 11.6</td>
<td>10.5 ± 1.5</td>
<td>8.8 ± 2.4</td>
</tr>
<tr>
<td>MFC-B</td>
<td>201.2 ± 11.1</td>
<td>12.9 ± 1.2</td>
<td>9.3 ± 2.3</td>
</tr>
<tr>
<td>MFC-C</td>
<td>223.7 ± 7.9</td>
<td>11.6 ± 0.6</td>
<td>9.7 ± 2.6</td>
</tr>
<tr>
<td>MFC-D</td>
<td>7.9 ± 0.4</td>
<td>8.3 ± 1.4</td>
<td>0.5 ± 0.1</td>
</tr>
</tbody>
</table>

6.6 ZERO SPAN TESTING OF MICROFIBRILLATED CELLULOSE NETWORKS

Results obtained from zero span testing can be used to estimate the bond strength between MFC within the networks using the relationship between the tensile strength of paper and bond strength introduced by Page (1969). The strength of a network is derived from the tensile strength of individual fibrils and the bond strength between fibrils, $B$, which can be calculated using the equation (Page, 1969)

\[
\frac{1}{T} = \frac{1}{Z} + \frac{1}{B}
\]  

(6.3)

Then,

\[
B = \frac{ZT}{Z-T}
\]  

(6.4)

where $Z$ and $T$ are zero and long span tensile indices (kN m kg$^{-1}$).
The zero strength and bond strength indices of MFC networks are reported in Table 6.6. It was found that the zero strength index, related to the fibre strength, of MFC-A networks were higher than that of MFC-B and MFC-C networks. This may be due to the damage from carboxymethylation pretreatment to MFC-B and MFC-C fibrils. The values of the bond strength of MFC-A, MFC-B and MFC-C networks were significantly higher than that of MFC-D networks. This can confirm why the fracture surface of MFC-D networks showed more significant fibril pull-out, whereas fibril breakage was mostly observed for the networks of MFC-A, MFC-B and MFC-C, as shown in Figure 6.2. It is worth noting that higher bond strengths are found for the networks of MFC-A, MFC-B and MFC-C, compared to typical paper hand sheets (less than 200 Nm g⁻¹) (I'Anson et al., 2006). This is possibly due to smaller fibrils, higher aspect ratio and therefore more contact area of MFC fibrils for bonding in the networks (Page, 1969; I'Anson et al., 2006; Retegi et al., 2010; Yoo and Hsieh, 2010). The low mechanical properties of networks of MFC made from Lyocell fibres, as discussed in Chapter 4.5, however, were thought to be due to the low bonding strength between MFC fibrils within the networks and high porosity in the networks.

The bond strength index has been found to be higher when handsheet paper is produced from beaten fibres. A value of 19 kNm kg⁻¹ of the bond strength for the handsheet paper formed from unbeaten fibres was reported, while values of 116 and 221 kNm kg⁻¹ were obtained from the handsheet paper prepared from beaten fibres using a PFI mill for 56,000 and 72,000 revolutions respectively (I'Anson et al., 2006). This is due to the fact that when the fibres are beaten, the surface area and contact area with neighboring fibrils increase (I'Anson et al., 2006).
According to Equation 6.4, if a value of the bond strength index, $B$, is considerably high, the value of $1/B$ in the equation 6.4 would be close to zero. Then, the ratio of the tensile strength index to the zero strength index, $T/Z$, can be equal to one (Page, 1969), meaning that the whole network acts as a whole fibre. This ratio, however, can be less than one if defects and voids in this material are taken into account. Interestingly, compared to values of the content of MFC fibrils in networks, $1 – \text{porosity} (\varepsilon_p)$, shown in Table 6.1, the values of $T/Z$ for the MFC networks were found to be similar.

Table 6.6 Calculated bonding index of MFC networks. Errors reported are standard deviations from the mean.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Zero strength index, $Z$ (kNm kg$^{-1}$)</th>
<th>Bond strength index, $B$ (kNm kg$^{-1}$)</th>
<th>$T/Z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFC-A</td>
<td>126.3 ± 8.5</td>
<td>499 ± 9</td>
<td>0.80</td>
</tr>
<tr>
<td>MFC-B</td>
<td>113.8 ± 6.1</td>
<td>669 ± 7</td>
<td>0.85</td>
</tr>
<tr>
<td>MFC-C</td>
<td>117.9 ± 8.8</td>
<td>1160 ± 10</td>
<td>0.91</td>
</tr>
<tr>
<td>MFC-D</td>
<td>77.7 ± 4.0</td>
<td>38 ± 5</td>
<td>0.33</td>
</tr>
</tbody>
</table>

6.7 RAMAN SPECTROSCOPY OF MICROFIBRILLATED CELLULOSE NETWORKS

Typical Raman spectra obtained from MFC networks (MFC-A, MFC-B, MFC-C and MFC-D) are shown in Figure 6.9. These spectra show a dominant peak, initially located at $\sim$1095 cm$^{-1}$, corresponding to the C-O ring stretching mode within the cellulose backbone structure (Wiley and Atalla, 1987; Eichhorn et al., 2001; Hsieh et al., 2008;
Bakri and Eichhorn, 2010), and possibly the glycosidic C-O-C stretching mode (Edwards et al., 1997; Gierlinger et al., 2006; Qin et al., 2008).

![Graph showing Raman spectra]

**Figure 6.9** Typical Raman spectra in the range 200 - 1600 cm\(^{-1}\) for MFC networks and, highlighting a Raman peak initially located at ~1095 cm\(^{-1}\).

### 6.8 REPEATABILITY OF THE MEASUREMENT OF RAMAN BAND POSITIONS OF MICROFIBRILLATED CELLULOSE NETWORKS

40 measurements of the position of the Raman band initially located at ~1095 cm\(^{-1}\), obtained from fixed and random locations of the laser beam on the MFC networks, were recorded to determine the reproducible of the position of this band as shown in Figures 6.10.
Figure 6.10 Distributions of the peak positions of the Raman band initially located at ~1095 cm\(^{-1}\) for 40 measurements taken from the same and different positions of the laser beam on (a) MFC-A, (b) MFC-B, (c) MFC-C and (d) MFC-D networks.
It can be seen that the values of standard deviation of the peak position obtained from the same and different locations of the laser beam on networks of MFC-A, MFC-B, MFC-C and MFC-D are similar, confirming that Raman results of these samples is reproducible. This indicates that Raman spectroscopy is a viable method for studying the deformation of MFC networks.

6.9 MOLECULAR ORIENTATION OF MICROFIBRILLATED CELLULOSE WITHIN NETWORKS

Figure 6.11 reports the normalised intensity of the Raman band initially located at ~1095 cm$^{-1}$ as a function of rotation angle between the sample axis and laser polarisation axis for MFC networks (MFC-A, MFC-B, MFC-C and MFC-D), compared to a highly oriented single Lyocell fibre, as has been discussed in detail in Section 5.3.

The intensity of this Raman band obtained from these MFC networks is found to be independent of the rotation angle, indicating the orientation of the cellulose molecules within the MFC networks is planar isotropic and random, as has been reported for bacterial cellulose networks (Hsieh et al., 2008). The intensity of this Raman band taken from a highly oriented single Lyocell fibre, however, is found to have a maximum when the fibre is aligned parallel to the laser direction, and a minimum when the fibre direction is perpendicular to the laser direction. This is thought to be due to the high degree of molecular orientation of the cellulose molecular chains along the fibre axis. Similar results have been previously reported for other highly aligned cellulose fibres, such as flax (Sturcova et al., 2005; Bakri and Eichhorn, 2010) and rayon fibres (Zimmerley et al., 2010)
Figure 6.11 Normalised intensity of the Raman band initially located at $\sim 1095$ cm\(^{-1}\) as a function of rotation angle between the sample direction and laser direction for MFC-A, MFC-B, MFC-C and MFC-D networks compared to a highly aligned Lyocell fibre.

6.10 MICROMECHANICAL DEFORMATION OF MICROFIBRILLATED CELLULOSE NETWORKS

When deformed in tension, the position of the Raman band initially located at $\sim 1095$ cm\(^{-1}\) for the MFC networks was observed to shift toward a lower wavenumber, as discussed in Section 2.4.4. Typical examples of the shifts of this Raman band for an MFC-C network in tension are shown in Figure 6.12.
Typical shifts towards a lower wavenumber of the Raman peak initially located at ~1095 during tensile deformation of an MFC-C network. Solid lines mark the position of the peak and are a guide for the eye only.

A summary of the Raman band shifts with respect to tensile strain and stress for MFC networks is reported in Table 6.9, and Figure 6.13 shows typical shifts of the Raman band initially located at ~1095 cm\(^{-1}\) for MFC networks with respect to tensile strain and applied stress. It has been found that the magnitude of the gradient of a linear fit to Raman data with respect to strain (shift rate with respect to strain) is related to the stress-transfer efficiency in cellulose networks and composites (Quero et al., 2011).

The values of Raman band shifts as a function of tensile strain determined from dense networks (MFC-A, MFC-B and MFC-C) were found to be higher, compared to that of MFC-D networks (-0.28 ± 0.02 cm\(^{-1}\) %\(^{-1}\)). This was thought to be due to a more opened
structure, larger fibril sizes and fewer fibril-fibril bonds. Importantly, a value of 138 GPa for the modulus of the cellulose I crystal has been reported, which is higher than that of 88 GPa obtained from the cellulose II crystal, the raw material of MFC-D networks (Nishino et al., 1995). These differences in crystal modulus could result in a lower Raman band shift rate and mechanical properties of the MFC networks prepared from Lyocell fibres. It is also worth mentioning that after being deformed in tension beyond 1% strain, the Raman band shift rate with respect to strain of MFC-D networks reaches a plateau. This plateau could be due to fibrils pulling out of the network, which is supported by the fracture surface shown in Figure 6.2.

Table 6.7 Raman band shifts as a function of strain and stress for MFC networks. Errors are standard deviations from the mean.

<table>
<thead>
<tr>
<th>Raman band shift against</th>
<th>MFC-A</th>
<th>MFC-B</th>
<th>MFC-C</th>
<th>MFC-D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strain (cm⁻¹ %⁻¹)</td>
<td>-0.45 ± 0.01</td>
<td>-0.40 ± 0.01</td>
<td>-0.44 ± 0.02</td>
<td>-0.28 ± 0.02</td>
</tr>
<tr>
<td>Stress (cm⁻¹ GPa⁻¹)</td>
<td>-7.1 ± 0.3</td>
<td>-7.4 ± 0.3</td>
<td>-6.8 ± 0.4</td>
<td>-21.9 ± 0.4</td>
</tr>
</tbody>
</table>
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Figure 6.13 Typical shifts of the Raman band initially located at 1095 cm$^{-1}$ for MFC-A, MFC-B, MFC-C and MFC-D networks as a function of (a) tensile strain and (b) stress. Error bars are standard deviations from the mean.
It is thought that the networks have a uniform strain microstructure, as has been previously proposed for fibrous networks (Kallmes et al., 1977). Therefore, the Raman band shift with respect to applied stress, \( \frac{d(\Delta \nu)}{d\sigma} \), of the networks can be given by (Young and Eichhorn, 2007; Bakri and Eichhorn, 2010).

\[
\frac{d(\Delta \nu)}{d\sigma} \propto \frac{1}{E}
\]

where \( E \) is the modulus of the material. This could explain why a value of Raman band shift with respect to applied stress (-21.9 ± 0.4 cm\(^{-1}\) GPa\(^{-1}\)), obtained from MFC-D networks, was found to be higher than those of MFC-A, MFC-B and MFC-C networks (-7.1 ± 0.3, -7.4 ± 0.3 and -6.8 ± 0.4 cm\(^{-1}\) GPa\(^{-1}\) respectively) since the Young’s modulus of the MFC-D networks was much lower than those of the other networks (MFC-A, MFC-B and MFC-C). It is worth noting that stress relaxation can be observed at high stress during the deformation micromechanics due to time consuming of 50 s to record one Raman spectrum. This stress relaxation, however, could not be found at low stress.

In addition, Even though when the MFC-D network was deformed in tensile fibril pull-out occurred at low strain, the effective modulus of MFC can be approximately estimated using the first few step of tensile strain before fibril pull-out occurred. A value of 17.4 ± 1.2 GPa for the effective modulus of single filament of MFC fibrillated from Lyocell fibres can be estimated. This value is lower than a value of ~98 GPa for the modulus of MFC prepared from Lyocell fibres using an AFM tip (Cheng et al., 2009). This is because MFC agglomerates and bigger MFC fibrils were observed within
the MFC-D network (Figure 6.1d), while an individual fibril of MFC was measured using an AFM method (Cheng et al., 2009).

6.11 CONCLUSIONS

The physical and mechanical properties of MFC networks were investigated. The fracture surfaces of these networks after tensile testing were found to vary depending upon porosity, bond strength and fibril size. The carboxymethylation pretreatment used to prepare MFC-B and MFC-C networks was found to modify the hydroxyl groups (-OH) to carboxyl groups (-COO), as confirmed by FTIR results. Mechanical treatment, however, did not appear to significantly affect the structure, again confirmed by FTIR spectra as well as X-ray diffraction. Both carboxymethylation pretreatment and additional passes through a microfluidiser have a combined influence on the thermal stability of MFC networks. No significant difference was observed for the mechanical properties of MFC networks prepared using the enzymatic and carboxymethylation pretreatment, but the additional number of passes through a microfluidiser affected the porosity of networks due to decrease in both fibril agglomerates and coarse fibrils, resulting in higher mechanical properties of the network.

Young’s modulus and tensile strength values of dense MFC networks (MFC-A, MFC-B and MFC-C) were observed to be significantly higher than those of MFC-D networks. This was thought to be due to the presence of finer fibrils and lower porosity in MFC-A, MFC-B and MFC-C, resulting in more contact area and stronger bonding strength in the networks. Additionally, the raw material used to produce MFC-D networks is a from a cellulose II source, which has a lower crystal modulus (88 GPa) compared to a value of
138 GPa for a cellulose I crystal, the raw material used to produce MFC-A, MFC-B and MFC-C networks.

Raman spectroscopy has been used successfully to follow the stress-transfer mechanisms in MFC networks. The presence of a Raman band initially located at ~1095 cm\(^{-1}\) was noted for MFC networks, making it possible to monitor its position during tensile deformation. This Raman band was observed to shift towards a lower wavenumber, thus indicating stress transfer between MFC fibrils within the network. A value of 17.4 ± 1.2 GPa for the effective modulus of single filaments of MFC prepared from Lyocell fibres can be estimated.

### 6.12 REFERENCES


Aulin C., Gallstedt M. and Lindstrom T. Oxygen and oil barrier properties of microfibrillated cellulose films and coatings. Cellulose. 2010; 17 (3): 559-574.


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CHAPTER 7

PHYSICAL AND MECHANICAL PROPERTIES OF MICROFIBRILLATED CELLULOSE REINFORCED POLY(LACTIC ACID) COMPOSITES

MFC networks, namely MFC-A, MFC-B, MFC-C and MFC-D, were used as reinforcements for poly(lactic acid) prepared using compression moulding. The effect of these MFC networks on the physical and mechanical properties of the composites is reported.

7.1 MORPHOLOGY OF MICROFIBRILLATED CELLULOSE REINFORCED COMPOSITES

SEM micrographs of the fracture surfaces for composites reinforced by MFC-A and MFC-D networks after tensile testing are shown in Figures 7.1 and 7.2 respectively. The fracture surface of MFC-B and MFC-C reinforced composites is similar to the MFC-A
reinforced PLA composite fracture surface. It is worth noting that interaction of the dense MFC networks (MFC-A, MFC-B and MFC-C) and PLA matrix can be observed between the surface of the network and PLA matrix with little penetration of PLA into the network. Similarly, the interfacial interaction between a dense network of bacterial cellulose and PLA has been reported, showing little penetration of the PLA into the bulk of the cellulose network (Quero et al., 2010). The porosity of this network of BC was ~10 % (Quero et al., 2010).

Figure 7.1 Typical SEM micrographs of the fracture surfaces of PLA composites reinforced by the MFC-A network from tensile testing with different magnifications.
PLA, on the other hand, is observed to penetrate within the pores of the MFC-D network due to higher porosity and larger pore size within MFC-D networks, as discussed in chapter 6.1., than MFC-A, MFC-B and MFC-C network. This results in what is thought to be a strong interface, allowing stress to transfer from PLA to the MFC fibrils (Figures 7.2) In addition, the fracture surface of the MFC-D reinforced PLA composite was found to be completely different compared to that of the MFC-D network (Figure 6.2d). This was thought to be because MFC fibrils were well-bonded with the PLA matrix. This enhanced bonding could lead to MFC fibrils being broken instead of pulling out (Imamoglu and Karademir, 2006).

![Figure 7.2 Typical SEM micrographs of the fracture surface of PLA composites reinforced by the MFC-D network from tensile testing with different magnifications.](image)

### 7.2 THERMOGRAVIMETRIC ANALYSIS OF MICROFIBRILLATED CELLULOSE REINFORCED COMPOSITES

The thermal stability of the MFC reinforced composites, compared to neat PLA, is shown in Figure 7.3, and a summary of the thermal stability of MFC reinforced PLA
composites and neat PLA is reported in Table 7.1. The weight of MFC reinforced PLA composites starts to reduce up to 100 °C, owing to the evaporation of moisture. It can be seen that all MFC reinforced composites are observed to degrade at lower temperatures, compared to the onset degradation temperature of ~332 °C for neat PLA. This is because MFC is sensitive to thermal decomposition. Similarly, the degradation temperature of cellulose-whisker reinforced PLA nanocomposites has been reported to slightly decrease due to the thermal sensitivity of acid treated cellulose nanowhiskers (Sanchez-Garcia and Lagaron, 2010). It has been noted that the thermal decomposition of cellulose-reinforced composites depends on the content and the thermal stability of cellulose in the composites (Tome et al., 2011; Sanchez-Garcia and Lagaron, 2010).

Table 7.1 Summary of thermal properties of MFC reinforced composites and neat PLA, reporting the onset degradation temperature ($T_{d_{\text{onset}}}$) and maximum degradation temperature ($T_{d_{\text{max}}}$). Errors reported are standard deviations from the mean.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$T_{d_{\text{onset}}}$(°C)</th>
<th>$T_{d_{\text{max}}}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>331.6 ± 5.8</td>
<td>354.9 ± 3.0</td>
</tr>
<tr>
<td>MFC-A/PLA</td>
<td>312.2 ± 3.4</td>
<td>338.8 ± 3.1</td>
</tr>
<tr>
<td>MFC-B/PLA</td>
<td>294.0 ± 1.7</td>
<td>319.7 ± 1.6</td>
</tr>
<tr>
<td>MFC-C/PLA</td>
<td>289.7 ± 2.5</td>
<td>315.0 ± 1.3</td>
</tr>
<tr>
<td>MFC-D/PLA</td>
<td>309.3 ± 4.1</td>
<td>331.9 ± 3.7</td>
</tr>
</tbody>
</table>
Figure 7.3 Thermogravimetric analysis curves representing (a) the weight loss and (b) derivative of weight loss with respect to temperature for MFC reinforced PLA composites compared to neat PLA films.
7.3 DIFFERENTIAL SCANNING CALORIMETRY OF MICROFIBRILLATED CELLULOSE REINFORCED COMPOSITES

Differential scanning calorimetry (DSC) was used to investigate the thermal behaviour of composites reinforced by MFC networks compared to neat PLA, as shown in Figure 7.4. A summary of the glass transition temperature ($T_g$), cold crystallisation temperature ($T_{cc}$), melting temperature ($T_m$) and heat of fusion ($\Delta H_m$) of neat PLA and PLA composites reinforced by MFC networks during the first heating and cooling cycles is reported in Table 7.2.

![Figure 7.4](image)

**Figure 7.4** Differential scanning calorimetry curves of MFC reinforced composites and neat PLA for the first heating and cooling cycles: $T_g$ is the glass transition temperature, $T_{cc}$ is the cold crystallisation temperature and $T_m$ is the melting temperature.
Table 7.2 Summary of differential scanning calorimetry data representing the glass transition temperature (T\textsubscript{g}), cold crystallisation temperature (T\textsubscript{cc}), melting temperature (T\textsubscript{m}) and heat of fusion (\(\Delta H_{m}\)) of neat PLA and composites reinforced by MFC networks obtained from the first heating scan. Errors reported are standard deviations from the mean.

<table>
<thead>
<tr>
<th>Materials</th>
<th>T\textsubscript{g} (°C)</th>
<th>T\textsubscript{cc} (°C)</th>
<th>T\textsubscript{m} (°C)</th>
<th>(\Delta H_{m}) (J g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PLA</td>
<td>59.2 ± 1.3</td>
<td>-</td>
<td>147.1 ± 0.7</td>
<td>1.6 ± 0.3</td>
</tr>
<tr>
<td>MFC-A/PLA</td>
<td>61.2 ± 0.3</td>
<td>110.6 ± 1.0</td>
<td>146.1 ± 0.7</td>
<td>4.7 ± 0.4</td>
</tr>
<tr>
<td>MFC-B/PLA</td>
<td>60.6 ± 0.3</td>
<td>111.6 ± 0.3</td>
<td>145.4 ± 0.2</td>
<td>5.6 ± 0.4</td>
</tr>
<tr>
<td>MFC-C/PLA</td>
<td>60.4 ± 0.4</td>
<td>111.7 ± 1.1</td>
<td>144.3 ± 0.5</td>
<td>7.6 ± 0.2</td>
</tr>
<tr>
<td>MFC-D/PLA</td>
<td>59.5 ± 0.2</td>
<td>107.5 ± 0.9</td>
<td>142.7 ± 0.5</td>
<td>7.7 ± 0.4</td>
</tr>
</tbody>
</table>

Thermal behaviours of MFC reinforced PLA composites were found to be similar to that of neat PLA films. The DSC curve for PLA exhibits two dominant transitions located at ~60 and 147 °C, corresponding to the glass transition temperature (T\textsubscript{g}) and melting temperature (T\textsubscript{m}) respectively. These peaks have been observed for typical semi-crystalline polymers such as polypropylene (Joseph \textit{et al.}, 2003) and poly(vinyl alcohol) (El-Zaher and Osiris, 2005; Lu \textit{et al.}, 2008). No crystallisation peak, however, could be observed from the cooling curve because the cooling rate used in the system, 10 °C min\(^{-1}\), does not provide enough time for PLA to crystallise (Iannace and Nicolais, 1997; Liu \textit{et al.}, 2010; Quero \textit{et al.}, 2010). This is due to the fact that PLA is a slow crystallisation polymer, similar to poly(ethylene terephthalate) (PET) (Wang \textit{et al.}, 2005; Quero \textit{et al.}, 2010; Suryanegara \textit{et al.}, 2010).
After embedding MFC networks in the PLA matrix, no significant change in the glass transition temperature ($T_g$) for the composites is detected. In whisker-reinforced composites, an increase of the glass transition temperature ($T_g$) has been reported, as the mobility of polymer chains is thought to be hindered by the whiskers (Siqueira et al., 2009; Sanchez-Garcia and Lagaron, 2010).

No peak, corresponding to the cold crystallisation temperature ($T_{cc}$) (Liu et al., 2010; Quero et al., 2010; Sanchez-Garcia and Lagaron, 2010; Suryanegara et al., 2010), can be observed for neat PLA matrix. However, after embedding MFC networks in the PLA matrix, there is a peak located at ~110 °C observed, suggesting MFC can nucleate crystallisation in composites, as previously reported for cellulose reinforced composites (Liu et al., 2010; Quero et al., 2010; Sanchez-Garcia and Lagaron, 2010; Suryanegara et al., 2010; Wang et al., 2011). The transcrystallisation process has been observed to occur along cellulose fibres in composites, increasing the degree of crystallinity of composites (Zafeiropoulos et al., 2001; Wang et al., 2011), although no evidence for this process can be found in the present study.

Compared to composites reinforced by MFC-A, MFC-B and MFC-C networks, MFC-D reinforced PLA composites exhibit a broader and larger cold crystallisation peak (a higher heat of fusion of crystallisation). This is due to the penetration of PLA through the MFC-D networks, supported by the fracture images shown in Figure 7.2. Therefore, MFC-D could potentially interact more readily with the PLA matrix.

The melting temperature ($T_m$) of MFC-PLA composites was found to be lower than that of neat PLA. This may be because of the good interaction between cellulose and the polymer chains, which limits the capability of spherulites to grow or possibly the
transcrystallisation process making small spherulites occurring in the composites (Samir et al., 2004; Roohani et al., 2008; Sanchez-Garcia and Lagaron, 2010). In addition, values of the heat of fusion ($\Delta H_m$), the area of the melting peak, were found to increase with the addition of MFC networks, indicating higher crystallinity in the composites.

### 7.4 MECHANICAL PROPERTIES OF MICROFIBRILLATED CELLULOSE REINFORCED COMPOSITES

The mechanical properties of MFC reinforced composites are reported in Table 7.3, and typical stress-strain curves for these composites, pure MFC networks and neat PLA films are shown in Figure 7.5. After embedding MFC networks in PLA, the strength and Young’s modulus of MFC reinforced composites were found to increase above that of the neat matrix. Strain at failure, however, decreased due to embrittlement caused by MFC. This enhancement of the mechanical properties of the PLA indicates stress is transferred from the matrix to the reinforcement phase i.e. the MFC fibrils.

It is assumed that MFC-A, MFC-B and MFC-D networks act as one piece of reinforcement material in the laminated composite. The rule of mixtures (discussed in Section 2.3.3), therefore, can be applied to estimate the modulus of the laminated composites with the dense MFC networks (MFC-A, MFC-B and MFC-C) using the equation

$$E_c = E_f V_f + E_m (1 - V_f)$$

(7.1)

where $E_c$, $E_f$ and $E_m$ are the composite, MFC network and matrix moduli respectively, and $V_f$ is the volume fraction of an MFC network in a composite. Values of the volume
fraction for networks of MFC-A, MFC-B and MFC-C in the composites are 0.34, 0.31 and 0.29 respectively. Therefore, theoretical values of 4.3, 4.2 and 4.2 GPa for the modulus of MFC-A, MFC-B and MFC-C reinforced composites can be obtained, which is similar to the experimental values shown in Table 7.3. This suggests a good interaction between the reinforcement and matrix phases.

On the other hand, it can be assumed that MFC is dispersed randomly in MFC-D/PLA composites. The modulus of this composite, therefore, can be estimated using (Hull and Clyne, 1996)

\[
E_c = \eta_0 E_f V_f + E_m (1 - V_f)
\]

(7.2)

where \(\eta_0\), an efficiency factor taking the effect of the orientation of MFC within a network into account, is 3/8, as already discussed in Chapter 5.5. The volume fraction of an MFC-D network \((E_f)\) in the composite is 0.21, and the modulus of a filament of MFC prepared from Lyocell fibres is 17.4 GPa, as discussed in Chapter 6.10. The value of 3.0 GPa for the modulus of MFC-D/PLA composites can be estimated using Equation 7.2. This value is close to the value from the experiment, 3.2 GPa, showing the good bonding between PLA and MFC in this composite.

Even though the mechanical properties of pure MFC-D networks were considerably lower than those of neat PLA, the tensile strength and Young’s modulus of the MFC-D reinforced PLA composites (55.8 MPa and 3.2 GPa) were higher than those of pure PLA films (49.0 MPa and 2.0 GPa) and close to those of composites reinforced with dense networks (MFC-A, MFC-B and MFC-C). This indicates that the combination of these materials leads to enhanced stress-transfer between the components. The fibril-
fibril interaction is thought to play a dominant role in the mechanical properties of the pure MFC networks. When these networks are combined with the PLA, stress-transfer from the PLA matrix to the fibrils plays an important role in the mechanical properties of the composites (Almgren et al., 2009). In addition, it has been shown that crack initiation and propagation in paper structures can be hindered by polymer impregnation (Imamoglu and Karademir, 2006). Similarly, the mechanical properties of PP composites reinforced with MFC mats prepared using compression moulding have been reported to increase compared to those of neat PP (Cheng et al., 2007). The mechanical properties of the composites reinforced by networks of MFC-A, MFC-B and MFC-C, however, mainly depend on the mechanical properties of the networks due to the interfacial interaction, as shown in Figure 7.1.

<table>
<thead>
<tr>
<th>Materials</th>
<th>σ (MPa)</th>
<th>ε (%)</th>
<th>E (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PLA</td>
<td>49.0 ± 2.7</td>
<td>9.2 ± 0.5</td>
<td>2.0 ± 0.1</td>
</tr>
<tr>
<td>MFC-A composite</td>
<td>64.3 ± 7.0</td>
<td>3.2 ±1.1</td>
<td>3.8 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>(123.9 ± 16.3)</td>
<td>(6.2 ± 1.5)</td>
<td>(8.7 ± 0.7)</td>
</tr>
<tr>
<td>MFC-B composite</td>
<td>60.5 ± 4.6</td>
<td>3.2 ± 0.5</td>
<td>3.6 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>(118.5 ± 12.5)</td>
<td>(4.6 ± 1.2)</td>
<td>(9.1 ± 0.7)</td>
</tr>
<tr>
<td>MFC-C composite</td>
<td>68.0 ± 5.1</td>
<td>4.7 ± 1.2</td>
<td>3.6 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>(100.3 ± 19.8)</td>
<td>(2.2 ± 1.5)</td>
<td>(9.6 ± 0.3)</td>
</tr>
<tr>
<td>MFC-D composites</td>
<td>55.8 ± 1.4</td>
<td>5.1 ± 0.9</td>
<td>3.2 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>(6.8 ± 0.3)</td>
<td>(2.4 ± 0.3)</td>
<td>(0.6 ± 0.1)</td>
</tr>
</tbody>
</table>
Figure 7.5 Typical stress-strain curves for MFC networks and MFC reinforced composites compared to neat PLA films.
7.5 RAMAN SPECTROSCOPY OF MICROFIBRILLATED CELLULOSE REINFORCED COMPOSITES

Figure 7.6 shows Raman spectra obtained from an MFC-A reinforced PLA composite, an MFC-A network and a neat PLA film in the range 1050 - 1150 cm\(^{-1}\). When an MFC network is embedded in the PLA matrix, even though PLA shows a small peak located at 1095 cm\(^{-1}\), it is possible to obtain the \(~1095\) cm\(^{-1}\) Raman band from MFC fibrils in the composite. This is because the peak obtained from PLA films is not of sufficient intensity to interfere with the signal from the cellulose.

![Figure 7.6 Typical Raman spectra in the range 1050 - 1150 cm\(^{-1}\) for an MFC-A network, an MFC-A reinforced PLA composite and neat poly(lactic acid, highlighting a Raman peak initially located at \(~1095\) cm\(^{-1}\).]
No shift of this Raman band for PLA with respect to tensile strain is observed, as shown in Figure 7.7. Similarly, the shift in the position of this Raman band from cellulose has been reported to be unaffected by the presence of the band in the same region arising from the PLA (Quero et al., 2010). This is thought to be due to the random conformations of the entangled network of polymer molecules within PLA, without any significant orientation. It is concluded, therefore, that the Raman method can be used to study the stress transfer processes in MFC-reinforced PLA composites. Similar spectra were obtained from composites reinforced with the other MFC networks.

![Figure 7.7 Typical shifts of the Raman band initially located at ~1095 cm⁻¹ as a function of tensile strain for neat PLA. Error bars are standard deviations from the mean.](image-url)
7.6 REPEATABILITY OF THE MEASUREMENT OF RAMAN BAND
POSITIONS OF MICROFIBRILLATED CELLULOSE REINFORCED
COMPOSITES

40 measurements of the position of the Raman band initially located at \(~1095\ \text{cm}^{-1}\),
obtained from fixed and random locations of the laser beam on the MFC reinforced
composites, were as shown in Figures 7.8 . It can be seen that the results of MFC
reinforced composites can be reproducible due to similar values of standard deviations
of the peak position obtained from the same and different locations of the laser beam on
the composite samples.
Figure 7.8 Distributions of the peak positions of the Raman band initially located at \( \sim 1095 \text{ cm}^{-1} \) for 40 measurements taken from the same and different positions of the laser beam on PLA composites reinforced by (a) MFC-A, (b) MFC-B, (c) MFC-C and (d) MFC-D networks.
7.7 MICROMECHANICAL DEFORMATION OF MICROFIBRILLATED CELLULOSE REINFORCED COMPOSITES

When deformed in tension, the position of the Raman band initially located at \( \sim 1095 \text{ cm}^{-1} \) obtained from the MFC-C/PLA composite was observed to shift toward a lower wavenumber, as discussed in Section 2.4.4, as shown in Figure 7.9.

Figure 7.9 Typical shifts towards a lower wavenumber of the Raman peak initially located at \( \sim 1095 \text{ cm}^{-1} \) during tensile deformation of a PLA composite reinforced with an MFC-C network. Solid lines mark the position of the peak and are a guide for the eye only.

Figure 7.10 reports shifts of the Raman band initially located at \( \sim 1095 \text{ cm}^{-1} \) with respect to strain for MFC networks and MFC-reinforced PLA composites. After embedding MFC networks into PLA, increased Raman shifts with respect to strain were obtained from all MFC-reinforced PLA composites, compared to those from the pure networks.
This change in the gradient of the shifts, going from a network to a composite material, is the direct evidence of stress transfer between the matrix and fibrils within the network.

Fibril-matrix debonding is observed for MFC-B and MFC-C reinforced composites (Figures 7.10b and c), where the data for the peak position level off to a plateau, as reported previously for laminated PLA and bacterial cellulose networks (Quero et al., 2010). MFC-A and MFC-D reinforced PLA composites, however, do not exhibit this behaviour. It is thought that the interaction between the MFC-B and MFC-C networks and PLA is weaker because of the denser networks, and less matrix penetration.

The stress-transfer process is further elucidated by plotting the position of the Raman band initially located at ~1095 cm$^{-1}$ with respect to stress (Figure 7.11). It is worth noting that the composite is best described using a uniform strain model of the structure i.e. the strain of reinforcement and matrix phases is equal, as discussed in Section 2.3.2.

Therefore, the Raman band shift with respect to stress ($d\nu/d\sigma$) has been reported to be proportional to the reciprocal of the modulus of a material ($1/E$) (Young and Eichhorn, 2007). If this is the case, then Raman band shifts with respect to stress for composites should be affected by a change in the slope of the stress-strain curves i.e. the modulus (see inset Figure 7.11). MFC reinforced PLA composites were found to yield at a high stress level. The yield point in the Raman band shift data with respect to applied stress for MFC-B and MFC-C reinforced composites may be difficult to see due to debonding of the fibrils from the matrix.
Figure 7.10 Typical shifts of the Raman band initially located at ~1095 cm\(^{-1}\) as a function of tensile strain for (a) MFC-A networks and MFC-A/PLA composites, (b) MFC-B networks and MFC-B/PLA composites, (c) MFC-C networks and MFC-C/PLA composites and (d) MFC-D networks and MFC-D/PLA composites. Error bars are standard deviations from the mean.
Figure 7.11 Typical shifts of the Raman band initially located at ~1095 cm\(^{-1}\) with respect to applied stress for (a) MFC-A, (b) MFC-B, (c) MFC-C and (d) MFC-D networks compared to composites reinforced by these networks. Insets show typical stress-strain curves of the MFC networks and MFC reinforced PLA composites during the deformation experiments using Raman spectroscopy. Error bars are standard deviations from the mean.
Increased Raman band position shift rates as a function of applied stress are obtained from PLA reinforced with dense networks (MFC-A, MFC-B and MFC-C) compared to those of pure MFC networks, indicating that the Young’s moduli of the composites are lower than those of networks (see inset Figure 7.11). Interestingly, MFC-D reinforced composites showed a value of \(-18.7 \pm 0.6 \text{ cm}^{-1} \text{ GPa}^{-1}\) for the Raman band shift with respect to stress, compared to \(-21.9 \pm 0.4 \text{ cm}^{-1} \text{ GPa}^{-1}\) for MFC-D networks. This indicates that after embedding MFC-D networks in PLA, the Young’s modulus of the composites was higher than that of the MFC-D networks. The change of Raman band shift with respect to stress confirms that stress is transferred from the PLA matrix to MFC fibrils when composites are subjected to tensile deformation (Quero et al., 2010).

7.8 CONCLUSIONS

PLA-based composites reinforced with MFC networks were prepared using compression moulding. MFC fibrils were thought to act as nucleating agents, inducing crystallisation. It can be clearly seen from SEM micrographs of MFC-D reinforced PLA composites that PLA can penetrate into the network of MFC-D during composite fabrication. A laminated structure, however, was observed for composites reinforced with dense networks (MFC-A, MFC-B and MFC-C); little penetration of PLA within networks was observed for these samples. This was thought to be due to the higher porosity and larger pore size of MFC-D networks than MFC-A, MFC-B and MFC-C networks. After embedding all networks in PLA, enhanced mechanical properties were obtained compared to neat PLA. This indicates that stress transfer occurs in the composites.
The stress-transfer mechanisms in MFC-reinforced PLA composites were monitored using Raman spectroscopy. The Raman band initially located at ~1095 cm\(^{-1}\) was observed to shift towards a lower wavenumber, thus indicating stress transfer between the PLA matrix and the reinforcing fibrils in the composite. The Raman band shifts as a function of tensile strain and stress were found to be different when comparing data for the networks to those of the composites. These differences indicate that stress is transferred from the PLA matrix to the MFC fibrils when composites are subjected to tensile deformation. In addition, the mechanical properties of composites reinforced with dense networks (MFC-A, MFC-B and MFC-C) are found to dominated by the properties of the networks, whereas the mechanical properties of MFC-D reinforced composites are controlled by the stress-transfer between the PLA matrix and the MFC fibrils.

7.9 REFERENCES


Tome L.C., Pinto R.J.B., Trovatti E., Freire C.S.R., Silvestre A.J.D., Neto C.P. and Gandini A. Transparent bionanocomposites with improved properties prepared from


CHAPTER 8

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

Conclusions of this study and suggestions for future work are provided in this chapter.

8.1 CONCLUSIONS

The effective Young’s modulus of single fibrils of MFC and the physical and mechanical properties of MFC networks prepared from different techniques and different cellulose sources have been studied. The effect of parameters such as porosity, fibril width and density of MFC networks on the physical and mechanical properties of MFC reinforced PLA composites has been investigated also.

The effective Young’s modulus of single fibrils of MFC prepared from wood pulp (MFC-A, MFC-B, MFC-C and MFC-D) determined using Raman spectroscopy with the VV and VH polarisation configurations was found to be in the range of 29 - 41 GPa, which is much lower than the modulus of a cellulose I crystal (138 GPa) as discussed in Chapter 5.5. When these dense MFC networks (MFC-A, MFC-B and MFC-C) were
deformed in tension, the fibril breakage was observed rather than fibril pull-out. This is thought to be strong bond strength between MFC fibrils in the networks. MFC networks with high porosity and low bonding strength, on the other hand, exhibited lower mechanical properties and fibril pull-out failure (MFC-D), as mentioned in Chapter 6.1. A value of 17.4 ± 1.2 GPa for the effective modulus of single fibrils of MFC fibrillated from Lyocell fibres was estimated.

The aim of using MFC filaments produced from pulp to enhance the mechanical properties of composites may be limited due to the low modulus of MFC filaments. Even though MFC and natural fibres have similar modulus, the use of MFC to enhance the mechanical properties of polymers is better than the use of typical natural fibres because of the higher aspect ratio and greater contact area. Likewise, MFC can be used to improve other properties of the composites, such as barrier properties.

The effect of polarisation configurations on the shifts of the Raman band initially located at ~1095 cm⁻¹ as a function of tensile strain obtained from randomly oriented networks of MFC-A, MFC-B and MFC-C was studied. This Raman band shift as a function of strain using the VV polarisation configuration for MFC networks was found to depend on the angle between the strain direction and the laser polarisation axis (Equation 5.10); however, the Raman band shift rate using the VH polarisation configuration was found to be independent of this angle (Equation 5.11). In addition, negative Poisson’s ratio was found for the networks of MFC-A, MFC-B and MFC-C. This may be due to the re-entrant structure of the networks.

The length of time used to fibrillate Lyocell fibres was found to affect the physical and mechanical properties of MFC. As the treatment time used to fibrillate MFC increased,
the degree of crystallisation and thermal degradation temperature of MFC decreased due to the degradation of MFC caused by the harsh mechanical treatment. The density and mechanical properties (strength and stiffness) of MFC networks, however, increased. This is thought to be more contact area of fine fibrils, increasing hydrogen bonding in the networks, as discussed already in Chapter 4. MFC networks with less porosity, stiffer fibrils, smaller fibre width and higher bonding strength, therefore, are thought to exhibit the optimum mechanical properties.

Enzymatic or carboxymethylation pretreatments followed by mechanical treatment were used to prepare MFC from pulp; these two methods provided MFC networks with similar specific mechanical properties, as shown in Section 6.5. Enzyme pretreated MFC, however, was found to be more thermally stable than carboxymethylated MFC. This is attributed to the fact that hydroxyl groups within cellulose of carboxymethylated MFC were converted to carboxyl groups, as confirmed by FTIR spectra shown in Chapter 6.2, reducing hydrogen bonds within and between the cellulose chains.

When MFC networks were embedded into PLA matrix, enhanced mechanical properties of the resulting composites were observed compared to neat PLA matrix. The degradation temperature behaviour of MFC reinforced PLA composites, however, decreased due to the thermal sensitivity of MFC. MFC fibrils were thought to act as a nucleating agent, leading the nucleation and growth of transcrystalline regions in the composites. This resulted in the higher degree of crystallinity of MFC reinforced composites, compared to that of neat PLA. The increased degree of crystallinity of a composite is another factor that can improve the mechanical properties of the composite, and has often been neglected in other studies.
The penetration of the PLA matrix through the voids within an MFC networks was found to depend on the porosity and average pore diameter within a network, as discussed in Chapter 6.1. When an MFC network with low density and larger fibrils, having thereby larger mean pore sizes and more porosity, was used to prepare a composite, it was possible for PLA to penetrate through the voids within the network. Interfacial interaction between the surface of the network and PLA matrix, on the other hand, was reported when a dense network (high density) with fine fibrils was used to prepare a composite. It is clear that the mechanics of the composites reinforced with low porosity networks of finer MFC fibrils rely mostly on the network properties, while those of composites reinforced by networks with high porosity have an additional component from the interaction between the PLA matrix and the bulk of an MFC network.

Raman spectroscopy has been used effectively to follow the stress-transfer mechanisms of MFC reinforced composites and MFC networks. It is difficult to investigate stress-transfer mechanisms in the networks and composites using standard techniques such as tensile testing, without making assumptions. Shifts in the position of the Raman band initially located at ~1095 cm\(^{-1}\), corresponding to the C-O stretching mode within the backbone structure of cellulose, were observed for both MFC networks and composites. Increased Raman band shifts with respect to tensile strain were found for MFC reinforced composites, compared to MFC networks, as mentioned in Chapter 7.7. This indicates that stress is transferred from the PLA matrix to MFC fibrils. Moreover, Raman band shifts as a function of stress for MFC networks and MFC reinforced composites are related to the reciprocal of the modulus of a material (1/E).
In summary, a network with finer fibrils, higher bonding strength and less porosity is suitable to be used as a packaging material, but this network may not be good enough to be used as a reinforcement for composites, compared to networks with higher porosity. This is because it is difficult for PLA to penetrate into the dense network, forming interaction only on the surface of the network and PLA matrix. Then, debonding failure may occur during usage. Also, the Young’s modulus of MFC fibrils should be considered if MFC is selected to reinforce a polymer matrix. Even though the Young’s modulus of a cellulose II crystal has been reported to be lower than a cellulose I crystal, MFC produced from Lyocell fibres provide uniform mechanical properties, and can be produced in mass production with a rapid rate because Lyocell fibres are continuous fibres, and are easy to be fibrillated. The aspect ratio of MFC can be controlled, and the mechanical properties of MFC fibrils can be enhanced with an increase of a draw ratio or the degree of polymerisation of Lyocell fibres. The degree of crystallinity of Lyocell fibres can be adjusted by the increase of the draw ratio. Then, nearly fully crystalline fibres with higher aspect ratio can be made, and used as a reinforcement in composites. These advantages, therefore, should overcome the problem of the lower modulus of cellulose II MFC fibrils.

8.2 SUGGESTIONS FOR FUTURE WORK

MFC networks have been proved to enhance the mechanical properties of the composites; however, this material should be further studied to investigate other properties, or should be used to prepare composites using other techniques. Some suggestions are provided.
8.2.1 Effect of Water and Moisture on Mechanical Properties of MFC Reinforced Composites

As the MFC reinforced composite material can be used as a biodegradable packaging product, the effect of environment on the mechanical properties of composites is an important issue which should be investigated. It has been reported that the mechanical properties of cellulose reinforced composite materials can be affected by water (Rusli et al., 2010; Mendez et al., 2011). The modulus of cellulose reinforced composites has been reported to significantly decrease when in a wet condition (Rusli et al., 2010; Mendez et al., 2011). Similarly decrease has been found for cellulose networks (Aulin et al., 2010; Quero et al., 2011). This is due to the fact that water can act as a plasticiser, which interrupts hydrogen bonding between cellulose fibrils (Aulin et al., 2010; Rusli et al., 2010; Quero et al., 2011). Also, it has been reported that the oxygen permeability of MFC coated PLA film is 1 ml m⁻² day⁻¹ Pa⁻¹ compared to a value of 746 ml m⁻² day⁻¹ Pa⁻¹ for a pure PLA film (Fukuzumi et al., 2009). This is due to the high crystallinity of MFC.

The MFC network in a composite prepared using compression moulding in this study is completely covered by a PLA matrix, as confirmed by SEM micrographs shown in Section 7.1. It is unlikely for MFC fibrils to directly contact with water or moisture. Also, a value of 0.4 wt.% of water uptake of PLA has been previously reported (Kovacs and Tabi, 2011). Therefore, this composite may be able to use in the wet condition and provide superior barrier properties. Importantly, both reinforcement and matrix phases of this composite are biodegradable.
8.2.2 Effect of Porosity of MFC Networks on the Penetration of a Matrix into a Network

It has been found that the penetration of a matrix into an MFC network with low porosity is difficult, as discussed in Chapter 7.1, having only the interfacial interaction between the surface of the network and matrix. The use of equipment such as a pin, a roller with pins or specific treatment for instance plasma or laser treatments, therefore, to create a large number of uniform tiny holes in a network may improve the penetration of the matrix into the network. Also, the size and number of holes can be adjusted to study the effect of these factors on the penetration of the matrix through the network and the mechanical properties of the composite materials.

8.2.3 Composites Reinforced by a Network with Aligned Fibrils

Generally, the alignment of MFC fibrils in composites prepared using a solvent casting method (Cheng et al., 2007; Lu et al., 2008; Cheng et al., 2009b) or melt compounding (Jonoobi et al., 2010; Suryanegara et al., 2010) is difficult to be controlled. Composites reinforced with a network of aligned fibrils, however, can be prepared. The networks of aligned fibrils can be fabricated using an electrospinning technique, and composites are subsequently prepared using compression moulding (Tang and Liu, 2008; Pankonian et al., 2011; Zucchelli et al., 2011). Then, the effect of weight fraction and porosity of the networks on the mechanical properties of composites can be investigated.
8.2.4 All-cellulose Composite from MFC Networks

All-cellulose composites can be further prepared from MFC networks. All-cellulose composites have been first introduced by Nishino et al. (2004). Unidirectionally aligned ramie fibres were dissolved in a cellulose matrix of kraft pulp dissolved in a solution of LiCl/DMAC (lithium chloride and dimethylacetamide). After that, an all-cellulose composite was formed (Nishino et al., 2004). Later, this method has been used to prepare all-cellulose composites from a variety of cellulose sources (Gindl and Keckes, 2005; Nishino and Arimoto, 2007; Soykeabkaew et al., 2008; Soykeabkaew et al., 2009; Pullawan et al., 2010). This technique, therefore, could be used to prepare all-cellulose composites from MFC networks. This all-cellulose composite can be then drawn in a wet condition to enhance their mechanical properties (Gindl and Keckes, 2007). The effect of porosity and density of the networks on the mechanical properties of this composite can be further studied.

8.2.5 Determination of Young’s Modulus of a Single Filament of MFC from Pulp Using Atomic Force Microscopy

The elastic modulus of a single fibril of cellulose nanofibres, prepared from a variety of cellulose such as Lyocell fibres (Cheng and Wang, 2008; Cheng et al., 2009a) and tunicate (Iwamoto et al., 2009), can be determined using atomic force microscopy (AFM) to employ the three-point bending test. This technique allows nano sized fibres to be deformed in the range of Angstroms. An AFM cantilever tip is used to apply a small load at the centre of a nanofibre sample suspended on a groove, as shown in Figure 8.1 (Cheng and Wang, 2008; Cheng et al., 2009a; Iwamoto et al., 2009). The
elastic modulus can be subsequently obtained. This technique, therefore, should be able
to measure the modulus of single filaments of MFC from pulp, and then the value
obtained from this method can be compared to that determined from Raman
spectroscopy.

![Figure 8.1 Schematic diagram of using an AFM cantilever to employ the three-point bending test for a single nanofibre. Reproduced with modification from Cheng and Wang (2008).](image)

8.3 REFERENCES

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APPENDIX A

MOLECULAR ORIENTATION WITHIN A NETWORK DURING TENSILE DEFORMATION

The normalised intensity of the Raman band peak initially located at ~1095 cm\(^{-1}\) with respect to the angle \(\phi\) between the laser polarisation direction and MFC network axis obtained from MFC-A networks at 0 and 1.5 % strain is shown in Figure A.1. It was found that during tensile deformation, no reorientation of cellulose molecular chains within a network of MFC-A can be found. Similar results were observed for MFC-B and MFC-C networks. This may be due to the fact that networks are highly dense with low porosity, and the bonding strength is considerably high (Table 6.6).
Figure A.1 Normalised intensity of the Raman band initially located at ~1095 cm$^{-1}$ as a function of the angle between the laser polarisation direction and the network axis at 0 and 1.5% strain of MFC-A networks. Black arrow indicates the tensile deformation direction.
APPENDIX B

PUBLICATIONS

Some parts of this work have been presented, and published before the submission of the thesis.

1. Publication


2. Conference Presentation

1) Poster presentation at “14\textsuperscript{th} European Conference on Composite Materials (ECCM 14)”, 7 - 10 July 2010, Budapest University of Technology and Economics, Budapest, Hungary. “Mechanical properties and micromechanics of nanofibrillated cellulose sheets”.