

Fabrication and Characterisation of Carbon Nanofibres from Cellulose Nanofibres

By

Ehsan Jazaeri

Submitted in fulfilment of requirements for the degree of

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Dedication

I dedicate my work to my parents Mr. Seyed Mohammadreza Jazaeri and Mrs. Nosrat Imani, my brothers Amir, Shahram, Peiman and Mohammadjavad for their endless love and support in my life.

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Publication List

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Abstract

Although the production of carbon fibres (CFs) from cellulosic precursors has been studied since the 1960s, the fabrication of nano-scale CFs from cellulose nanofibres (CellNFs) is fairly new and many aspects of this research area are still unknown. In addition, the properties of CellNF precursors are expected to greatly affect those of the carbon nanofibres (CNFs) and yet only few types of CellNF precursors have been investigated. Up to date, there has been little research conducted on the carbonisation of CellNFs originated from softwood pulp, due to unavailability of appropriate fabrication methods. Our recent successful fabrication of CellNFs from renewable natural plant products using a green and scalable technique, has led us to investigate the possibility of fabricating CNFs from such materials.

Although carbonisation of micron-sized cellulose fibres have been widely investigated in the past, in this thesis, the novel CellNFs obtained from ball-milled softwood pulp was used to investigate the carbonisation process. Various pyrolysis conditions including the effect of heating stages, heating rates and maximum temperatures in each stage, and holding time at the maximum temperatures were investigated for their effects on the morphological, structural and chemical properties of resulting carbon residues. It was found that the methods to dry CellNF precursors significantly affected the morphology of resulting CNFs. Heat treatment conditions around the thermal decomposition temperature of cellulose also greatly influenced the morphological properties of CNFs. Longer holding time at 240°C and slower heating rate from 240°C to 400°C were critical to preserve the original fibrous structures of the precursor CellNFs after pyrolysis. In addition, the method to dry CellNF precursor influenced the yield of resulting CNFs. Although mass loss occurred during carbonisation, due to the removal of oxygen, hydrogen and carbon, appropriate pyrolysis conditions could reduce the total mass loss after carbonisation. Furthermore, the possibility of graphitizing CNFs at temperatures above 1600°C was demonstrated. Since graphitization starts from the fibre surface and develops towards the core of the fibre, smaller diameters would help the graphitization process to be initiated at lower temperatures. It was shown that a certain crystal structure was developed in the carbonised fibre at lower temperatures (1600°C) than the graphitization temperature of conventional CFs (~ 2800°C).

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Glossary

CF: Carbon Fibre

CellNF: Cellulose NanoFibre

CNF: Carbon NanoFibre

FT-IR: Fourier Transform Infra Red

PAN: PolyAcryloNitrile

SEM: Scanning Electron Microscopy

TEM: Transmission Electron Microscopy

XRD: X Ray Diffraction

Chapter 1: Introduction

1.1 Significance of research

1.1.1 Research problem

The production of micron-scale carbon fibres (CFs) from cellulosic precursors has been studied since the 1960s. However, the fabrication of nano-scale CFs from cellulose nanofibres (CellNF) is fairly new and many aspects of fabrication processes are still unknown. In addition, the properties of CellNF precursors are expected to greatly affect those of the carbon nanofibres (CNF) and yet only few types of CellNF precursors have been investigated. To date, there has been little research conducted on the carbonisation of CellNFs originated from softwood pulp, due to unavailability of appropriate fabrication methods. Recently, Deakin University demonstrated successful fabrication of CellNFs from renewable natural plant products using a green and scalable technique. This has led us to investigate the possibility of fabrication of CNFs from such materials. In the current project, fabrication of CNFs from such CellNFs by pyrolysis is investigated.

1.1.2 Research aim

In order to study the potential of producing CNFs from plant-based CellNFs, this research project focuses on the following three specific aims:

1- Study of the effects of carbonisation conditions, on the structural properties of carbon residues

In this project, the production of CNFs is studied using pyrolysis. These carbonisation conditions are expected to affect the structural properties of the carbon residues such as crystallinity and morphology, because heat treatment conditions influence the depolymerisation of the cellulose molecular chains and the formation of new atomic bonding between carbon atoms during pyrolysis. Hence, the effects of pyrolysis conditions on the structural properties of carbon residues are studied. The process parameters studied in each heating stage include (i) a heating rate by which the sample is heated to a certain temperature, (ii) a maximum temperature to which the sample reaches

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in each stage and (iii) holding time at the maximum temperature. All the heat treatments are conducted in an inert gas atmosphere under nitrogen gas flow.

2- Study of the effects of the methods to dry CellNF precursors on the structural properties of carbon residues

The spatial distance between the fibres may play an important role in maintaining the fibrous morphology in carbon residues. Oven-drying techniques result in a cellulosic film that contains highly compact fibres. On the other hand, freeze-drying techniques yield a 3-dimensional loose nanofibre network. Therefore, carbonisation of oven-dried and freeze-dried CellNFs will lead to carbon residues with different structural and morphological properties. In this project, the effect of the techniques to dry CellNF precursors, on the morphological properties of carbon residues is studied, using oven-drying and freeze-drying techniques.

3- Feasibility of the graphitization of amorphous CNFs

Graphitization of carbonised nanofibres is expected to occur when the nanofibres are exposed to very high temperatures above 2000°C. Normally, graphitization of conventional micron-sized fibres requires temperatures above 2800°C. Since graphitization starts from the fibre surface, it is expected that the graphitization takes place at lower temperatures in nanofibres than in conventional micron-sized fibres. This means that graphitized CNFs may be produced with less energy and cost, than conventional CFs. In this study, after the carbonisation conditions are optimized and CNFs with improved structural and morphological properties are produced, the possibility of graphitizing carbonised nanofibres is investigated at the temperatures between 1600°C and 2800°C.

1.2. Thesis outline

This thesis consists of seven chapters including this chapter. The outlines of each chapter are described as follow:

Chapter 2 is a literature review about CNFs as well as conventional micron-sized CFs. The chapter describes the advances in CF research, the properties of CFs, commercial production methods and industrial applications of CFs. The descriptions of CNFs

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including their properties, production methods and various applications are also described.

Chapter 3 gives the experimental procedures. The methods to prepare CellNF precursors, pyrolysis conditions, drying techniques, characterisation instruments and their set-ups are explained.

Chapter 4 presents the study on the pyrolysis of oven-dried CellNFs. The effects of heating rates and holding time in each pyrolysis stage were studied. Oven-dried CellNFs were pyrolysed in three heating stages: 25-170°C, 170-240°C and 240-350°C. The heating stages were designed on the basis of the thermal behaviour of CellNFs. The samples were characterised after each pyrolysis stage to understand the effect of heating conditions on the morphology, crystal structure and chemical bonds of CellNFs.

Chapter 5 presents the study on the pyrolysis of freeze-dried CellNFs. The pyrolysis conditions such as heating rate and holding time were investigated. Based on the thermal behaviour of CellNFs, three heating stages were selected: 25-170°C, 170-240°C and 240-400°C. CNFs were successfully fabricated from freeze-dried CellNFs. It was found that the heating conditions largely affect the fibrous morphology during carbonisation. Comparing the results in Chapter 4 and Chapter 5, the effects of drying techniques on the morphological properties of carbon residues are discussed.

Chapter 6 investigates graphitization of CNFs. Amorphous CNFs obtained from the pyrolysis at 400°C were heated to higher temperatures (1600°C, 1800°C, 2000°C, 2200°C, 2500°C and 2800°C) and the effect of the temperature on the morphological, crystalline and chemical properties were investigated.

Chapter 7 summarizes the main findings of the project about the effects of drying methods and pyrolysis conditions of CellNFs, on the properties of carbon residues. Proposed future works are also presented.

Chapter 2: Literature review

In this chapter, the advances in CF research, the properties of CFs, commercial production methods and industrial applications of CFs are presented. The descriptions of CNFs including their properties, production methods and various applications are also described.

2.1. Carbon fibre

2.1. 1. Overview

CFs have $> 92\%$ carbon atoms in their structure. Such structures can be amorphous, semi crystalline or crystalline. Crystalline CFs have the hexagonally oriented rings of graphite. Carbon atoms have connected to each other via covalent bonding and form hexagonal rings. Such rings then connect in the cylindrical plane to form graphitic layers. These layers have connected in directions perpendicular to the layer, via van der Waals bonding. Such a molecular configuration gives the CFs two properties: a) they are good electrical and thermal conductors in the planes and good thermal insulators in the direction perpendicular to the planes and b) they have high strength (high modulus of elasticity) in the planes and low strength (low modulus of elasticity) in the direction perpendicular to the planes [1]. In CFs graphitic layers are highly aligned along the fibre axis. This gives the fibres high elastic modulus, large crystallite sizes (D_{cr}), high density, high tensile modulus, high electrical and thermal conductivities along the fibre axis. The highly aligned graphitic layers along the fibre axis also give electrical and thermal insulation properties to the fibre axis [2]. Graphite is made up of graphene layers that are stacked up in a way that only half of one graphene layer (layer A) is on top of another layer (layer B). This orientation is called ABAB sequence. Graphene layers can also be stacked up in ABCABC sequence which is found when half of layer B is on top of layer A while half of layer C is on top of layer B. While most of the graphitic materials have ABAB or ABCABC sequences [3-5], graphene layers in CFs can be stacked up parallel to one another but with no particular sequence. They can also be amorphous and are stacked up unparallel to each other although the layers were highly developed in the direction parallel to the fibre axis.

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Table 2.1. some properties of synthetic fibres [6, 7].

Material	Density (g/cm³)	Tensile Strength (GPa)	Modulus of elasticity (GPa)	Ductility (%)	Melting temp (°C)	Specific modulus (10⁶ m)	Specific strength (10⁴ m)
E-glass 2.55	2.55	3.4	72.4	4.7	<1725	2.9	14
S-glass 2.50	2.5	4.5	86.9	5.2	<1725	3.56	18
SiO ₂ 2.19	2.19	5.9	72.4	8.1	1728	3.38	27.4
SiO ₂ 3.95	3.95	2.1	380	0.55	2015	9.86	5.3
ZrO ₂ 4.84	4.84	2.1	340	0.62	2677	7.26	4.3
CF (high-strength)	1.5	5.7	280	2	3700	18.8	19
CF (high-modulus)	1.5	1.9	530	0.36	3700	36.3	13
Cellulose	-	0.9	41	2.5	-	-	-
BN	1.9	1.4	90	1.6	2730	4.78	7.4
Boron	2.36	3.4	380	0.89	2030	16.4	9.9
B ₄ C	2.36	2.3	480	0.48	2450	20.9	5.1
SiC	4.09	2.1	480	0.44	2700	12	0.3
TiB ₂	4.48	0.1	510	0.02	2980	11.6	7.1
Be	1.83	1.28	300	0.4	1277	19.7	2
W	19.4	4	410	0.98	3410	2.2	27.4
Polyethylene	0.97	2.59	120	2.2	147	12.4	25.7
Kevlar	1.44	4.5	120	3.8	500	8.81	53.3
Al ₂ O ₃ whiskers	3.96	21	430	4.9	1982	11	47
BeO whiskers	2.85	13	340	3.8	2550	12.3	56.1
B ₄ C whiskers	2.52	14	480	2.9	2450	19.5	66.5
SiC whiskers	3.18	21	480	4.4	2700	15.4	44.5
Si ₃ N ₄ whiskers	3.18	14	380	3.7	-	12.1	12
Graphite whiskers	1.66	21	703	3	3700	43	128
Cr whiskers	7.2	8.9	240	3.7	1890	3.4	12

Table 2.1 compares the properties of CFs with those of some other fibres. It is noted that ‘high-strength CFs’ have the highest tensile strength among all fibres (5.7 GPa) while ‘high-modulus CFs’ have the highest modulus of elasticity (530 GPa). Moreover, CFs

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exhibit the lowest density among the fibres (1.5 g/cm^3) which makes the specific modulus (modulus/density) of CFs significantly higher than that of even Kevlar fibres.

Commercial CFs are produced for three main purposes:

- 1- General purpose CFs: They are mainly amorphous in structure with low modulus, strength and production cost.
- 2- High performance CFs: They are graphitic in structure with high modulus, strength and higher price than general purpose CFs.
- 3- Activated CFs: They are porous in their micro structures which make them highly adsorptive to other chemicals [8].

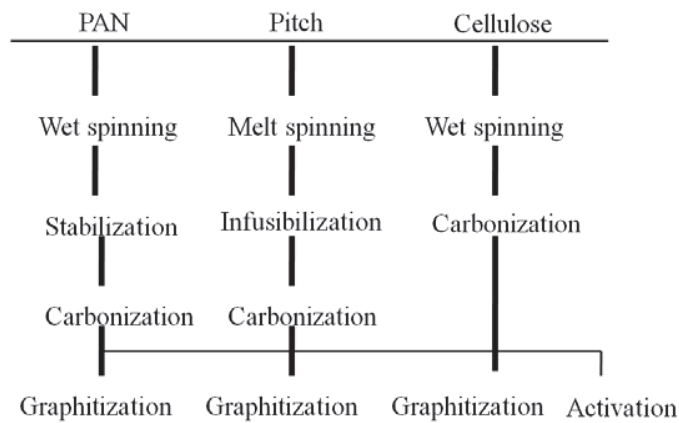


Figure 2.1. Schematic processes of CFs production [9-11].

2.1.2. Production

2.1.2.1. Overview

Commercially available CFs are mainly produced from pyrolysis of synthetic precursors such as polyacrylonitrile (PAN), oil- or coal-based precursors such as pitch, and natural precursors such as cellulose (Figure 2.1). Pitch-based CFs have higher strength than PAN-based CFs, since pitch can be better graphitized in higher temperatures. The cost of producing CFs from PAN is higher than pitch or cellulose (Table 2.2) [10].

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Table 2.2. Cost of CF production [10].

	Cost of precursor (\$/kg)	Cost of CFs (\$/kg)
PAN-based	0. 4	60
Cellulose	0. 31	4
Isotropic pitch-based	0. 6	22

Polymeric precursors such as polyvinylidene chloride, polyvinyl alcohol and PAN are commonly used for CF production. Table 2.3 shows the mass loss during carbonisation of PAN, pitch and cellulose fibres.

Table 2.3. precursor mass loss during carbonisation [12, 13].

Precursor fibres	Weight loss (%)
Pitch	30
PAN	60, 67
cellulose	88

2.1.2.2. Pitch

Pitch is a black/brown sticky material that is usually solid at room temperature and melts at higher temperatures. It can be produced from partial pyrolysis of some polymers such as polyamides and polyesters, or coal and petroleum [14]. Pitch is a combination of some monomers that form a three- to eight-ring molecular structure with a molecular weight of 300 to 400 [15].

In order for pitch to be used as the precursor in the production of CFs, pitch should fulfil certain requirements. It should be free from metallic ions and insoluble particles that would reduce the mechanical properties of CFs [16]. In addition, it should have high carbon content and be mesophase in its structure. Mesophase pitch is a mixture of aromatic hydrocarbons containing anisotropic liquid-crystalline particles that can be obtained by heat treatment of pitch at 250-400°C. Mesophase helps produce fibres with high molecular orientation that are suitable for CF production [17, 18], because liquid-crystalline materials orient easily during fibre formation [19].

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CFs with high degrees of molecular orientation have high elastic moduli and thermal conductivities whereas CFs with more discontinuous and less ordered fibrillar structures have higher tensile strengths. The latter can be used as reinforcement components for high-strength composites [20, 21]. By increasing the molecular orientation during fibre formation, the strength of pitch-based CFs can be improved [22, 23]. Linearizing the molecular orientation during fibre formation can yield pitch-based fibres with improved thermal conductivities. Controlling such structures during fibre formation can optimize CF as well as improve processing conditions [21, 24].

The crystal structure of pitch is isotropic in nature and hence pitch requires some heat treatment to become anisotropic suitable for fibre spinning. In order for the pitch to become anisotropic, it is held at 400°C for some time (14-32 h [25]). Spinning of anisotropic pitch into pitch fibres is not an easy process, and several alternative methods, such as melt spinning, jet spinning and centrifugal spinning, were proposed to obtain pitch fibres. Melt spinning is however the most favourable method among all. Conventional melt spinning methods can be used to prepare pitch fibres. Molten anisotropic pitch with a certain viscosity passes through spinnerets that forms continuous pitch filaments. Air is blown to the spun filaments to cool them, and then the filaments are collected [7, 26-28]. In order to obtain CFs with high tensile strength and high modulus, pitch fibres are drawn to increase molecular orientation during the spinning process. The stretching can be done within 5mm of the spinneret while the pitch fibres are still hot enough to be stretched. Pitch fibres are then carbonised to obtain CFs. The spinneret shape and the pressure applied to the molten pitch during spinning govern the mechanical and structural properties of the resultant CNFs. For instance, stirring the molten pitch in the spinneret nozzles helps formation of more oriented and even fibres. Applying the correct pressure during spinning also avoids the off-gassing phenomenon.

Pitch-based CFs are produced by pyrolysis at various temperatures. It is critical to maintain their fibrous structure and avoid infusibility during pyrolysis. Stabilization is a process to partially introduce oxygen atoms in pitch polymer molecules in order to prevent the pitch fibres from fusing together during the carbonisation (Figure 2.2) [29-32]. Surface oxidation helps pitch fibres to behave as if they are thermoset fibres instead of thermoplastic fibres, so that the fibrous structures are retained during carbonisation [33].

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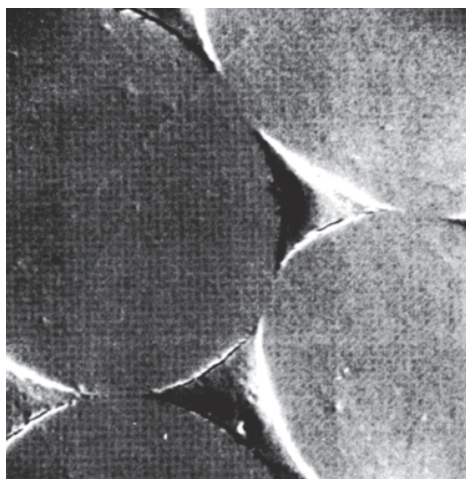


Figure 2.2. Fusion of fibres during carbonisation [34].

The oxidative stabilization step is normally performed at 350°C. Pitch fibres are then suspended in graphite or carbon black to enhance the fibre stability during carbonisation. Stabilized pitch fibres are then carbonised in a series of ascending heating temperatures. CFs are then graphitized at above 2000°C.

2.1.2.3. PAN

PAN is a polymer with the molecular weight of 120,000 g/mol and acrylonitrile content of >85%. PAN is widely used for the production of CNFs (Figure 2.3). Its decomposition temperature is below melting point (350°C). Hence PAN fibres could not be produced by melt-spinning. Commercial production of PAN fibres uses wet spinning techniques with dimethyl formamide (DMF) as a solvent for PAN.

As a precursor of commercial CFs, high purity PAN is not commonly used. PAN precursors usually contain other monomers such as itaconic acid, acrylic acid, and methacrylic acid [35]. Although mass loss is higher with PAN than pitch, PAN is a cheaper and more favourable precursor than pitch in CF production [36].

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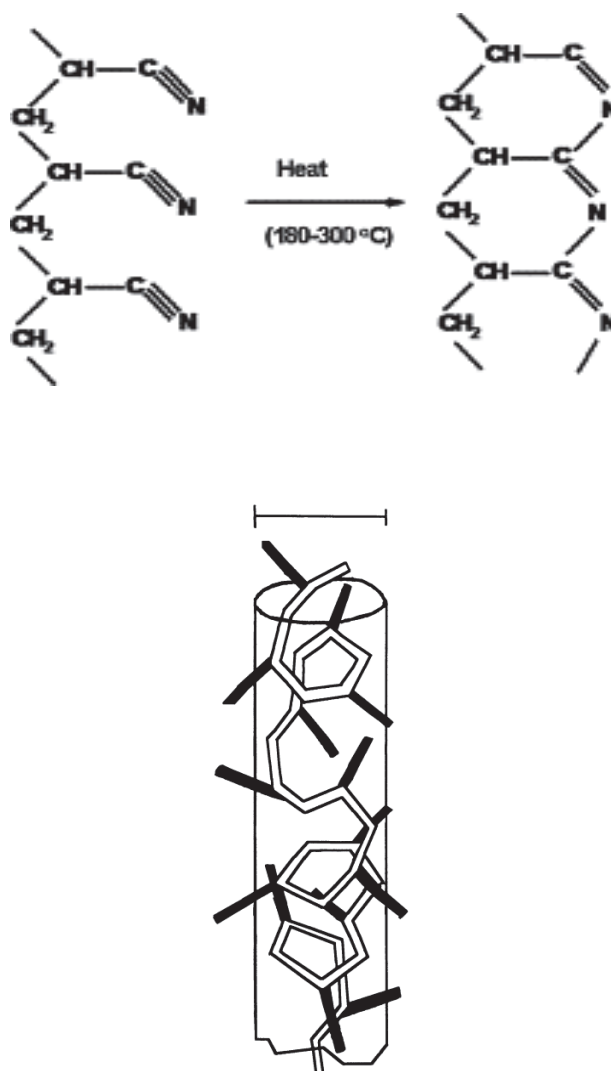


Figure 2.3. Schematic structure of PAN molecules [37-39].

The process to produce PAN fibre precursors is critical to assuring the high quality in resulting CFs. All stages of the fibre production process should be done accurately in order to obtain PAN fibres with least defects in their molecular structures. The molecular defects such as amorphous regions, folded and entangled parts can reduce fibre strength [40]. To minimize such defects, partial oxidation of PAN fibres during stabilization [41-43] and stretching [44-47] is applied. However, this causes reduction of the tensile strength and elongation at break of PAN fibres [48-50].

Once PAN fibres are spun via wet spinning, they undergo stabilization at 300°C and carbonisation above 1000°C to convert into CFs. The stabilization stage comprises three main reactions; cyclization, dehydrogenation and oxidation. The stabilization stage is necessary to increase carbon yield in the carbonisation stage [9]. During cyclization

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reaction, $\text{C}\equiv\text{N}$ groups are converted into $\text{C}=\text{N}$ and benzene rings are formed along the fibre axis. Dehydrogenation reaction comprises removal of H atoms from the benzene rings and formation of $\text{C}=\text{C}$ groups in the rings [51]. During oxidation process, OH groups are formed on the rings to further stabilize the fibres. Up to 180°C , the heating rates can be as high as $5^\circ\text{C}/\text{min}$ [52-55]. However, it should be maintained from 180°C up to 350°C [56-59]. The maximum temperature should be kept below the decomposition temperature of PAN to let the volatile gases released from the fibres before chain scission and to obtain higher carbon yield [35, 46, 54, 60-64]. During the carbonisation, nitrogen, oxygen and hydrogen are released from the molecules in the form of gaseous by-products [54, 58, 65-71]. This stage is then completed at 1000°C and CFs with carbon content of $>92\%$ in the molecules are left.

During carbonisation, volatile gases such as HCN, NH_3 , CH_4 and H_2 are formed and released from the structure [12]. Heating rates below 600°C should be less than $5^\circ\text{C}/\text{min}$ to allow the volatile gases to be removed from the fibres with least damage to the fibre structure. Above 600°C , higher heating rates can be applied since only carbon and nitrogen are left in the fibre molecules [72]. Carbonisation of PAN fibres are completed at 1500°C where the residual nitrogen is removed from the fibre structure and CFs with $< 95\%$ carbon in the molecule is produced [73-75]. Although graphitization or carbonisation takes only minutes to complete, the stabilization stage takes some hours [76]. This makes carbonisation of PAN fibres costly. In addition, the mass loss during carbonisation is over 50%. These factors add to the final price [77] and make PAN-based CFs expensive. HCN which is released during carbonisation is an extremely toxic gas with a linear molecule comprising the molecular structure of $\text{H}-\text{C}\equiv\text{N}$. The treatment of such highly toxic by-product gas during the production also adds to the final price of PAN-based CFs.

The structural properties of CFs greatly influence their electrical, mechanical and thermal properties. Important structural aspects are: (i) crystallinity such as crystallite size (D_{cr}), degree of crystallinity (I_{cr}) and interlayer spacing d , (ii) graphene layers orientation along and perpendicular to the fibre axis (texture), and (iii) shape and orientation of defects and voids [78-90]. Generally larger crystallite sizes, higher degrees of crystallinity, lower interlayer spacing and higher graphene alignments along the fibre axis result in CFs with greater tensile and modulus values and electrical and thermal conductivities [91-96]. However, fibre production methods, especially heat treatment and processing, affect the

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structures of CFs and influence such properties. PAN-based CFs exhibit different structures in the fibre core from that of the skin [97-103]. Heat treatment to over 2000°C results in graphitic layers along the fibre surface. Graphene layers along the skin prohibit the heat to get absorbed into the fibre core and hence the core does not develop the graphitic structure. Therefore, PAN-based CFs cannot be graphitized as much as pitch-based CFs [104-108]. Shorter distances between graphene layers, d , results in higher mechanical strength and improved electrical and thermal conductivities along the fibre axis [109]. Figure 2.4. shows the scanning electron microscopy image of typical PAN-based CFs [110].

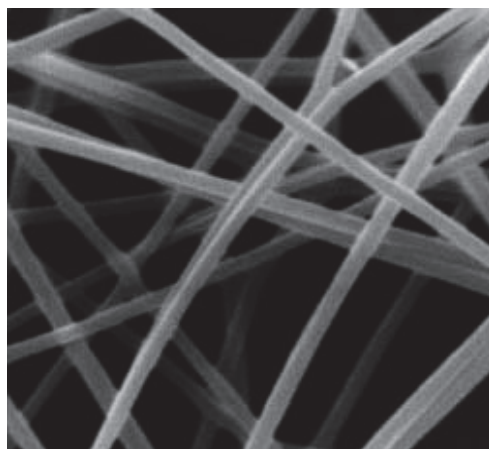


Figure 2.4. SEM image of PAN-based CF [110].

2.1.2.4. Cellulose

Compared to pitch or PAN precursors, cellulose is more widely available and comparably cheaper. Cellulose is a renewable raw material and widely available on earth with the estimated yearly-production of 10^{10} tons. Cellulose is found in plants, sea shelves and some animals such as tunicates and fungi [111-114]. It consists of a long linear homopolymer of 1→4-β-D-glucosidic rings with the formula of $(C_6H_{10}O_5)_n$ (n =degree of polymerization of glucose) that are combined to form a highly ordered cellulosic chains (Figure 2.5) [115, 116]. Natural cellulose has the cellulose-I structure (Figure 2.6) with a high degree of polymerization (DP) of over 10000 but processing of cellulose-I often reduces the DP to 2500 [10]. These chains form parallel nanoscale fibrillar structures which again link together via strong hydrogen bonds to form cellulose fibres [117]. These intermolecular hydrogen bonds break in the aqueous state because hydroxyl groups (OH) in water compete with those in the cellulose. The intra-molecular hydrogen bonds are

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comparatively stiff and make the anhydro-glucose rings stable. Intermolecular hydrogen bonds are responsible for the fibrillar nature of cellulose [118-120]. The distance between chains is ~ 0.45 nm and the distance between two adjacent rings is ~ 0.5 nm.

Cellulose has a high carbon content of 44.4 wt% in addition to 49.4 wt% of oxygen and 6.2 wt% of hydrogen [121, 122]. When cellulose is heated to its decomposition temperature ($\sim 320^\circ\text{C}$), the polymeric chains break down and volatile gases such as CO , CO_2 and H_2O are formed, and hence cellulose loses around 40% of its weight [123-127].

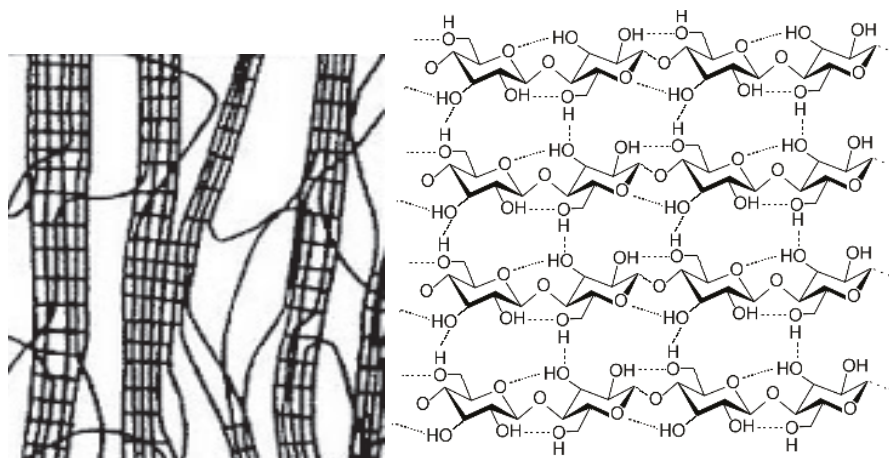


Figure 2.5. Molecular configuration of cellulose [128].

The degree of crystallinity varies in different celluloses from 30% to over 70%. Chemical and mechanical treatment can reduce the crystallinity to less than 50% [129-137]. Highly crystalline cellulose has long cellulosic chains parallel to one another and oriented along the direction of the chains (Figure 2.5) [138, 139]. Mechanical properties such as tensile strength also increase when crystallinity improves [140, 141].

Cellulose crystals have several polymorphs [142]. Native plant cellulose has crystal structures of I_α or I_β . It is known that treatment of native cellulose under different temperatures and chemical environments can transform the crystal structure to many other forms [142]. Both cellulose I_α and I_β consist of sheets placed parallel to each other [144]. In the cellulose I_β structure, the sheets are placed parallel to the unit cell axis b . On the other hand, in the cellulose I_α structure, the sheets are placed parallel to the diagonal direction of the cell axis a and b . Due to the close similarity in the structure, it is difficult to distinguish cellulose I_α and I_β structures by X-ray powder diffraction [144]. Normally nuclear magnetic resonance spectroscopy or 2-dimensional X-ray diffraction study is used to identify these crystal phases.

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It has been reported that cellulose I β form dominates in softwoods [143].

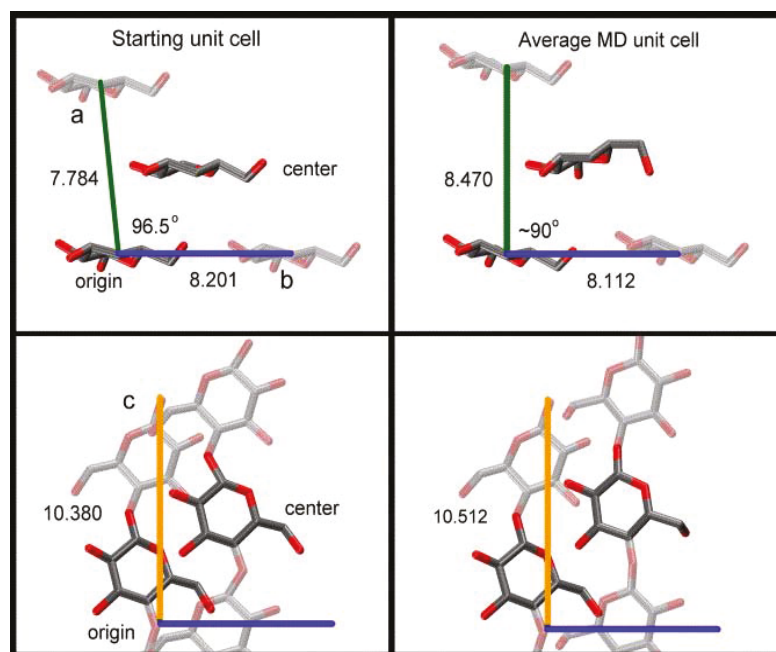


Figure 2.6. Crystal structure of cellulose-I [145].

Cellulose was used as a precursor to produce CFs in Thomas Edison's laboratory in 1880 in search of finding a filament for his light bulbs. However, it took another 80 years, in 1959, before the National Carbon Company used cellulose-based precursor to produce CFs. Since then, many researchers have studied the production of CFs by pyrolysis of cellulose using various heat treatments.

Currently most of the commercial CFs with micron size diameters are produced by the pyrolysis of precursors made from fossil fuels, such as PAN [146] or oil-/coal-based pitch [147]. Viscose rayon precursors have also been used while prepared by some hazardous chemicals to enhance the properties. Hence those methods pose environmental and cost-related concerns. Despite this drawback, the investigation of CF production by the pyrolysis of renewable materials such as native cellulose has rarely appeared in the literature [148, 149]. Although the pyrolysis of bulk cellulosic materials has been extensively investigated in the past, most of the studies focused on the production of energy or bulk char rather than fibres [111, 149-160]. The formation of CFs by pyrolysis of cellulose is more challenging than the formation of activated carbon, as the fibrous structure needs to be preserved during carbonisation. In particular, the formation of volatile and often sticky tar (levoglucosan) should be avoided.

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2.1.3 Properties

2.1.3.1. Mechanical properties

Mechanical properties of CFs are usually explained by tensile strength and Young's modulus. The actual tensile strength of CFs is lower than the theoretical one, because the alignment of graphitic layers along the fibre axis is not perfect and crystallite size is lower than the ideal CFs [161]. Table 2.4 shows the theoretical and actual values for tensile strength and Young's modulus of CFs [162].

Table 2.4. Mechanical properties of CFs [146].

CF precursor	Tensile strength		Young's modulus	
	theoretical value (GPa)	actual value (GPa)	theoretical value (GPa)	actual value (GPa)
Pitch	25	3-4	2000	500
PAN	15	2-3	1000	250
cellulose	8	0.8-1	1000	80

Tensile strength depends on the orientation of the graphene layers along the fibre axis as well as the interlayer spacing; the higher the alignment and lower interlayer spacing (d), the higher the tensile strength. The tensile strength increases as the fibre diameter decreases [163]. In addition, pitch-based CFs show higher tensile strength than PAN- or cellulose-based CFs, because the graphene layers are highly oriented along the fibre axis in pitch-based CFs. However, increase in tensile strength results in decrease in shear modulus, since the higher orientation of graphene layers along the fibre axis makes fibres weaker to shear forces.

2.1.3.2. Electrical properties

Although CFs are electrically conductive to a certain extent, their conductivity is much lower than that of metals except for highly graphitic CFs. One method to increase the electrical conductivity of CFs is intercalation [162]. In this method, metal particles such as copper [164], nickel [165, 166] or bromine [167, 168] are inserted in between graphene layers so as to increase the electrical conductivity up to 70% [169]. This

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method is only possible in graphitic CFs which have well-developed graphitic structures [170, 171].

2.1.3.3. Thermal properties

Thermal conductivity of highly graphitized CFs is generally higher than that of metals such as copper [172, 173]. In addition, increase in tensile strength increases the thermal conductivity due to the more developed graphitic structure. [174-176].

2.1.3.4. Chemical properties

Graphitized CFs exhibit high chemical resistance in harsh chemical environments. Due to highly oriented graphene layers as well as highly stable benzene rings, graphitized CFs have low tendency to react with acidic or basic agents [177-180].

CFs can be oxidised to modify some physico-chemical properties such as polarity. Polar CFs have enhanced electromechanical properties suitable for electrical and composite applications [181-186]. Partial oxidation may increase the weight while complete oxidation results in 100% mass loss depending on the oxidation duration.

2.1. 4. Application

CFs are widely used in the production of composite materials for various purposes. Excellent mechanical properties and lightweight of CFs are suitable as reinforcement components in polymer and many other matrices.

2.1.4.1. Structural composites

Inclusion of CFs in polymer matrices can increase electrical and thermal conductivity, chemical resistivity and also mechanical strength [187]. Pitch- or PAN-based CF/cement composites show lower deflection than cement matrix when a given load is applied [188]. The composites can be used in a variety of applications from aerospace to sport and biomedical applications. Some examples are given in the following sections.

2.1.4.2. Biomedical composites

CF composites are used to produce artificial feet (Figure 2.7) [189]. The strength and flexibility of CFs enable the artificial feet to adjust to the person's pace and direction.

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Figure 2.7. Use of CFs in artificial feet [187].

CFs are also widely used in medical applications such as in dental [190, 191] and surgical instruments [192-194].

2.1.4.3. Polymer composites for sports and leisure

CFs are widely used in the production of sport equipment such as bicycle, yacht, body-building equipment, hockey, golf shaft, tennis and badminton rackets, fishing and ski equipment in a form of polymer composites [195, 196]. CF bicycles are much lighter than conventional aluminium bicycles with the same or better strength and flexibility. A 100% CF bicycle can weigh only 1.05 kg. CF composites reduce production costs significantly while enhancing the performance [197-199].

2.2. Carbon nanofibre

2.2.1. Overview

Due to their excellent mechanical, thermal and electrical properties, CNFs have attracted much attention in many applications. Graphitic CNFs have successfully used in nanocomposites in automotive [200-202] and sensors and electrode in electronics [203], gas sensor [204, 205] and solar cells [206, 207]. Graphitized CNFs consist of long graphitic layers that are oriented along the fibre axis and stacked up perpendicular to the fibre axis [5-7]. Such structural orientation has provided CNFs with very attractive properties such as ultra high aspect ratios (the ratio of fibre length to its diameter) and high specific surface area. They exhibit very high tensile strength and modulus which are

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comparative with metals. Superior properties of CNFs have promised bright future in many applications where strength is needed combined with flexibility.

2.2.2. Properties

2.2.2.1. Mechanical property

Theoretically, CNFs show tensile strength of 100 GPa and modulus of 1000 GPa. However, in reality, CNFs from various precursors would have tensile strength and modulus of 2-5 GPa and 300-700 GPa, respectively. Some factors, such as defects on the surface or within the fibres, handling procedures and impurities in the nanofibre structure, affect the mechanical properties of CNFs [105].

The aspect ratio of nanofibres is another important property that influences the mechanical properties of composites. Since CNFs have diameters in nano-scale and lengths of up to several micro meters, their high aspect ratio enables them to distribute the load evenly throughout the matrix with no fibres pulled out of the matrix, and hence increase the reinforcement effects in composites [208, 209].

2.2.2.2. Thermal property

Thermal stability of CNFs depends on the atmosphere in which they are used. CNFs can be oxidized in air and great mass loss occurs above 400°C [210]. Graphitized CNFs show higher stability than un-graphitized CNFs. However, mass loss still occurs above 600°C. Therefore, if CNFs are to be used in atmospheric environments, their working temperature should be below 400°C. Thermal stability of CNFs also depend on the amount of impurities such as Na, Si, Mg and Ca [211]. Although these impurities may increase thermal conductivity, they lower the stability of CNFs at high temperatures [212].

2.2.2.3. Electrical property

Oxidation reduces the electrical conductivity of CNFs. Oxidation occurs when CNFs are exposed to air at high temperatures (>600°C) [213]. Electrical resistivity is increased by oxidation and higher initial resistivity leads to larger increase in resistivity [214]. Electrical conductivity depends greatly on the physical deformation or damage in CNF, because any change in the cross-section and length of the graphitic layers would reduce the conductivity [215].

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Electrical properties are influenced by the production conditions. For instance, PAN based CNFs become semi-conductive when they are partially oxidized in air and heat treated at 700-900°C [216]. Electrical conductivity can be increased by optimizing the carbonisation stages of the precursor fibres [217].

As shown in Table 2.5, thermal and electrical properties of CNFs along the fibre axis and perpendicular to the fibre axis vary due to the anisotropic graphitic structure of the CNFs.

Table 2.5. Properties of CNFs along and perpendicular to the fibre axis.

Property	Along the fibre axis	Perpendicular to the fibre axis
Coefficient of thermal expansion 0–1000 °C (K ⁻¹)	3.0×10^{-6}	2.8×10^{-6}
Electrical resistivity (Ωm)	1.1×10^{-3}	4.1×10^{-3}

2.2.3. Applications

2.2.3.1. Biological applications

Any material that is going to be used inside human body has to be safe, non-toxic and non-reactive in acidic or basic environments [218]. Use of CNFs in biomedical applications such as tissue engineering, implant and wound healing has been studied and fibres with specific properties suitable for such end-uses have been successfully commercialized [219, 220]. For example, CNFs were used to reinforce calcium phosphate composites for bone replacement [221].

2.2.3.2. Electrical applications

Because of their high electric conductivity, CNFs can be used as an anode in batteries [222]. They have also been used in transmitters as electrodes [223]. CNFs are also used as an anode material in fuel cells due to their capacity to store hydrogen (Figure 2.8) [187].

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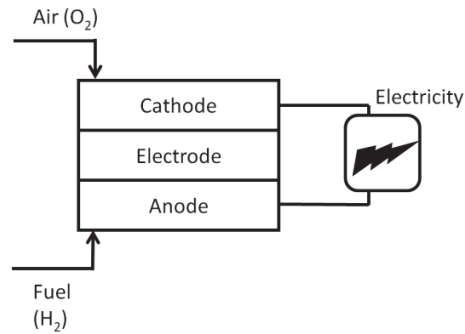


Figure 2.8. Schematic illustration of the structure of a fuel cell [172].

2.2.3.3. Thermal applications

CNFs are used as heat insulating and fire resistant materials [224, 226]. They are mixed with phenol resin and carbonised at high temperatures ($>1000^{\circ}\text{C}$). These products are used in aircraft seats as fire blocking materials in post-crash fires, insulators in aircraft body between the exterior and interior, and personal fire retardants [226-228].

2.2.3.4. Aerospace applications

Use of CNFs in aerospace industry is increasingly becoming diverse. They are now used in army and civil aircrafts and helicopters as composite reinforcement agents in nose, engine blades, interior body, exterior body, wings, stabilizers, etc (Figure 2.9) [229-231]. CNFs not only bring strength to the structure, but also reduce the overall aircraft weight by up to 1.5 tons. CNFs are also used in aerospace industry as a sound insulator.

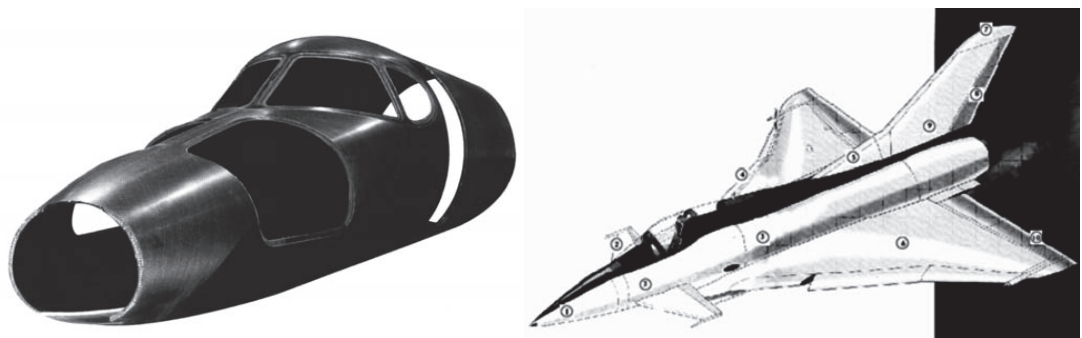


Figure 2.9. Cabin of Proteus aircraft fabricated by Viper 7-axis fibre placement system [187].

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2.2.5. Production

CNFs are produced using 2 main methods: (i) chemical vapour deposition (CVD) and (ii) pyrolysis.

2.2. 5. 1. Chemical vapour deposition (CVD)

In this method, CNFs are produced from carbonaceous gases such as acetylene, methane, natural gas, benzene and ethylene in the presence of catalytic particles [232]. The catalysts are mainly iron, nickel, copper, cobalt or palladium [233]. At accelerating temperatures carbonaceous gases are flown onto the catalytic particles which have certain diameters [234]. The diameters of CNFs are normally determined by the diameter of catalyst nanoparticles.

The growth process comprises endothermic and exothermic reactions which occur on the particles surface. Carbon atoms are adsorbed on the hotter side of the catalyst's surface in which the exothermic reaction occurs. Then a CF starts to grow on the cooler side of the catalyst particles where the endothermic reaction occurs (Figure2.10). This process continues and more and more carbon atoms are built up on top of each other in the form of benzene rings. The growth develops along the fibre axis as well as in the direction perpendicular to the fibre axis (fibre thickening) (Figure 2.11). Hence CVD methods normally results in the production of nanotubes, although CNFs have also successfully produced using CVD. As the fibre grows, the thickness of the fibres can be increased by increasing the gas concentration. The fibre growth can be stopped by reducing the gas concentration [236-239].

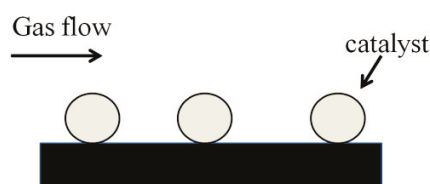


Figure2. 10. CNF growth using CVD methods.

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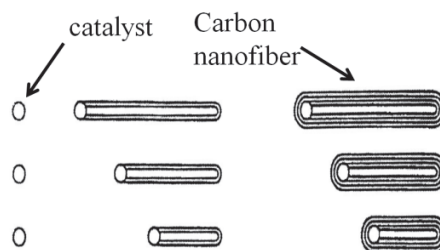


Figure 2.11. CNF lengthening [240].

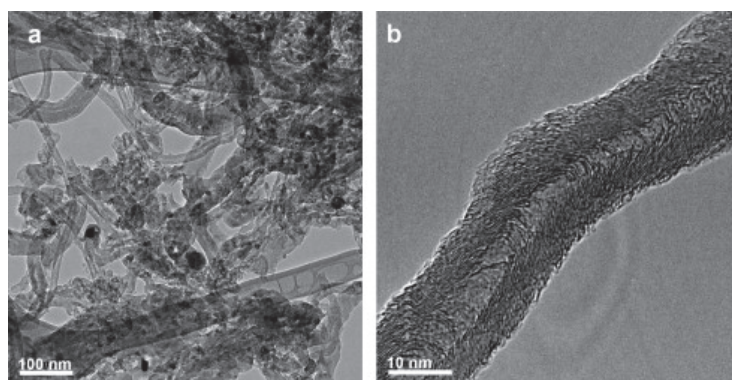


Figure 2.12. TEM image of a CVD grown CNF [241].

CVD grown CNFs (Figure 2.12) have high mechanical strength due to their highly graphitized structure. They show modulus of >200 GPa and tensile strength of >2 GPa [242].

2.2.5.2. Pyrolysis

Pyrolysis comprises a series of heat treatment stages where each stage has a particular heating rate, maximum temperature and holding time [243, 244]. Mainly organic materials are pyrolysed for the production of activated carbon, CFs and CNFs [245-247]. The type of atmosphere used in the pyrolysis of various materials can be inert such as N_2 and Argon or oxidative such as O_2 , depending on the desired properties of the resultant carbon material. However, the atmosphere and the gas flow rate should be carefully controlled during the pyrolysis [248, 249]. The molecular structure of precursors breaks down during the pyrolysis which leads to the formation of gaseous species, tar and a carbon rich residue (Figure 2.13) [250-253].

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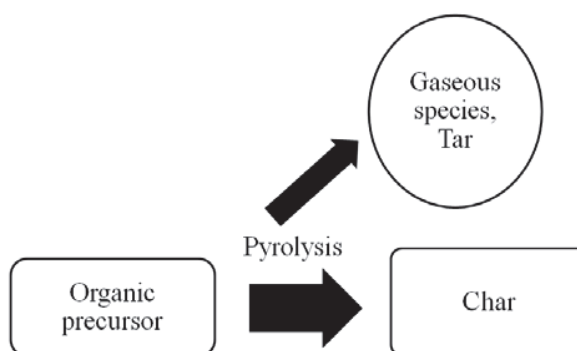


Figure 2.13. Schematic illustration of the pyrolysis of organic materials.

For the production of CNFs by pyrolysis, there are two classes of precursor nanofibres that can be used. One is polymeric nanofibres made using electrospinning techniques. Another is CellNFs extracted from naturally occurring materials.

2.2.5.2.1. Pyrolysis of Electrospun nanofibres

Electrospinning was first invented in the early 20th century. But it was until the early 21st century when the real novelty and functionality of this technique was realized [254]. Electrospinning setup comprises a high voltage power supply, an electrically conductive polymer solution, an electrode collector and an injection tip (usually syringe needle) [255]. Electrically charged polymer solution is exposed to an electric field which leads to the formation of droplets at the tip of the needle. As a result, the electric field forces the droplet to draw towards the opposite electrode that also serves as a collector. As the droplet travels along the electric field, it is then exposed to the electric field resulting in the formation of filaments before hitting the electrode collector [256].

Electrospun nanofibres present excellent characteristics such as [257]:

- High surface area;
- High porosity;
- High mechanical and structural strength;
- Low weight;
- Ability to integrate with other materials;
- Ability to form different fibre diameter and length and chemical and mechanical properties.

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Electrospun nanofibres are used in many applications such as filtration [258], catalyst support [259], biomedical [260-262] and sensors in electronics [263, 264].

CNFs can be produced from electrospun nanofibres by undergoing carbonisation in an inert atmosphere [54, 265, 266]. Zhou et al. used PAN-based electrospun nanofibre precursors to produce CNFs of 200-300 nm in diameter using pyrolysis in an inert gas [216]. They applied tension during the stabilization process which increased the structural order within the fibres. Thus, the pyrolysed CNFs were more graphitic than the ones with no applied tension. The CNFs produced by this method showed tensile strength of 300-600 MPa, modulus of 40-60 GPa and improved electrical conductivity. Figure 2.14 shows the typical TEM images of PAN-based electrospun carbon nanofibres.

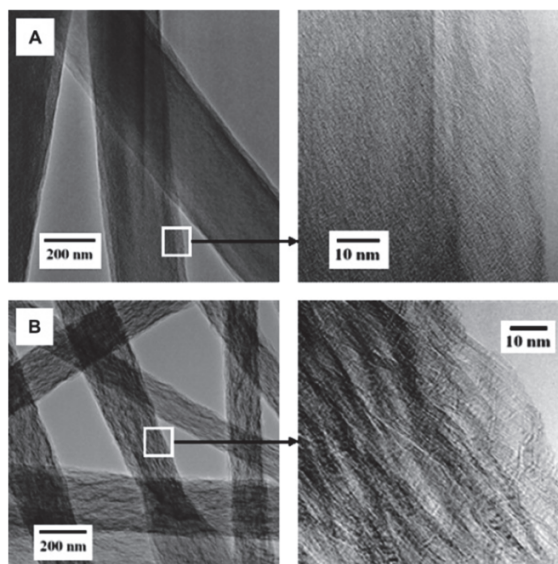


Figure 2.14. TEM images of the PAN-based electrospun CNFs [216].

Nataraj et al. studied the use of various acids for the preparation of PAN nanofibres and their effects on the morphological and electrical properties of resulting CNFs [267]. They reported that the CNFs showed improved morphological and electrical properties by using heteropolyacids with 5% concentration.

CNFs inherit their properties from their precursors. For example, precursors with high tensile strength and modulus will produce CNFs with similar properties [216]. Thus, electrospun-based CNFs display very high surface area, low weight and high mechanical and structural strengths, because of the properties of electrospun PAN fibres. Electrospun

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CNFs are used in many applications such as batteries, hydrogen storage, catalyst supports, nanocomposites and fuel cells [268, 269].

CNFs with smaller diameters, when used as a structural material in composites, enhance the integration between the matrix and the fibres and hence distribute the applied force more evenly throughout the network. As a result, the composite has a longer life span and higher mechanical strength. Typical electrospun-based CNFs have diameters of >100 nm [270, 271]. Smaller diameters are difficult to obtain mainly due to the limitations in electrospinning techniques where the attempt in producing finer diameter fibres leads to an increase in the formation of beads (defects) within the nanofibre network [266]. Electrospinning requires a polymer solution, such as chloroform and methylene chloride [272], in which the polymer is well dispersed. The evaporation of such solvents during fibre formation can cause health risks.

2.2.5.2.2. Pyrolysis of CellNFs

The pyrolysis of CellNFs is expected to result in the formation of CNFs. Due to their small diameter, cellulose-based CNFs may require lower temperature for graphitization [273]. However, little research has been reported on the production of nano-scale CFs by pyrolysis of CellNFs. It is expected that the molecular and morphological properties of precursors strongly affect those of the pyrolysed carbon material [203]. Ishida et al. investigated the carbonisation of freeze-dried bacterial and tunicate CellNFs and found that the carbon residue retained its fibrous morphology by using HCl as a pyrolytic atmosphere and a pretreatment chemical [149]. Another study showed that the effect of surface area and thermal stability of chitin and softwood CellNFs was considered to be the main factors in altering the fibrous morphology in the resultant carbon residues. However, these studies did not report successful retention of the fibrous structure of softwood-based CellNFs in the carbon residue.

Recently, Deakin University has successfully developed the technology to produce CellNF from natural plant products [274]. Mechanical ball-milling was used in order to obtain CellNFs. It is known that when cellulose fibres are placed in water, the hydroxyl groups (OH) of water competes with the ones in cellulose to form hydrogen bonding. This can help separate cellulose fibres from each other [275-277]. Ball-milling of cellulose in aqueous suspension breaks down the raw fibres into CellNFs suitable for CNF production. Successful fabrication of CellNFs using such green and scalable

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technique was a major step toward CNF fabrication. Unlike CVD or electrospinning, pyrolysis does not require the precursor to undergo pre-treatment using hazardous chemicals. Once the optimum conditions are found, carbonisation of cellulose can be undertaken in inert atmosphere.

2.2.6. Thermal decomposition mechanism of cellulose

Cellulose undergoes thermal decomposition without going through the melting stage and thus it does not behave like other precursors such as PAN or pitch [78, 278, 279]. If the decomposition of cellulose was an idealistic dehydration reaction, then the following reaction would happen [10]:



However, cellulose decomposition is a complex phenomenon comprising a series of reactions occurring in succession or concurrently, which eventually leads to mainly three products: (a) water, (b) gases and (c) char. There have been many studies investigating cellulose decomposition and theories developed explaining the phenomenon [149, 200, 1202, 279-284]. However, since cellulose itself has many physical forms in nature, the decomposition mechanism is influenced by its structural configuration. Hence it is difficult to obtain a general explanation of the decomposition mechanism. However, the current consensus can be summarised as follow [10]. The thermal decomposition of cellulose occurs in several stages:

- External dehydration (120–180°C)

When cellulose is heated to 120°C, physically absorbed water molecules are released (external dehydration). The hydrogen bonds between water molecules and OH groups in cellulose are replaced with the hydrogen bonding between OH groups in cellulose.

- Internal dehydration (180 – 250°C)

As the temperature increases to around 180°C the energy is sufficient to excite some bonds within the cellulose molecules such as —OH and —H atoms ready to break the bonds [126, 127, 285, 286]. This causes dehydration from the cellulose glycosidic rings (internal dehydration) and elimination of water molecules from the rings [279]. Whether the OH and H from one glycosidic ring or from two neighbouring rings link together is still being debated.

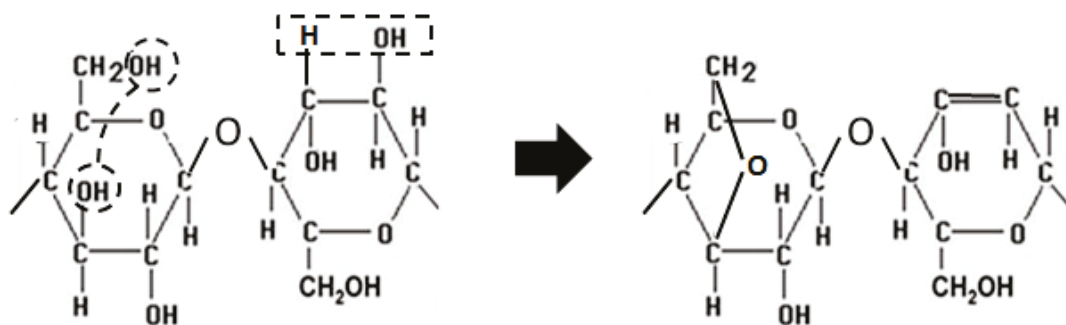


Figure 2.15. Internal dehydration of cellulose.

- Initial chain scission (180–250°C)

At ~250°C, levoglucosan (1-6-anhydro- β -D-glucopyranose) is formed by an intra-chain dehydration reaction between an OH group in CH_2OH and the oxygen in 1-4 glycoside links (Figure 2.16) [275-277, 287]. Levoglucosan is volatile and, at higher temperatures, breaks down into tar and some other by-products such as char, CO_2 and furan [288, 289]. Tar is a brown sticky by-product of levoglucosan decomposition [290-296]. Levoglucosan is also responsible for the flammability of cellulose since its structural breakdown results in the formation of flammable gases. Hence, the prevention of levoglucosan formation will increase the yield of carbon residue [152-154, 160, 297-299]. The use of fire retardants such as ZnCl_2 [300-302] was studied in order to reduce the amount of levoglucosan that was produced during cellulose decomposition [52, 303-306].

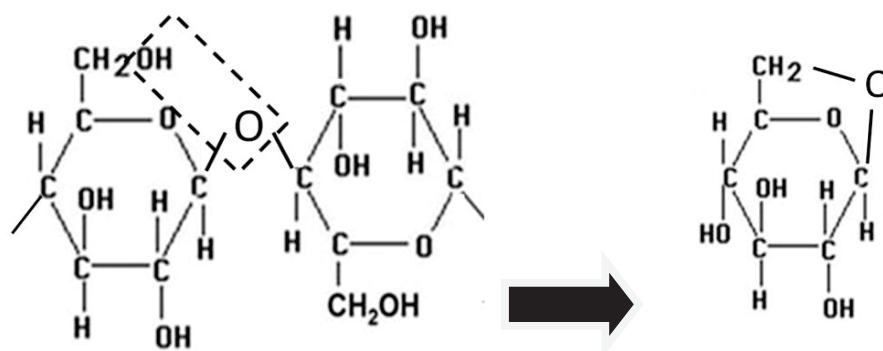


Figure 2.16. Formation of levoglucosan.

- Depolymerization (250–400°C)

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Above 250°C, the scission of glycosidic rings occurs that leads to the formation of CO, CO₂, H₂O and char (Figure 2.17) [157, 307, 308]. However, the scission is not a straight reaction but a series of other reactions leading to such a phenomenon. A glycosidic ring has four OH groups located at 2-, 3-, 4- and 6-C [309]. On one hand, the removal of these OH groups from the rings results in the formation of C=C and C=O bonds, while the chair/bed [112, 310] conformation of cellulose is still maintained [311-314]. On the other hand, levoglucosan is also formed at above 250°C. These two reactions are always concurrent and compete with each other [10].

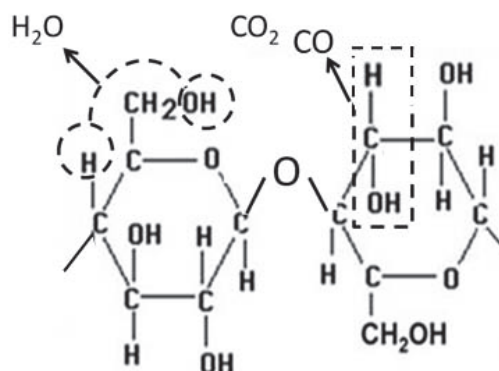


Figure 2.17. Chain scission of cellulose and formation of gaseous species.

- Aromatization (>400°C)

Depolymerization is completed at 400°C and further increase in temperature initiates aromatization of CFs. At the completion of cellulose decomposition, carbon atoms connect with each other and form hexagonal rings similar to graphite. However, the paths in which carbon atoms connect and form rings are not fully understood. It was suggested that longitudinal polymerization occurs where carbon atoms join to form carbon chains and chains connect to form rings (Figure 2.18). However, this model has little experimental support [317]. Davidson [318] suggested that increasing temperature causes the carbon chains to get closer to each other and join to form rings. Losty [159, 319] suggested that elimination of pyranose rings and glycoside links create aromatic rings with hydrogen attached to them. Attached hydrogen atoms act as isolators and keep the rings separate from each other [158]. The rings then connect and form graphitic layers at higher temperatures.

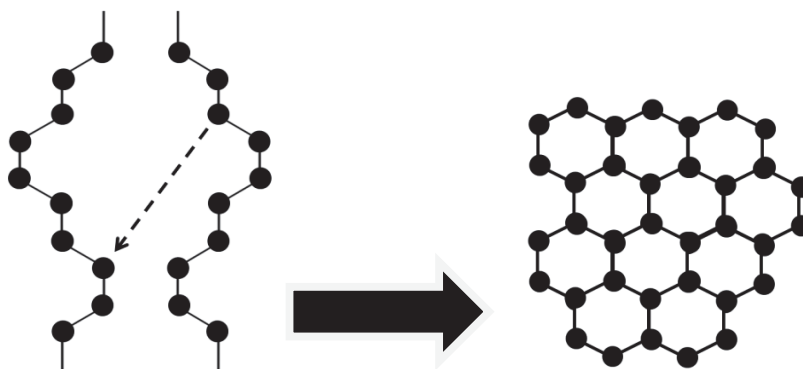


Figure 2.18. Aromatization of chains and formation of graphitic carbon.

2.3. Summary

CNFs are a new class of materials with many new applications from which various industries from automobile and aerospace to electronics and medicine can greatly benefit. While micron sized CFs are widely used, CFs with diameters in nanometer range exhibit improved properties such as mechanical strength and electrical conductivities. In addition, CNFs have high aspect ratios and high specific surface areas, which enable them to greatly interact with other materials and distribute the desired function evenly across the host material. In the past, some studies have been conducted on the development of new techniques to produce CNFs and utilisation of various precursors including natural polymers such as cellulose. The common methods to produce CNFs are CVD, electrospinning and pyrolysis techniques. CVD uses carbonaceous gases as a precursor and metallic catalysts as a platform to grow CNFs. Electrospinning produces precursor nanofibres using charged polymeric solutions and an electric field initiating the fibre-spinning process, and the resulting polymer fibres are subsequently carbonised. Both CVD and electrospinning have major drawbacks. CVD grown CNFs often contain a high percentage of impurities. Electrospinning methods result in precursor nanofibres with diameters larger than 100 nm. In addition, the cost of CVD and electrospun CNFs is high due to slow and rather difficult production processes. The environmental concerns of CVD and electrospun CNFs, due to the involvement of hazardous chemical treatments, limit the horizons for the commercial development of such techniques.

Carbonisation of cellulose using pyrolysis has some advantages:

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1. Cellulose is a renewable material which is widely available on earth and hence the cost of the precursor is low. The environmental benefit is high, as it does not rely on petrol-based raw materials;
2. Precursor preparation does not require hazardous chemical treatments, which add another environmental benefit;
3. Pyrolysis does not require facilities as complex as for CVD;
4. Pyrolysis of plant-based cellulose is theoretically carbon-neutral and hence has reduced environmental impacts compared with CVD and electrospinning techniques;
5. The pyrolysis process is relatively easy to scale up for commercial purposes.

Although the pyrolysis of bacterial cellulose or chitin-based celluloses has been investigated in the past, the use of plant-based CellNFs as a precursor has rarely appeared in the literature. This research was conducted to fill this knowledge gap by investigating the potential to produce CNFs by pyrolysis of plant-based CellNFs.

Chapter 3: Experimental

In this chapter, the details of the materials, instruments, experimental procedures and characterisation methods used in this research work are presented.

3.1. Cellulose nanofibre preparation

3.1.1. Overview

The fabrication procedure of CellNFs has been detailed elsewhere [274]. Briefly, softwood pulp was suspended in deionised water, blended in a mixer and stirred for 48 h. The pulp suspension was then ball-milled for 90 min using zirconia balls. The suspension was then dried (using oven-drying or freeze-drying techniques) for carbonisation.

3.1.2 Cellulose pulp suspension

Cellulose pulp (NIST standard material RM 8495 Northern Softwood Bleached Kraft Pulp) was kindly donated by the Australian Pulp and Paper Institute in Monash University. Cerium-doped zirconium oxide balls (Zirconox 0.4-0.6 mm in diameter) were purchased from Jyoti Ceramic Industries Pvt. Ltd.

Cellulose pulp sheeting was cut into 5×5 cm pieces and soaked in deionised water in the fridge overnight. The weight ratio between the pulp and water was 99:1. Wetted cellulose was then defibrillated using a conventional kitchen blender and then stirred at 70°C overnight. The cellulose suspension, thus obtained, was kept in the fridge and used as required.

3.1.3. Ball milling

In order to mill the pulp suspension, 45 g of cerium-doped zirconia balls and 20 mL of deionised water were added to 20 g of 1wt% pulp suspension in a 70 ml polypropylene container. Ball-milling was performed in a Spex 8000M shaker mill for 90 min (Figure 3.1). The CellNF suspension was then filtered to remove balls and clotted fibres using a polyethylene terephthalate mesh with a mesh opening of 125 µm.

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Figure 3.1. Spex 8000M shaker mill.

3.1.4. Drying

For oven drying, the CellNF suspension was poured into a purpose-made aluminium foil container and placed in a laboratory oven at 60°C overnight. A translucent CellNF film was collected and used for carbonisation and characterisation.

For freeze-drying, a small amount of CellNF suspension was poured in a flask and dipped and stirred in liquid nitrogen. The CellNF suspension was then vacuum dried using a Labconco freeze-drier for 72 h. CellNFs with a spongy appearance were collected and used for carbonisation and characterisation.

3.2. Carbonisation

3.2.1. Below 1000°C

A pyrolysis method was selected to carbonise CellNFs. A tubular furnace (TF55035C-1, Lindberg/Blue M) were used with a quartz tube with the length of 68 cm and diameter of 2.7 cm (Figure 3.2). A small piece of sample (~ 15 mg) was placed on an alumina boat of 85×10 ×13 mm inside the quartz tube. A nitrogen gas flow at the rate of 70 ml/min was introduced into the tube to create an inert atmosphere and also to constantly remove the evolved gases from the system. Higher flow rates would blow the samples off the tube while lower flow rates would not remove the by-product gases and water from the system. The furnace temperature was accurately calibrated so that the temperature variation was negligible. The heating elements were aligned along and around the tube hole so that a uniform heating area was facilitated for accurate sample heating. The nitrogen flow rate, heating rate, maximum temperature and holding time were controlled throughout the experiment.

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Figure 3.2. Tube furnace, TF55035C-1, Lindberg/Blue M.

3.2.2. Above 1600°C

Graphitization experiments at temperatures above 1600°C were conducted using a Tanmann furnace (Figure 3.3) in the laboratory of Professor Toyoda (Applied chemistry, Faculty of Engineering, Oita University). The heat treatment was carried out under vacuum in a graphite container. The heating rate was fixed to 10°C/min.



Figure 3.3. Tanmann furnace, school of applied chemistry, faculty of Engineering, Oita University.

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3.3. Characterisation of nanofibres

3.3.1. Scanning Electron Microscopy (SEM)

The morphological properties of fibres were studied with scanning electron microscopy (SEM, SUPRA 55P). Unlike optical microscopes that use light for imaging, SEM microscope uses electrons to interact with the sample and produce images of the sample surface. An electron beam sends out electrons to the sample. These electrons then interact with the atoms which make up the sample and send back electrons with specific energies (secondary electrons). These electrons are then collected and used for producing images containing information about the surface morphology of the samples. The low energy of secondary electrons allows them to escape only from near the sample surface (a few nm) and hence SEM is an excellent method to analyse surface morphology of nano-scale objects.

A small amount of sample was placed on a sample holder using carbon tape and was sputter coated with gold or carbon, using a Baltec SCD50 sputter coater. Due to the sensitivity of samples to high voltage, all images were taken at an acceleration voltage of ~ 1 kV with magnifications of 5,000-10,000. The SEM images were used to calculate the average fibre diameters using an image analysis software (Image Pro-Plus 4. 5, Media Cybernetics Co., Santa Clara, CA).

For the analysis of fibre diameters, SEM images were taken from randomly selected spots on the sample. All the fibers in one image were measured using Image Pro Plus software. Since all the fibres in one image were measured, the bias in the selection of fibres was minimal. On average 7-15 images were taken from one sample and fiber diameter of all the fibers in the images were measured.

In this research, different magnification was used for different samples to estimate the fibre diameter. The magnifications of SEM images were selected based on the limitations arising from the sample damage caused by the electron beam. Higher magnification means higher concentration of electrons in one spot. It was noticed that, under high magnifications, cellulose fibers could be damaged by the electron beam before being measured. The degree of damage varied among the samples even using the same magnification, which reason should be further investigated. Therefore, different

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magnifications were chosen depending on the sample's characteristics to tolerate electron beams.

3.3.2. Transmission Electron Microscopy (TEM)

TEM observations of the samples were undertaken on a JEM-2100 TEM. Similar to SEM technique, in TEM microscopy an electron beam sends out electrons to a thin sample (< 100 nm in thickness). The electrons interact with the sample atoms as they pass through the thickness of the sample. Electrons that were not scattered by the sample were transmitted through and were collected for producing images containing information about crystalline, chemical and electronic properties of the sample. Because of the very small wavelength of electrons (~ 2.5 pm for 200 keV) compared to visible light (400 – 750 nm), TEM enables the observation of nanoscale objects.

All the samples were ultrasonically dispersed in ethanol and then a drop of the dispersion was dried on a copper grid covered with a carbon film. TEM images were observed through a Gatan image filter at an accelerating voltage of 200 keV.

3.3.3. Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier transform infrared (FT-IR) spectra were recorded by an FT-IR spectrophotometer (Bruker Vertex 70) to study the chemical configuration of the samples. Fourier transform infrared spectroscopy is a technique to analyse the chemical and crystalline properties of the sample. It uses a beam of infrared light that hits the sample in a wide range of wavelengths and measures that how much of the light is absorbed/transmitted. The atomic bonds that make up the sample absorb a particular wavelength of light depending on the characteristics of the chemical bonds. Hence the information about the types of chemical bonding that are present in the sample is recorded in the spectrum.

The spectra were obtained under the condition of 64 scans per spectra at 4 cm^{-1} resolution. All test runs were undertaken in a controlled environment ($20\pm 2^\circ\text{C}$ and $65\pm 2\%$ relative humidity). The data were analysed using OPUS 5.5 software. Samples pallets were produced using the KBr method. The samples were diluted and evenly distributed in the KBr disks so that appropriate effective thickness was achieved not to saturate the FTIR signal.

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3.3.4. X-ray Diffraction (XRD)

The crystallinity of the samples was studied by X-ray diffraction analysis. X-ray diffraction technique is used to analyse the crystal structures of materials. When a monochromatic X-ray beam is projected onto a crystalline sample, X-ray diffraction occurs only in certain diffraction angles, depending on the crystal structure of the sample. Most atoms scatter X-ray through destructive interference in most directions whereas atoms that are in one lattice plane scatter the X-ray in a certain angle through constructive interference (Bragg's law). The constructive interference leaves high intensity spots (or peaks) on the detector which is then used to analyse the crystal properties such as crystal symmetry, crystallite size and crystallinity. It can also be used to analyse chemical compositions by identifying the crystalline phases of known materials in the observed diffraction patterns.

An X-ray diffraction instrument (Panalytical X'Pert PRO MRD XL) was used to obtain the curves at 2θ between 5° to 80° , step size of 0.01, time per step of 3 sec, and Cu $k\alpha$ ($\lambda=1.54\text{\AA}$) radiation generated at 40 kV and 30 mA. All tests were undertaken at room temperature and atmospheric pressure. Samples were put on glass holders and flattened before measurement.

Crystallite sizes were calculated using the Bragg-Scherrer equation:

$$D = \frac{K\lambda}{\beta \times \cos \theta} \quad (3.1),$$

where θ is the Bragg angle in radian and λ is the wavelength of the incident radiation, 0.154 nm. K is the Scherrer constant, 0.94, and β is the diffraction peak's full width at half maximum in radian.

The degree of crystallinity was estimated using the Segal method that is frequently used for cellulose [320]:

$$I_{cr} = \frac{I_{max} - I_{min}}{I_{max}} \times 100 \quad (3.2),$$

where I_{max} is the maximum intensity of the peak at 22.5° and I_{min} is the peak intensity of the amorphous fraction represented by the diffraction intensity at 19° .

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Interplanar spacing, d , is the distance between adjacent planes in the set (hkl) crystal plane. The cellulose I β structure has a monoclinic $P2_1$ unit cell containing two non-equivalent chains. The periodic chains run parallel to each other forming single planar sheets that stack into 3D crystals [321].

3.3.5. Thermal Gravimetry/ Differential Scanning Calorimetry (TG/DSC)

Thermal properties of the samples were investigated with TG/DSC using a Netzsch 407 PC Luxx instrument with the NETZSCH Proteus analysis software. In thermal gravimetry analysis (TGA), the changes in weight are measured to analyse the thermal behaviour/reaction of the sample. This requires precise measurements in weight, temperature and temperature change. By heating the sample to above decomposition temperature, at least one component decomposes into gas and is released from the sample by which the weight change can be measured. The data give information about the thermal characteristics of the material. In Differential Scanning Calorimetry (DSC) analysis, the difference in the required amount of heat energy to increase the temperature of a sample and reference is measured. DSC allows the detection of phase changes as the appearance of peaks associated with endothermal or exothermal reactions, or the change in specific heat as the change in the slope of temperature-heat curve.

Samples of 5-10 mg were placed in an alumina crucible and measured at the heating rate of 10°C/min in a nitrogen atmosphere. The measurements were carried out in the temperature range between 30°C-1000°C under atmospheric pressure.

3.3.6. Raman spectroscopy

Raman spectroscopy reveals the vibrational mode of atoms and molecules using a monochromatic light. The shift in the wavelength of detected light from the wavelength of incident light, Raman shift, is associated with the energy of atomic or molecular vibrations/ rotations that are excited by the incident light. The vibrational/rotational energy is specific to chemical bondings and molecular structures. For example, the peaks at 1350 and 1580 cm^{-1} in Raman spectra of carbonaceous materials represent the vibration in defective graphitic structure and the tangential vibration of carbon atoms in graphitic layers, respectively. By comparing these two peaks, the extent of carbonisation can be analysed.

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Raman spectra were obtained using an InVia Confocal microscope system (Renishaw, Gloucestershire, UK) with 514 nm excitation from a Modu-Laser Stellar-Pro ML/150 argon ion laser through a X20 (0.4 na) objective. Nanofibre samples were packed into a 2 mm cavity cell held on a 250 mm $\times$ 750 mm plate. Incident laser power was 1.1 mW and coaxial backscatter geometry was employed. Use of higher laser power was found to cause decomposition of the nanofibres. Laser power was measured at the sample using an Ophir Nova power meter fitted with a PD300-3W head. Spectra were collected over the range 3200 cm^{-1} to 200 cm^{-1} and averaged over at least 5 scans, each with an accumulation time of 40 s. Signal to noise was further reduced by averaging a minimum of two spectra obtained from different areas of the sample. These spectra were found to be highly reproducible. The Raman shifts were calibrated using the 520 cm^{-1} line of a silicon wafer. The spectral resolution was $\sim 1 \text{ cm}^{-1}$.

Chapter 4: Carbonisation of oven-dried cellulose nanofibre

4.1. Introduction

In this chapter, the pyrolysis of oven-dried CellNFs under atmospheric pressure and inert environment was investigated using controlled heating conditions. An oven-drying method was selected as the first drying technique to investigate its suitability for the production of carbon nanofibres, as the method is simple and easily scalable. The oven drying method leaves a compact network of nanofibres due to strong hydrogen bonding between nanofibres. The effect of heat treatment conditions on the properties of carbonised residue was investigated using TGA, SEM, XRD and FT-IR.

4.2. Experimental procedure

4.2.1. Carbonisation equipment

The pyrolysis of oven-dried CellNFs was carried out using the tube furnace as described in Chapter 2. In order to study the pyrolysis effect on the original CellNFs and for the experimental accuracy, one batch of oven-dried CellNFs was split into two identical batches. Small pieces of one batch of oven-dried CellNFs (1cm×1 cm) were placed on the boat and placed in the middle of a quartz tube. The other batch was used for comparison with the pyrolysis results.

4.2.2. Carbonisation conditions

As discussed in chapter 2, it has been reported that the pyrolysis of cellulose comprises four stages: dehydration of physically absorbed water (25°C - 180°C), inter and intra molecular dehydration (180-250°C), depolymerisation (240 -350°C) and aromatization (over 350°C). Therefore, separate investigations in these temperature ranges are crucial to understand the pyrolysis characteristics of oven-dried CellNF.

Heating the CellNFs above 180°C is expected to cause the internal dehydration from the cellulose molecules. H₂O is formed by connection of an OH group and hydrogen in the

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cellulose molecules. Cellulose dehydration continues up to 250°C where the major stage in decomposition is initiated. It was suggested that if hydrogen and oxygen were completely released from the cellulose molecules prior to the decomposition stage, the interference of these elements with carbon atoms would be minimum during cellulose decomposition. This has two advantages: 1) less carbon atoms are released from the molecules in the form of gas, so that less mass loss occurs, 2) upon completion of the decomposition, presence of oxygen and hydrogen complexes in the carbon residue would be minimal. Thus, holding CellNFs below 180°C would affect the CellNF properties and the pathways in which cellulose converts into carbon. The carbon residue would retain its original cellulosic morphology. In order to study such effects, three holding times of 1, 2 and 3 h at 170°C, a slightly lower temperature than 180°C where the internal dehydration starts, were investigated. Likewise, heating conditions up to 240°C, a slightly lower temperature than 250°C where the decomposition starts, were investigated.

Table 4.1 shows the heat treatment conditions selected for carbonisation of oven-dried CellNFs. Past studies showed that higher heating rates leads to higher mass loss and formation of tarry by-products whereas lower heating rates prohibits such results, for conventional micron sized cellulose [146]. Hence, different heating rates of 1°C/min, 2°C/min and 10°C/min, were selected in this temperature range.

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Table 4.1. Heat treatment conditions.

Sample ID		Target temperature 1			Target temperature 2			Target temperature 3
	Heating rate (°C/min)	Temp. (°C)	Residence time (h)	Heating rate (°C/min)	Temp. (°C)	Residence time (h)	Heating rate (°C/min)	Temp. (°C)
NF1	1	170	—	—	—	—	—	—
NF2	2	170	—	—	—	—	—	—
NF3	10	170	—	—	—	—	—	—
NF4	10	170	1	—	—	—	—	—
NF5	10	170	2	—	—	—	—	—
NF6	10	170	3	—	—	—	—	—
NF7	10	170	1	1	240	—	—	—
NF8	10	170	1	2	240	—	—	—
NF9	10	170	1	10	240	—	—	—
NF10	10	170	1	1	240	1	—	—
NF11	10	170	1	1	240	2	—	—
NF12	10	170	1	1	240	3	—	—
NF13	10	170	1	1	240	3	1	400
NF14	10	170	1	1	240	3	2	400
NF15	10	170	1	1	240	3	10	400

4.3. Results and discussion

4.3.1. Characteristics of oven-dried CellNFs before heat treatment

4.3.1.1. Morphology

Figure 4.1 (a) shows the SEM image of the oven-dried CellNFs. Oven-drying left a very compact film of fibres and little spatial gaps exist between the fibres. This suggested that cellulosic chains from neighbouring nanofibres could form hydrogen bonding and joined together. Figure 4.1(b) shows the fibre diameter distribution analysed from SEM images.

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The fibre diameter distribution is in good agreement with the previous report by Zhang et al. [274].

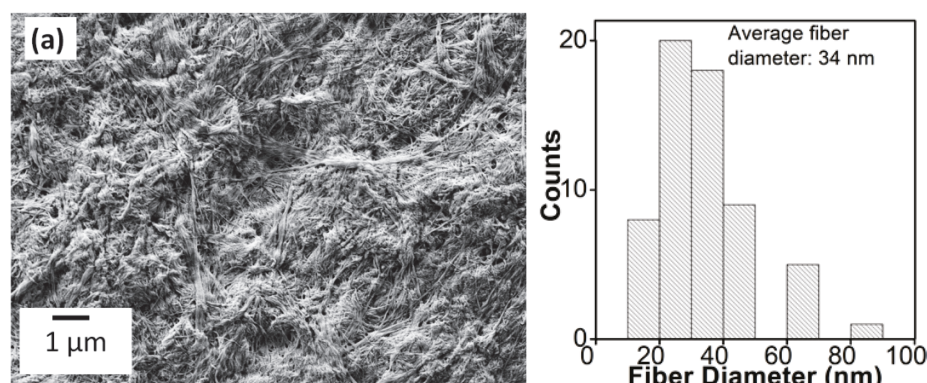


Figure 4.1. (a) SEM image of the oven-dried CellNFs and (b) fibre diameter distribution analysed from SEM images.

4.3.1.2. Crystallinity

Figure 4.2 shows the XRD graphs of the oven-dried CellNFs and softwood pulp. It is shown that the characteristic peak of cellulose occurs at 22.5° , indicating that the cellulose-I crystal structure was maintained after ball-milling and drying. CellNFs show main peaks at 15° , 16° , 22.5° and 34.1° associating with the (1 $\bar{1}$ 0), (110), (200) and (004) lattice planes.

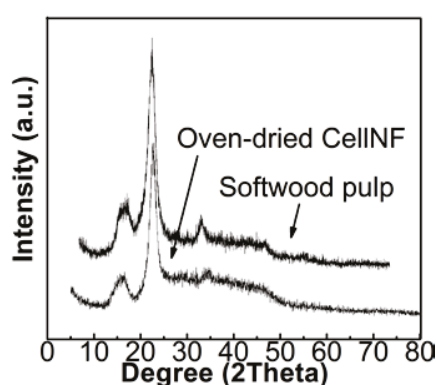


Figure 4.2. XRD graphs of softwood pulp and oven-dried CellNFs.

Table 4.2 shows the crystalline properties of softwood pulp and oven-dried CellNFs. Preparation of CellNFs including ball-milling did not drastically change the crystal properties.

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Table 4.2. Crystal size D , index of crystallinity I_{cr} , and interplanar distances d , of raw pulp and oven-dried CellNFs, estimated from XRD patterns.

	2 theta (deg)	hkl	d (Å)	D_{cr} (nm)	I_{cr} (%)
Softwood pulp	16.1°	110, 1-10	5.4	—	—
	22.5°	200	4.1	3.6	73
	34.1°	004	2.6	—	—
Oven-dried CellNFs	16.1°	110, 1-10	5.5	—	—
	22.5°	200	3.9	3.5	71
	34.1°	004	2.6	—	—

4.3.1.3. Chemical bonding

Figure 4.3 shows the FT-IR spectra of softwood pulp and oven-dried CellNFs. The spectra are identical with each other which indicate that CellNF preparation did not change the molecular structure of CellNFs.

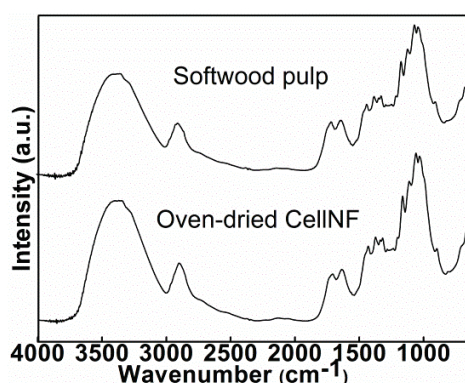


Figure 4.3. FT-IR spectra of softwood pulp and oven-dried CellNFs.

4.3.1.4. Thermal properties

Figure 4.4 shows the thermal behaviour of the oven-dried CellNFs when heated with a rate of 10°C/min up to 600°C. The chemical breakdown process started from around 250°C and completed at ~360°C. From the TG graph, it was evident that the sample lost 80% of its original weight. From the DSC graph, it was noted that a peak occurred at 353°C and indicates that the decomposition stage is an endothermic process.

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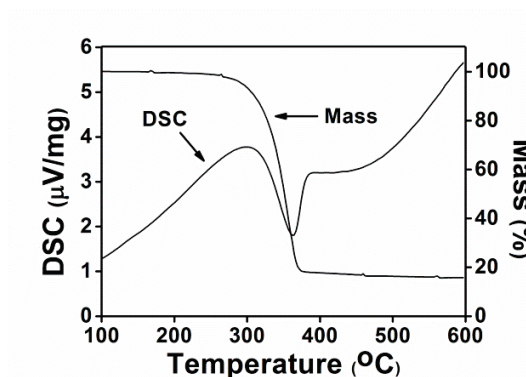


Figure 4.4. TGA/DSC graphs of CellNFs.

4.3.2. Effects of heating conditions below 170°C

4.3.2.1. Morphology

Figure 4.5 shows the SEM images of the samples heated to 170°C with heating rates of 1, 2, and 10°C/min. The fibrous morphology was retained during the heat treatment under the three heating rates. The macroscopic morphology of the resultant materials was similar to the original CellNFs (Figure 4.1). It is also evident from the SEM images that nanofibres were greatly compacted after heating and little space was remained between the fibres.

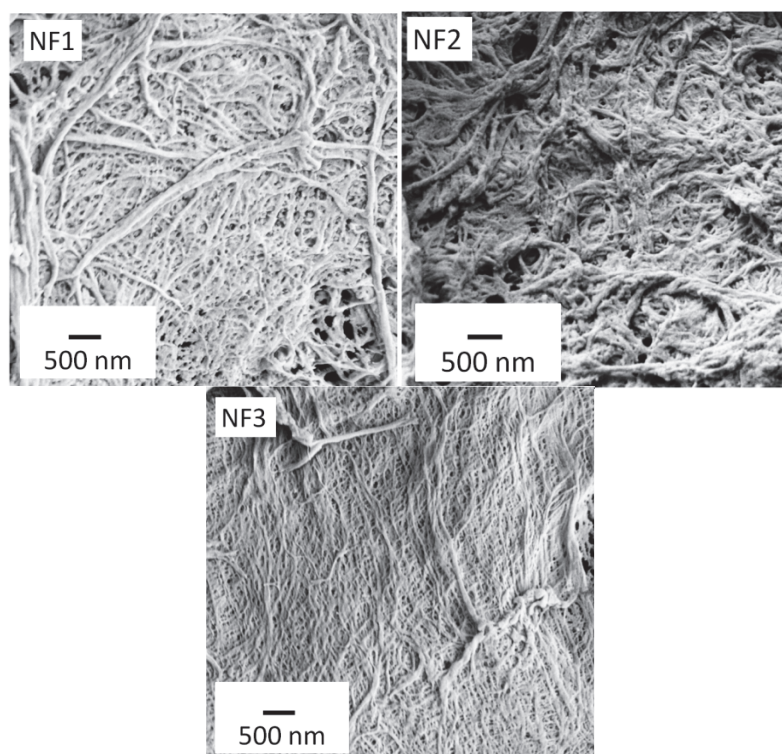


Figure 4.5. SEM images of heat treated samples to 170°C with heating rate of 1°C/min (NF1), 2°C/min (NF2) and 10°C/min (NF3).

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4. 3. 2. 2. Crystallinity

Figure 4.6 Shows the XRD patterns of the samples heat treated with the three heating rates. The position of the main peak at $\sim 22.5^\circ$ did not change with the heating rate. However, the peak at $\sim 15^\circ$ shifted to a slightly higher angle in the samples NF1 and NF2 with low heating rate (1 and $2^\circ\text{C}/\text{min}$ respectively). This may suggest the formation of a disordered state of cellulose-I β structure [322], but further detailed investigation is required to confirm the structural change during heat treatment at such a low temperature range.

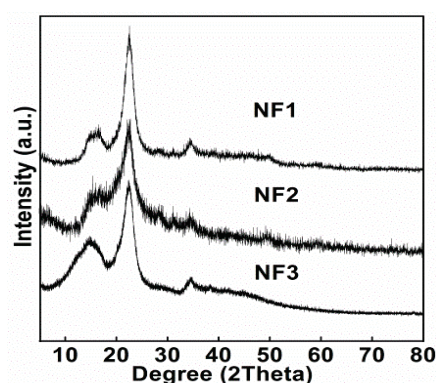


Figure 4.6. XRD graphs of heat treated samples with heating rates of $1^\circ\text{C}/\text{min}$ (NF1), $2^\circ\text{C}/\text{min}$ (NF2) and $10^\circ\text{C}/\text{min}$ (NF3).

Table 4.3 lists the estimated crystal size D , index of crystallinity I_{cr} , and interplanar distances d , after heat treatment. It is evident that heating the CellNFs up to 170°C did not affect the crystallinity and crystallite size (see Tables 4.2 and 4.3). Hence, the crystal structure of CellNFs showed little change up to this temperature irrespective of heating rate.

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Table 4.3. Crystal size D , index of crystallinity I_{cr} , and interplanar distances d , of heat treated samples with various heating rate, estimated from XRD patterns.

Heating rate	2 theta (deg)	hkl	d (Å)	D_{cr} (nm)	I_{cr} (%)
1°C/min	16.1°	110, 1-10	5.4	—	—
	22.5°	200	3.9	3.7	73
	34.1°	004	2.6	—	—
2°C/min	16.1°	110, 1-10	5.7	—	—
	22.5°	200	4.0	3.6	70
	34.1°	004	3.3	—	—
10°C/min	16.1°	110, 1-10	5.8	—	—
	22.5°	200	3.9	3.7	71
	34.1°	004	2.3	—	—

4.3.2.3. Chemical structure

Figure 4.7 shows the FT-IR spectra of CellNFs heated to 170°C with the three heating rates. Characteristic peaks of cellulose occur between 1000 cm^{-1} to 1500 cm^{-1} as shown in Figure 4.7(b). These peaks were assigned to the chemical bonds in the cellulose molecules (Table 4.4). Figure 4.7 shows that these three spectra are identical and no peak shift was observed. This indicates that heating to 170°C does not alter the chemical configuration of CellNFs and that the heating rate does not influence the chemical bondings in CellNFs.

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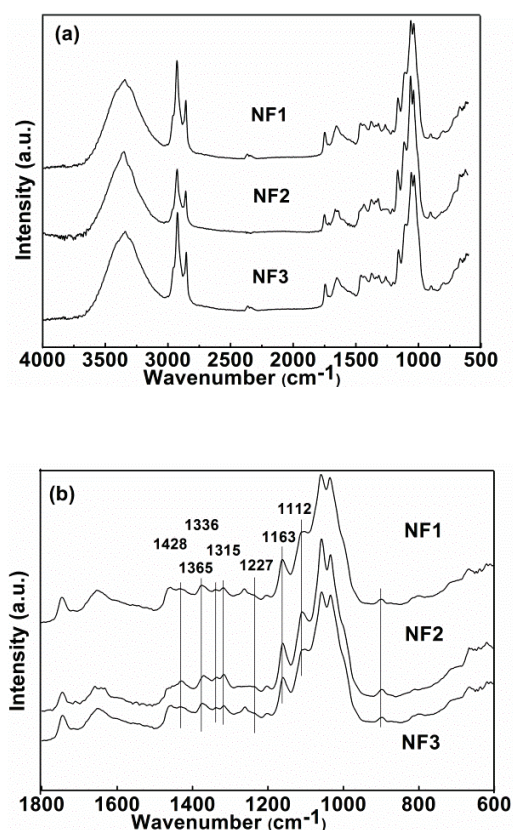


Figure 4.7. FT-IR spectra of heat treated CellNFs with heating rates of 1°C/min (NF1), 2°C/min (NF2) and 10°C/min (NF3); (a) 4000-800 cm^{-1} , (b) 2000-800 cm^{-1} .

Table 4.4. Assignment of FT-IR peaks to chemical bonds.

Wavenumber (cm^{-1})	Chemical bond
1112	C-OH
1163	C-O
1227	O-H
1277	C-H
1315	CH_2
1336	O-H
1365	C-H
1428	CH_2

4.3.3. Effect of holding time at 170°C

4.3.3.1. Morphology

Figure 4.8 shows the SEM images of the CellNFs held at 170°C for 1, 2 and 3 h, respectively. These images indicate that the morphological properties remained intact although dehydration and formation of H_2O from the cellulose molecule have already

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started (180°C -250°C) (see the TG/DSC data Figure 4.4). The average fibre diameter before and after each experiment was calculated from the SEM images and are shown in Figures 4.1(b) and 4.9. The Average fibre diameter did not show remarkable changes before and after heat treatment at 170°C for various holding times. This suggests that major decomposition process of cellulose was not initiated at this temperature.

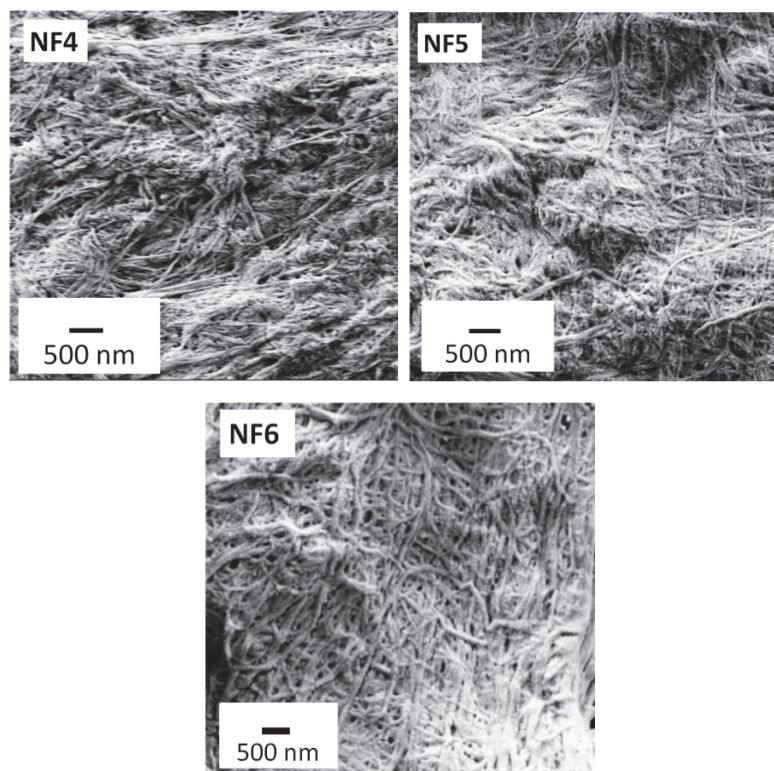


Figure 4.8. SEM images of heat treated samples at 170°C, with holding times of 1 h (NF4), 2 h (NF5) and 3 h (NF6).

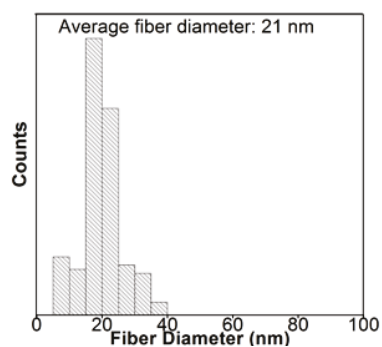


Figure 4.9. Fibre diameter distribution (average of three samples) of NF4, NF5 and NF6 estimated from SEM images.

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4.3.3.2. Crystallinity

Figure 4.10 Shows the XRD graphs of CellNF samples heated to 170°C and held for various times. These three XRD patterns of heat treated samples show similar patterns to that of CellNFs before heat treatment. The position of the main peak at $\sim 22.5^\circ$ did not change with heating rate. However, the peak at $\sim 15^\circ$ shifted to a slightly higher degree in the samples NF4 and NF5 with long holding times (2 and 3 h respectively). This may suggest the formation of a disordered state of cellulose-I β structure [322], but further detailed investigation is required to confirm the structural change during heat treatment at such a low temperature range.

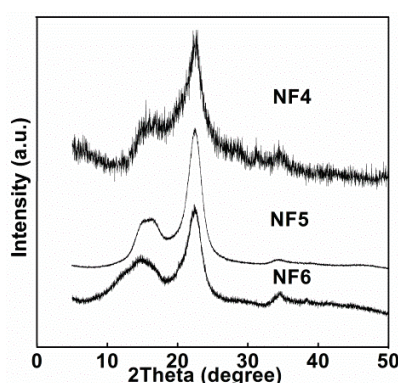


Figure 4.10. XRD graphs of heat treated samples at 170°C with holding times of 1 h (NF4), 2 h (NF5) and 3 h (NF6).

Table 4.5. Crystal size D , index of crystallinity I_{cr} , and interplanar distances d , of heat treated samples with various holding times, estimated from XRD patterns.

Holding time	2 theta (deg)	hkl	d (Å)	D_{cr} (nm)	I_{cr} (%)
3 h	16.1 °	110, 1-10	4.3	—	—
	22.5 °	200	3.8	3.8	72
	34.1 °	004	2.9	—	—
2 h	16.1 °	110, 1-10	5.1	—	—
	22.5 °	200	4.3	3.5	70
	34.1 °	004	3.3	—	—
1 h	16.1 °	110, 1-10	5.5	—	—
	22.5 °	200	3.9	3.9	72
	34.1 °	004	2.9	—	—

Table 4.5 lists the estimated crystal size D , index of crystallinity I_{cr} , and interplanar distances d , after heat treatment. It is noted that the crystalline properties of heat treated

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CellNFs did not change dramatically. This indicates that heat treatment at 170°C has little effect on the structure of the material irrespective of holding time.

4.3.3.3. Chemical structure

Figure 4.11 shows the FT-IR spectra of CellNFs heat treated at 170°C for 1, 2 and 3 h. It is noted that the FT-IR spectra of heat treated cellulose resemble the one before heat treatment (Figure 4.3) indicating that external dehydration, not internal one, was mainly taking place at this temperature.

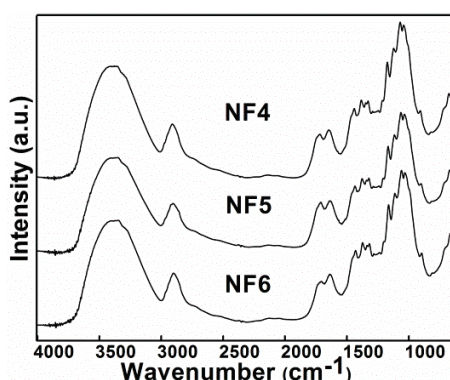


Figure 4.11. FT-IR spectra of heat treated CellNFs with holding times of 1 h (NF4), 2 h (NF5) and 3 h (NF6).

4.3.4. Effect of heating rate between 170°C to 240°C

4.3.4.1. Morphology

Figure 4.12 shows the SEM images of the samples after heating up to 240°C with various heating rates. These images show that fibrous morphologies from different heating rates resemble the original ones. Between 170°C to 240°C internal dehydration mainly takes place which comprises connection of OH groups with H atoms in the cellulose molecules and formation of water molecules.

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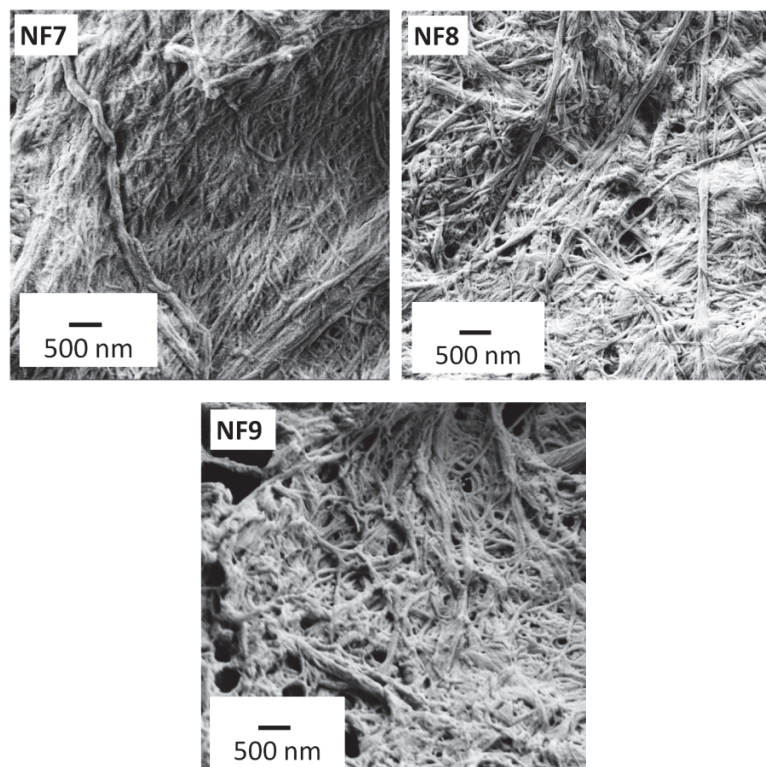


Figure 4.12. SEM images of samples heat treated to 240°C, with heating rates of 1°C/min (NF7), 2°C/min (NF8) and 10°C/min (NF9).

4.3.4.2. Crystallinity

Figure 4.13 shows the XRD patterns of the samples before and after heating up to 240°C. The sharp peak at 22.5° indicates that the cellulosic structure still remained at 240°C and that the difference in heating rate in the temperature range between 170°C and 240°C does not influence the crystal structure.

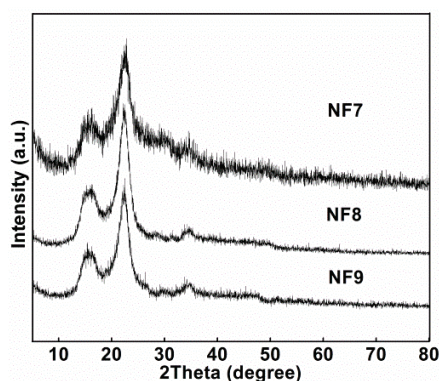


Figure 4.13. XRD patterns of heat treated CellNFs, with heating rates of 1°C/min (NF7), 2°C/min (NF8) and 10°C/min (NF9).

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Table 4.6. Crystal size D , index of crystallinity I_{cr} , and interplanar distances d , of heat treated samples with various heating rates between 170°C to 240°C, estimated from XRD patterns.

Heating rate	2 theta (deg)	hkl	d (Å)	D_{cr} (nm)	$I_{cr}(\%)$
1°C/min	16.1 °	110, 1-10	3.8	—	—
	22.5 °	200	3.6	3.1	70
	34.1 °	004	2.7	—	—
2°C/min	16.1 °	110, 1-10	4.3	—	—
	22.5 °	200	5.1	2.9	70
	34.1 °	004	3.7	—	—
10°C/min	16.1 °	110, 1-10	5.1	—	—
	22.5 °	200	3.8	3.7	71
	34.1 °	004	2.6	—	—

4.3.4.3. Chemical structure

Figure 4.14 shows FT-IR spectra of the samples heat treated to 240°C. The FT-IR spectra of the samples were identical to that of CellNFs before heat treatment, except the 1700 cm^{-1} band which was not identified and is a subject of further study. 1112 cm^{-1} and 1165 cm^{-1} bands assigned to CH_2 and OH groups were still present in the FT-IR spectra. The results indicate that cellulosic chemical configuration seemed to have not changed by the heat treatment regardless of heating rate.

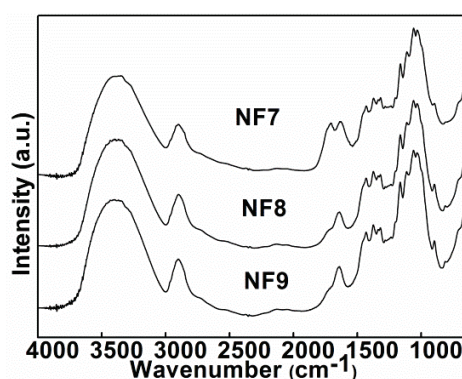


Figure 4.14. FT-IR spectra of heat treated samples, with heating rates of 1°C/min (NF7), 2°C/min (NF8) and 10°C/min (NF9).

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4.3.5. Effect of holding time at 240°C

4.3.5.1. Morphology

Figure 4.15 shows the SEM images of oven-dried CellNFs held at 240°C for 1, 2 and 3 h. It is noted that CellNFs still maintained their fibrous morphologies. The average fibre diameter was measured for three heat treated samples separately and averaged in order to analyse the fibre diameter after heat treatment. The average fibre diameter was 33.58 nm which is identical the oven-dried CellNFs (Figure 4.16).

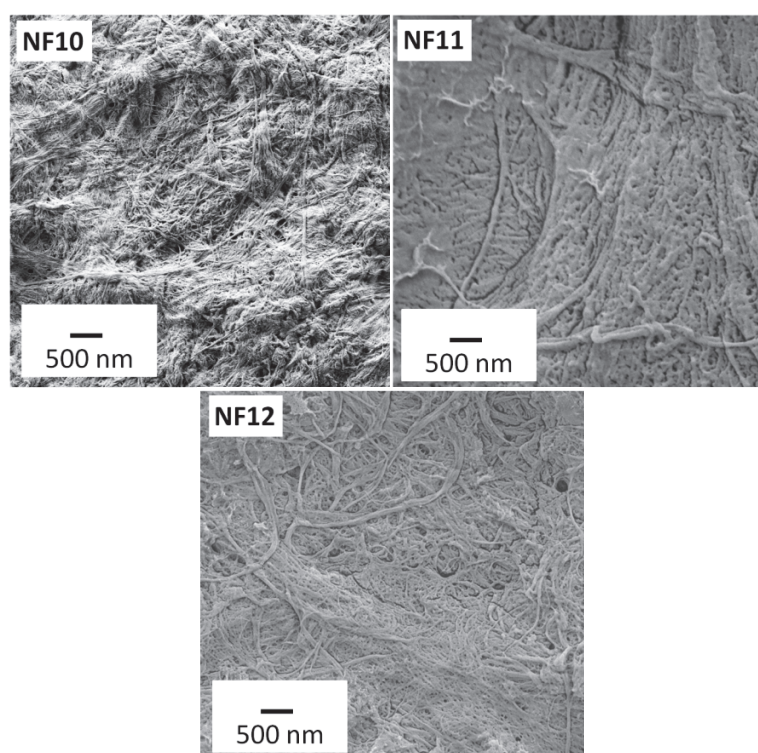


Figure 4.15. SEM images of samples held at 240°C, with holding times of 1 h (NF10), 2 h (NF11) and 3 h (NF12).

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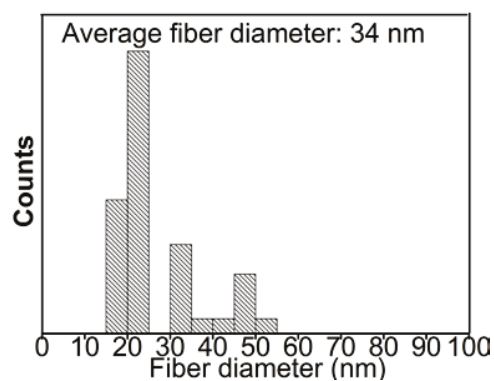


Figure 4.16. Fibre diameter distribution (average of NF-10, NF11 and NF12) estimated from SEM images.

4.3.5.2. Crystallinity

Figure 4.17 shows the XRD results for the samples held at 1, 2 and 3 h. The peak at 22.5° was evident in all samples indicating that the cellulose-I crystal structure was retained [145].

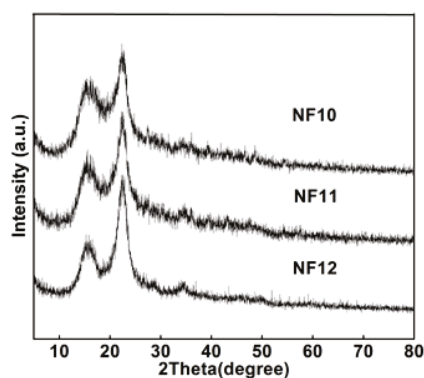


Figure 4.17. XRD graphs of samples heat treated at 240°C , with holding times of 1 h (NF10), 2 h (NF11) and 3 h (NF12).

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Table 4.7. Crystal size D , index of crystallinity I_{cr} , and interplanar distances d , of heat treated samples with various holding time at 240°C, estimated from XRD patterns.

Holding time	2 theta (deg)	hkl	d (Å)	D_{cr} (nm)	I_{cr} (%)
3 h	16.1 °	110, 1-10	4.3	—	—
	22.5 °	200	4.2	3.7	70
	34.1 °	004	3.1	—	—
2 h	16.1 °	110, 1-10	5.3	—	—
	22.5 °	200	3.5	2.9	68
	34.1 °	004	3.8	—	—
1 h	16.1 °	110, 1-10	5.4	—	—
	22.5 °	200	3.3	3.9	69
	34.1 °	004	2.4	—	—

4.3.5.3. Chemical structure

Figure 4.18 shows FT-IR spectra of heat treated samples heat treated at 240°C. The FT-IR spectra show rather similar spectra to that of freeze-dried CellNFs before heat treatment. Cellulosic peaks in the spectra were identical for the three different holding times. No major change in the band position or disappearance of bands from the spectra was recorded. The result indicates that the difference in holding time at 240°C did not influence the chemical structure of cellulose. This is in agreement with the XRD results (Figure 4.17) indicating that the crystalline structure of the cellulose was also maintained.

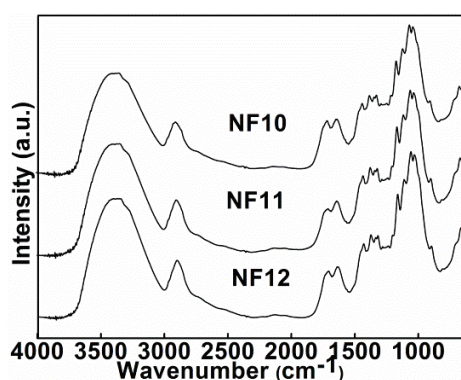


Figure 4.18. FT-IR spectra of heat treated samples, with holding times of 1 h (NF10), 2 h (NF11) and 3 h (NF12).

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4.3.6. Effect of heating rate between 240°C to 400°C

4.3.6.1. Morphology

Figure 4.19 shows the SEM images of the samples heat treated at 400°C. It is shown that the fibrous morphology was greatly damaged and a film-like structure was formed. Some traces of fibres were evident in the sample heated with the heating rate of 1°C/min. It is also shown that heating rate of 10°C/min resulted in agglomerated particles on the surface.

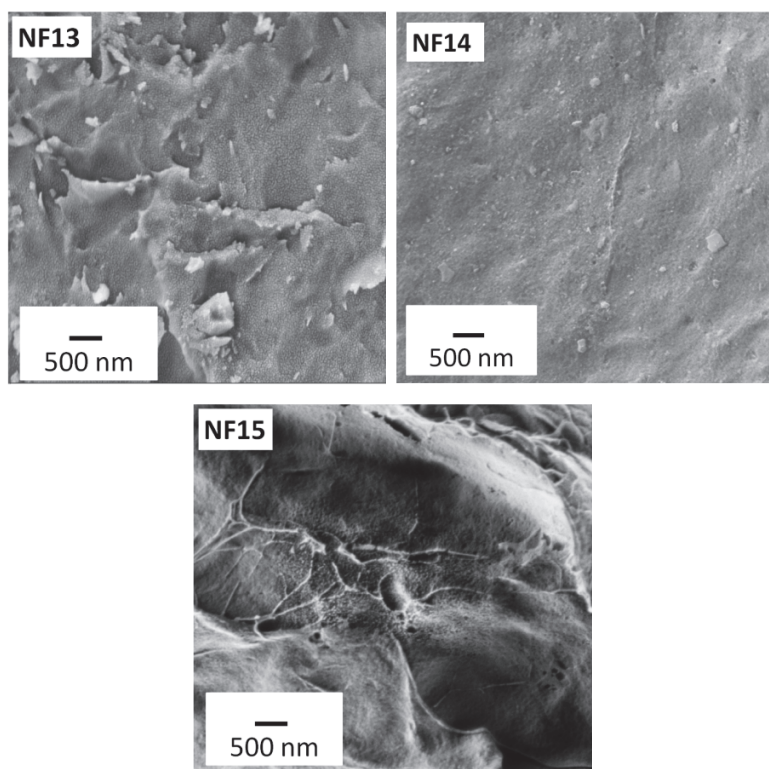


Figure 4.19. SEM images of heat treated samples to 400°C, with heating rates of 1°C/min (NF13), 2°C/min (NF14) and 10°C/min (NF15).

4.3.6.2. Crystallinity

Figure 4.20 shows the XRD patterns of the samples when heated to 400°C. The diffraction peak at 22.5° that is associated with cellulose-I structure disappeared. This indicates that the resultant material was amorphous.

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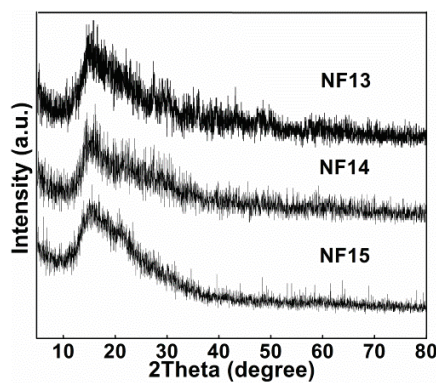


Figure 4.20. XRD graphs of samples heat treated at 400°C, with heating rates of 1°C/min (NF13), 2°C/min (NF14) and 10°C/min (NF15).

4.3.6.3. Chemical structure

Figure 4.21 shows the FI-TR spectra of the samples heated to 400°C. Cellulosic characteristic bands were no longer observed in these samples. The peaks at 1603 cm^{-1} and 1703 cm^{-1} were assigned to C=O and C=C groups. The formation of C=C is the first step in progressing into graphitization at higher temperatures. However, the XRD results indicate that no long range atomic order associated with the graphene structure was formed at this temperature.

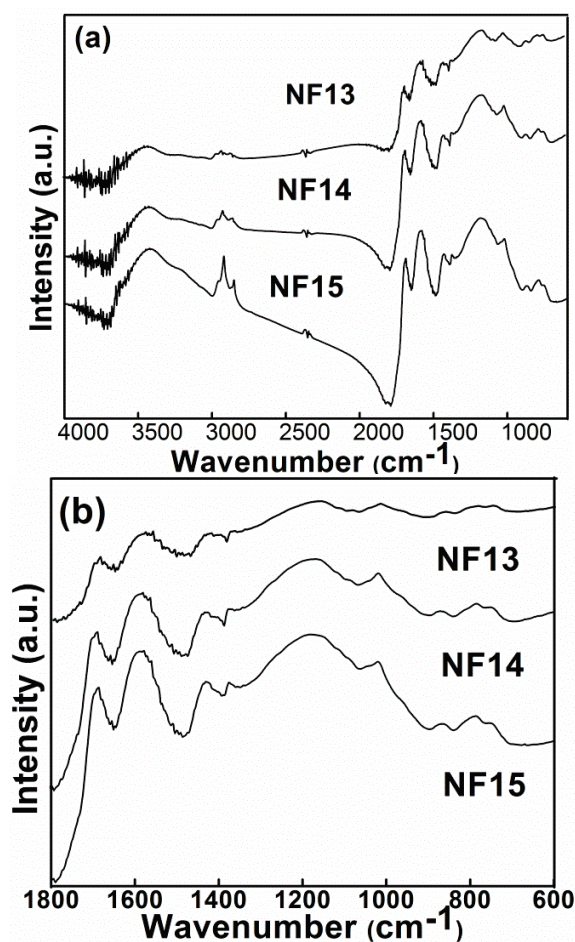


Figure 4.21. FT-IR spectra of samples, with heating rates of 1°C/min (NF13), 2°C/min (NF14) and 10°C/min (NF15); a) 4000-800cm⁻¹, (b) 2000-800cm⁻¹.

4.4. Conclusion

In this chapter, the effect of low-temperature heat treatment of oven-dried CellNFs on the morphology, crystal structure and chemical bonding was studied. Cellulose decomposition comprises 3 main stages: (i) physical dehydration from the surface, (ii) internal dehydration from the cellulose molecule and (iii) the breakdown of the glycosidic rings into volatile gases and water. The effects of pyrolysis conditions such as heating rate, holding time and maximum temperature in each decomposition stage were investigated.

Oven-drying left a compact network of cellulose fibres which connected to each other via hydrogen bonding. Between 25°C to 170°C, neither the heating rate nor the holding time altered the cellulosic structure. The glycosidic rings still maintained the chain-like structure of cellulose alongside with the strong hydrogen bonding.

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However, XRD study showed that holding the oven-dried CellNFs at 170°C altered the crystal structure to cellulose-I β . Further study is required to confirm the phase transition, preferably by using synchrotron radiation. The change in crystal phase, however, did not break the glycosidic rings and the fibrous structure.

Furthermore, the oven-dried CellNFs samples showed little response to heat treatment to 240°C. Various heating rates did not change the cellulosic chemical or crystal structures; hence the samples maintained their fibrous morphology. Holding time at 240°C did not cause changes in cellulosic chemical and crystalline properties. The nanofibres retained their original fibrous morphology after various holding times.

Heating the samples up to 400°C caused cellulosic rings to break down. As a result, a carbon rich residue was formed. The morphological properties were independent of heating rate from 240°C to 400°C. Furthermore, the crystal and chemical properties of the samples were not influenced by heating rates.

Upon carbonisation, the original fibrous morphologies were lost. It appeared in the SEM images that the oven-dried CellNF sheets were transformed into sheet-like carbon residues. This may be caused by the fact that the distance between CellNFs was close enough to form bridging between fibres during carbonisation. As will be investigated in the next chapter, different drying technique resulting in wider spatial distance between fibres may results in different morphological characteristics of residual carbon.

Chapter 5: Carbonisation of freeze-dried cellulose nanofibre

5. 1. Introduction

In the previous chapter, it was shown that oven-drying of CellNFs aqueous suspensions results in a compact network of nanofibres which were closely packed in the form of a translucent sheet-like structure. It was suggested that this close packing of CellNFs led to the destruction of fibrous structures in carbonised samples. On the other hand, freeze drying of CellNFs would retain the spatial gap between the fibres, and hence the carbonisation of freeze dried CellNFs would show characteristics different to that of carbonised oven-dried CellNFs. In this chapter, pyrolysis of freeze-dried CellNFs under atmospheric pressure and inert environment was investigated using controlled heating conditions. The freeze drying method leaves a network of nanofibres with spatial distance between the fibres and turns them into spongy looking masses. The effect of heat treatment conditions on the freeze-dried CellNFs and the carbonised residues was investigated using TGA, SEM, XRD and FT-IR. The results were compared with those from oven-dried CellNFs and the decomposition mechanism of CellNFs was discussed.

5.2. Experimental procedure

5.2.1. Freeze-drying

The procedure to produce CellNFs was described in chapter 3. A small amount of CellNF suspension was poured in a flask and dipped and stirred in liquid nitrogen. The CellNFs were then vacuum dried using a Labconco freeze-drier for 72 h during which water is removed. A spongy looking CellNF mass was collected which was used for carbonisation and characterisation.

5.2.2. Pyrolysis

Freeze-dried CellNFs were pyrolysed using a Lindberg tube furnace by gradually increasing the temperature to 400°C. The instrument calibration was carried out prior to experiments so that temperature variation was negligible.

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An alumina boat was used to hold the samples in the tube. The macroscopic appearance of freeze-dried CellNFs was a spongy looking patch containing nanofibres. Small pieces of samples (1cm×1 cm) were cut and placed on the boat and was then put in the tube. Nitrogen gas was blown into the tube to create an inert atmosphere in the system. The flow rate was chosen to be 70 ml/min. Higher flow rates would blow the sample off the system whereas lower flow rates would not remove the by-product gases and water (which were produced from cellulose decomposition) from the system during pyrolysis.

5.2.2. Carbonisation of freeze-dried CellNFs

Table 5.1 shows the heat treatment conditions selected for carbonisation of freeze-dried CellNFs. The heating parameters were selected because of the same reasons as for oven-dried samples described in the previous chapter.

Table 5.1. Heat treatment conditions.

Sample ID		Target temperature 1			Target temperature 2	
	Heating rate (°C/min)	Temp. (°C)	Residence time (h)	Heating rate (°C/min)	Temp. (°C)	Residence time (h)
NF16	10	170	0	—	—	—
NF17	10	170	2	—	—	—
NF18	10	170	3	—	—	—
NF19	10	170	0	1	240	—
NF20	10	170	0	2	240	—
NF21	10	170	0	10	240	—
NF22	10	240	1	—	—	—
NF23	10	240	3	—	—	—
NF24	10	240	17	—	—	—
NF25	10	240	17	1	400	—
NF26	10	240	17	10	400	—
NF27	10	240	1	1	400	—

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Figure 5.1(a) shows the TG/DSC curves of freeze-dried CellNFs. Below 170°C, the mass loss was insignificant (<1%). Upon further heating to 240°C, the mass loss started to increase. The DSC curve in Figure 5.1(a) shows a peak at 360°C due to an endothermic reaction associated with the breakage of glycosidic rings of cellulose. CellNFs lost 81% of their weight between 240°C and 370°C. Further heating above 370°C caused negligible mass loss, indicating the near completion of the decomposition of cellulose and formation of a carbonaceous residue above 370°C. Figure 5.1(b) shows the mass loss of the sample during isothermal heat treatment at 240°C. After heat treatment for 1100 min, the mass loss nearly reached a plateau during which ~40% of its weight was lost. Based on this result, the effect of holding times of 0 h, 3 h (where weight loss was ~ 20%) and 17 h (where weight loss was ~ 40%) was investigated.

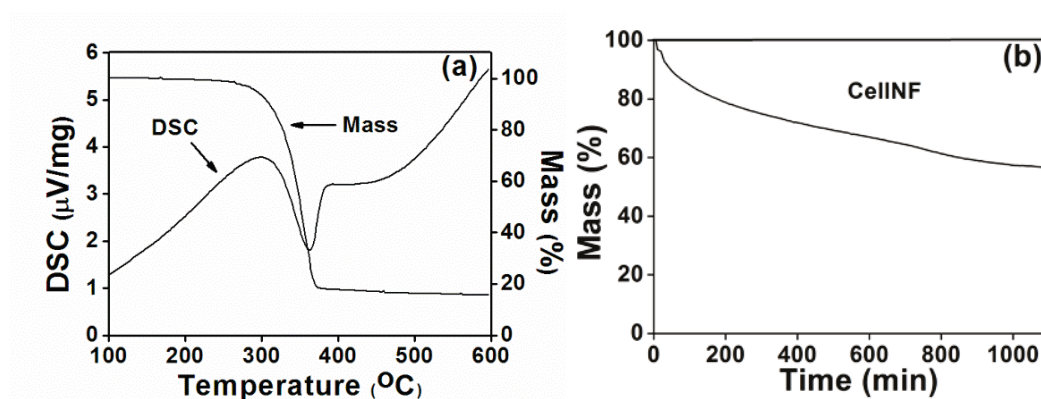


Figure 5.1. (a) TG/DSC graphs of CellNFs and (b) mass loss at 240°C as a function of holding time.

5.3. Results and Discussion

5.3.1. Effect of holding time at 170°C

5.3.1.1. Morphology

Figure 5.2 shows the SEM images of the samples at 170°C held for 0, 2 and 3 h. The fibre diameter distributions are also shown in Figure 5.2. It is noted that the fibrous morphology was retained after heat treatment. The average fibre diameter for the three heat treatment conditions is shown in Figure 5.2. The fibres show average diameters of < 50 nm.

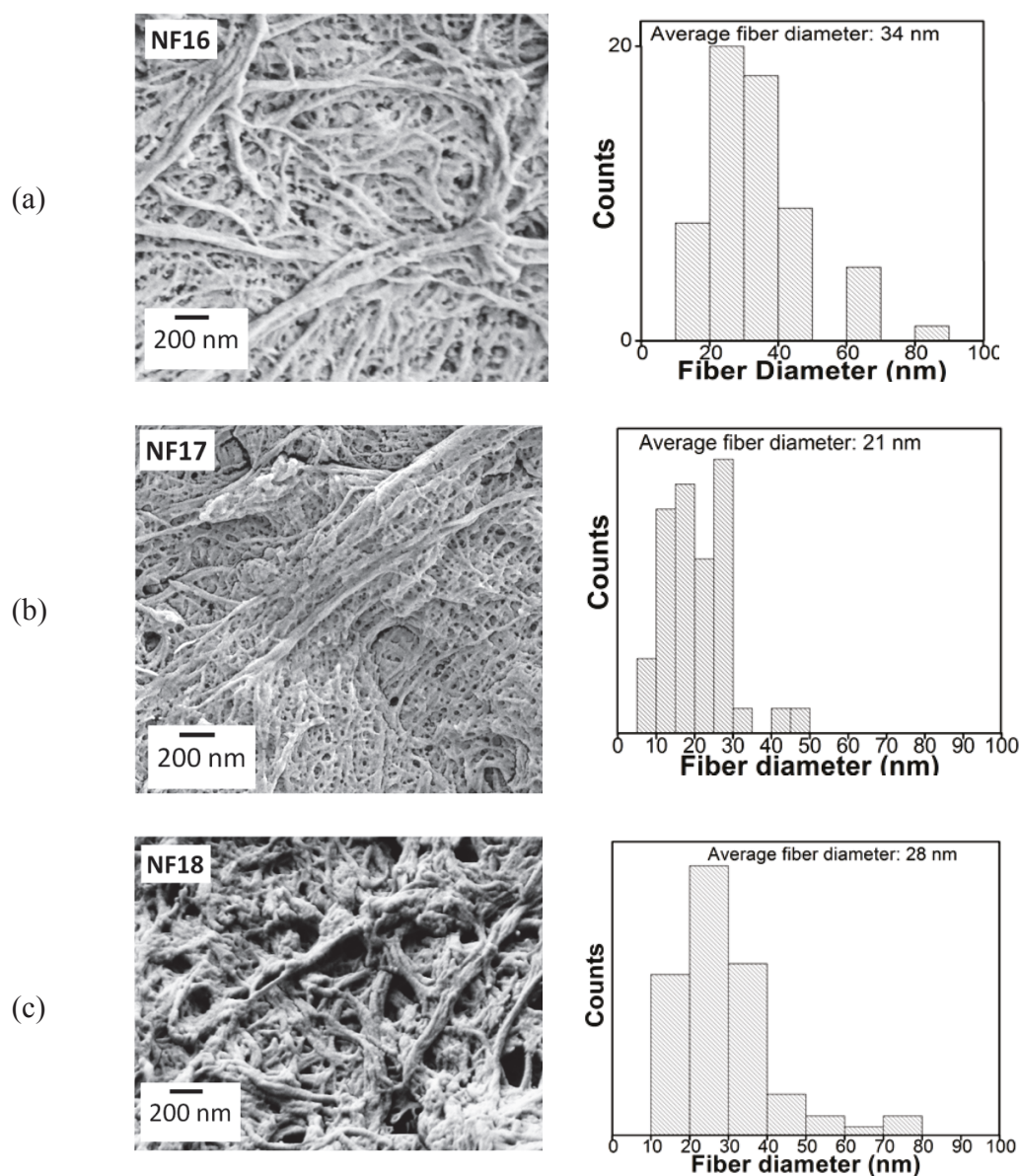


Figure 5.2. SEM images and fibre diameter distributions of heat treated samples at 170°C, with holding time of (a) 0 h (NF16), (b) 2 h (NF17) and (c) 3h (NF18).

5.3.1.2. Crystallinity

Figure 5.3 Shows the XRD patterns of the samples heat treated with three holding times at 170°C. The XRD pattern of freeze dried CellNFs before heat treatment is also shown for comparison. Freeze-dried CellNFs show a sharp peak at 22.5°. This peak was assigned to the (200) lattice plane in cellulose-I crystal structure. This peak was observed in all the samples heat treated with various holding times indicating that the glycosidic rings have not been deformed by such pyrolysis conditions. As for the oven-dried

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samples (Figure 4.10), the peak at $\sim 15^\circ$ shifted to a slightly higher degree in the samples NF17 and NF18 with long holding times (2 h and 3 h respectively), suggesting the formation of a disordered state of cellulose-I β structure.

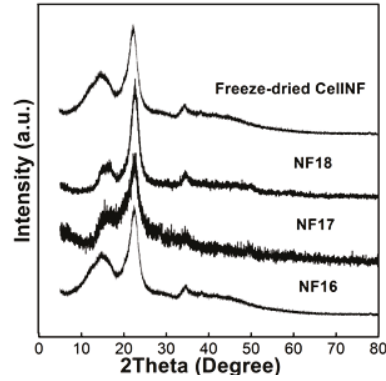


Figure 5.3. XRD patterns of freeze-dried sample before heat treatment and heat treated samples at 170°C, with holding time of 0 h (NF16), 2 h (NF17) and 3h (NF18).

Table 5.2. Crystal size D , index of crystallinity I_{cr} , and interplanar distances d , of heat treated samples at 170°C with various holding times, estimated from XRD patterns.

Holding time	2 theta (deg)	hkl	d (Å)	D_{cr} (nm)	I_{cr}
3 h	16.1°	110, 1-10	4.3	—	—
	22.5°	200	3.8	3.5	69
	34.1°	004	2.9	—	—
2 h	16.1°	110, 1-10	5.1	—	—
	22.5°	200	4.3	3.5	70
	34.1°	004	3.3	—	—
1 h	16.1°	110, 1-10	5.5	—	—
	22.5°	200	3.9	3.9	72
	34.1°	004	2.9	—	—

The crystal parameters of the heat treated CellNFs was calculated from the XRD patterns as shown in Table 5.2. It is evident that the crystal properties of heat treated CellNFs did not change dramatically with holding time.

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5.3.1.3. Chemical bonding

Figure 5.4 shows the FT-IR spectra of freeze-dried CellNFs and heat treated samples at 170°C. The peaks were assigned to the chemical bonds listed in Table 4.4. For the sample with holding time of 0 and 2 hrs, the FT-IR spectra were nearly identical to that of un-heat treated sample. However, in the spectrum of the sample held for 3 h (NF18), the relative intensities of the peaks at 1025 cm⁻¹ and 1050 cm⁻¹ (associated with C-OH bonds at the 1st and 2nd alcohols in the glucose rings), compared to the peak at 1112 cm⁻¹ (associated with C-O-C glycoside links in the cellulose chain), were reduced. This suggests that internal dehydration started to occur after holding the temperature at 170°C for 3 h.

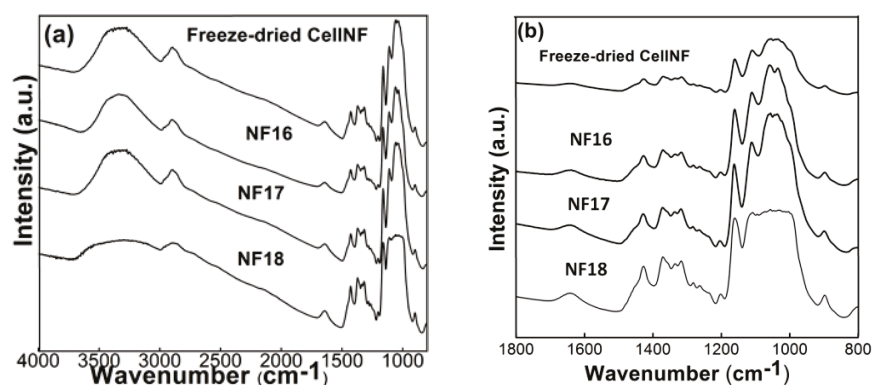


Figure 5.4. FT-IR spectra of heat treated samples at 170°C with holding times of (a) 0 h (NF16), (b) 2 h (NF17) and (c) 3h (NF18); (a) 4000-800 cm⁻¹, (b) 2000-800 cm⁻¹.

5.3.1.4. Discussion on the effect of holding time at 170°C

The SEM images show that the temperature at 170°C was not enough to initiate decomposition of cellulosic rings (glycosidic rings) and hence the fibrous structure was maintained during heat treatment. According to the FT-IR spectra, internal dehydration may have started at 170°C though XRD study showed that the cellulose-I crystal structure was still retained.

5.3.2. Effect of heating rate between 170°C to 240°C

For the heat treatment up to 240°C, a residence time of 0 h was selected at 170°C.

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5.3.2.1. Morphology

Figure 5.5 shows SEM images of the samples heat treated from 170°C to 240°C with heating rates of 1°C/min, 2°C/min and 10°C/min. The nanofibres retained their fibrous morphology with heating rates of 1°C/min and 2°C/min. The average fibre diameter measured for three samples showed similar value of 27 nm. It is noted that a heating rate of 10°C/min caused some damage to the fibrous structure in some areas, as indicated with arrows in Figure 5.5.

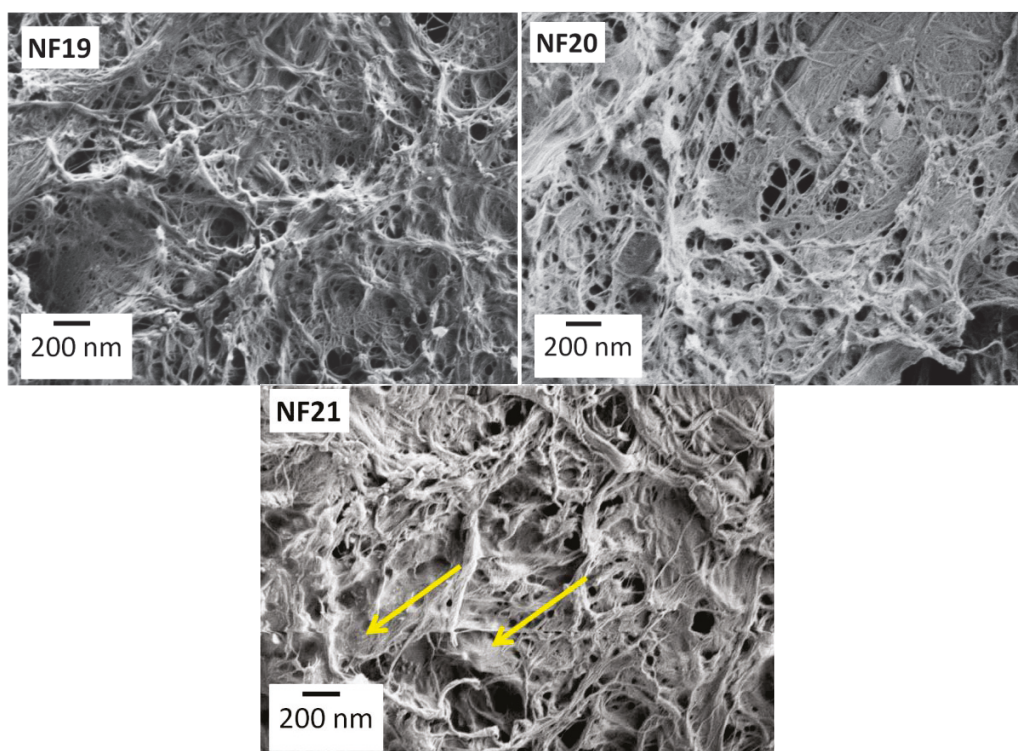


Figure 5.5. SEM images of freeze-dried samples heat treated samples to 240°C with heating rates of 1°C/min (NF19), 2°C/min (NF20) and 10°C/min (NF21).

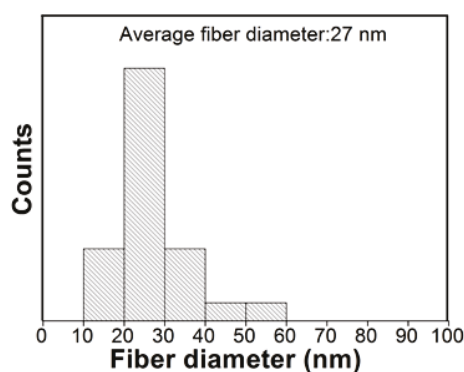


Figure 5.6. Fibre diameter distribution (average of NF19, NF20 and NF21) estimated from SEM images.

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5.3.2.2. Crystallinity

Figure 5.7 shows the XRD patterns of the samples with different heating rates. The peak associated with the cellulose-I structure was observed at 22.5° for these samples. A broad peak at 16.1° also indicates that crystallinity has not been altered severely. Difference in heating rates between 170°C to 240°C did not greatly influence the crystal structure. Table 5.3 lists the crystal properties of the samples NF19, NF20 and NF21. The crystal size was reduced as the heating rate decreased.

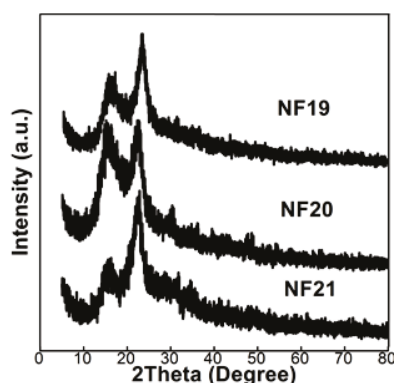


Figure 5.7. XRD graphs of freeze-dried samples heat treated to 240°C with heating rates of $1^\circ\text{C}/\text{min}$ (NF19), $2^\circ\text{C}/\text{min}$ (NF20) and $10^\circ\text{C}/\text{min}$ (NF21).

Table 5.3. Crystal size D , index of crystallinity I_{cr} , and interplanar distances d , of heat treated samples at 240°C with various heating rates estimated from XRD patterns.

Heating rate ($^\circ\text{C}/\text{min}$)	2 theta (deg)	hkl	d ($\text{\AA}$)	$D_{\text{cr}}(\text{nm})$	I_{cr}
1	16.1°	110,1-10	4.5	—	—
	22.5°	200	3.4	2.2	69
	34.1°	004	3.1	—	—
2	16.1°	110,1-10	4.2	—	—
	22.5°	200	4.2	3.9	70
	34.1°	004	3.3	—	—
10	16°	110,1-10	4.6	—	—
	22.5°	200	3.9	3.6	72
	34.1°	004	2.89	—	—

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5.3.2.3. Chemical structure

Figure 5.8 shows the FT-IR spectra of samples heated to 240°C with three different heating rates. Peaks at 1336 cm⁻¹ and 1365 cm⁻¹ corresponding to O-H and C-H were still present in the spectra. Hence the difference in heating rates between 170°C to 240°C did not cause noticeable structural change within the molecule.

As described earlier, the bands at 1025 cm⁻¹ and 1050 cm⁻¹ were assigned to the vibration of C-OH bonds at the 1st and 2nd alcohols in the glucose rings, and 1112 cm⁻¹ was assigned to C-O-C glycoside links in the cellulose chain [323-326]. It is evident in Figure 5.8(b) that the relative intensities of the peaks at 1025 cm⁻¹ and 1050 cm⁻¹, compared to the peak at 1112 cm⁻¹, were reduced as the heating rate decreased. This indicates that, longer heat treatment between 170°C and 240°C induced more removal of the OH bonds via dehydration processes, while glycoside link remained intact.

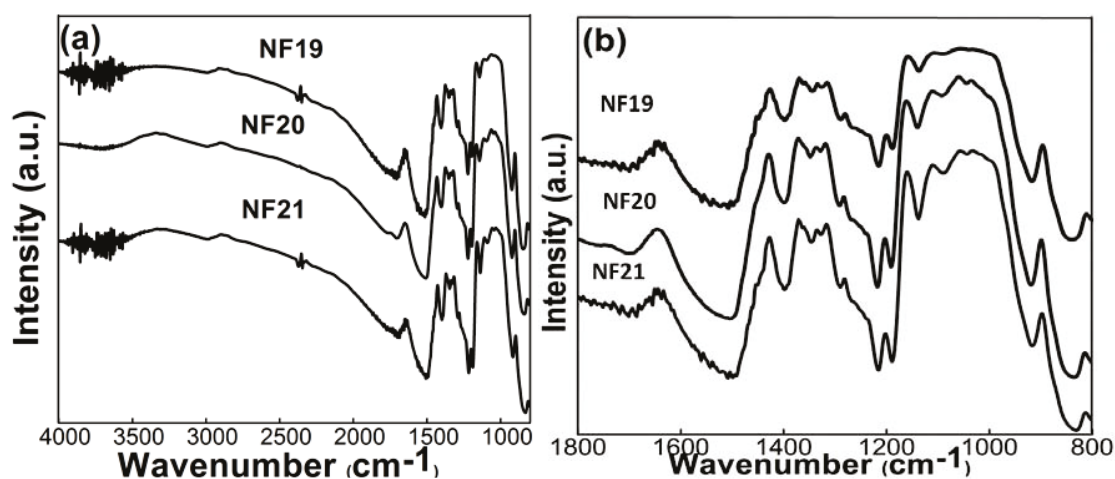


Figure 5.8. FT-IR spectra of freeze-dried samples heat treated to 240°C with heating rates of 1°C/min (NF19), 2°C/min (NF20) and 10°C/min (NF21); (a) 4000-800 cm⁻¹, (b) 2000-800 cm⁻¹.

5.3.2.4. Discussion on the effect of heating rate between 170°C and 240°C

The SEM images show that fast heating rate of 10°C/min between 170°C and 240°C may influence the morphology by causing fusion of fibres and formation of film-like structures. However, according to the data shown in Figure 5.7 and Figure 5.8, the difference in heating rate caused no significant changes in crystal structures. However, further internal dehydration was initiated when the sample was heated longer. These

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results show that slow heating rate between 170°C and 240°C is necessary to maintain the fibrous morphology of heat treated samples.

5.3.3. Effect of holding time at 240°C

5.3.3.1. Morphology

Figure 5.9 shows the SEM images of the samples held at 240°C for 0h, 3h and 17 h. The images did not show any distinct difference in morphology between the samples heat treated for different holding times at 240°C. The average fibre diameter was measured for three samples and was ~27 nm.

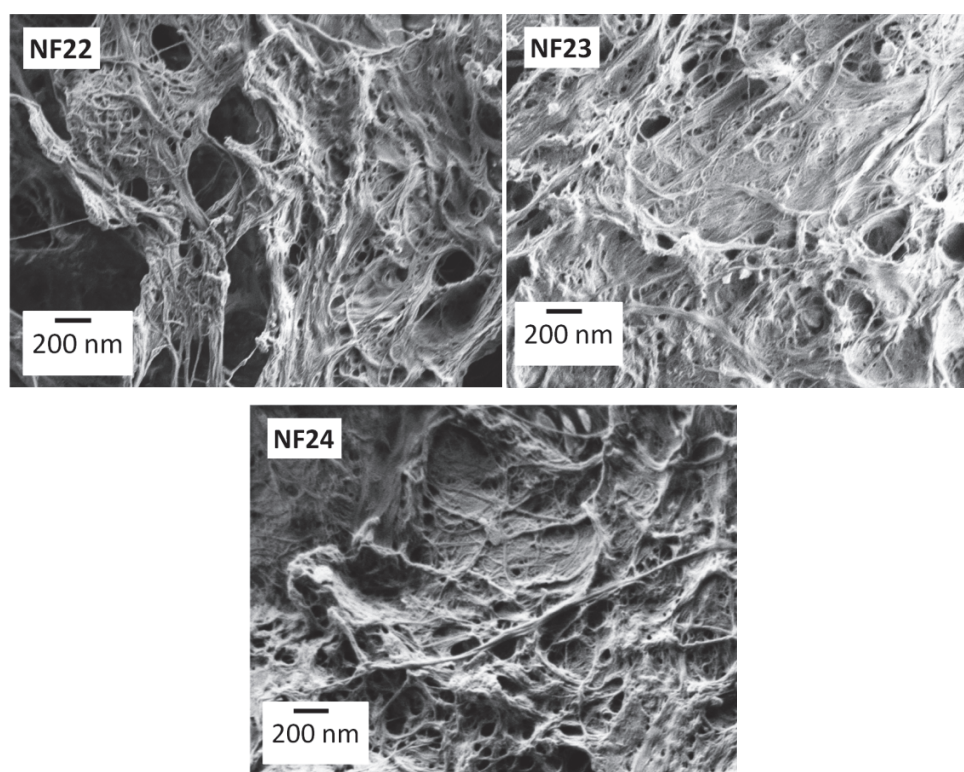


Figure 5.9. SEM images of freeze-dried samples heat treated to 240°C with holding times of 0 h (NF22), 3 h (NF23) and 17 h (NF24).

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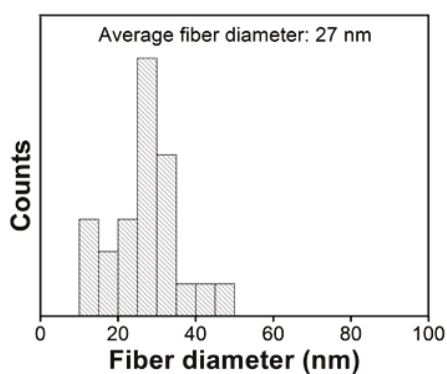


Figure 5.10. Fibre diameter distribution (average of NF22, NF23 and NF24) estimated from SEM images.

5.3.3.2. Crystallinity

Figure 5.11 shows the XRD patterns of the samples when held at 240°C for 0h, 3h and 17h. Table 5.4 shows the crystal properties of the samples estimated from the diffraction peaks at 16.1°, 22.5° and 34.1°. The values of d and D are similar to these of the samples held at 170°C. The results indicate that cellulose has retained its crystal structure irrespective of holding times.

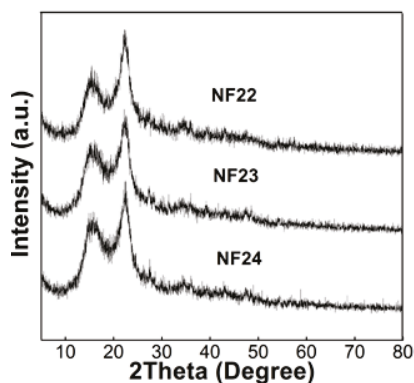


Figure 5.11. XRD graphs of freeze-dried samples heat treated to 240°C with holding times of 0 h (NF22), 3 h (NF23) and 17 h (NF24).

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Table 5.4. Crystal size D , index of crystallinity I_{cr} , and interplanar distances d , of heat treated samples with various holding times at 240°C estimated from XRD patterns.

Holding time (h)	2 theta (deg)	hkl	d (Å)	D_{cr} (nm)	I_{cr}
0	16.1°	110, 1-10	4.7	—	—
	22.5°	200	4.1	2.5	62
	34.1°	004	—	—	—
3	16.1°	110, 1-10	4.6	—	—
	22.5°	200	3.8	3.9	60
	34.1°	004	—	—	—
17	16.1°	110, 1-10	4.2	—	—
	22.5°	200	4.6	3.9	60
	34.1°	004	—	—	—

5.3.3.3. Chemical structure

Figure 5.12 shows the FT-IR spectra of the freeze-dried samples when held at 240°C for 0, 3 and 17 h. The spectra of samples NF16-NF23 resembled the spectrum of CellNFs. The bands at 1025 cm^{-1} and 1050 cm^{-1} were assigned to the vibration of C-OH bonds at the 1st and 2nd alcohols in the glucose rings, and 1112 cm^{-1} was assigned to C-O-C glycoside links in the cellulose chain (Figure 5.12b) [323-326]. It is evident that the relative intensities of the peaks at 1025 cm^{-1} and 1050 cm^{-1} , compared to the peak at 1112 cm^{-1} , were further reduced in NF24 from that in CellNFs. This indicates again that longer heat treatment below 240°C induced the removal of the OH bonds by internal dehydration processes, while glycoside link remained intact.

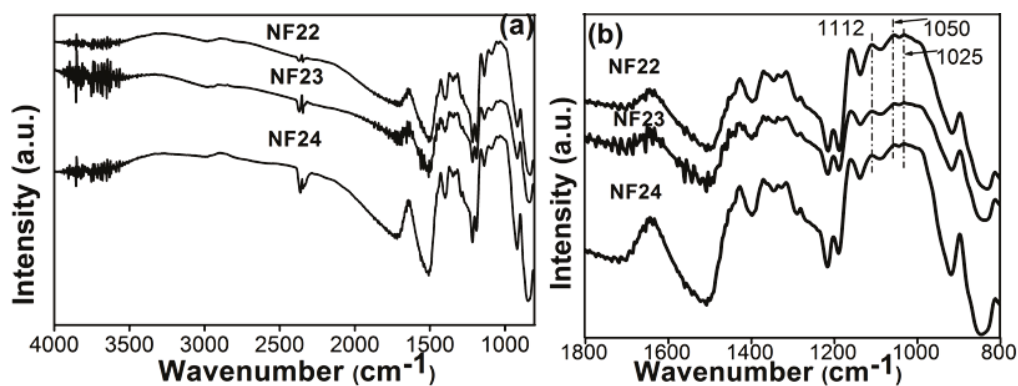


Figure 5.12. FT-IR spectra of freeze-dried samples heat treated to 240°C with holding times of 0 h (NF22), 3 h (NF23) and 17 h (NF24); (a) 4000-800 cm^{-1} , (b) 2000-800 cm^{-1} .

5.3.3.4. Discussion on the effect of holding time at 240°C

The results show that holding time at 240°C did not influence the morphology and crystal structure of heat treated samples. It is interesting to note that, even after 17 h of holding time, cellulose-I crystal structure was retained even after the mass loss of $\sim 40\%$. Similar results were also reported by Davidson and Losty [159]. The removal of hydrogen and oxygen from cellulose molecules continued as the heat treatment prolonged. Based on the results, two possible explanations can be drawn: a) dehydration was mostly taking place which was temperature-sensitive and b) the C=O formation seems to be reversible due to release of hydroxyl groups. The data indicates that glycosidic rings or C-O-C bonds (1, 4- β linkage) have been partially deformed although the bed/chair configuration has still been present in the molecule resulting the XRD peaks at 16.1° and 22.5° .

5.3.4. Effect of heating rate to 400°C

In order to investigate the effect of heat treatment condition in 240-400°C, the samples were heated to 240°C where they were held for 1h and 17 h. They were then heated to 400°C by $1^\circ\text{C}/\text{min}$ and $10^\circ\text{C}/\text{min}$. Such experimental procedure was designed in order to distinguish the effects of heating rate and holding time.

5.3.4.1. Morphology

Figure 5.13 shows SEM images of the samples treated under various heat treatment conditions (NF25-NF27). These samples have undergone carbonisation and their appearance changed from a white spongy mass to a black char (Figure 5.15). The SEM

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images of NF26 and NF27 show that, during carbonisation, the fibres were damaged by fusing together and forming bundles of carbon char rather than fibres. Although some fibres retained their fibrous structures, they did not retain their original high aspect ratios. On the other hand, the SEM image of NF25 shows the morphology similar to its cellulosic precursor with high aspect ratios. On the other hand, the SEM image of NF25 shows the morphology similar to its cellulosic precursor with high aspect ratios. Figure 5.14 shows the fibre diameter distribution of the sample NF25. The average diameter was around 25 nm, close to that of commercial multiwall carbon nanotubes.

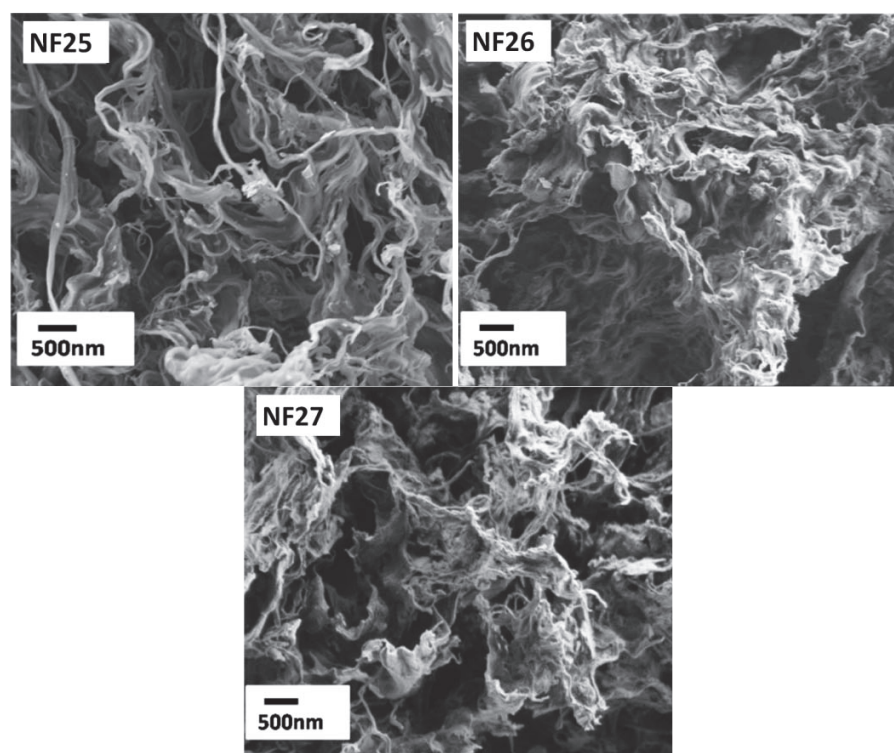


Figure 5.13. SEM images of samples heat treated to 400°C under different conditions; holding time at 240°C and heating rate to 400°C are 17 h and 1°C/min (NF25), 17 h and 10°C/min (NF26), and 1 h and 1°C/min (NF27).

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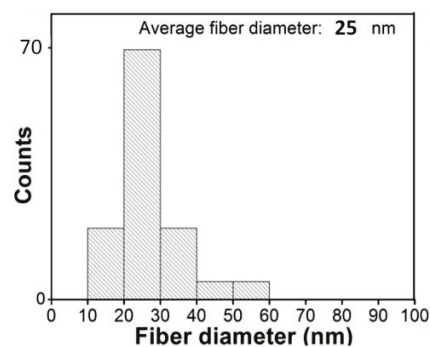


Figure 5.14. fibre diameter distribution of sample NF25 estimated from SEM images.

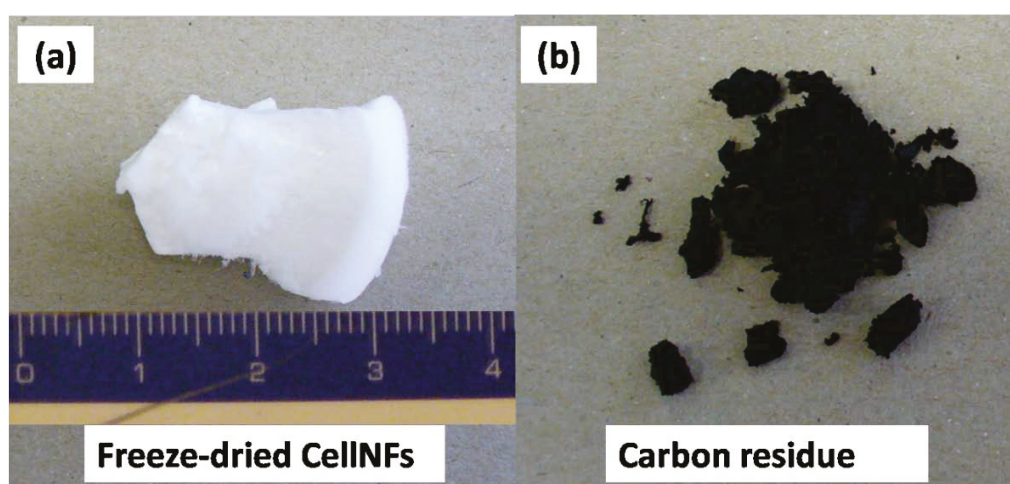


Figure 5.15. Appearance of (a) freeze-dried CellNFs and (b) carbon residue after heat treatment at 400°C.

5.3.4.2. Crystallinity

The crystal structure of the precursor cellulose is expected to influence the decomposition and subsequently the resultant carbon materials [146]. Figure 5.16 shows XRD patterns of NF25-NF27. The peaks associated with cellulose-I crystal structure was no longer evident in the XRD patterns. Instead, the patterns showed an amorphous-like feature.

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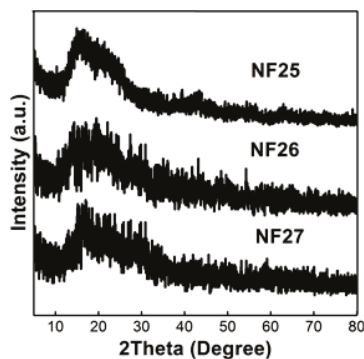


Figure 5.16. XRD graphs of samples heated to 400°C under different conditions; holding time at 240°C and heating rate to 400°C are 17 h and 1°C/min (NF25), 17 h and 10°C/min (NF26), and 1 h and 1°C/min (NF27).

5.3.4.3. Chemical structure

Figure 5.17 shows the FT-IR spectra of samples under different heat treatment conditions. These samples show rather different curves to that of the CellNF precursors. The carbon residue shows peaks at 1603 cm^{-1} and 1703 cm^{-1} which were assigned to C=O and C=C bands respectively. The latter group did not appear in the samples heat treated below 400°C. This indicates the breakdown of glycosidic rings resulting in the formation of carbon rich char. However, oxygen was still present in the carbon chemical structure, as the peak corresponding to C=O was present in the spectra. It is suggested that complete removal of oxygen and hydrogen from the molecule occurs at above 400°C [279].

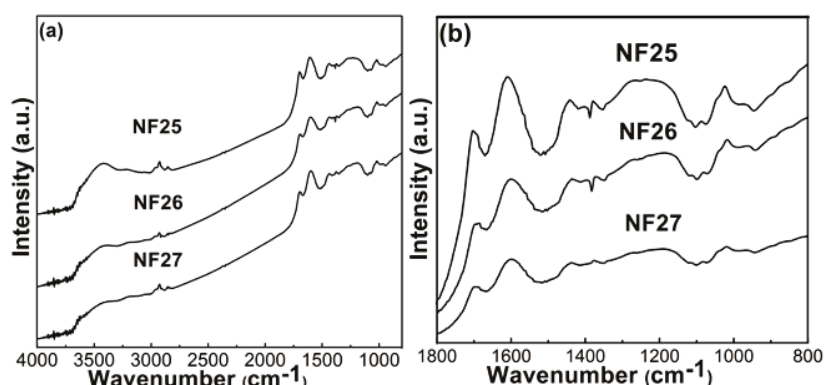


Figure 5.17. FT-IR spectra of samples heat treated to 400°C under different conditions; holding time at 240°C and heating rate to 400°C are 17 h and 1°C/min (NF25), 17 h and 10°C/min (NF26), and 1 h and 1°C/min (NF27); (a) 4000-800 cm^{-1} , (b) 2000-800 cm^{-1} .

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5.3.4.4. Discussion on the effect of heating rates and holding time

The XRD study confirmed that the decomposition of cellulose-I crystal structure takes place in the temperature range of 240-350°C. The FT-IR data indicated that the decomposition of cellulose-I crystal structure is accompanied by the breakdown of glycosidic rings. The SEM study showed that the decomposition reactions are sensitive to heating rate; higher heating rates severely damage the fibrous morphology. The heating rate dependency of the morphology of carbon residue indicates the possibility of two or more competing reactions occurring during the decomposition of the cellulose-I crystal structure; one is to destroy cellulose chains that is favourable at high heating rates, another is to carbonise cellulose without chain scission that is favourable at low heating rates. These two reactions will be discussed further in the later sections.

In addition, holding time at 240°C has influence on the morphological properties of the resultant residue. Longer holding time of 17 h resulted in better preservation of the fibrous morphology. TG data showed that extensive mass loss occurred at 240°C (Figure 5.1) while retaining the original cellulose-I crystal structure. The mass loss reached ~40 % after 17 h of isothermal heating. Since intra and inter molecular dehydration occur at 240°C, it is expected that longer holding time at 240°C removed much of the oxygen and hydrogen from the cellulose molecules. This will help prevent the formation of levoglucosan and the scission of cellulosic chain (Figure 2.17).

5.4. Discussion on the effect of heat treatment conditions and drying methods

5.4.1. Sensitivity of heat treatment conditions to the formation of CNFs

The results showed that heat treatment conditions around the thermal decomposition temperature greatly influence the morphological properties of CNFs. Longer holding time at 240°C and slower heating rate from 240°C to 400°C were necessary to preserve the original fibrous structures of CellNFs in CNFs. This may be explained from the viewpoint of intermolecular dehydration.

According to the results of XRD and SEM studies, the crystal structure, crystallinity and morphology were not significantly affected by the heat treatment conditions below 240°C. However, TG data showed that extensive mass loss occurred at 240°C (Figure 5.1). The mass loss reached ~40 % after 17 h of isothermal heating. The FT-IR

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results indicate that the mass loss is associated with the loss of OH groups and hence is caused by intra- or inter-chain dehydration.

An intra-molecular dehydration model between two OH groups has frequently been used for explaining the mass loss of cellulose below 300°C [10]. This model predicts the formation of C=C and C=O bonds (Figure 5.18). However, as can be seen in the FT-IR spectrum of NF24, C=C or C=O bands in the aromatic rings did not appear after heat treatment for 17 h at 240°C. The result implies that the dehydration process occurred mainly between the interchain OH groups, but not between the OH groups in the same pyranose rings.

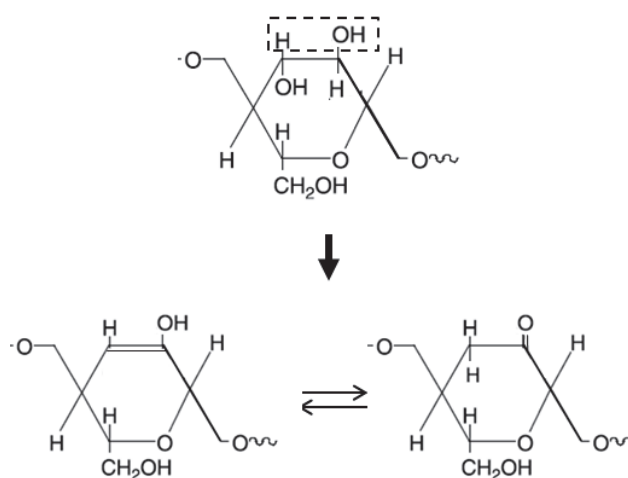


Figure 5.18. Intramolecular dehydration in cellulose chains.

In cellulose crystals, straight cellulose chains are interconnected with other chains through strong hydrogen bonds between the OH groups. Dehydration at 240°C may result in covalent bonding between cellulose single chains and help preserve fibrous structures upon carbonisation. In addition, the removal of OH from $-\text{CH}_2\text{OH}$ groups may prevent (i) the chain scission at glycoside links and (ii) the formation of volatile and viscous tar (levoglucosan) (Figure 5.19), which may play a critical role in preserving the original fibrous structures (Figure 5.20).

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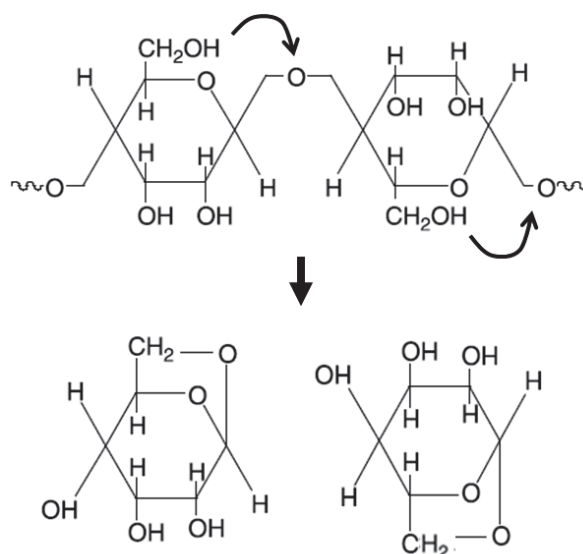


Figure 5.19. Formation of levoglucosan associated with depolymerisation.

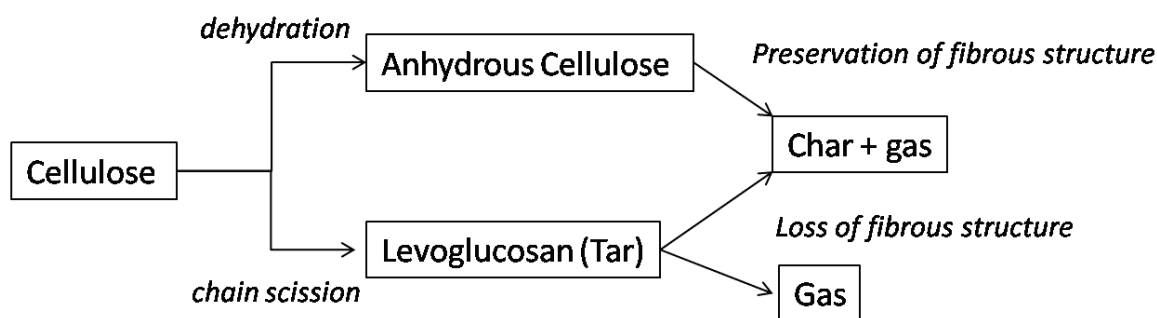


Figure 5.20. Model of cellulose pyrolysis [327].

The D-glucose unit in cellulose has 3 OH groups and their loss is equivalent to the mass loss of ~33 %. This value is smaller than the observed mass loss of 40 % during the isothermal heating at 240°C. Hence, apart from dehydration, the evolution of some gaseous species such as CO, CO₂ and CH₄ may have occurred at 240°C, without affecting the crystal structure of cellulose. Further study is required to identify these gases evolved during the isothermal heat treatment at 240°C by, for example, FT-IR or mass spectroscopy [328].

The SEM images of NF25 and NF26 show that, even after dehydration at 240°C for 17 h, fast heating rate can still destroy the original fibrous structure. This result suggests that the removal of remaining oxygen in the pyranose rings and glycoside links could lead to depolymerisation at fast heating rates (e.g. 10°C/min). The slow heating rate (1°C/min) may provide the carbon atoms with sufficient time to diffuse inside the nanofibres and

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form aromatic rings without causing morphological damages. In addition, it has been reported that more oxygen and hydrogen can escape the cellulosic chains during carbonisation if slower heating rates are applied between 240°C to 350°C [1, 203]. This helps reduce oxygen-to-carbon ratio within the carbon structure, contributing to the preservation of fibrous structures in carbon residues.

5.4.2. Influence of drying methods on the morphology of carbon residue.

The difference in fibrous morphology of the carbon residues between the two drying methods can be explained from the viewpoint of the spatial distance between the fibres.

It is known that, cellulose goes through thermal decomposition between 180-400°C and further aromatization above 400°C starting with a dehydration (180-240°C) followed by depolymerisation (240-400°C) [283]. Tang et al. suggested that between 240-400°C cellulosic rings start to break down which leads to the formation of highly active free radicals. They cause formation of gaseous products such as CO₂ and CO as well as H₂O and tar [279]. Due to the hydrophilic property of cellulose and upon oven-drying the CellNFs, the hydroxyl groups tend to bridge between the cellulosic chains of neighbouring nanofibres via hydrogen bonds. Thus the fibres tend to be in close contact with each other in the oven-dried sample. Viscous tar may connect fibres with each other when their distance is very short, leading to the disappearance of fibrous structure in oven-dried samples. On the other hand, freeze drying creates sufficient space between the individual fibres whereby removal of gaseous and tarry by-products from the sample becomes faster by the flow of an inert gas, which allows individual fibres to remain relatively isolated from adjacent fibres.

The difference in spatial distance between the fibres may also contribute to the difference in the formation of tar/levoglucosan. As shown in Figure 4.10, after isothermal heat treatment at 170°C, the FT-IR spectra of oven-dried sample did not show much change in the 1000–1100 cm⁻¹ region. On the other hand, the FT-IR spectra of freeze-dried sample did show changes in the 1000–1100 cm⁻¹ region as a function of holding time at 170°C; the relative intensities of the peaks at 1025 cm⁻¹ and 1050 cm⁻¹ (associated with C-OH bonds at the 1st and 2nd alcohols in the glucose rings), compared to the peak at 1112 cm⁻¹ (associated with C-O-C glycoside links in the cellulose chain), were reduced as the isothermal heat treatment time increased. The same trend was observed during heating from 170°C to 240°C. As shown in Figures 4.13 and 5.8, the FT-IR spectra of oven-dried

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sample did not show much change in the 1000–1100 cm^{-1} region, whilst the FT-IR spectra of freeze-dried sample did show changes in the 1000–1100 cm^{-1} region, as a function of heating rate. In freeze-dried sample, lower heating rate (i.e., longer heat treatment time) caused reduced relative intensity of the peaks at 1025 cm^{-1} and 1050 cm^{-1} , compared to the peak at 1112 cm^{-1} . The results indicate that internal dehydration process occurs below 240°C in freeze-dried samples but not in oven-dried samples. This may be because water molecules can escape cellulose easier from the open network structure in freeze-dried samples than from tightly fused structures in oven-dried samples.

Thus, large spatial distance between fibres in the precursor CellNFs can serve two purposes to preserve original fibrous structures in the carbon residue; (1) by promoting internal dehydration to prevent the formation of tar and chain scission, and (2) by preventing tar from bridging neighboring fibres so as not to form fusion between carbonised fibres.

5.5. Conclusion

In this chapter, the effects of heat treatment conditions on amorphous CNFs and their precursor CellNFs were investigated. Amorphous CNFs were produced by the pyrolysis of CellNFs below 400°C. It is shown that heat treatment conditions around the thermal decomposition temperature greatly influence the morphological properties of CNFs. Longer holding time at 240°C and slower heating rate from 240°C to 400°C were critical to preserve the original fibrous structures of the precursor CellNFs after pyrolysis. It was suggested that intermolecular dehydration was induced during the prolonged isothermal heat treatment at 240°C and that the removal of OH groups reduced the chance of chain scission and the formation of tar. This in turn contributed to the retention of the original fibrous structure during carbonisation between 240°C and 400°C. Slow heating rate helps the carbon chains to join neighbouring chains to form aromatic rings within the nanofibre boundaries without causing morphological damage to the nanofibre. These heat treatment conditions will have stronger influence on the morphology of resulting carbon residues in nanofibres than in conventional micron-diameter fibres, as the fibrous structures can be altered by atomic diffusion over much shorter distances in nanofibres than in micron-diameter fibres. This study demonstrated that, upon optimization of heat treatment

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conditions, CNFs with diameters of <100 nm can be produced from renewable raw materials in a simple and scalable manner.

Chapter 6: Graphitization of **carbon nanofibres from freeze-** **dried cellulose nanofibre**

6.1. Introduction

In the previous chapter, CNFs were successfully fabricated from freeze-dried CellNFs. However, the fibres were made in an amorphous structure. In order to increase the mechanical properties, the fibres need to be graphitized. In this chapter, CNFs were heat treated at high temperatures. The effect of the graphitization temperatures on the properties of CNFs were investigated using TEM, SEM, XRD, FT-IR and Raman spectroscopy.

6.2. Experimental

CNFs were prepared by the pyrolysis of freeze-dried CellNFs under the optimized conditions described in Chapter 5. Amorphous CNFs were heated to 1600°C, 1800°C, 2000°C, 2200°C, 2500°C and 2800°C to study the effect of temperature on the properties of CNF. Each sample was held at these temperatures for 30 min before cooling down to room temperature. The heating rate of 10°C/min was used for all the heat treatment.

CVD grown CNFs with average fibre diameters of 200-500 nm and lengths of 10-40 µm were purchased from Nanostructured and Amorphous Materials Inc., USA and used as received. Graphite powder was purchased from Asbury Graphite Mills, USA and used as received. The CVD grown CNFs and graphite powders were used as reference samples in Raman spectroscopy.

6.3. Results and discussion

6.3.1. Morphology

Figure 6.1 shows TEM images of the heat treated samples between 1600 and 2800°C. After heating up to 1600°C, aligned crystalline regions have been formed in some parts of

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the fibres. The crystallized fibres were observed only in a localized area and the bulk for the samples did not show this feature. Nonetheless, it is interesting to note that the growth of crystalline structures started from such low temperatures. Ishida et al. suggested that the crystallization at low temperature will lead to the crystal structure different from graphite [149]. However, detailed structural analysis is required as a part of future work, by electron diffraction study. Upon increasing the heat treatment temperature from 1600°C, most of the fibrous structures were lost. Furthermore, in all samples, there were particles in different sizes. These particles developed hexagonal shapes as the temperature reached 2800°C.

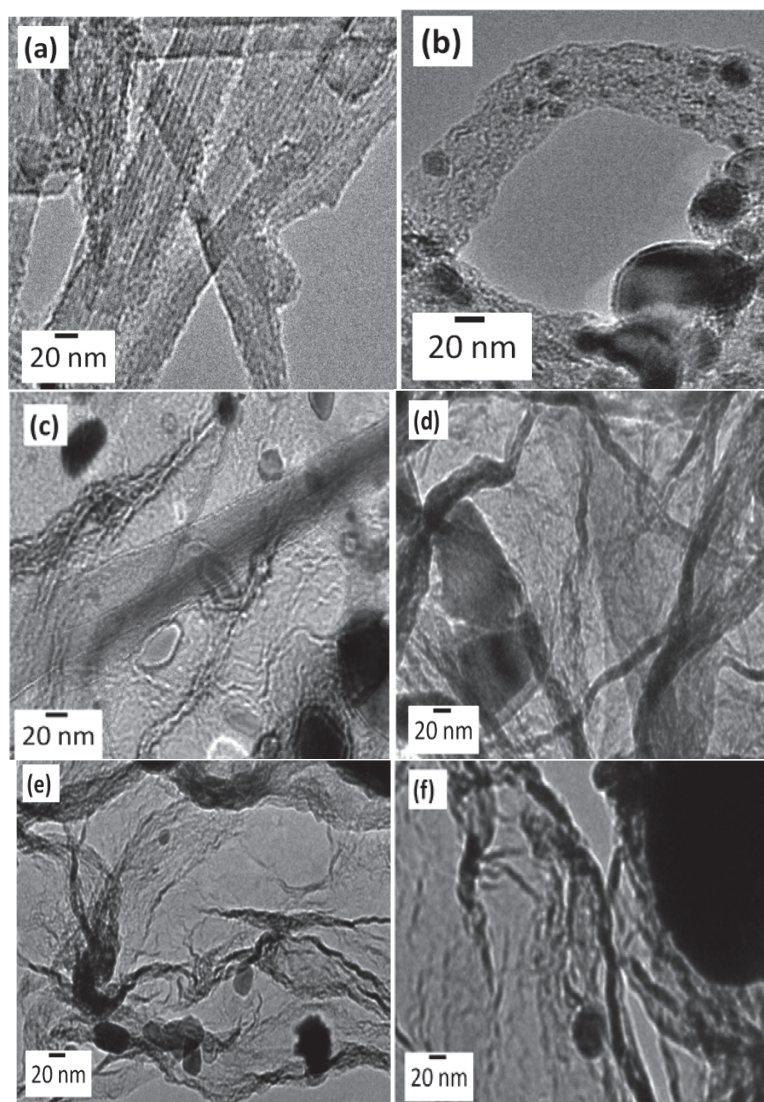


Figure 6.1. TEM images of heat treated samples; a) 1600°C, b) 1800°C, c) 2000°C, d) 2200°C, e) 2500°C and f) 2800°C.

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Figure 6.2 shows the SEM images of the heat treated samples between 1600°C and 2800°C. It appears that the fibres of ~20 nm in diameters are entangled and fused in a network structure or a film-like structure. Free nanofibres with high aspect ratios were rarely observed.

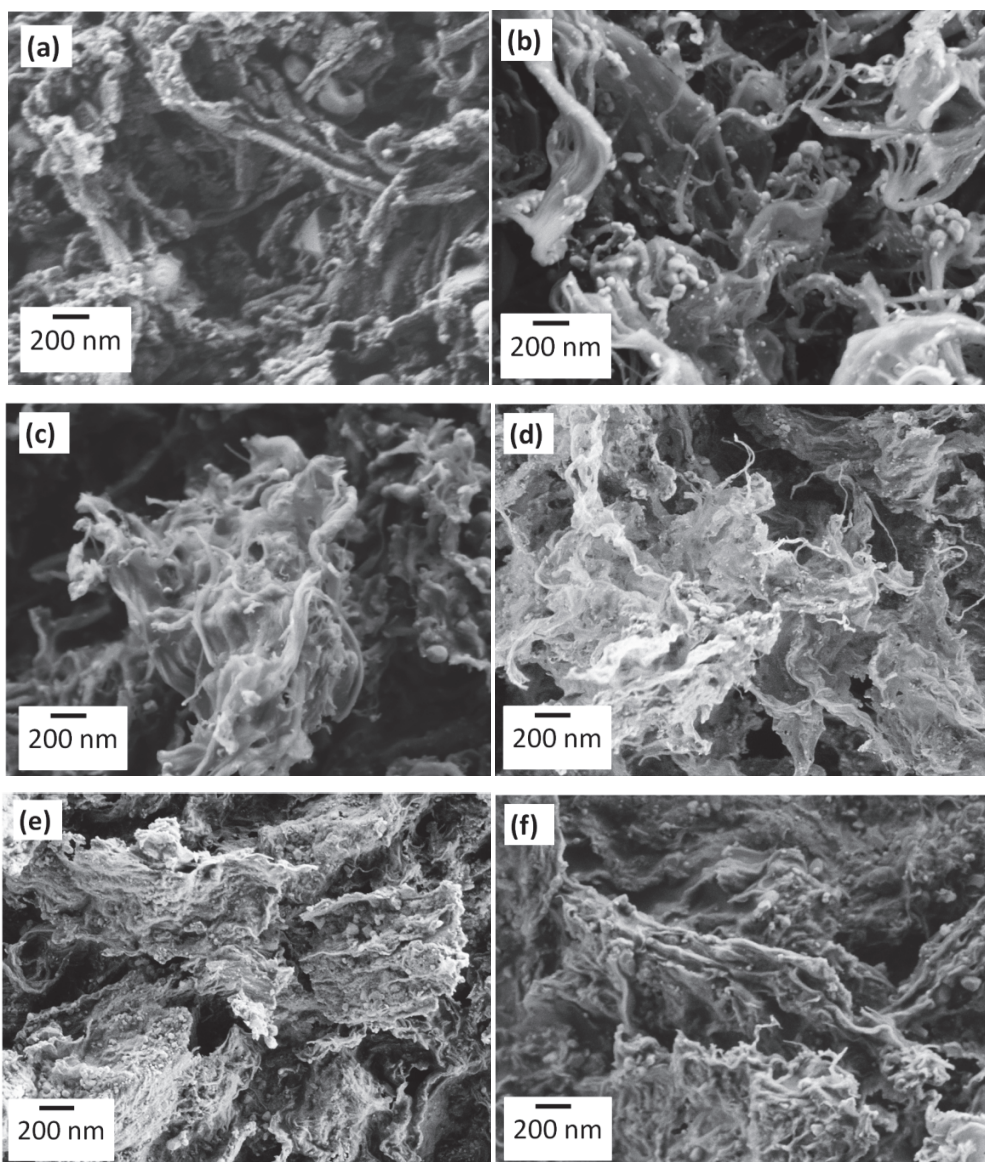


Figure 6.2. SEM images of heat treated samples; a) 1600°C, b) 1800°C, c) 2000°C, d) 2200°C, e) 2500°C and f) 2800°C.

Figure 6.3 shows the SEM images of the sample graphitized at 2000°C. Some fine fibrillar structures of ~5 nm in diameter were formed between two parts of the carbon residues. They were aligned in one direction and stretched parallel to each other. Further

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investigation needs to be undertaken to understand how these fibrillar structures are formed.

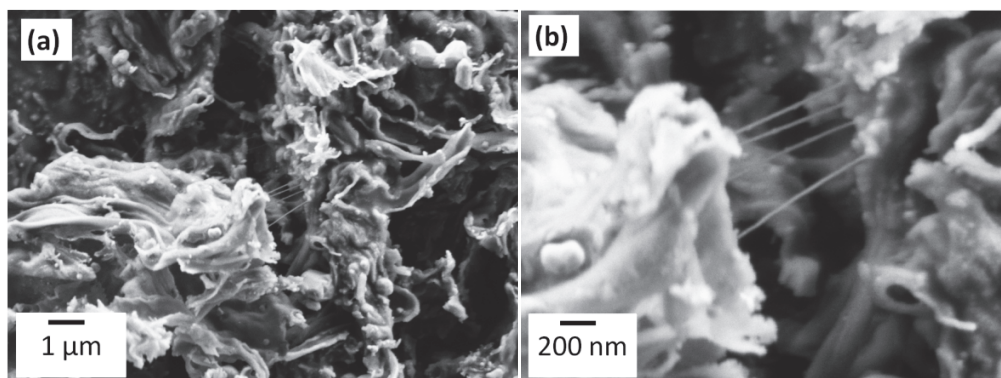


Figure 6.3. SEM images of fine fibrillar structure in 2000°C sample; a) lower magnification and b) higher magnification.

6.3.2. XRD analysis

Figure 6.4 shows the XRD patterns of heat treated samples at various temperatures. All samples showed broad peaks at 15° similar to CNFs at 400°C (Figure 5.16). However, above 2000°C, the samples show crystalline peaks at 33°, 39°, 55°, 65° and 69°. The peaks were identified to be associated with zirconium carbide. No peak associated with graphite was observed.

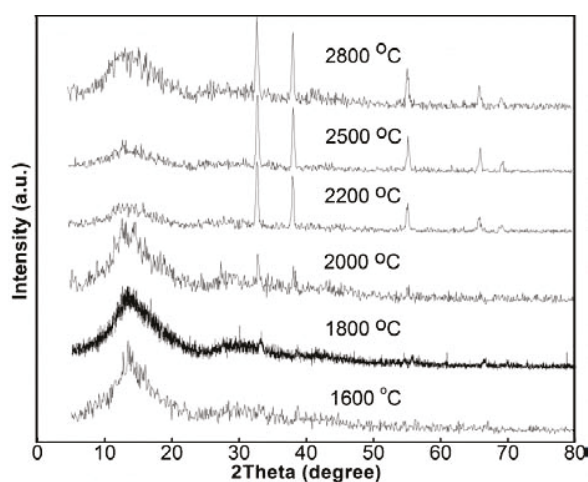


Figure 6.4. XRD patterns of heat treated samples.

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6.3.3. FT-IR analysis

Figure 6.5 shows the FT-IR spectra of samples heat treated at various temperatures. The peaks at 1112cm^{-1} and 1163cm^{-1} that are associated with oxygen bonds were still present. A sharp peak was present at 1380cm^{-1} associated with the strong Zr—O covalent bonds [329-331].

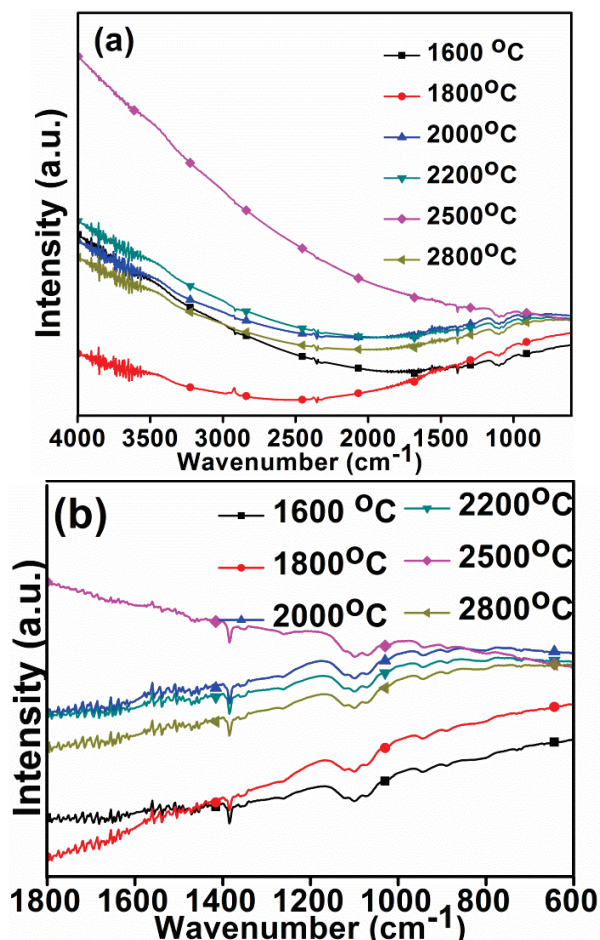


Figure 6.5. FT-IR spectra of heat treated samples; a) $4000\text{--}800\text{ cm}^{-1}$, (b) $2000\text{--}800\text{ cm}^{-1}$.

6.3.4. Raman analysis

Figure 6.6 shows Raman spectra of heat treated samples and Figure 6.7 shows Raman spectra of graphite and CVD CNFs. Compared to graphite, heat treated CNFs exhibit broader peaks at 1350 cm^{-1} and 1580 cm^{-1} . These peaks are associated with D and G bands, respectively. D band shows the defective graphitic structure and G band is associated with the tangential vibration of carbon atoms in graphitic layers. The D/G ratio

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gives an understanding about how much of the material is graphitic. A larger D/G value indicates more disordered structure [332-335].

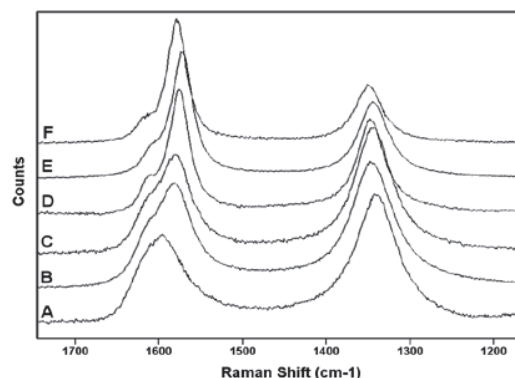


Figure 6.6. Raman spectra of heat treated samples; a) 1600°C, B) 1800°C, C) 2000°C, D) 2200°C, E) 2500°C and F) 2800°C

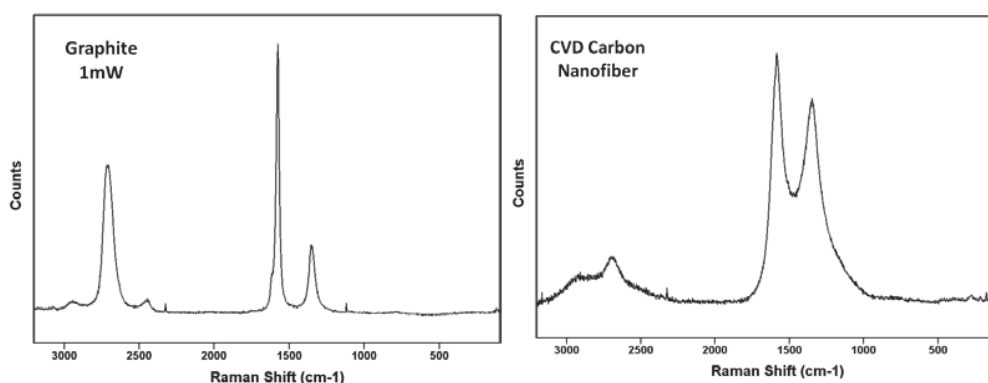


Figure 6.7. Raman spectra of CVD grown CNF and graphite.

Table 6.1 shows the D and G band parameters associated with the graphitized samples. Figure 6.8 shows the D/G peak intensity ratio as a function of heat treatment temperature. As shown in Figure 6.8, D/G ratio decreased as the heat treatment temperature increased, indicating the progress of graphitization with increasing the heat treatment temperature. It is noted that the D/G ratio of the samples heat treated above 2200°C is between the D/G ratios of CVD CNFs and graphite. Hence the degree of graphitization in the samples heat treated in this temperature range is as high as that of commercial CVD-based CNFs. Figure 6.9 shows the Raman shift of the peak G as a function of heat treatment temperature. The peak position shifted toward lower wavenumber as the heat treatment temperature increased. This result indicates that the number of graphite stacking layers increased as a function of heat treatment temperature [336]. These results indicate that

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graphitization started at around 1600°C. The investigation about the effect of holding time on the degree of graphitization is suggested for future study.

Table 6.1. D and G band parameters.

Sample	D/G	G (cm^{-1})	D (cm^{-1})
1600°C	1.447	1596	1340
1800°C	1.192	1582	1347
2000°C	1.270	1581	1345
2200°C	0.762	1577	1348
2500°C	0.611	1572	1345
2800°C	0.487	1579	1351
CVD CNF	0.809	1587	1350
Graphite	0.238	1579	1353

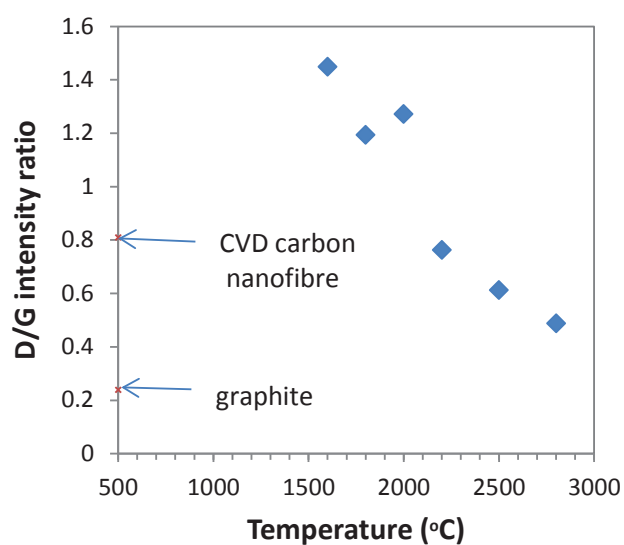


Figure 6.8. D/G peak intensity ratio as a function of heat treatment temperature.

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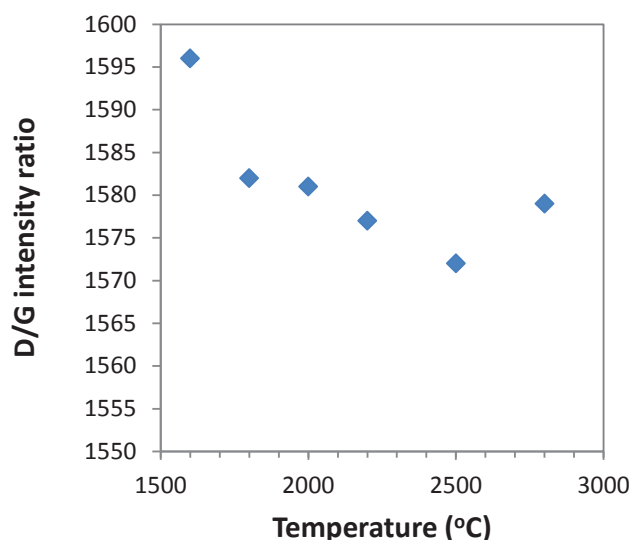


Figure 6.9. Raman shift of the peak G as a function of heat treatment temperature.

6.3.4. Source of contaminant particles

As shown in Figures 6.1 and 6.4, a significant quantity of contaminant particles was observed in the heat treated samples. The contaminants were identified as ZrC. It is likely that the contaminants stemmed from the milling balls made of ceria doped zirconia. The reaction between zirconia (ZrO_2) and carbon to form ZrC via the following reaction is thermodynamically favourable above 1700°C ;



Thus ZrC particles were formed during heat treatment in the Tanmann furnace. It was assumed that the fragments of milling balls were not detected by XRD before graphitization, possibly because the quantity and crystallite sizes of the fragments were small compared to CellNFs.

6.4. Conclusion

In this chapter, CNFs obtained from freeze-dried CellNFs were heat treated at various temperatures above 1600°C . The effects of heat treatment temperatures on the graphitization and morphology of CNFs were characterised by TEM, SEM, XRD, FT-IR and Raman spectroscopy.

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TEM and SEM studies showed that the original fibrous morphology was not retained during graphitization. XRD results showed that the samples were mainly amorphous, apart from ZrC crystal contaminants. FT-IR spectra of samples showed that oxygen related bonds were still present in samples after heat treatment. However, a small part of the sample heat treated at 1600°C showed crystal-like structures under TEM. Raman spectroscopy also indicated that graphitization started gradually from above 1600°C. The number of graphite stacking layers increased steadily as a function of heat treatment temperature. It was also found that in the sample heat treated at 2000°C, some fine fibres of around 5 nm in diameter were bridged between bundles of fibres. They were aligned in one direction and were parallel to each other.

A significant quantity of contaminant particles was observed in the heat treated samples. The contaminants were not detected before high temperature heat treatment. As the contaminant particles may act as catalysts, it is critical to minimize the amount of contaminant arising from milling balls in order to control the graphitization reaction in CNFs. Further study is required to optimize the heat treatment conditions to retain fibrous structures during high temperature heat treatment.

Chapter 7: Conclusion and future work

7.1. Main conclusions

In this thesis, the potential of pyrolysis methods to form CNFs from CellNFs was investigated. Although carbonisation of micron-sized cellulose fibres has been widely investigated in the past, in this thesis, the novel CellNFs obtained from ball-milled softwood pulp was used to investigate the carbonisation process. Various pyrolysis conditions including the effect of heating stages, heating rate in each stage, maximum temperature in each stage and holding time at the maximum temperature were investigated for their effects on the morphological and structural properties of resulting carbon residues. By the use of freeze-dried CellNFs and optimized heat treatment conditions, CNFs with diameters of <100 nm were produced from renewable raw materials in a simple and scalable manner. Several conclusions were drawn from the investigation as listed below:

1) Heat treatment conditions below 400°C affect the morphology of the resulting carbon nanofibres.

CNFs were produced by the pyrolysis of CellNFs below 400°C. It is shown that heat treatment conditions around the thermal decomposition temperature greatly influence the morphological properties of CNFs. Longer holding time at 240°C and slower heating rate from 240°C to 400°C were critical to preserve the original fibrous structures of precursor CellNFs in CNFs. It was suggested that intermolecular dehydration was induced during the prolonged heat treatment below 240°C and that the removal of OH groups reduced the chance of chain scission and the formation of tar/ levoglucosan. This in turn contributed to the retention of the original fibrous structure during carbonisation between 240°C and 400°C. Slow heating rate helps the carbon chains to join neighbouring chains to form aromatic rings within the nanofibre boundaries without causing morphological damage to the nanofibre.

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2) The method to dry CellNF precursors affects the morphology of resulting carbon nanofibres.

The freeze drying method left a network of nanofibres with wider spatial distance between the fibres than oven-dried samples, and turned them into spongy looking masses. Hydrogen bonding still occurred between nanofibres and connected the fibres together in an open-network structure.

The open structure allowed effective removal of oxygen and hydrogen from the cellulose molecules during heat treatment below 240°C. This prevents the formation of levoglucosan and the scission of cellulosic chain during decomposition of cellulose between 240°C and 400°C and, in turn, the retention of the original fibrous structure.

On the other hand, oven-drying left a compact network of fibres which connected to each other via hydrogen bonding. During heat treatment below 240°C, the oxygen and hydrogen were not efficiently removed from the cellulose molecules. This may be due to the closely packed structure without much open space between fibres. As a result, the formation of levoglucosan and the scission of cellulosic chain were promoted during decomposition of cellulose between 240°C and 400°C, resulting in the loss of original fibrous structure. The viscous tar that was formed from levoglucosan may bridge the closely packed fibres, which further contributed to the loss of original fibrous structure.

It was also found that the method to dry CellNF precursors affects the yield of resulting CNFs. Oven-dried and freeze-dried CellNFs show mass loss of 80-85% and 90-95% respectively after carbonisation to 400°C. Greater mass loss in freeze-dried CellNFs may be the result of adjacent nanofibres having greater spatial distance which facilitates higher rates of oxygen and hydrogen removal from the cellulose molecules.

3) The possibility of graphitizing carbon nanofibres at temperatures above 1600°C was demonstrated.

Since graphitization starts from the surface and develops to the core of the fibre, having finer diameter would help the graphitization process to initiate at lower temperatures. It was shown that crystal-like structures were developed at lower temperatures (1600°C). However, the development of such crystals was localized in a small area of the sample and the bulk of the samples did not show such structures. Nonetheless, the results of Raman spectroscopy showed that formation of crystalline regions in the carbon residues

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started at about 1600°C. Furthermore, severe contamination was reported occurring. It is speculated that the contaminant derived from zirconia milling balls and that zirconium carbide contaminants were formed during heat treatment at high temperatures. FT-IR analysis showed that oxygen related bonds were still present in samples after heat treatment at high temperatures

In summary, this thesis has provided a new understanding of the carbonisation of CellNFs. It was demonstrated that pyrolysis of CellNFs produces CNFs of < 100 nm in diameter which have potential in various applications such as biomedical, electronic and structural devices.

7.2. Suggested future work

While interesting and encouraging results were drawn, a lot of new horizons have been opened which need to be studied in the future. Based on the conclusions made in this work, future works are proposed to further deepen the understanding towards the carbonisation and graphitization processes of CellNFs:

- 1- Although the effect of heat treatment on the oven-dried CellNFs was investigated, the heat treatment conditions used were not exactly the same as those for freeze-dried CellNFs. This occurred because the experiments on freeze-dried samples were conducted after oven-dried samples when additional knowledge was accumulated. Thus, using the heat treatment conditions optimized for freeze-dried samples, the experiments on oven-dried samples should be conducted and the results should be compared between the two drying methods.
- 2- The formation of gaseous species during carbonisation between 240-400°C should be investigated using mass spectroscopy or FT-IR. It is thought that identification of gaseous species would provide better insight on the breakdown of cellulosic rings and complex reactions that occur between 240-400°C.
- 3- Graphitization should be thoroughly investigated using pure CellNFs free from contamination. Starting temperature should be around 1600°C with longer holding time. It is suggested that longer holding times may provide enough time and energy for the graphitized regions to develop across the fibres.

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4- Investigations should be re-visited by addressing the yield of CNFs. Most of the investigations in this thesis were focused on the effects of heat treatment and drying conditions on the morphological feature of carbon residues. The optimization of pyrolysis conditions from the minimisation of mass loss should be investigated. Levoglucosan is volatile and breaks down into tar and some other by-products such as char, CO₂ and furan at higher temperatures. Once pyrolysis conditions were optimized, hydrogen and oxygen atoms could be eliminated from the cellulosic chains. Thus, less carbon atoms reacted with hydrogen and oxygen and released from the chains, and the formation of levoglucosan will be suppressed. This in turn had two effects:

- a. A smaller mass loss occurred;
- b. Fibrous structure was maintained.

Both effects are desirable and improve the cost-related issues and CNF properties.

5- The effect of atmospheric conditions during pyrolysis should be investigated. In this thesis, only nitrogen gas was used. Reducing atmosphere using hydrogen or ammonium gas may influence the decomposition processes of cellulose and in turn change the morphological and structural properties of carbon residues.

6- A thorough investigation should be carried out on how chemical pre-treatments on the CellNF precursors will affect the yield and morphology of carbonised fibres. Use of fire retardants for mass loss reduction should be investigated. The presence of chemicals absorbed onto CellNF precursors may also influence the decomposition reaction of CellNFs and in turn affects the chemical and physical structures of carbon residues.

7- Another method to increase the spatial distance between CellNFs upon drying should be explored. It is suggested that chemical treatment of the CellNFs within the suspension may avoid the formation of hydrogen bonding between CellNFs during drying. Hence, upon drying, the fibres will remain independent from each other. This will help retain the fibrous morphology during carbonisation.

8- The method to quantitatively analyse the fibre morphology should be developed. In this thesis, the retention of fibrous morphology was assessed qualitatively based on the SEM image. Quantitative analysis is required to further investigate the effect of drying and heat treatment conditions on the morphological properties of carbon residue

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in detail. For example the use of specific surface area measurements should be considered.

9- In depth statistical analysis should be undertaken to source and eliminate fiber diameter measurements using Image Pro Plus software. Sources of error include:

- a) Operator eye
- b) Number of images
- c) Scale bar
- d) Fiber uniformity
- e) Angle of bar to fiber axis

Since the diameter is in nanometer range, these factors could potentially affect the fiber diameter.

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