



**This electronic thesis or dissertation has been
downloaded from Explore Bristol Research,
<http://research-information.bristol.ac.uk>**

Author:
Filby, Jyoti

Title:
Cellulose Composite Fibres for Potential Engineering and Bio-medical Applications

General rights

Access to the thesis is subject to the Creative Commons Attribution - NonCommercial-No Derivatives 4.0 International Public License. A copy of this may be found at <https://creativecommons.org/licenses/by-nc-nd/4.0/legalcode>. This license sets out your rights and the restrictions that apply to your access to the thesis so it is important you read this before proceeding.

Take down policy

Some pages of this thesis may have been removed for copyright restrictions prior to having it been deposited in Explore Bristol Research. However, if you have discovered material within the thesis that you consider to be unlawful e.g. breaches of copyright (either yours or that of a third party) or any other law, including but not limited to those relating to patent, trademark, confidentiality, data protection, obscenity, defamation, libel, then please contact collections-metadata@bristol.ac.uk and include the following information in your message:

- Your contact details
- Bibliographic details for the item, including a URL
- An outline nature of the complaint

Your claim will be investigated and, where appropriate, the item in question will be removed from public view as soon as possible.

Advanced Composite Collaboration for Innovation and Science



Cellulose Composite Fibres for Potential Engineering and Bio-medical Applications

A Thesis submitted for the Degree of MSc. Aerospace Engineering in
Composites Research

February 2018

Supervisor:

Dr. Sameer S Rahatekar,

Prof. Michael Wisnom

Jyoti Filby

Bristol Composites Institute
Queens School of Engineering

Author's Declaration

I, Jyoti Filby, hereby declare that this work has been carried out based on the requirements of the university rules under the supervision of Dr. Sameer Rahatekar and Prof Michael Wisnom.

All the results in this thesis are conducted by the author unless exclusively stated before the results.

List of Publication from the thesis:

Marta Gina Coscia¹, JyotiBhardwaj¹, Nandita Singh, M. Gabriella Santonicola, Robert Richardson, Vijay Kumar Thakur, Sameer Rahatekar. Manufacturing & characterization of regenerated cellulose/curcumin based sustainable composites fibers spun from environmentally benign solvents. Volume 111, January 2018, Pages 536-543.

Signature: Jyoti Filby

Dated: 2nd of March, 2018

Abstract

With the continuous use of fossils and metals, the resources are depleting very fast and in order to maintain the supply with demand there is a need to find the best suitable alternative. Composites have brought a revolutionary change in the field of engineering, along with the very serious concerns for the environment too. In addition, the conventional fibre reinforced composites are polluting the environment very severely, hence disturbing the whole life cycle. To maintain the balance between nature and technology, there is a need to make most of the natural resources without making any harm to the environment. Following this idea, there is a lot of research going in the field of natural fibres. Despite the extra ordinary performance of carbon and glass fibres, its manufacturing, processing and decomposition compromises the environment health, hence leaving serious concerns. On the other hand, cellulose fibres which are not only manufactured from benign material but also are very less harmful for the environment along with its important properties making it efficient enough to be used in the engineering, textile, medical, food and cosmetics industry.

“Considerable growth is expected in the production of man-made cellulose textile fibres.” [1]

In this thesis the manufacturing and characterization of the best cellulose fibres produced is discussed. The cellulose fibres were produced by dissolving 4wt% and 6 wt. % DP890 in ionic liquid and also were later produced with Cellulose Nano crystals dispersion, winding speed was kept at 200rpm (approximately), needle diameter 340 um and spinning temperature between 50-60 degree Celsius. Fine fibres with diameter ~21um were manufactured and tested for mechanical properties and characterization. It was found that the tensile strength of the cellulose fibres was increased from 276 (± 10.7) MPa to 630 (± 35.5) MPa and the young's modulus was increased from 21 (± 1.2) GPa to 43 (± 1.7) GPa when the fibres were dispersed with Cellulose Nano Crystals. The cellulose

MSc. R. Aerospace Engineering

fibres were briefly studied for curcumin dispersion as well. These were tested for mechanical properties in this thesis.

Keywords: Nano Cellulose, Cellulose Nanocrystals, bio-composites.

Reference:

1. Lauri K. J. Hauru, Michael Hummel, Anne Michud, Herbert Sixta, Dry jet-wet spinning of strong cellulose filaments from ionic liquid solution, Springer Netherlands, Cellulose, volume 20, issue 6, pages 4471-4481.

Acknowledgement

I hereby would like to acknowledge the help, guidance and support I received from my supervisor, Dr. Sameer Rahatekar. I would also like to thanks Dr. Steven Rae, Dr. Julie Etches, Dr. Sean Davis, Prof Robert Richardson, Dr. Avinash Patil, the workshop team, all the ACCIS lab, ACCIS support staff and faculty team to arrange the resources making this research to run efficiently.

I would also like to thank Prof. Michael Wisnom for his support to complete my Thesis and for encouraging me to finish it on time with regular updates. My special thanks to HiPerDuct funding to support the work and to cover the expense for the conferences and travel.

I also would like to acknowledge Marta Gina Coscia for initiating the work to manufacture cellulose/curcumin based composite fibres, which I have reproduced in this thesis and have worked on its further characterization.

My special thanks to Dr Nandita Singh for her support and guidance in this learning process. And to my Family for the moral and financial support.

Contents

Author's Declaration	i
Abstract	ii
Acknowledgement	iv
Project Aim	xii
Objectives	xii
Chapter 1	1
1.1 Introduction	1
1.1.1 Cellulose	1
1.1.2 Morphology of Cellulose	1
1.1.3 Structure of Cellulose	2
1.1.4 Applications	3
1.2 Nano-Cellulose	4
1.2.1 Introduction and Historical Outline	4
1.2.2 CNC Morphology, Structure and Resources	5
1.2.3 Mechanical Properties and Applications	7
1.3 Fibre spinning	7
1.3.1 Dry Spinning.....	7
1.3.2 Wet Spinning	7
1.3.3 Dry-Jet Wet Spinning	8
1.4 Drawing techniques	9
1.4.1 Effect of Fibre Spinning and Stretching	9
1.4.2 Mechanical Properties of the fibres	10
1.4.3 Water Resistance.....	10

1.5	Refernces	Error! Bookmark not defined.
Chapter 2	15
Literature Review	15
Chapter 3	25
Experimental	25
3.1 Materials	25
3.1.2 Cellulose	25
3.1.3 Cellulose Nano-Crystals	25
3.1.4 Ionic liquids	25
3.2 Methods	26
3.2.1 4% DP890 fibre spinning	26
3.2.2 4% DP890 Fibre Stretching	26
3.3 Characterization of fibres	27
3.3.1 Scanning electron microscopy	27
3.3.2 Fourier Transform Infrared Spectroscopy (FTIR):	27
3.3.3 Mechanical properties	27
3.4 Discussion and Conclusion	29
3.5 Reference:	29
Chapter 4	30
Marrying Cellulose Nanocrystals with Wood Pulp Cellulose to Manufacture High Modulus Cellulose Nanocomposite Fibres	30
4.1 Introduction:	30
4.2 Experimental Section	32
4.2.1 Materials	32

MSc. R. Aerospace Engineering

4.2.2 Preparation of Cellulose Nanocrystals suspension.....	32
4.2.3 Cellulose Dope Preparation	33
4.2.3.1 Neat cellulose.....	33
4.2.3.2 Cellulose Solution with nanocrystals dispersion.....	33
4.2.4 Fibre Preparation.....	33
4.2.5 Fibres Characterization	34
4.2.5.1 Scanning Electron Microscopy (SEM).....	34
4.2.5.2 Mechanical Testing.....	36
4.2.5.3 Fourier transform infrared (FTIR) Spectroscopy	36
4.2.5.4 2D Wide Angle X-ray Diffraction.....	37
4.3 Results	37
4.3.1 Scanning Electron Microscopy	37
4.3.2 Mechanical Properties.....	37
4.3.3 FTIR Spectroscopy	39
4.3.4 Wide Angle X-ray Diffraction of the fibres	39
4.4 Discussions	41
4.4.1 Wet Spinning of Cellulose Fibres.....	41
4.4.2 Structure and Morphology of the Spun Fibre	42
4.4.3 Orientations and Mechanical Properties.....	43
4.5 Conclusion.....	46
4.6 References	47
Chapter 5.....	51
Characterization of Regenerated Cellulose/Curcumin Composites Fibres	51

5.1 Introduction	51
5.2 Materials and Methods	53
5.2.1 Cellulose/curcumin fibres formation	53
5.2.2 Statistical analysis.....	55
5.3 Results	55
5.3.1 Surface Morphology	55
5.3.2 Scanning electron microscopy.....	55
Cross-section Observation of Cellulose Fibres	55
5.3.3 Mechanical properties.....	60
5.3.4 FTIR spectroscopy	60
5.3.5 Wide Angle X-ray Diffraction (WAXD) of the Fibres	62
5.3.6 Orientation Factor	63
5.3.7 Crystallinity Index	64
5.4 Discussion	64
5.5 Conclusion	67
5.7 References:	68
Conclusion and Future Work	75

List of Figures

Figure 1: Graphical representation of the project vision.xii

Figure 2: Beta-D-Glucopyranose [4] 1

Figure 3: Hydrogen bonding within Cellulose. [4].....2

Figure 4: Cellulose structure with defined different levels.3

Figure 5: Non-crystalline and crystalline regions in cellulose fibres. [6]5

Figure 6: AFM topography images showing height measurements of ECN (left) and CNC (right) [10].....6

Figure 7: TEM images for Tunicate-sulphate (left) and wood sulphate (right) [10]6

Figure 8: Schematic of dry-jet wet fibre spinning process.8

Figure 9: Wet fibre stretching Demonstration. [2]26

Figure 10: Design of a tensile sample with one fibre filament between two cardboard frames. [3]27

Figure 11: Graphical representation of the spinning process.30

Figure 12: Dry Jet Wet Spinning System.34

Figure 13: A, B: The SEM images of neat cellulose fibres(A) and cellulose fibres dispersed with CNC (B).....35

Figure 14: FTIR spectrum for cellulose fibres, neat cellulose and EMIM DEP confirming complete removal of ionic liquid.39

Figure 15: W-XRD diffraction pattern for two type of fibres- Neat Cellulose (A) and Neat Cellulose with Tunicate CNC (B).40

Figure 16: TEM images of cellulose fibres with Cellulose Nano-crystals, darker regions representing the presence of dispersed CNC in the amorphous cellulose matrix.42

Figure 17: Stress Strain curve for cellulose fibres obtained with neat cellulose with and without tunicate CNC dispersions.44

Figure 18: The mechanical properties comparison of the fibres manufactured in this report with the previous work.46

Figure 19: Microscopic image for cross-sections of the cellulose fibres with (A) 0% curcumin fibres. (B) 1% curcumin fibres. (C) 5% curcumin fibres. (D) 10% curcumin fibres.56

Figure 20: SEM images for the Cellulose fibres with 10% curcumin representing the decrease in diameter with increase in the winding speed from 1.5×10^{-1} m/s, 2.9×10^{-1} m/s and 4.8×10^{-1} m/s.57

Figure 21: A, B, C, D represents (macro-level) images of the fibres of the bundle of cellulose fibres with 0%, 1%, 5% and 10% curcumin respectively- Indicating the colour change with increase in curcumin concentration.58

Figure 22: Graphic representation of fibre diameter at different winding velocities: 1.5×10^{-1} m/s, 2.9×10^{-1} m/s and 4.8×10^{-1} m/s. significant statistical variation was seen in the fibre diameter with different winding speed.59

Figure 23: FTIR spectra of EMIM DEP solvent and the regenerated cellulose and cellulose/curcumin fibres.60

Figure 24: FTIR spectra of EMIM DEP solvent and the regenerated cellulose and cellulose/curcumin fibres; none of the regenerated cellulose fibres show the P=O bond peak at 1238cm^{-1} indicating that the solvent is completely removed from the fibres.61

Figure 25: WAXD image of (a) pure cellulose fibre (b) 10% curcumin/cellulose fibre.62

Figure 26: Radial Scan of WAXD of (a) pure cellulose fibre (b) 10% curcumin/cellulose fibre.....62

Figure 27: Variation of orientation factor of the fibres while processing in ionic liquid with the increase of curcumin.....63

List of Tables

Table 1: Dimensional characterisation of cellulose nano-crystals obtained from various sources [1, 6].5

Table 2: Mechanical Properties of Stretched and un-stretched 4%DP890 fibres.28

Table 3: Mechanical Properties comparison between current cellulose fibres with CNC before and after carbonisation with wood, silk, glass and carbon fibres.....38

List of Abbreviations

CNC – Cellulose Nano Crystal

EMIM DEP- 1-ethyl-3-methylimidazolium diethyl phosphate.

EMIM OAc - 1-ethyl-3-methylimidazolium diethyl Acetate.

GPa – Gega Pascals

MPa – Mega Pascals

SEM – Scanning Electron Microscopy

WXRD – Wide angle X-ray diffraction

FTIR – Fourier-transform infrared spectroscopy

Project Aim

This project aims to fully understand - how to use a dissolution method to develop a manufacturing process for regenerated cellulose fibres with improved mechanical properties using ionic liquids as benign solvents.

To manufacture and study Curcumin based cellulose composite fibres for bio-medical applications.

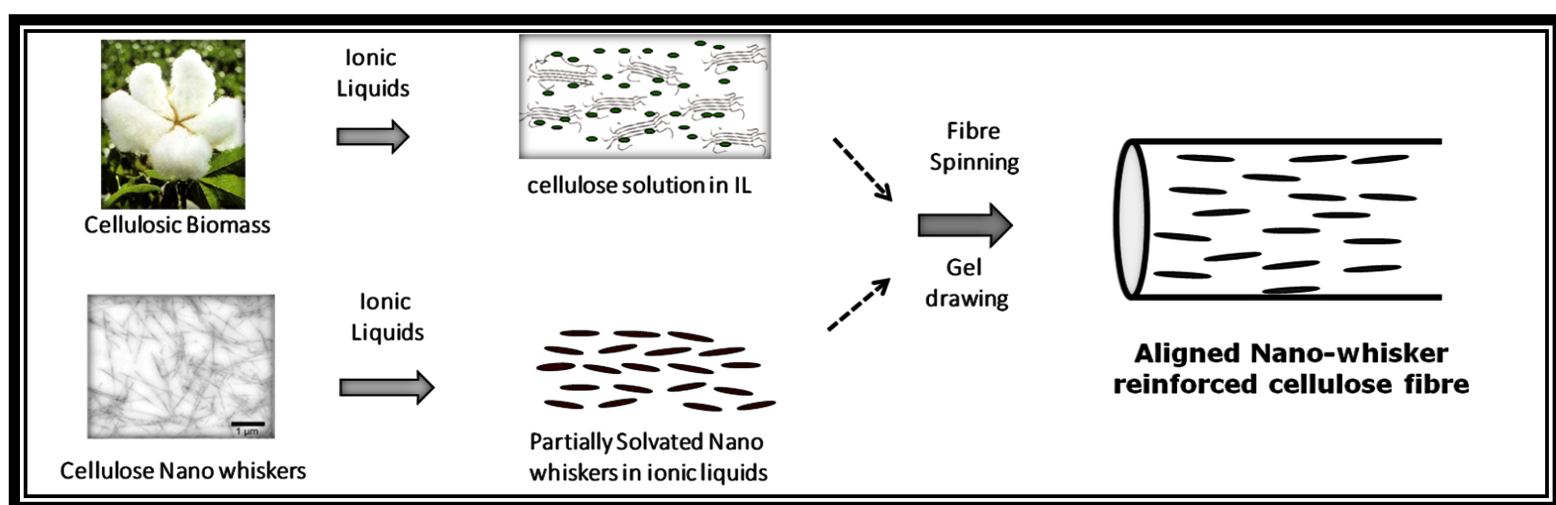


Figure 1: Graphical representation of the project vision.

Objectives

In order to achieve the overall aims, the objectives are outlined as below:

1. To gain an in-depth understanding of cellulose dissolution and Nano-particles dispersion.
2. To manufacture regenerated cellulose fibres reinforced with cellulose Nano-crystals with high stiffness and strength.
3. To develop cellulose fibres in order to replace glass fibres.
4. To deliver more sustainable composites via novel, environmentally benign manufacturing method to spin high performance regenerated cellulose fibres.

MSc. R. Aerospace Engineering

5. To investigate the effects of different parameters on the mechanical performance, e.g. temperature, winding speed, cellulose concentration, etc.
6. To establish threshold parameters for maximum stable winding speed and cellulose concentration for improved mechanical properties.
7. To control and optimize the dispersion process of curcumin in cellulose matrix.

Chapter 1

1.1 Introduction

1.1.1 Cellulose

Cellulose is one of the most abundant materials on the surface of the Earth, it is considered to be a source of raw material that is inexhaustible - thus making it a highly sought after material. For this reason, wood and other cellulose-rich resources are commonly used as sustainable and renewable materials within many of today's industries.

It can also be described as the biopolymer that is naturally found in the cotton and wood plant cells.

Cellulose is found in plants like wood and cotton. The highest concentration of cellulose, around 90%, is found in cotton plant, 40-50% in wood and the bast fibres like hemp, ramie or flax contribute about 70-80%. It is the main constituent in the cell wall of plants and trees and is the most abundant polymer in nature. Tunicates, algae, various bacterial species etc. are few other resources of cellulose. [1][2]

1.1.2 Morphology of Cellulose

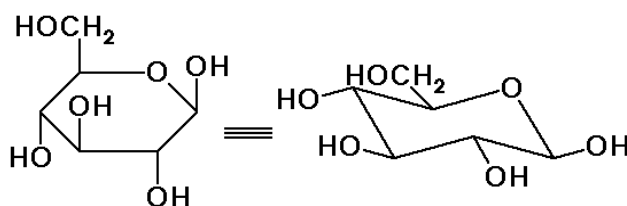


Figure 2: Beta-D-Glucopyranose [4]

Cellulose is an unbranched homopolysaccharide that is composed of β -D-Glucopyranose units linked together by 1, 4 glycosidic bonds. β -D-Glucopyranose is the beta isoform of D-Glucopyranose that is more commonly referred to as Beta-D-Glucose. β -D-Glucose cannot be hydrolysed into a simpler form, making it a monosaccharide. When two monosaccharides

undergo a condensation reaction, a molecule of H₂O is removed and an alpha-linkage or beta-linkages is formed. Both the α - and β -linkages confer to very different structural properties even though the sequences are otherwise identical in composition. When a glycosidic linkage forms between two units of β -D-Glucose, the disaccharide cellulose is produced. The glycosidic linkage between two monosaccharides is found between the anomeric carbon of one monosaccharide and a hydroxyl group of another- a hemiacetal group reacts with an alcohol group to form an acetal. The acetal that forms are configurationally stable under most conditions because once a glycosidic bond is formed, its configuration is maintained indefinitely. Also as a result of the bonds stability, no oxidation or reduction can take place at an anomeric centre that is involved in a glycosidic bond. [3]

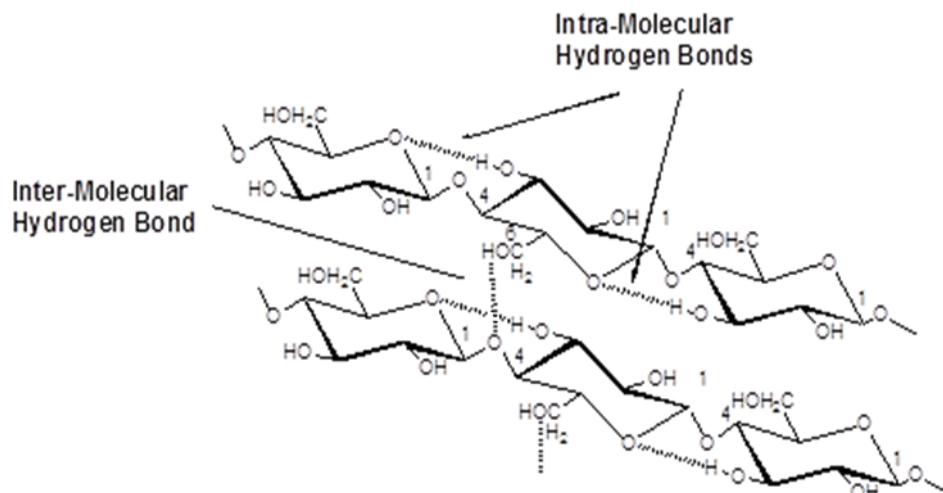


Figure 3: Hydrogen bonding within Cellulose. [4]

1.1.3 Structure of Cellulose

While studying the structure of a cellulose fibre, it can be divided into three different levels: the molecular level, the supramolecular level, and the morphological level. The molecular level is as described in the beginning of this section and represented in figure 3. The supramolecular level defines the polymer chains ordered in crystalline and non-crystalline regions due to

hydrogen bonding. The morphological level defines the cellulose fibre and its cell walls as shown in figure 4. [1]

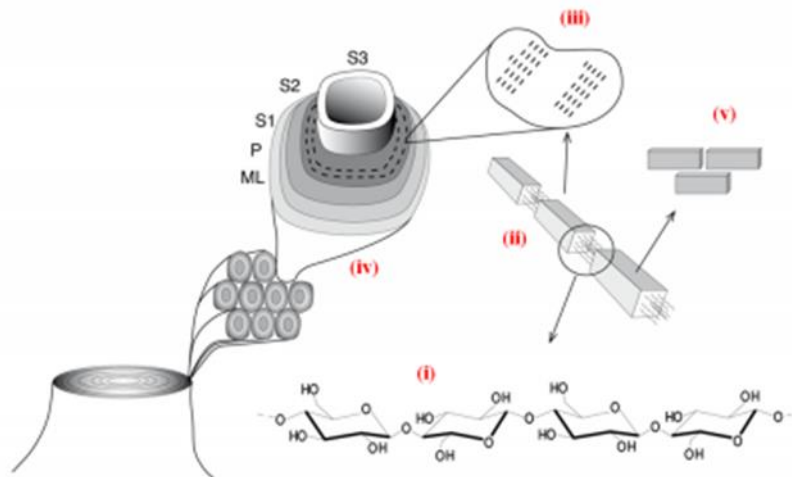


Figure 4: Cellulose structure with defined different levels.

The above figure shows the defined structural levels of the cellulose fibres where the cellulose polymers

- (i) are aggregated to form micro fibrils
- (ii) Micro fibrils- long bundles of cellulose molecules which are stabilised by hydrogen bonding.
- (iii) Micro fibrils- oriented in different layers in the cell wall.
- (iv) And the different layers differ in fibril densities, direction, and textures. [1]

1.1.4 Applications

“The cellulose is a renewable and biodegradable polymer which has been known for about 150 years” [1]. It has been used as building material, energy source, and clothing, for a long time.

1.1.4.1 Medical and hygiene products: Nano cellulose has good absorption properties. Hence, the fibres dispersed with CNC can be used in non-woven products, tissues, or diapers. [1]

1.1.4.2 Food industry: emulsions and dispersions can be prepared using Nano cellulose. It is also suitable for use in food products as stabilizers or as thickeners [1][2].

1.1.4.3 Other applications: Cosmetics, automotive, films, painting, etc. are some of the other application areas of cellulose fibres.

1.2 Nano-Cellulose

1.2.1 Introduction and Historical Outline

There are different types of Nano cellulose depending on the cellulose origin source and pre and post treatments. Hence, they have different aspect ratios (L/d , where L is the length and d is the diameter) and as well as mechanical properties [1].

The cellulose Nano-crystals have been considered as superior entities in terms of the mechanical properties when compared with recrystallized bio-materials. It has proven to have best fracture properties which has been published in recent studies as well. [5]

There are some reviews about the research in the field of Nano cellulose. Most of them are about Nano cellulose as a reinforcement material in bio composites. Reviews are also found on the use of bacterial Nano cellulose (BNC) in medical or surgical products. New avenues in product development can be opened by expanding the knowledge in the area of Nano cellulose and by finding better techniques to control its properties during processing. Fossil fuel-based products can be replaced by bio based products with outstanding properties [1].

Nano cellulose shows extra ordinary properties when compared with Kevlar, stainless steel, carbon fibres or the bulk materials. The first pilot plant for CNC manufacturing was opened in 2011 in Sweden and the production factory was

opened in 2012 in Canada. And the most recent in North Sweden in 2016. Here they source the CNC from the paper industry and the pulp sludge. [1] [6]

1.2.2 CNC Morphology, Structure and Resources

When a cellulose fibre or crystal measuring at least one of its dimension in nanometer size range, it termed as Nano cellulose or Nano whiskers. [7]

“For the synthesis of cellulose nanocrystals, the monocrystalline regions are hydrolyzed and the remaining crystals are in nanometer size range in all dimensions as shown in figure 5” [6, 1]

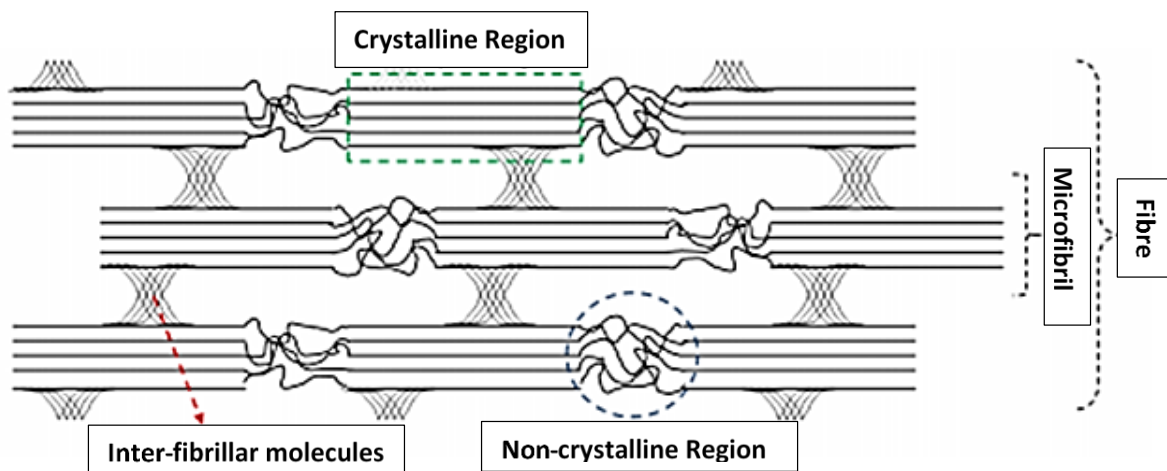


Figure 5: Non-crystalline and crystalline regions in cellulose fibres. [6]

Cellulose source	Length, L (nm)	Cross section, D (nm)	Axial ratio, L/D
Wood	100-300	3-5	30-70
Cotton	100-400	7-15	10-20
Algae (Valonia)	100nm to um	10-20	N/A
Bacterial Cellulose	100nm to um	5-10	N/A
Tunicate Cellulose	100nm to um	10-20	67
Sugar beet pulp	210	5	40
Wheat straw	220	5	45

Table 1: Dimensional characterisation of cellulose nano-crystals obtained from various sources [1, 6].

The nano-crystal charge depends upon the acid used during the hydrolysis reaction. Depending on the concentration of CNC diluted in water, the stable colloidal dispersion is promoted by the charged sulphate groups on the nano-crystals surface. The Aspect ratio and the dimension of different type of CNC's from various sources: [1] [8] [9]

Figure 6 and 7 shows the AFM and TEM images of tunicate and wood Nano crystals. "It is shown that the modulus of the tunicate cellulose is very high, at about 143 GPa".

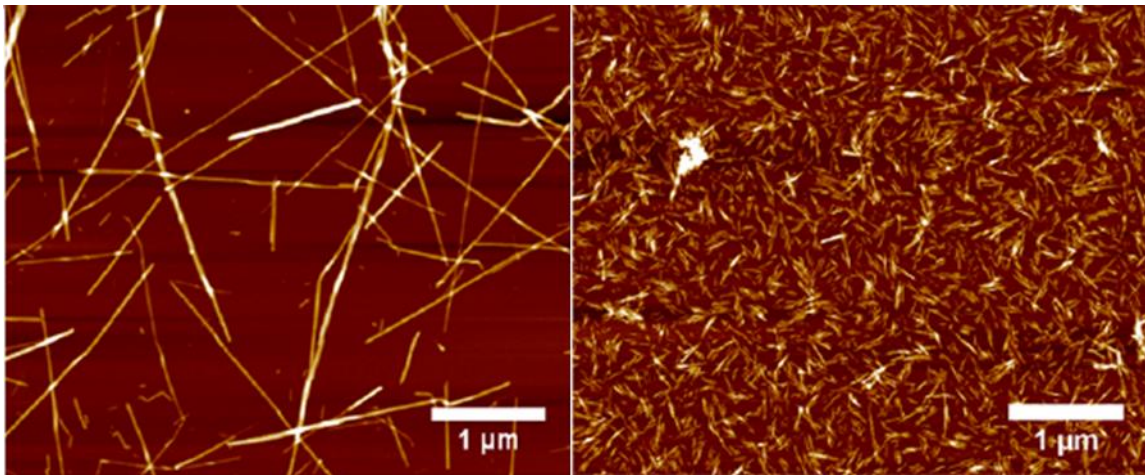


Figure 6: AFM topography images showing height measurements of ECN (left) and CNC (right) [10].

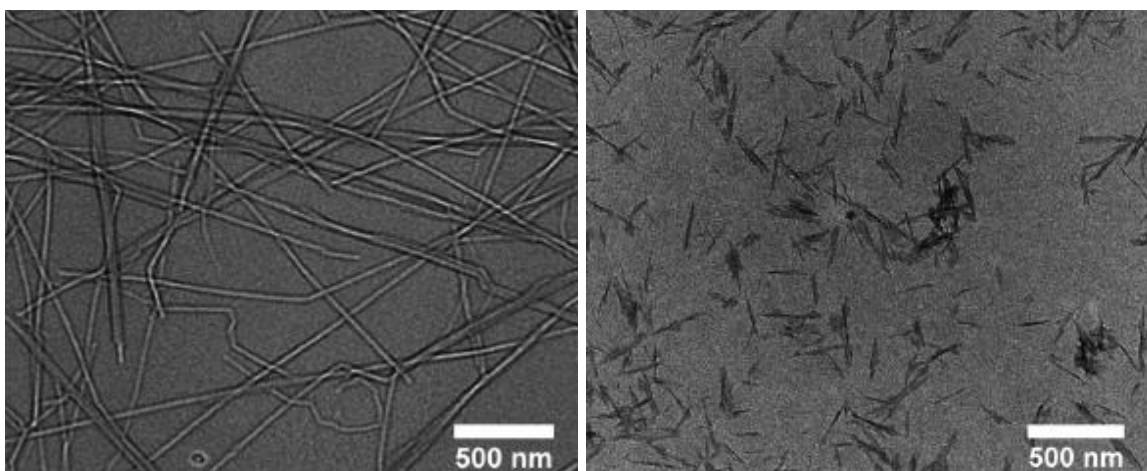


Figure 7: TEM images for Tunicate-sulphate (left) and wood sulphate (right) [10]

1.2.3 Mechanical Properties and Applications

A lot of research was previously carried out in the field of cellulose fibres and due to its strengthening properties and applications. “Macro-scale fibres composed of Nano-fibrillated chitin and cellulose (NFCh, NFC) inducing a high degree of orientation and alignment scales macro-scale mechanical stiffness, with the NFC-based fibres (ENFC = 33 GPa) outperforming the NFCh-based ones (ENFCh = 12 GPa) considerably have been manufactured.” [11, 12]

Following different techniques to manufacture cellulose fibres, gives different properties. Also the strength and stiffness of the regenerated fibres depends on the solvent and the other manufacturing techniques. Where spinning fibres with pure cellulose with high alignment gives very good strength, same place it has been proven that addition of Nano cellulose crystals can enhance the fibres properties along with pre and post processing even up to 100%. [11, 13, 14, 6]

1.3 Fibre spinning

The Types of Spinning and the method chosen for this study are described as below:

1.3.1 Dry Spinning

Dry Spinning is a method used for polymers that have a melting temperature which is similar to their thermal decomposition temperature and that cannot be melt spun. During this process the polymer is dissolved in a volatile solvent, extruded through a spinneret, heated by hot air after emerging to remove the solvent through evaporation and is then collected by winding.

1.3.2 Wet Spinning

Wet spinning is another spinning method that can be used on polymers that can thermally degrade before melting but can also be dissolved in solvents. During this process, the polymer is dissolved or suspended in the solvent, drawn

through the spinneret directly into a liquid coagulation bath (no air gap) and then wound.

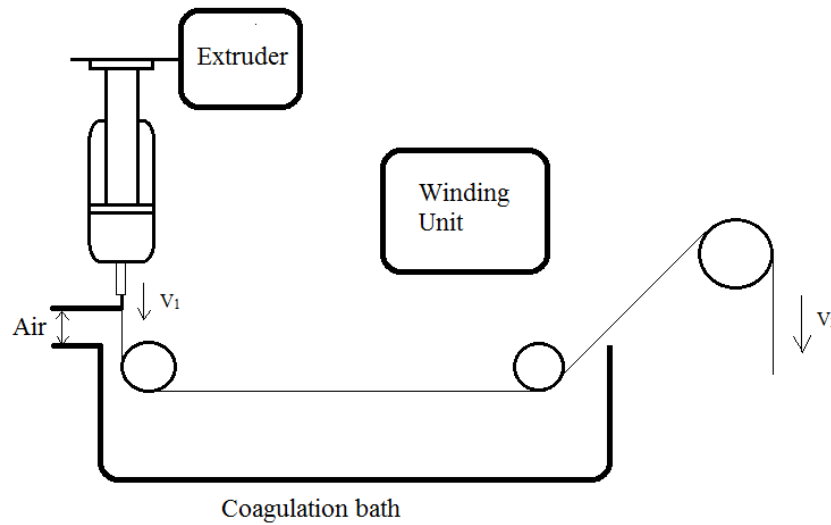


Figure 8: Schematic of dry-jet wet fibre spinning process.

1.3.3 Dry-Jet Wet Spinning

Dry-jet wet spinning is a combination of dry spinning and wet spinning, involving both evaporation and extraction for solvent removal. This technique is used for polymers with melting temperatures that are very close to their decomposition temperature. The schematics of dry-jet wet fibre spinning, as shown in figure 8, consist of four steps;

1. Extrusion of Cellulose/EMIM DEP solution (solution dope) through a nozzle (spinneret) of the extruder.
2. Stretching of the emerging fluid into a filament of the desired diameter through the air gap between the extruder and the coagulation bath.
3. Immersing of the solvent-rich filament into the liquid media coagulation bath, where the solvent is removed from the filament.
4. The winding of the coagulated filament using a motor-controlled winding unit.

Cellulose is a biological polymer that thermally degrades before melting so only wet spinning, dry spinning and dry-jet wet spinning can be used to manufacture fibres. Dry-jet wet spinning has been chosen in this study because it is believed to be the process which is best adapted to cellulose fibre production [20].

1.4 Drawing techniques

The fibres can be drawn in two ways:

- An integral part of the spinning operation, or
- In a separate step.

The cellulose fibres can be drawn without any requirement of the external heat source. This process is known as cold drawing. Fibres like polypropylene and nylon can be drawn at temperature around 60 to 70 degree Celsius. Fibres spun at high temperatures are partially crystallized and partially oriented. Partially oriented fibres are more brittle. To improve these properties, the fibres are hot or cold drawn according to the desired properties soon after the spinning. Fibres like PET require immediate hot drawing in order to control the brittleness. Some other examples of hot spun fibres are Nylon, Kevlar 29 and Nomex, where the stiffness is nearly doubled the original value after the hot drawing [15].

1.4.1 Effect of Fibre Spinning and Stretching

The long polymers that form spun filaments by the spinning process described in the previous chapter produce orientation to some extent. Orientation can be completed by drawing or stretching the filament. Stretching is a process that pulls the long polymer chains and align those along the longitudinal axis of the fibre, closely packed together with better cohesion. During the stretching process, the atoms tend to arrange themselves in an ordered manner and forms tightly packed bundles, called crystallites. The term crystallites indicate the regular and precise arrangement of these atoms. There are still some regions where molecules do not get align in a precise manner, called non-crystalline or

amorphous regions. Hence, while considering the fibre structure, these polymer chains maybe considered as the structure embedded with amorphous and crystalline regions.

The polymer chains slide over each other while pulled along the longitudinal axis of the fibre during the drawing operation. As the operation proceed, more molecules come to a state where they are closely packed alongside one another forming a crystallite. Hence, due to intermolecular forces, these tightly held molecules resist further movement with respect to one another. For example, in case of nylon, after spinning, it can only be stretched to as much as five times its original length. After this limit it resists stretching and hence breaks. This is called the threshold point where all the possible atoms have been aligned into crystallites and are held together tightly. This results in improved mechanical properties of the fibres. Hence the fibres can work with large load without any further stretching. [15]

1.4.2 Mechanical Properties of the fibres

The properties of a fibres depend on the degree of alignment of the molecule in several ways. The ultimate strength or the breaking strength of the fibre increases with increase in the degree of alignment. This also results in decrease in the strain range or the elongation limit of the fibre before it reaches its breaking point. This because, as most of the molecules are highly aligned and there is less tendency for them to slide over each other, as they could before the stretching operation. The high degree of orientation also results in higher stiffness or tensile modulus. When the load crosses the elastic limit of the fibre, the fibre ruptures.

1.4.3 Water Resistance

The increase in degree of alignment also resists water absorption. This is due to the reason that the crystalline region resists water penetration and the amorphous region inhibits the water absorption. It affects the dyeing properties

the fibres with high alignment. The increased resistant to water in fibre also resists the molecules of dye to migrate from the dye bath to the spaces between the fibre molecules. Since the highly aligned molecules are relatively less prone to the chemical attack, general chemical stability of a fibre also gets improved. Stretching also improves the appearance of the fibres. Fibres, e.g. cellulose is normally dull and opaque before drawing or stretching. The filaments acquire the luster and transparency characteristics when the molecules are highly aligned after stretching.

A lot of work has been done in this sector. According to Saleh Hshmand study, they reported the CNC when spun with HEC shown improved mechanical properties up to 70% as compared to CNF spun itself. HEC also contributed towards the increase in alignment when lower concentration of CNC was spun. It also improved the wet strength of the fibres by decreasing the hydrophilicity [16]. The mechanical properties of the filaments increased with an increase in the spinning rate due to the higher degree of orientation along the axial direction of the filaments [17]. Lihong Gang reported that the increased strength and modulus values when CNF was wet spun. The flue induced alignment and the contact-induced alignment contributed towards the highly oriented filaments [18].

The effect of degree of alignment can also be seen in case of carbon Nano tubes, as Belén Alemán reported in 2015[19].

In this research work, cellulose fibres with pure cellulose (chapter 3) and with Nano cellulose crystals dispersions (chapter 4) has been manufactured and been tested mechanically for characterization. The effect of fibre stretching and variation in diameter on fibres mechanical properties is studied in chapter 3 and 4.

Along with engineering applications, we have also looked into bio-medical and food packaging industry and have manufactured curcumin and cellulose based fibres as detailed in chapter 5.

1.5 References

1. Mikaela Börjesson and Gunnar Westman , Crystalline Nanocellulose — Preparation, Modification, and Properties, In: Matheus Poletto, Heitor Luiz Ornaghi (Eds.), Cellulose - Fundamental Aspects and Current Trends, 2015, chapter 7, <http://dx.doi.org/10.5772/61899>
2. Ström G, Öhgren C, Ankerfors M. Nanocellulose as an additive in foodstuff. Innven- tia; June 2013, Report No.: 403.
3. Essentials of Glycobiology. 2nd edition. Chapter 2 Structural Basis of Glycan Diversity. Carolyn R Bertozzi and David Rabuka. Cold Spring Harbor (NY): Cold Spring Harbor Laboratory Press; 2009.
4. Varshney VK, Naithani S. Chemical Functionalization of Cellulose Derived from Nonconventional Sources. In: Kalia S, Kaith BS, Kaur I, editors. Cellulose Fibres: Bio and Nano-Polymer Composites. Berlin: Springer; 2011. p. 43–60. DOI: 10.1007/978-3- 642-17370-7.
5. Cellulose Nanofibril- and Chitin Nanofibrilbased Materials: Fibres, Scaffolds and Tubes. Von der Fakultät für Mathematik, Informatik und Naturwissenschaften, der RWTH Aachen University zur Erlangung des akademischen Grades eines Doktors der, Naturwissenschaften genehmigte Dissertation. 2016
6. Klemm D, Kramer F, Moritz S, Lindström T, Ankerfors M, Gray D, et al. Nano celluloses: A New Family of Nature-Based Materials. AngewChemInt Ed. 2011; 50:5438– 5466. DOI: 10.1002/anie.201001273.

7. TAPPI's International Nanotechnology Division. Roadmap for the Development of International Standards for Nanocellulose [Report]. October 2011.
8. Marchessault RH, Morehead FF, Walter NM. Liquid crystal systems from fibrillar polysaccharides. *Nature*. 1959;184: 632–633. DOI: 10.1038/184632a0.
9. Dong XM, Kimura T, Revol J-F, Gray DG. Effects of Ionic Strength on the Isotropic Chiral Nematic Phase Transition of Suspensions of Cellulose Crystallites. *Langmuir*. 1996, 12, pp 2076–2082.
10. Iulia A. Sacui, Ryan C. Nieuwendaal, Daniel J. Burnett, Stephan J. Stranick, MehdiJorfi, Christoph Weder, E. Johan Foster, Richard T. Olsson, and Jeffery W. Gilman, Comparison of the Properties of Cellulose Nanocrystals and Cellulose nanofibrils Isolated from Bacteria, Tunicate, and Wood Processed Using Acid, Enzymatic, Mechanical, and Oxidative Methods, *ACS Appl. Mater. Interfaces*, **2014**, 6 (9), pp 6127–6138
11. Jose Guillermo Torres-Rendon, Felix H. Schacher, ShinsukeIfuku, and Andreas Walther, Mechanical Performance of Macrofibres of Cellulose and Chitin Nanofibrils Aligned by Wet-Stretching: A Critical Comparison, *Biomacromolecules*, 2014, 15(7), pp 2709-17.
12. Baochun Wang, Jose Guillermo Torres-Rendon, Jinchao Yu, Yumei Zhang, and Andreas Walther. Aligned Bioinspired Cellulose Nanocrystal-Based Nanocomposites with Synergetic Mechanical Properties and Improved Hygromechanical Performance. *ACS Appl. Mater. Interfaces*, **2015**, 7 (8), pp 4595–4607.
13. Stephen J. Eichhorn, Cellulose Nano whiskers: promising materials for advanced applications, *Soft Matter*, 2011, **7**, pp 303-315.

14. Lin Liu, Xiaogang Yang, Houyong Yu, Chao Ma and Juming Yao, Biomimicking the structure of silk fibres via cellulose nanocrystal as b-sheet crystallite, *RSC Adv.*, 2014,4, pp 14304-14313.
15. <https://www.britannica.com/technology/man-made-fibre#ref82580>
16. Saleh Hoshmand, Yvonne Aitomaki, Linn Berglund, Aji P. Mathew, Kristiina Oksman, Enhanced alignment and mechanical properties through the use of hydroxyethyl cellulose in solvent-free native cellulose spun filaments, *Composites Science and Technology* 150, 2017, 79-86.
17. Baochun Wang, Jose Guillermo Torres-Rendon, Jinchao Yu, Yumei Zhang, and Andreas Walther. Aligned Bioinspired Cellulose Nanocrystal-Based Nanocomposites with Synergetic Mechanical Properties and Improved Hygromechanical Performance. *ACS Appl. Mater. Interfaces*, 2015, 7 (8), pp 4595–4607.
18. Lihong Geng, Binyi Chen, Xiang Fang Peng, Tairong Kuang. Strength and modulus improvement of wet-spun cellulose I filaments by sequential physical and chemical cross-linking; *Materials & design* 136 2017.09.054.
19. Belén Alemañ, Víctor Reguero, Bartolomé Mas, and Juan J. Vilatela. Strong Carbon Nanotube Fibres by Drawing Inspiration from Polymer Fibre Spinning. *ACS Nano*, 2015; 9(7):7392-8.
20. Lauri K. J. Hauru, Michael Hummel, Anne Michud, Herbert Sixta; Dry jet-wet spinning of strong cellulose filaments from ionic liquid solution, Springer Netherlands, *Cellulose*, 2014, 20(6), pages 4471-4481.

Chapter 2

Literature Review

Among different bio renewable materials, cellulose is one of the most common natural polymers found in higher plants, algae, bacteria, fungi and marine animals. It is a linear polymer that consists of two glucose sugar units that are linked by β -1, 4 glycosidic linkage to form a dimer known as cellubiose[1, 2]. The length of cellulose chains can be very different due to the number of repeating units of glucose (from 20 to 10 000 or more), also called degree of polymerization or DP [3]. Several studies have shown that cellulose and its derivatives have a good biocompatibility and in addition, can be regarded as slowly degradable materials [4-8]. Due to its excellent mechanical and barrier properties, biocompatibility and low cost, cellulose is used in many biomedical applications, like orthopedic devices and tissue engineering [9-10] and is an excellent candidate for food packaging [12, 13].

Several studies have indicated that some herbal supplements contain phytochemicals that are able to prevent various relevant and wide-spread pathologies, including diabetes, cancer and autoimmune diseases [14-16]. Among these many studies have reported that curcumin, a polyphenol derived from *Curcuma longa*, commonly called turmeric, has excellent pharmacological properties like antimicrobial, antiviral, anti-inflammatory and anti-tumor activities [17, 18]. Previous studies on wound healing in diabetic rats as well as genetically diabetic mice have shown the efficacy of curcumin treatment both by the oral and topical application. There was an improved neovascularization, earlier re-epithelialization, increased migration of various cells including fibroblasts, and dermal myofibroblasts, when curcumin was used to treat the wounds of animals [3, 19]. Furthermore, curcumin has been widely used as an active component in the food industry to create new packaging films with antioxidant and antimicrobial activities [20, 21].

Ionic liquids (ILs) are a new class of benign solvents that can be liquid at room temperature (usually $T_{\text{melt}} < 100$ °C)[22]. Over the past 20 years, many studies have shown the countless properties of ionic liquids, in particular their low volatility that makes them benign solvents as compared to traditional volatile and aggressive solvents used for dissolving cellulose (Carbon disulphide, sulfuric acid etc.). ILs has good chemical and thermal stability, high ionic and thermal conductivity, high heat capacity and easy recyclability. All these properties can reduce many health and environmental related issues when ILs is used as solvents for the dissolutions of natural polymers like cellulose, lignin, starch and chitin [22-26]. There are several ILs that can directly dissolve cellulose upon heating, such as 1-allyl-3-methylimidazolium chloride (AMIM-Cl) and 1-ethyl-3-methylimidazolium acetate (EMIMAc) [25,27]. Furthermore, in recent years there has been a great interest of the international scientific community on ILs, used as pharmaceutical ingredients that can modify the pharmacokinetics and pharmacodynamics of drugs [28, 29].

Cellulose nanocrystals (CNCs), the novel, high-performance materials have been the subject of extensive research, during the last couple of decades. Depending on the source and the chemical treatment, CNCs can vary in surface chemistry, morphology, degree of crystallinity, crystal structure, and aspect ratio[30]. From previous studies[31-34]ⁱ, CNC aspect ratios have been measured to range from 148 ± 147 for tunicate-CNCs to 23 ± 12 for wood-CNCs. The Young's modulus of a single cellulose nanocrystal (CNC) has been estimated to be between 100 GPa to 160 GPa[35, 36, 39], which is significantly higher than modulus of glass fibres and is comparable to early generations of carbon fibres. This combination of renewability, low density, excellent mechanical properties and high aspect ratio makes CNCs ideal candidates for reinforcements in high performance fibres which are potential upgrades and replacements to heavy

glass fibres used in composite materials serving the automotive, aerospace, civil and sports industries.

A number of researchers have used CNCs to spin continuous fibres from aqueous suspensions of CNCs using hydrodynamic alignment[37], spinning and stretching of cellulose and chitin nanocrystals[38], CNC hydrogel stretching and spinning[39],as well as syringe spinning followed by high speed winding of CNC suspensions. These methods have yielded continuous fibres with good tensile moduli (12 GPa to 33GPa) and moderate tensile strengths (120 MPa to 300 MPa). However, these methods also result in highly porous structures containing voids that make it difficult to consolidate the fibres. More recently, researchers have spun CNC-reinforced polymer Nano-composite fibres with polyvinyl alcohol, polyacrylonitrile and cellulose acetate matrices. However, the polymer matrix used was either water soluble (polyvinyl alcohol), or had poor mechanical properties (cellulose acetate) or was derived from non-renewable resources (polyacrylonitrile) making it difficult to use them in for high performance composite applications.

Ionic liquids have emerged as excellent solvents to dissolve a wide range of cellulosic biomass such as wood chips, lignocellulose, pure cellulose etc.,[40, 41] and are found have a much lower environmental impact compared with the previous generation of solvents [38, 42]. In our previous work we have shown how ionic liquids solvents can be used to achieve uniform dispersion of carbon nanotubes[40]. Thus ionic liquids offer an excellent common medium to dissolve cellulose as well as disperse cellulose nanocrystal for seamless manufacturing of all cellulose composite where cellulose fibre matrix is reinforced with cellulose nanocrystals.

Here we marry the cellulose nanocrystals derived from tunicate nanocrystals with wood pulp cellulose using ionic liquids common solvent medium. With this approach, we report for the first time manufacturing of strong cellulose

fibres with very good combination of strength ranging from 410 to 660 MPa as well as modulus from 32 to 43 GPa depending fibre spinning conditions. We further carry out the carbonisation of the cellulose fibres to produce carbon fibre with very good mechanical properties (Strength 1.2GPa and modulus 97 GPa) which are superior than glass fibres currently used in automotive, sports and civil construction industries. The strong consolidated CNC reinforced cellulose nanocomposite fibres can be used to replace heavy glass fibres as well as can act as a renewable precursor to produce carbon fibres to replace the non-renewable PAN precursors. Our unique all cellulose nanocomposite fibre manufacturing method in the long run will allow replacing heavy glass fibres (which also take a very high energy to manufacture) and non-renewable precursors of carbon fibres to help make the composite industry more sustainable.

In biomedical applications and tissue engineering, there is need for soft polymers which show more compatibility with the soft tissue as compared to the stiff ones [43]. While taking this into account, cellulose is not only biocompatible and green, but also has advance applications while working under biological conditions[44, 45].

In view of its bio-applications, and to reap the benefits of a pharmacological drug, we have incorporated curcumin at different percentage by weight in a matrix of cellulose dissolved by ionic liquid to manufacture curcumin incorporated fibres. The focus of current work is to develop a simple but effective manufacturing method which will allow continuous manufacturing of strong cellulose/curcumin fibres. The strong cellulose/curcumin fibres thus obtained has the potential to be woven into bandages and to use in drug, food and cosmetic industry for various low cost affordable health care.

The initial part of the fibre manufacturing protocol for curcumin based fibres was developed by Marta Gina Coscia as a part of her short internship at

University of Bristol. The author has reproduced those fibres based on this protocol. The characterization (Reproduction of fibres using the previous protocol, SEM, Optical Microscopy, FTIR, X-ray diffraction, fibre orientation factor measurements and crystallinity Index) of the fibres was done by the author of this thesis.

References:

1. Eichhorn, S.J., et al., Review: current international research into cellulose nanofibres and nanocomposites. M. et al. *J Mater Sci*, 2010. **45**(1): p. 1-33.
2. Kontturi, E., T. Tammelin, and M. Österberg, Cellulose—model films and the fundamental approach. *Chemical Society Reviews*, 2006. **35**(12): p. 1287-1304.
3. Sidhu, G.S., et al., Enhancement of wound healing by curcumin in animals. *Wound Repair and Regeneration*, 1998. **6**(2): p. 167-177.
4. Martson, M., et al., Is cellulose sponge degradable or stable as implantation material? An in vivo subcutaneous study in the rat. *Biomaterials*, 1999. **20**(21): p. 1989-1995.
5. Granja, P., et al., Mineralization of regenerated cellulose hydrogels induced by human bone marrow stromal cells. *Eur Cell Mater*, 2005. **10**(1): p. 31-37.
6. Miyamoto, T., et al., Tissue biocompatibility of cellulose and its derivatives. *Journal of biomedical materials research*, 1989. **23**(1): p. 125-133.
7. Müller, F.A., et al., Cellulose-based scaffold materials for cartilage tissue engineering. *Biomaterials*, 2006. **27**(21): p. 3955-3963.
8. Czaja, W.K., et al., The future prospects of microbial cellulose in biomedical applications. *Biomacromolecules*, 2007. **8**(1): p. 1-12.

9. Poustis, J., C. Baquey, and D. Chauveaux, Mechanical properties of cellulose in orthopaedic devices and related environments. *Clinical Materials*, 1994. **16**(2): p. 119-124.
10. Granja, P.L., et al., Cellulose phosphates as biomaterials. Mineralization of chemically modified regenerated cellulose hydrogels. *J. Mater. Sci.*, 2001. **36**(9): p. 2163-2172.
11. Svensson, A., et al., Bacterial cellulose as a potential scaffold for tissue engineering of cartilage. *Biomaterials*, 2005. **26**(4): p. 419-431.
12. de Moura, M.R., L.H.C. Mattoso, and V. Zucolotto, Development of cellulose-based bactericidal nanocomposites containing silver nanoparticles and their use as active food packaging. *Journal of Food Engineering*, 2012. **109**(3): p. 520-524.
13. Imran, M., et al., Cellulose derivative based active coatings: Effects of nisin and plasticizer on physico-chemical and antimicrobial properties of hydroxypropyl methylcellulose films. *Carbohydr. Polym.*, 2010. **81**(2): p. 219-225.
14. Aggarwal, B.B., et al., Potential of spice-derived phytochemicals for cancer prevention. *Planta medica*, 2008. **74**(13): p. 1560.
15. Kaefer, C.M. and J.A. Milner, The role of herbs and spices in cancer prevention. *The Journal of Nutritional Biochemistry*, 2008. **19**(6): p. 347-361.
16. Mahmood, K., et al., Recent developments in curcumin and curcumin based polymeric materials for biomedical applications: A review. *International journal of biological macromolecules*, 2015. **81**: p. 877-890.
17. Ramsewak, R.S., D.L. DeWitt, and M.G. Nair, Cytotoxicity, antioxidant and anti-inflammatory activities of Curcumins I–III from *Curcuma longa*. *Phytomedicine*, 2000. **7**(4): p. 303-308.

18. Ruby, A.J., et al., Anti-tumour and antioxidant activity of natural curcuminoids. *Cancer Letters*, 1995. **94**(1): p. 79-83.
19. Sidhu, G.S., et al., Curcumin enhances wound healing in streptozotocin induced diabetic rats and genetically diabetic mice. *Wound Repair and Regeneration*, 1999. **7**(5): p. 362-374.
20. Sonkaew, P., A. Sane, and P. Suppakul, Antioxidant activities of curcumin and ascorbyl dipalmitate nanoparticles and their activities after incorporation into cellulose-based packaging films. *Journal of agricultural and food chemistry*, 2012. **60**(21): p. 5388-5399.
21. Vimala, K., et al., Fabrication of curcumin encapsulated chitosan-PVA silver nanocomposite films for improved antimicrobial activity. *Journal of Biomaterials and Nanobiotechnology*, 2011. **2**(01): p. 55.
22. Holbrey, J. and R. Rogers, *Ionic liquids in synthesis*. Wiley VCH Verlag GmbH and Co. KGaA, 2002.
23. Silva, S.S., et al., Green processing of porous chitin structures for biomedical applications combining ionic liquids and supercritical fluid technology. *Acta biomaterialia*, 2011. **7**(3): p. 1166-1172.
24. Pu, Y., N. Jiang, and A.J. Ragauskas, Ionic liquid as a green solvent for lignin. *Journal of Wood Chemistry and Technology*, 2007. **27**(1): p. 23-33.
25. Wu, R.-L., et al., Green composite films prepared from cellulose, starch and lignin in room-temperature ionic liquid. *Bioresource Technology*, 2009. **100**(9): p. 2569-2574.
26. Wang, H., G. Gurau, and R.D. Rogers, Ionic liquid processing of cellulose. *Chemical Society Reviews*, 2012. **41**(4): p. 1519-1537.
27. Haward, S.J., et al., Shear and extensional rheology of cellulose/ionic liquid solutions. *Biomacromolecules*, 2012. **13**(5): p. 1688-1699.

28. Stoimenovski, J., et al., Crystalline vs. Ionic Liquid Salt Forms of Active Pharmaceutical Ingredients: A Position Paper. *Pharmaceutical Research*, 2010. **27**(4): p. 521-526.
29. Moniruzzaman, M., et al., Ionic liquid-assisted transdermal delivery of sparingly soluble drugs. *Chem. Commun.*, 2010. **46**(9): p. 1452-1454.
30. Habibi, Y.; Lucia, L. A.; Rojas, O. J., Cellulose nanocrystals: chemistry, self-assembly, and applications. *Chem Rev* **2010**,110 (6), 3479-500.
31. Azizi Samir MAS, A. F., Dufresne A. , Review of Recent Research into Cellulosic Whiskers, Their Properties and Their Application in Nanocomposite Field. *Biomacro-molecules* **2005**,6, 612-626.
32. Eichhorn, S. J., Cellulose nanowhiskers: promising materials for advanced applications. *Soft Matter* **2011**,7 (2), 303-315.
33. Sturcová A1, D. G., Eichhorn SJ., Elastic modulus and stress-transfer properties of tunicate cellulose whiskers. *Biomacromolecules* **2005**,6(2) (2005 Mar-Apr), 1055-61.
34. Iulia A. Sacui, R. C. N., Daniel J. Burnett, Steph-an J. Stranick, Mehdi Jorfi, Christoph Weder, E. Johan Foster, Rich-ard T. Olsson, and Jeffery W. Gilman, Comparison of the Properties of Cellulose Nanocrystals and Cellulose Nanofibrils Isolated from Bacteria, Tunicate, and Wood Processed Using Acid, Enzymatic, Mechanical, and Oxidative Methods. *ACS Appl. Mater. Interfaces* **2014**,6, 6127–6138.
35. István Siró, D. P., Microfibrillated cellulose and new nanocomposite materials: a review. *Cellulose* **2010**,17 (3), 459-494.
36. Won Jun Lee†, A. J. C., Eero Kontturi‡§||, Alexander Bismarck§||, and Milo S. P. Shaffer*†, Strong and Stiff: High-Performance Cellulose Nanocrystal/Poly(vinyl alcohol) Composite Fibres. *ACS Appl. Mater. Interfaces* **2016**,8 (46), 31500–31504.

37. Karl M. O. Håkansson, A. B. F., Fredrik Lundell, Shun Yu, Christina Krywka, Stephan V. Roth, Gonzalo Santoro, Mathias Kwick, Lisa Prahl Wittberg, Lars Wågberg & L. Daniel Söderberg, , Hydrodynamic alignment and assembly of nanofibrils resulting in strong cellulose filaments. *Nature Communications*, Article number: 4018 (2014) 5.
38. Jose Guillermo Torres-Rendon, F. H. S., Shinsuke Ifuku‡, and Andreas Walther*, Mechanical Performance of Macrofibres of Cellulose and Chitin Nanofibrils Aligned by Wet-Stretching: A Critical Comparison. *ACS Biomacromolecules* **2014**,15 (7) (June 20, 2014), 2709–2717.
39. Meri J. Lundahl, A. G. C., Ester Rojo, Anastassios C. Papageorgiou, Lauri Rautkari, Julio C. Arboleda, and Orlando J. Rojas, Strength and Water Interactions of Cellulose I Filaments Wet-Spun from Cellulose Nanofibril Hydrogels. *Sci Rep.* **2016**,6, 30695.
40. Sameer S. Rahatekar, A. R., Rahul Jain, Mauro Zammarano, Krzysztof K. Koziol, Alan H. Windle, Jeffrey W. Gilman, Satish Kumar, Solution spinning of cellulose carbon nanotube composites using room temperature ionic liquids. *Elsevier Polymer* **2009**,50 (19), 4577–4583.
41. Sixta, L. K. J. H. H. M., Dry jet-wet spinning of strong cellulose filaments from ionic liquid solution. *Cellulose Fibres: Bio and Nano-Polymer Composites.* **2014**,21 (6), 4471–4481.
42. Northolt, M. G.; Boerstoel, H.; Maatman, H.; Huisman, R.; Veurink, J.; Elzerman, H., The structure and properties of cellulose fibres spun from an anisotropic phosphoric acid solution. *Polymer* **2001**,42 (19), 8249-8264.
43. Foster, S.M.C.R.M.J.G.P.E.J., Mechanically switchable polymer fibres for sensing in biological conditions. *J. Biomed. Opt.*, 22(2), 027001 (2017).
44. Rramaswamy Ravikumar, M.G., Udumansha Ubaidulla, Eun Young Choi, Hyun Tae Jang, Preparation, characterization, and in vitro diffusion

MSc. R. Aerospace Engineering

study of nonwoven electrospun nanofibre of curcumin-loaded cellulose acetate phthalate polymer. Saudi Pharm J, 2017 Sep; 25(6): 921–926.

45. Norhidayu Zainuddin, I.A., Hanieh Kargarzadeh, Suria Ramli, Hydrophobic kenaf nanocrystalline cellulose for the binding of curcumin. Carbohydrate Polymers, 2017. **163**: p. 261-269.

Chapter 3

Experimental

3.1 Materials

3.1.2 Cellulose

The cellulose used in this project was purchased in the form of pulp sheets with degree of polymerization (DP) of 890, manufactured by an American company-Rayonier in Jacksonville.

3.1.3 Cellulose Nano-Crystals

The freeze dried Cellulose Nan- Crystals were obtained from Maine University.

3.1.4 Ionic liquids

Ionic liquids are a salt in which the cations and anions are large and asymmetrical, meaning the ions cannot pack closely together and will remain liquid while still having the properties of a salt. One useful property of ionic liquids is that they do not evaporate like typical solvents; this is caused by a number of strong columbic interactions acting between the ions in the structure. Furthermore, ionic liquids can dissolve a large number of chemicals and materials because of these free moving ions that make up its structure.

1-Ethyl-3-methylimidazolium diethyl phosphate $\geq 98.0\%$: EMIM DEP was chosen as the solvent for cellulose in this study because upon the addition of EMIM DEP, the hydroxyl hydrogen atoms from the dispersed cellulose form strong hydrogen bond associations with the phosphate anion of EMIM DEP, this is effectively makes the hydroxyl groups unavailable for inter- and intra-hydrogen bonds in cellulose. This is very important as it means the fibres produced cannot bundle up into a larger structure, for example, a micro fibril.

The experimental procedure follows the method established by Dr. Sameer Rahatekar's group at University of Bristol previously [1]. The process was modified by dispersing Nano particles and by altering the spinning parameters in order to optimize the fibres properties. The fibres mechanical testing and

characterization follows the ASTM standards of single fibre testing for the composite fibres.

3.2 Methods

Using hotplate magnetic stirrer, 4% DP890 was dissolved slowly in EMIM DEP at 80 degrees with constant stirring for 6 hours. The degassing of solution was done for (12-16) hours before spinning.

3.2.1 4% DP890 fibre spinning

Using the syringe pump the 4% DP890 solution was spun at room temperature with water bath acting as the coagulation bath. The winding speed was controlled by a voltage controller.

3.2.2 4% DP890 Fibre Stretching

The fibres were wet stretched under water manually up to 40% of its originally length as demonstrated in the below figure 9.

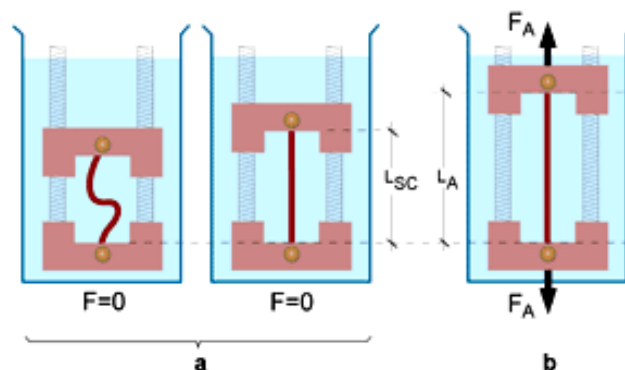


Figure 9: Wet fibre stretching Demonstration. [2]

F = Force under no load.

F_A = Force under tension.

3.3 Characterization of fibres

3.3.1 Scanning electron microscopy

TM3030 Plus Scanning Electron Microscope, was used for measuring the fibre diameter and for its characterisation.

Scanning electron microscopy (SEM) was performed on stretched and un-stretched fibres in order to observe the diameters of the fibres. The SEM images were taken and were evaluated using Image j software in order to measure the diameter.

The diameter of the un-stretched fibres was measured as ~ **21um**

The diameter of the stretched fibres was ~ **16 um**.

3.3.2 Fourier Transform Infrared Spectroscopy (FTIR):

To confirm that EMIM DEP was completely removed from the cellulose fibres, FTIR was performed using Parking Elmer Fourier Transform Infrared Spectroscopy testing machine

3.3.3 Mechanical properties

This set of testing took place so that the stress-strain behaviors of the fibres could be understood. It was ensured that all the samples that were tested were prepared in the exact same method as shown in figure 10, so that they could prevent any damage to the samples prior to testing.

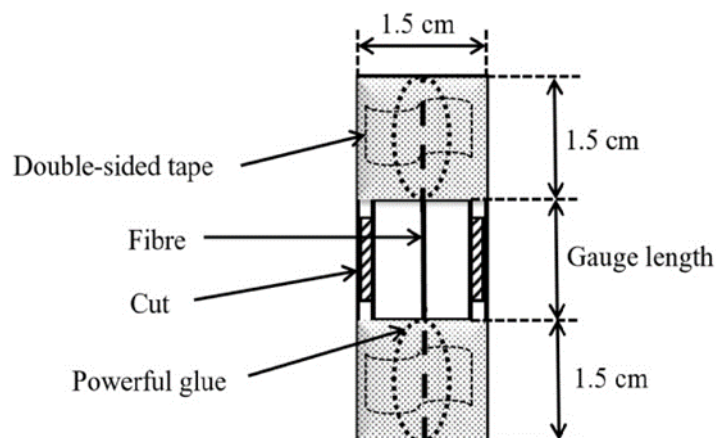


Figure 10: Design of a tensile sample with one fibre filament between two plastic tabs held on a frame. [3]

The fibres were mounted on plastic tabs with gauge length of 2mm. UV curing adhesive glue was used to fix the sample ends. The glue was cured for 30 mins before testing.

Dia-Stron Ltd. (Andover, UK) was used to perform the tensile testing of the fibres at 25 °C, using 20N load cell under a constant deformation rate of 2 mm/min. The gauge length of the fibres was taken as 2cm. The ultimate tensile strength and strain were determined at the breaking point of the fibres. The Young's modulus was calculated from the slope of the linear portion of the stress–strain curve before the yield point.

The mechanical properties of the stretched and un-stretched fibres as tested are shown in table 2. E.g., ‘266MPa’ is the average tensile strength of the un-stretched cellulose fibres taken by testing 10 successful fibre test trials; ‘(±85)’ indicates the standard deviation from the 10 tested samples.

Fibres Type	Tensile Strength (MPa)	Young's Modulus (GPa)	Strain (mm/mm)
4% DP 890 Un-stretched Fibres	266.3 (±85)	17.6 (±4.2)	5.6 (±1.2)
4% DP 890 Stretched Fibres	308 (±48)	20.4 (±2.3)	3.8 (±0.8)

Table 2: Mechanical Properties of Stretched and un-stretched 4%DP890 fibres.

3.4 Summary

As we can clearly see the diameter of the fibres decreased with stretching. Decreased diameter represents the high alignment and more closely packed molecules. Hence, the improved mechanical properties. The mechanical properties results stated above justify this statement, where the tensile strength improved by ~40MPa and the stiffness value improved by 3GPa. This is due to the fact that the atoms are closely packed up to its maximum possible stable stretch and hence formed a crystalline phase. Hence, there is a drop in the strain value of the fibre at the breaking point.

This chapter gives a brief introduction of the characterization of the fibres. The mechanical properties and characterization of the fibres are discussed in detail in the next chapter.

3.5 Reference:

1. Sameer S.Rahatekar, Asif Rasheed, Rahul Jain, Mauro Zammarano, Krzysztof K.Koziol, Alan H.Windle, Jeffrey W.Gilman, Satish Kumar; Deformation mechanisms in ionic liquid spun cellulose fibers; <https://doi.org/10.1016/j.polymer.2016.07.007>; Volume 99, 2 September 2016, Pages 222-230.
2. <http://www.tms.org/pubs/journals/JOM/0502/Fig6a.large.gif>
3. HANS-GEORG ELIAS, Mega Molecules, Springer link (1987)

Chapter 4

Marrying Cellulose Nanocrystals with Wood Pulp Cellulose to Manufacture High Modulus Cellulose Nanocomposite Fibres

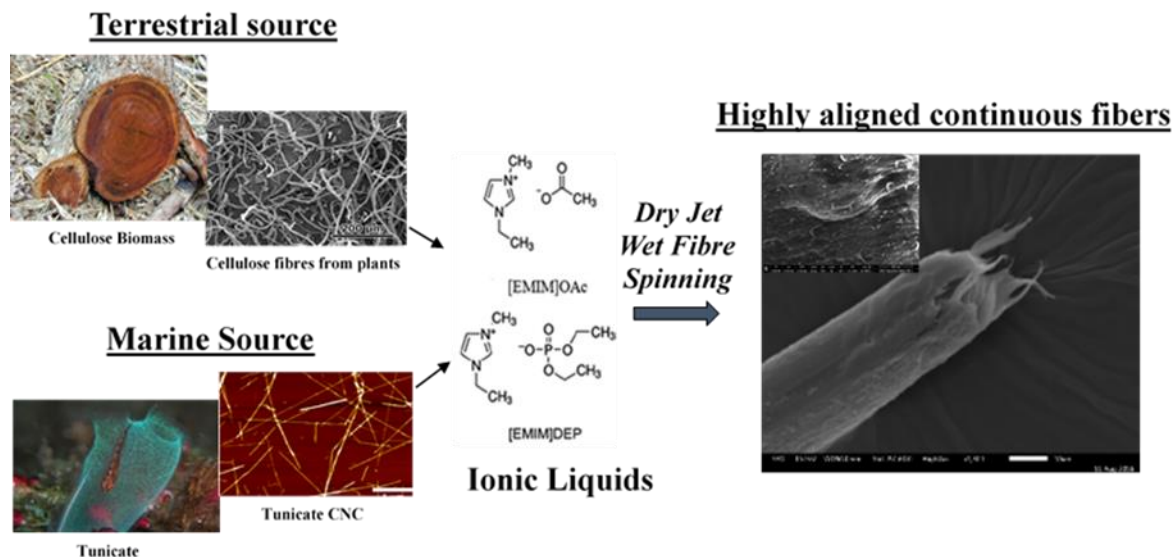


Figure 11: Graphical representation of the spinning process.

4.1 Introduction:

Cellulose nanocrystals (CNCs), the novel, high-performance materials have been the subject of extensive research, during the last couple of decades. Depending on the source and the chemical treatment, CNCs can vary in surface chemistry, morphology, degree of crystallinity, crystal structure, and aspect ratio[1]. From previous studies[2-5]ⁱⁱ, CNC aspect ratios have been measured to range from 148 ± 147 for tunicate-CNCs to 23 ± 12 for wood-CNCs. The Young's modulus of a single cellulose nanocrystal (CNC) has been estimated to be between 100 GPa to 160 GPa[6, 7, 10], which is significantly higher than modulus of glass fibres and is comparable to early generations of carbon fibres. This combination of renewability, low density, excellent mechanical properties and high aspect ratio makes CNCs ideal candidates for reinforcements in high performance fibres which are potential upgrades and replacements to heavy glass fibres used in composite materials serving the automotive, aerospace, civil and sports industries.

A number of researchers have used CNCs to spin continuous fibres from aqueous suspensions of CNCs using hydrodynamic alignment[8], spinning and stretching of cellulose and chitin nanocrystals[9], CNC hydrogel stretching and spinning[10],as well as syringe spinning followed by high speed winding of CNC suspensions. These methods have yielded continuous fibres with good tensile moduli (12 GPa to 33GPa) and moderate tensile strengths (120 MPa to 300 MPa). However, these methods also result in highly porous structures containing voids that make it difficult to consolidate the fibres. More recently, researchers have spun CNC-reinforced polymer Nano-composite fibres with polyvinyl alcohol, polyacrylonitrile and cellulose acetate matrices. However, the polymer matrix used was either water soluble (polyvinyl alcohol), or had poor mechanical properties (cellulose acetate) or was derived from non-renewable resources (polyacrylonitrile) making it difficult to use them in for high performance composite applications.

Ionic liquids have emerged as excellent solvents to dissolve a wide range of cellulosic biomass such as wood chips, lignocellulose, pure cellulose etc.,[11, 12] and are found have a much lower environmental impact compared with the previous generation of solvents [9, 13]. In the previous work done by DR Sameer Rahatekar, they have shown how ionic liquids solvents can be used to achieve uniform dispersion of carbon nanotubes[11]. Thus ionic liquids offer an excellent common medium to dissolve cellulose as well as disperse cellulose nanocrystal for seamless manufacturing of all cellulose composite where cellulose fibre matrix is reinforced with cellulose nanocrystals.

Here we marry the cellulose nanocrystals derived from tunicate nanocrystals with wood pulp cellulose using ionic liquids common solvent medium. With this approach, we report for the first time manufacturing of strong cellulose fibres with very good combination of strength ranging from 410 to 660 MPa as well as modulus from 32 to 43 GPa depending fibre spinning conditions. We

further carry out the carbonisation of the cellulose fibres to produce carbon fibre with very good mechanical properties (Strength 1.2GPa and modulus 97 GPa) which are superior than glass fibres currently used in automotive, sports and civil construction industries. The strong consolidated CNC reinforced cellulose nanocomposite fibres can be used to replace heavy glass fibres as well as can act as a renewable precursor to produce carbon fibres to replace the non-renewable PAN precursors. Our unique all cellulose nanocomposite fibre manufacturing method in the long run will allow replacing heavy glass fibres (which also take a very high energy to manufacture) and non-renewable precursors of carbon fibres to help make the composite industry more sustainable.

4.2 Experimental Section

4.2.1 Materials

Cellulose pulp sheets with a degree of polymerization (DP) of 890 were obtained from Rayonier (Jacksonville, US). Cellulose nanocrystals were obtained for Maine University and KTH. Ionic liquid 1-ethyl-3-methylimidazolium diethyl phosphate (EMIM DEP, >98%), used here as a solvent, was obtained from Sigma Aldrich. Silverson L5M high shear mixer and VCX-750 Sonicator were used to prepare the cellulose nanocrystals suspension. IKA magnetic stirrer hotplates were used to prepare the cellulose solution. A gear pump (model: Nexus 6000) purchased from KR Analytical Ltd. was used to extrude the solution from the syringe. 60ml three-part plastic syringes with luer-lock and BD 23G grade needles were used to spin the fibres. A voltage controller was used to control the winding speed of fibres.

4.2.2 Preparation of Cellulose Nanocrystals suspension

The aqueous CNC suspension was freeze dried to remove the water overnight for 48 hours. The new CNC suspension in ionic liquid was prepared by mechanical homogenization of the freeze-dried pulp and was slowly diluted. A

ceramic mortar and pestle was used for mechanical homogenization followed by high shear mixing, followed by pulse sonication.

4.2.3 Cellulose Dope Preparation

Two types of solutions were prepared:

4.2.3.1 Neat cellulose: cellulose pulp derived from wood was dissolved in EMIM DEP to achieve the required mass solution by heating at 90° C with constant stirring for 4 hours.

4.2.3.2 Cellulose Solution with nanocrystals dispersion: First, the desired amount of the CNC was dispersed in EMIM DEP using a combination of high shear mixing and sonication. Wood pulp cellulose was added slowly with constant stirring at 100rpm. The solution was kept at 90° C while mixing for 4 hours.

This solution was further transferred to a 60ml three-part BD plastic syringe with luer-lock and was kept in vacuum oven for 12 hours to 24 hours at 60°C to remove air bubbles.

4.2.4 Fibre Preparation

Continuous cellulose microfibrils were prepared by dry jet wet fibre spinning, as shown in figure 12. The cellulose solution was extruded using a syringe pump with piston speed of 33.3mm/s. An air gap of 3cm between the needle and water bath was maintained. The fibres were wound at the downstream end using a winding speed of 200mm/s. After the initial winding and coagulation of the fibres they were kept in water for two days for complete removal of the ionic liquid. The fibres were dried at room temperature for two days making sure there is no moisture content and were stored until tested.

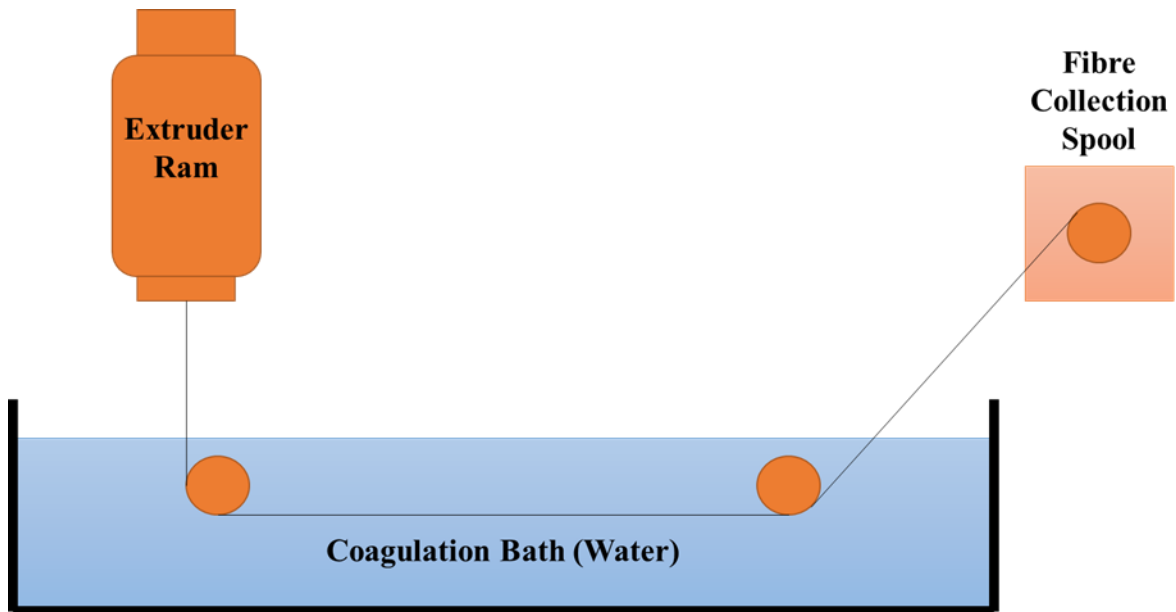


Figure 12: Dry Jet Wet Spinning System.

While still maintaining the stability and continuity of the fibres, the spinning was slowly accelerated to test the maximum achievable winding speed. The final fibres were spun at the two most stable winding speeds of 600.4mm/s and 750mm/s, keeping the extrusion speed constant at 91.83mm/s.

The final fibres were spun at 750 mm/s were taken under consideration for further characterization.

4.2.5 Fibres Characterization

4.2.5.1 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was used to study the fractured cross-section of the fibres broken under tension as well as to measure the diameters of

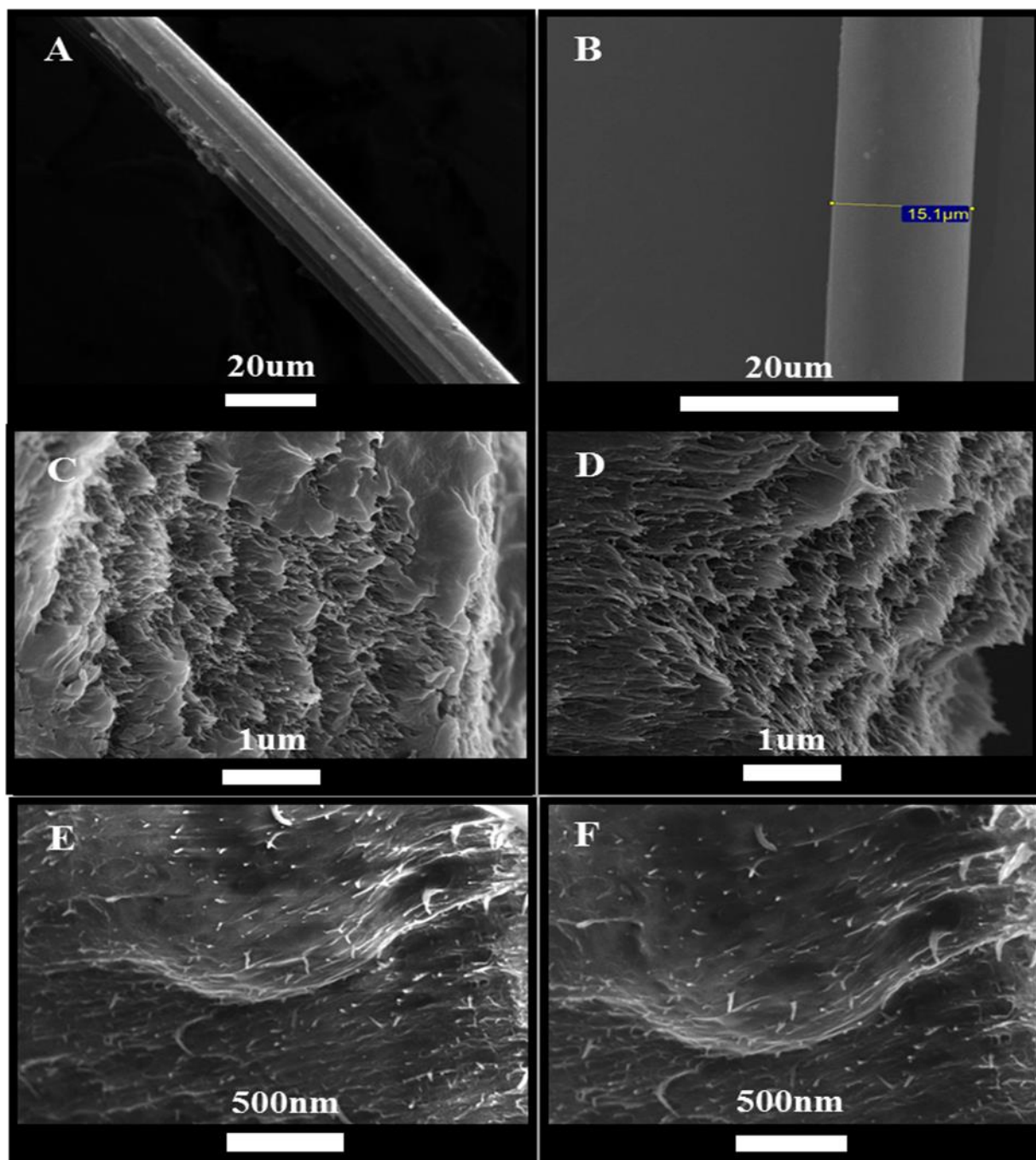


Figure 13: A, B: The SEM images of neat cellulose fibres(A) and cellulose fibres dispersed with CNC (B).

C and D shows the pulled cross-section of the Cellulose fibres and Cellulose fibres with Tunicate Cellulose Nano Crystals respectively from the surface under tensile load.

E and F are the high-resolution SEM images for the fibres cross-section taken at different angle.

measured for 7 fibres of each type. The average diameter and standard deviation (SD) of each fibre sample were calculated based on results from twenty measurements. The measurements were taken as found using Image J software, as shown in figure 13. The sample cross-sections were coated with 1-2 nm layer of gold-palladium to render them conductive. The sample was then imaged at 5 kV in a scanning electron microscopy (SEM) using a high-performance ion conversion and electron detector to investigate the dispersion of CNCs. Focused Ion Beam milling was employed to prepare electron transparent transmission electron microscopy (TEM) samples. TEM imaging was done at 300kV, with a 10-micron objective aperture using a 10eV wide energy filter centered at zero loss. This imaging was done in order to study the possible orientation of the CNC dispersion in the polymer matrix and on the surface of the filaments as shown in Figure 13.

4.2.5.2 Mechanical Testing

The Dia-Stron Ltd. (Andover, UK) was used to perform the single fibre tensile tests at 25 °C. A 20N load cell under a constant deformation rate of 2 mm/min was used. 20 samples of gauge length = 2 cm were tested. Each sample was glued to a tab to reduce the influence of clamping. The stress–strain curve for each fibre was obtained considering the mean cross-sectional area of the fibres as measured by SEM. The ultimate tensile strength and strain were determined at the fibre breaking point from the observations. The Young’s modulus was taken as the slope of the linear fitted curve of the stress–strain graph before the yield point indicating the stiffness of the fibres.

4.2.5.3 Fourier transform infrared (FTIR) Spectroscopy

In order to investigate the presence of residual EMIM DEP in the fibres after the water bath, Fourier transform infrared (FTIR) spectroscopy was performed on a PerkinElmer Spectrum 100 instrument. The resolution was set at 4 cm⁻¹ and the measurements were made from 4000 cm⁻¹ to 600 cm⁻¹ in transmittance mode.

4.2.5.4 2D Wide Angle X-ray Diffraction

The SAXSLAB GANESHA 300 XL SAXS system was used in order to study the alignment of the fibres. Four fibres of each type were mounted straight on the sample holder, placed on a sample stage between the X-ray and the two-dimensional detector. Each fibre was exposed for around 8 hours to the Cu K α radiation with a wavelength of 0.154 nm in a vacuum chamber to obtain the Wide-Angle X-ray Diffraction patterns for single fibre filaments. The sample-to-detector distance was kept at 100 mm. The beam size and beam stop were 0.8 mm and 2 mm, respectively. IDL and SAXSGUI software were used for data reduction and analysis. XRD spectra and images of pure cellulose fibres and those with CNC reinforcements was obtained.

4.3 Results

4.3.1 Scanning Electron Microscopy

The diameters of the neat cellulose and tunicate CNC reinforced fibres were found to be **21.9 $\mu\text{m} \pm 0.22 \mu\text{m}$ and 15.2 $\mu\text{m} \pm 0.73 \mu\text{m}$** , respectively. The diameter of the fibres with and without CNC varied between 21 μm to 15 μm when the winding speed was increased from 600 mm/s to 750 mm/s respectively and spinning temperature around 40 - 50 °C.

The Figure 13C and 13D shows the fracture behavior of the fibre under tension. It can be seen that unlike neat cellulose fibres, the fibres with CNC dispersion show long pulled fibrils at cross-section indicating the presence of high aspect ratio Nano cellulose crystals.

4.3.2 Mechanical Properties

The ultimate tensile strength and Young's modulus of the spun fibres are shown in Table 3. It was found that the tensile strength of the fibres increased significantly from ~276 MPa to ~660 MPa when reinforced with CNCs and the Young's modulus increased from ~21 GPa to ~43 GPa. Although there was a

drop in the strain value of cellulose fibres on addition of CNC due to the low strain range for the CNC, hence decreasing the ductility. “Based on a rule of mixture-based micromechanical model, usually implemented for short-fibre composites [16], the modulus of the CNC was estimated to be **~131.7 GPa**(considering the cellulose density = 1.64g/cm³ and the CNC density = 1.37 g/cm³ [14, 15]) as below which is close to the most commonly measured value of about **120 ~ 150 GPa** [16].

Fibres	Tensile Strength MPa	Young's Modulus GPa	Strain (%)
Cellulose Fibres	276 (±10.7)	21 (±1.2)	5 (±0.5)
Cellulose Fibres with CNC	630 (±35.5)	43 (±1.7)	4 (±0.5)
Carbonized Cellulose Fibres	~1000-1200	~97	~2.5

Table 3: Mechanical Properties comparison between current cellulose fibres with CNC before and after carbonisation with wood, silk, glass and carbon fibres.

$$E_1 = E_{cnc}V_{cnc} + E_{dp890}V_{dp890}43 \text{ GPa} = E_{cnc} * 0.199 + 21$$

$$E_{cnc} = 131.66 \text{ GPa}$$

4.3.3 FTIR Spectroscopy

The samples of cellulose fibres, neat cellulose and EMIM DEP were observed under FTIR in order to study the complete removal of ionic liquid from the fibres. The figure 14 shows the comparisons of the FTIR spectrum of the cellulose fibres to the ones obtained from EMIM DEP and neat cellulose.

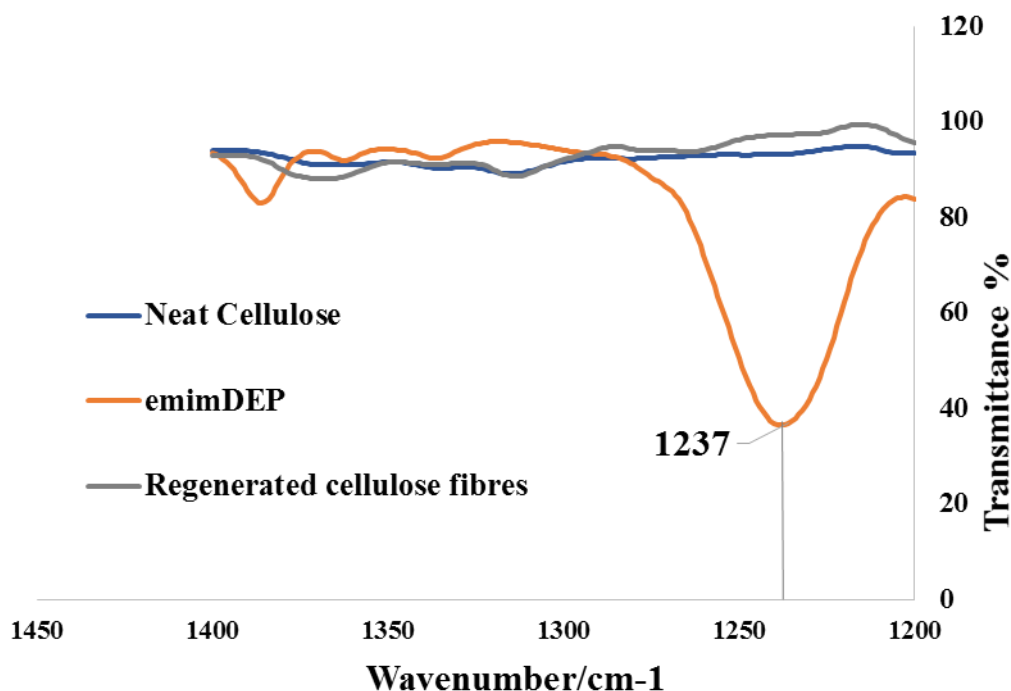


Figure 14: FTIR spectrum for cellulose fibres, neat cellulose and EMIM DEP confirming complete removal of ionic liquid.

From Figure 14, The absence of the peaks corresponding to the C=N (1575 cm^{-1}) [9] and P=O (1250 cm^{-1}) [17-19][18], represents the near complete removal of EMIM DEP. The typical excitations of cellulose C-H ring vibrations (896 cm^{-1}) and C-O-C pyranose ring skeletal vibration (1160 cm^{-1}) [20, 21] can be observed which indicates the presence of the neat cellulose and cellulose fibres.

4.3.4 Wide Angle X-ray Diffraction of the fibres

The XRD diffractogram of the cellulose fibres with and without CNC are shown in Figure 15A and 15B. The Bragg peaks shown in the figure reflect the cellulose II structure, thereby confirming the crystallinity pattern of the

regenerated cellulose after dissolution [11, 22, 23]. There are secondary Bragg peaks at 20.4° and 22.1° (corresponding to lattice planes (110) and (020), respectively) and three short and broad shoulders around 12.8° , 15.5° and 33.1° (lattice plane (110), (200) and (004), respectively), assigned to the diffraction of cellulose I. [16]

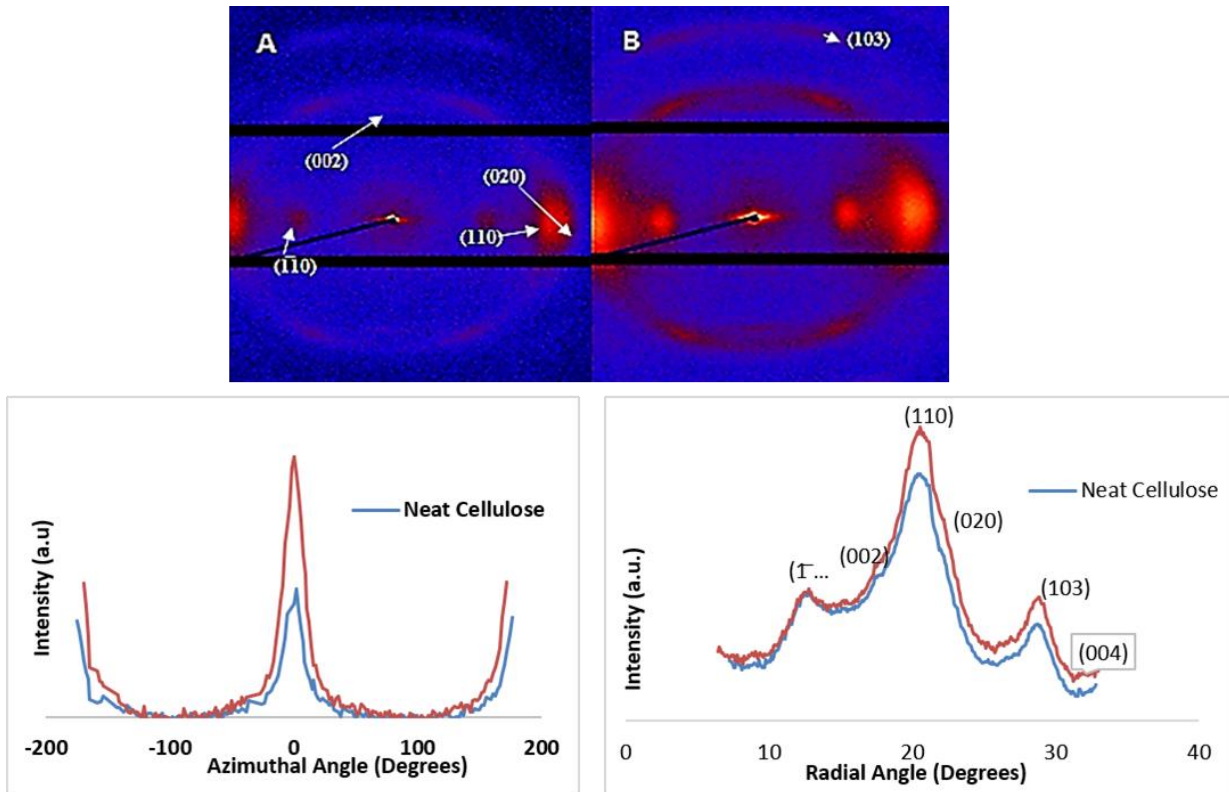


Figure 15: W-XRD diffraction pattern for two type of fibres- Neat Cellulose (A) and Neat Cellulose with Tunicate CNC (B).

The radial scanning data and Azimuthal scanning data is shown in above figure 15. The Azimuthal scanning data was used to find the cellulose fibres crystal alignment. Orientation Factor P2 Average = 0.85 and 0.81 indicates the high alignment in the Fibres.

The crystallinity index of the cellulose fibres was calculated to be ~65% which is similar to [11] and [24], based on the Segal's method, which gives a relative measure of the crystallinity [16].

$$\text{CrI (\%)} = \frac{I_{\text{total}} - I_{\text{am}}}{I_{\text{total}}} \times 100 = \frac{68.21 - 23.45}{68.21} \times 100 = 65.62\%$$

Where, I_{002} = peak intensities of crystalline region. And I_{am} = Peak intensity for the amorphous region.

In order to characterize the cellulose crystallite orientation in our fibres, the orientation factor 'f' is determined from the scattering data for each fibre as;

$$f = \langle P_2(\cos \theta) \rangle = \frac{(3 \langle \cos^2 \theta \rangle - 1)}{2} = (-2) \frac{\int_0^\pi \rho(\phi) P_2(\cos \phi) \sin \phi d\phi}{\int_0^\pi \rho(\phi) \sin \phi d\phi}$$

Here,

P_2 is the second order Legendre function. θ is the average polar disorientation angle of a crystallite with respect to the fibre axis. ϕ is the azimuthal angle of the scattering in the diffraction pattern. $f = -0.5$ and $f = 1$, indicates the perfect orientation of cellulose crystallites would have perpendicular and parallel to the fibre axis respectively. [1, 9, 25-27]. Using the intensity spectra shown in Figure 6, the orientation parameter was calculated by the Davidson method and was found to be 0.85 and 0.81 for the neat cellulose and cellulose with reinforcements, respectively, representing high alignment of cellulose chains in the polymer.

4.4 Discussions

4.4.1 Wet Spinning of Cellulose Fibres

The shear thinning behavior was observed while preparing the CNC suspension in ionic liquid which has been found in previous studies also [28]. Hence increasing the tendency to increase the cellulose percentage in the solution. Also it's been proven in previous studies that with the increase in the fraction of cellulose nanocrystals, the strain tendency of the filaments decreases [14]. Hence,

in this case, the neat cellulose and CNC weight fraction ratio was kept around 7:3 in order to get the continuous fibres with maximum possible ductility.

The key challenge here was due to the air gap, to maintain the stability and continuity of the fibres, which was optimized by controlling extrusion rate, winding speed and the spinning temperature.

4.4.2 Structure and Morphology of the Spun Fibre

As from figure 17, fibres show the flexibility of the filaments after drying at the room temperature. The ductility of the fibres was studied from the SEM images of the fibres showing long pulled fibres at the cross-section. It was observed that the length of the pulled fibres increased when dispersed with CNC, which might be due to the high aspect ratio of the tunicate cellulose nanocrystals.

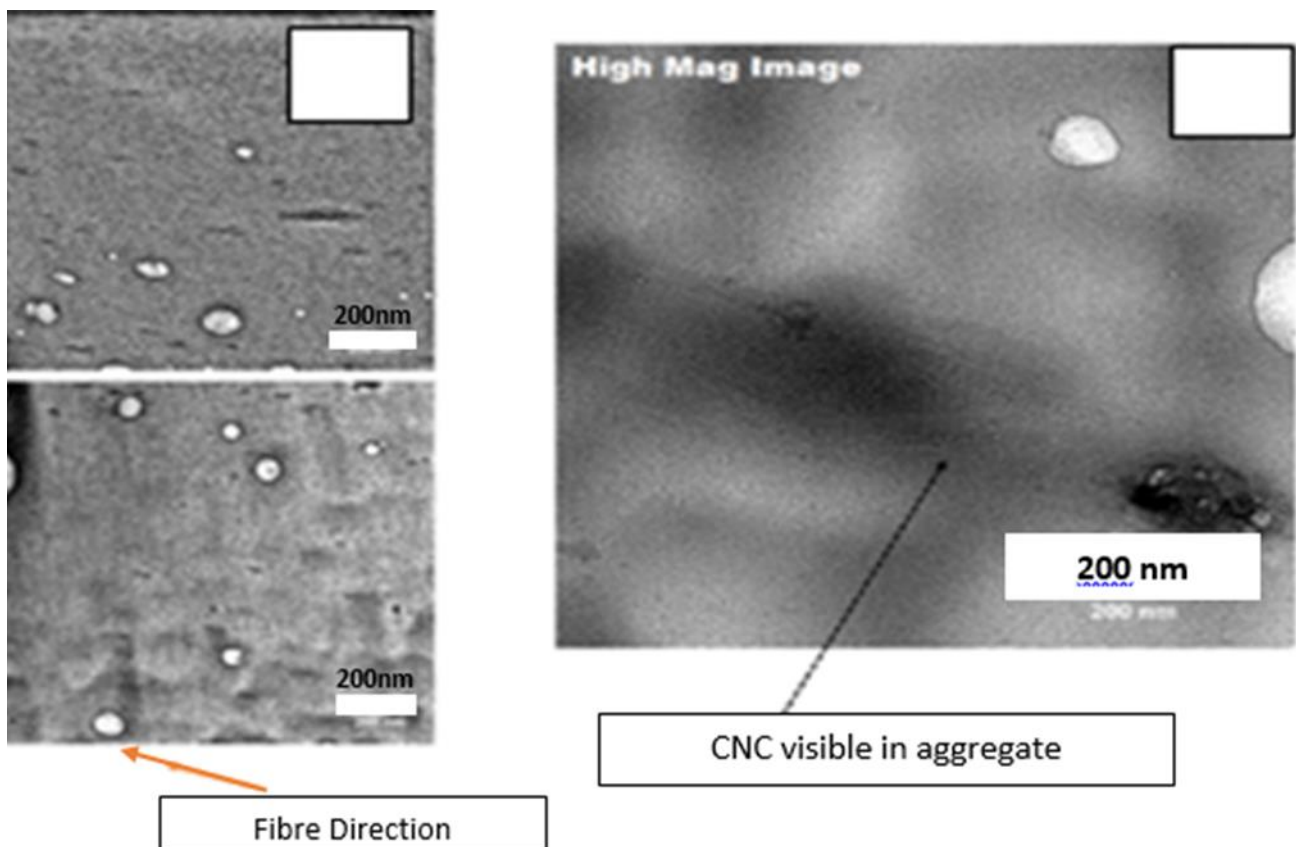


Figure 16: TEM images of cellulose fibres with Cellulose Nano-crystals, darker regions representing the presence of dispersed CNC in the amorphous cellulose matrix.

The high resolution SEM images show the CNCs sticking out from the surface. Further to investigate the CNC dispersion, the TEM imaging was done at zero loss filtering which enhances the contrast arising from the density variations. The crystalline CNCs are expectedly denser than a large amorphous cellulose matrix. No staining was done. The resulting images clearly show CNCs as a darker phase, well dispersed and distributed in light cellulose matrix as in figure 16. There are also some aggregates, but the morphology overall is well dispersed due to the matrix-filler compatibility. The CNCs appear to be aligned along the fibre axis and shows consistency in overall images.

4.4.3 Orientations and Mechanical Properties

The orientation parameter was calculated by using SaxsGui software and St. Davidson method. These fibres show a similar trend has been found in the previous studies [11, 14, 23]. A slight increase in the orientation parameter was observed with an increase in the spinning rate for the fibres.

According to the previous studies [16], “the increase in the speed rate will provide high shear force, subsequently increasing the alignment of the CNC in the fibre direction.”

The solvents used in this study are far better than what already have been done using the sulphuric acid and other harmful chemicals which are not very convenient and not easy to handle [9, 13]. The process implemented in this study is very conventional and has produced one of the best fibres with 43.2 GPa (± 1.7) stiffness. The stiffness and tensile strength of the Cellulose fibres with tunicate CNC were improved from 35 GPa to 43 GPa and 471 MPa to 660 MPa respectively by changing the winding speed and hence finer diameter and improved alignment. Figure 17 shows the stress strain curve of the fibres with and without tunicate cellulose nanocrystals.

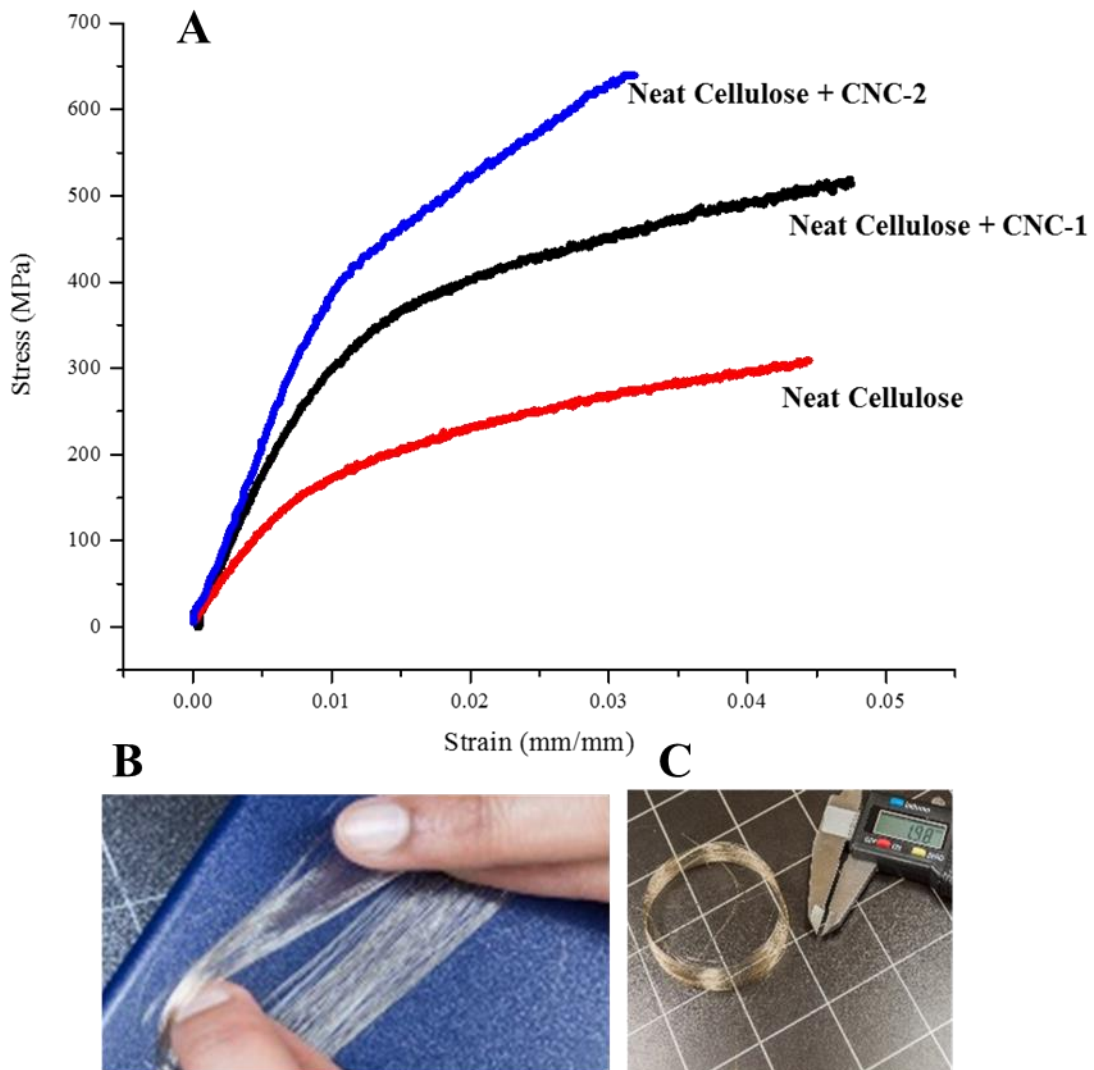


Figure 17: (A) Stress Strain curve for cellulose fibres obtained with neat cellulose with and without tunicate CNC dispersions.

B & C: showing the flexibility of the cellulose fibres bundle.

Here,

Neat Cellulose + CNC-1 = Fibres spun at lower winding speed.

Neat Cellulose + CNC-2 = Fibres spun at higher winding speed, hence more stretched.

It is clear from the figure 17 that the tensile strength and the tensile modulus of the fibres increased when CNC was dispersed in the cellulose matrix. Whereas,

on further stretching/drawing of CNC dispersed cellulose fibres shows improved tensile modulus but it also results in reduced strain range of the fibres, which is a critical mechanical behavior in the field of composites.

Figure 18 shows the mechanical properties comparison of the fibres manufactured in this report with the previous work done by Oksman-2015[14], Orlando J. Rojas-2016[10] and L. Daniel Soñderberg-2014[8] using the similar concentration of cellulose Nano-crystal and with Glass fibre type-E. From the Tensile Strength/Density vs Stiffness/Density graph, it is clear that the mechanical properties of current cellulose fibres reinforced with CNC are better than the previous work and the carbonized fibres show better Stiffness and similar tensile strength while compared with Glass fibres considering the fibres density. Current cellulose fibres show better young's modulus than what already have been achieved and with tensile strength in the range what already been achieved. The carbonized fibres show the similar trend when compared with Glass Fibres-E.

In recent studies by Sinan[29], where CNCs interaction with the cellulose matrix has been studied using a simulation model to improve the mechanical properties of the Nano paper. This model shows the relation between the mechanical properties of the CNC Nano paper and the increasing CNC overlap length and interfacial energy. It has been proven from the results of this study that the modulus and the strength both increases with increase in the overlap length of CNC. Hence, it supports our results from figure 17.

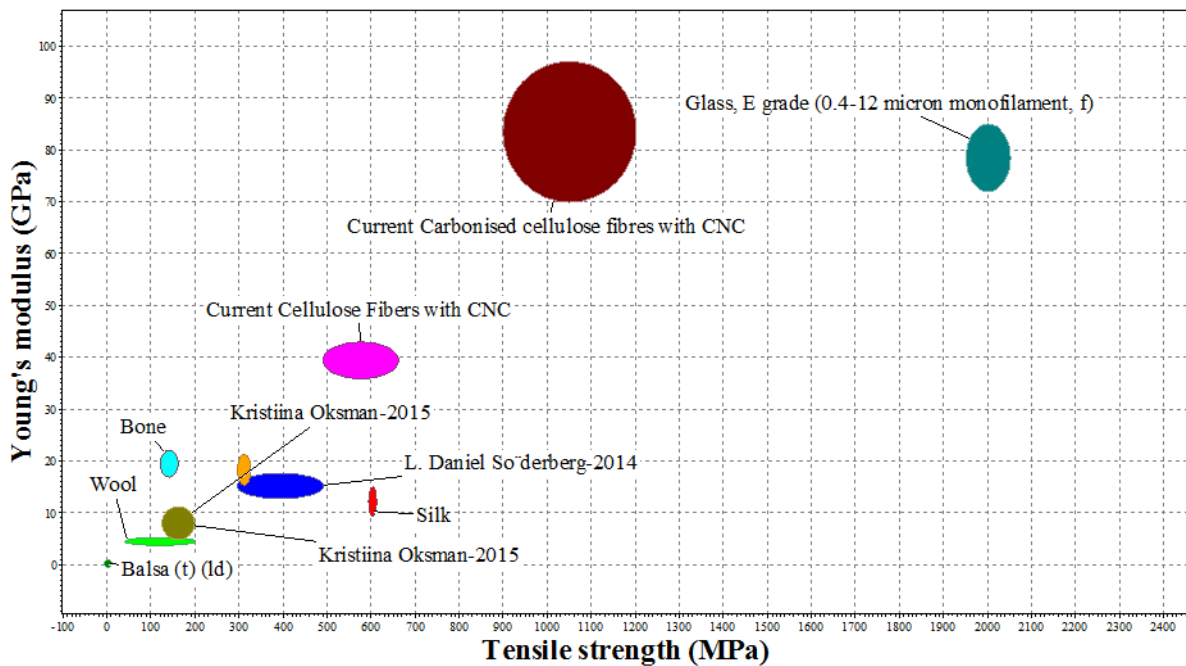


Figure 18: The mechanical properties comparison of the fibres manufactured in this report with the previous work.

4.5 Summary

We have been successful in manufacturing one of the highest modulus cellulose Nano-composite fibres using combination of wood pulp cellulose and tunicate derived cellulose nanocrystals. Ionic liquid namely Ethyl Methyl Diethyl phosphate was found to be very effective in dissolving the wood pulp cellulose as well as disperse the tunicate cellulose nanocrystals in the cellulose solution dope. The modulus of cellulose fibres spun from neat cellulose increased from 21 GPa to up to 43GPa due to addition of cellulose nanocrystals and varying winding speed(drawing). The SEM studies revealed that the cellulose nanocomposite fibres show protrusion of nanofibres which strongly indicates strong reinforcement due using tunicate nanocrystals. The X-ray diffraction studies indicated excellent alignment of cellulose chains along the fibre axis which can also explain good mechanical properties of the cellulose nanocomposite fibres. The specific modulus of cellulose nanocomposite fibres produced in this work exceeds to that of glass fibres. Hence our cellulose

nanocomposite fibres offer an excellent alternative to potentially replace heavy glass fibres for wide range of applications for renewable composite in automotive, sports and construction industries.

4.6 References

1. Habibi, Y.; Lucia, L. A.; Rojas, O. J., Cellulose nanocrystals: chemistry, self-assembly, and applications. *Chem Rev* **2010**,110 (6), 3479-500.
2. Azizi Samir MAS, A. F., Dufresne A. , Review of Recent Research into Cellulosic Whiskers, Their Properties and Their Application in Nanocomposite Field. *Biomacro-molecules* **2005**,6, 612-626.
3. Eichhorn, S. J., Cellulose nanowhiskers: promising materials for advanced applications. *Soft Matter* **2011**,7 (2), 303-315.
4. Sturcová A1, D. G., Eichhorn SJ., Elastic modulus and stress-transfer properties of tunicate cellulose whiskers. *Biomacromolecules* **2005**,6(2) (2005 Mar-Apr), 1055-61.
5. Iulia A. Sacui, R. C. N., Daniel J. Burnett, Steph-an J. Stranick, Mehdi Jorfi, Christoph Weder, E. Johan Foster, Rich-ard T. Olsson, and Jeffery W. Gilman, Comparison of the Properties of Cellulose Nanocrystals and Cellulose Nanofibrils Isolated from Bacteria, Tunicate, and Wood Processed Using Acid, Enzymatic, Mechanical, and Oxidative Methods. *ACS Appl. Mater. Interfaces* **2014**,6, 6127–6138.
6. István Siró, D. P., Microfibrillated cellulose and new nanocomposite materials: a review. *Cellulose* **2010**,17 (3), 459-494.
7. Won Jun Lee†, A. J. C., Eero Kontturi‡§||, Alexander Bismarck§||, and Milo S. P. Shaffer*†, Strong and Stiff: High-Performance Cellulose Nanocrystal/Poly(vinyl alcohol) Composite Fibres. *ACS Appl. Mater. Interfaces* **2016**,8 (46), 31500–31504.
8. Karl M. O. Håkansson, A. B. F., Fredrik Lundell, Shun Yu, Christina Krywka, Stephan V. Roth, Gonzalo Santoro, Mathias Kvik, Lisa Prahl

Wittberg, Lars Wågberg & L. Daniel Söderberg, , Hydrodynamic alignment and assembly of nanofibrils resulting in strong cellulose filaments. *Nature Communications* 5 **2014**, Article number: 4018 (02 June 2014).

9. Jose Guillermo Torres-Rendon, F. H. S., Shinsuke Ifuku‡, and Andreas Walther*, Mechanical Performance of Macrofibres of Cellulose and Chitin Nanofibrils Aligned by Wet-Stretching: A Critical Comparison. *ACS Biomacromolecules* **2014**,15 (7) (June 20, 2014), 2709–2717.

10. Meri J. Lundahl, A. G. C., Ester Rojo, Anastassios C. Papageorgiou, Lauri Rautkari, Julio C. Arboleda, and Orlando J. Rojas, Strength and Water Interactions of Cellulose I Filaments Wet-Spun from Cellulose Nanofibril Hydrogels. *Sci Rep.* **2016**,6, 30695.

11. Sameer S. Rahatekar, A. R., Rahul Jain, Mauro Zammarano, Krzysztof K. Koziol, Alan H. Windle, Jeffrey W. Gilman, Satish Kumar, Solution spinning of cellulose carbon nanotube composites using room temperature ionic liquids. *Elsevier Polymer* **2009**,50 (19), 4577–4583.

12. Sixta, L. K. J. H. H. M., Dry jet-wet spinning of strong cellulose filaments from ionic liquid solution. *Cellulose Fibres: Bio and Nano-Polymer Composites.* **2014**,21 (6), 4471–4481.

13. Northolt, M. G.; Boerstoel, H.; Maatman, H.; Huisman, R.; Veurink, J.; Elzerman, H., The structure and properties of cellulose fibres spun from an anisotropic phosphoric acid solution. *Polymer* **2001**,42 (19), 8249-8264.

14. Horwitz, E. M.; Gordon, P. L.; Koo, W. K. K.; Marx, J. C.; Neel, M. D.; McNall, R. Y.; Muul, L.; Hofmann, T., Isolated allogeneic bone marrow-derived mesenchymal cells engraft and stimulate growth in children with osteogenesis imperfecta: Implications for cell therapy of bone. *P Natl Acad Sci USA* **2002**,99 (13), 8932-8937.

15. Zhao, Y. D.; Li, J. B., Excellent chemical and material cellulose from tunicates: diversity in cellulose production yield and chemical and

morphological structures from different tunicate species. *Cellulose* **2014**,21 (5), 3427-3441.

16. Saleh Hooshmand†, Y. A., Nicholas Norberg§, Aji P. Mathew†, and Kristiina Oksman*†, Dry-Spun Single-Filament Fibres Comprising Solely Cellulose Nanofibres from Bioresidue. *ACS Appl. Mater. Interfaces* **2015**,7 (23), 13022–13028.

17. Moon, R. B., Stephanie; Rudie, Alan, Chapter 1 Cellulose Nanocrystals - A material with Unique Properties and Many Potential Applications. In: *Production and applications of Cellulose Nanomaterials*, Chapter 1, TAPPI Press 2013 **2013**, 9-12.

18. Jones, R. M., *Mechanics of Composite Materials*. Hemisphere Publishing Corporation, New York **1975**, 90-92.

19. Moon RJ, M. A., Nairn J, Simonsen J, Youngblood J. , Cellulose nanomaterials re- view: Structure, properties and nanocomposites. *Chemical Society Reviews* **2011**,40, 3941–3994.

20. Bartholomew, R. F., Structure and properties of silver phosphate glasses — Infrared and visible spectra. *Journal of Non-Crystalline Solids* **1972**,7 (3), 221-235.

21. Han JS, R. J., Chemical Composition of Fibres. In: Rowell RM., Young RA., Rowell J., editors. *Paper and Compo-sites from Agro-Based Resources*. In London: CRC Press, 1996; pp 83–130.

22. Moon RJ, F. C., Wegner T. , *Nanotechnology Applications in the Forest Products Industry*. *Forest Products* **2006**,56, 4–10.

23. S., K., Nanotechnology and its applications in lignocellulosic composites, a mini review. *Express Polymer Letters* **2007**,1 (14 June 2007), 546–575.

24. Haisong Qi, C. C., Lina Zhang, Effects of temperature and molecular weight on dissolution of cellulose in NaOH/urea aqueous solution. *Springer Cellulose* **2008**,15 (6), 779–787.

25. Mariko Ago, T. E., Takahiro Hirotsu, Crystalline transformation of native cellulose from cellulose I to cellulose ID polymorph by a ball-milling method with a specific amount of water. *Springer Cellulose* **2004**,11 (2), 163-167.
26. Chenchen Zhu, R. M. R., Kevin D. Potter, Anastasia F. Koutsomitopoulou, Jeroen S. van Duijneveldt, Sheril R. Vincent, Nandula D. Wanasekara, Stephen J. Eichhorn, and Sameer S. Rahatekar, High Modulus Regenerated Cellulose Fibres Spun from a Low Molecular Weight Microcrystalline Cellulose Solution. *ACS Sustainable Chemistry and Engineering* **2016**,4 (9), 4545-4553.
27. Varshney VK, N. S., Chemical Functionalization of Cellulose Derived from Nonconventional Sources. In: Kalia S, Kaith BS, Kaur I, editors. . *Cellulose Fibres: Bio and Nano-Polymer Composites*. **2011**, 43–60.
28. Mikaela Börjesson and Gunnar Westman (December 9th 2015). *Crystalline Nanocellulose — Preparation, Modification, and Properties*, Cellulose Matheus Poletto and Heitor Luiz Ornaghi Junior, IntechOpen, DOI: 10.5772/61899. Available from: <https://www.intechopen.com/books/cellulose-fundamental-aspects-and-current-trends/crystalline-nanocellulose-preparation-modification-and-properties>
29. Ström G, Ö. C., Ankerfors M., Nanocellulose as an additive in foodstuff. *Invention* **June 2013**,403.
30. JK Pandey, H. T., AN Nakagaito, HJ Kim, *Handbook of polymer nanocomposites. Processing, performance and application: volume C: polymer nanocomposites of cellulose nanoparticles*. Springer Materials **2014**, ISBN 978-3-642-45232-1.
31. Keten, X. Q. S. F. Z. M. S., Optimizing the mechanical properties of cellulose nanopaper through surface energy and critical length scale considerations. *Cellulose* 2017(24), 3289-3299.

Chapter 5

Characterization of Regenerated Cellulose/Curcumin Composites Fibres

5.1 Introduction

Among different bio renewable materials, cellulose is one of the most common natural polymers found in higher plants, algae, bacteria, fungi and marine animals. It is a linear polymer that consists of two glucose sugar units that are linked by β -1, 4 glycosidic linkage to form a dimer known as cellubiose[1, 2]. The length of cellulose chains can be very different due to the number of repeating units of glucose (from 20 to 10 000 or more), also called degree of polymerization or DP [3]. Several studies have shown that cellulose and its derivatives have a good biocompatibility and in addition, can be regarded as slowly degradable materials [4-8]. Due to its excellent mechanical and barrier properties, biocompatibility and low cost, cellulose is used in many biomedical applications, like orthopedic devices and tissue engineering [9-11] and is an excellent candidate for food packaging [12, 13].

Several studies have indicated that some herbal supplements contain phytochemicals that are able to prevent various relevant and wide-spread pathologies, including diabetes, cancer and autoimmune diseases[14-16]. Among these many studies have reported that curcumin, a polyphenol derived from *Curcuma longa*, commonly called turmeric, has excellent pharmacological properties like antimicrobial, antiviral, anti-inflammatory and anti-tumor activities [17, 18]. Previous studies on wound healing in diabetic rats as well as genetically diabetic mice have shown the efficacy of curcumin treatment both by the oral and topical application. There was an improved neovascularization, earlier re-epithelialization, increased migration of various cells including fibroblasts, and dermal myofibroblasts, when curcumin was used to treat the wounds of animals.[3, 19]. Furthermore, curcumin has been widely used as an

active component in the food industry to create new packaging films with antioxidant and antimicrobial activities [20, 21].

Ionic liquids (ILs) are a new class of benign solvents that can be liquid at room temperature (usually $T_{\text{melt}} < 100\text{ }^{\circ}\text{C}$) [22]. Over the past 20 years many studies have shown the countless properties of ionic liquids, in particular their low volatility that makes them benign solvents as compared to traditional volatile and aggressive solvents used for dissolving cellulose (Carbon disulphide, sulfuric acid etc.). ILs have good chemical and thermal stability, high ionic and thermal conductivity, high heat capacity and easy recyclability. All these properties can reduce many health and environmental related issues when ILs are used as solvents for the dissolutions of natural polymers like cellulose, lignin, starch and chitin [23-26]. There are several ILs that can directly dissolve cellulose upon heating, such as 1-allyl-3-methylimidazolium chloride (AMIM-Cl) and 1-ethyl-3-methylimidazolium acetate (EMIMAc) [25,27]. Furthermore, in recent years there has been a great interest of the international scientific community on ILs, used as pharmaceutical ingredients that can modify the pharmacokinetics and pharmacodynamics of drugs [28, 29].

In biomedical applications and tissue engineering, there is need for soft polymers which show more compatibility with the soft tissue as compared to the stiff ones [30]. While taking this into account, cellulose is not only biocompatible and green, but also has advance applications while working under biological conditions [31, 32].

In view of its bio-applications, and to reap the benefits of a pharmacological drug, we have incorporated curcumin at different percentage by weight in a matrix of cellulose dissolved by ionic liquid to manufacture curcumin incorporated fibres. The focus of current work is to develop a simple but effective manufacturing method which will allow continuous manufacturing of strong cellulose/curcumin fibres. The strong cellulose/curcumin fibres thus

obtained has the potential to be woven into bandages and to use in drug, food and cosmetic industry for various low cost affordable health care.

The initial part of the fibre manufacturing protocol was developed by Martha Gina Coscia as a part of her short internship at University of Bristol. The author has reproduced those fibres based on this protocol. The characterization (Reproduction of fibres using the previous protocol, SEM, Optical Microscopy, FTIR, X-ray diffraction, fibre orientation factor measurements and crystallinity Index) of the fibres was done by the author of this thesis.

5.2 Materials and Methods

Cellulose pulp sheets (A4 size cardboard sheets) with a degree of polymerization of 890DP were purchased from Rayonier (Jacksonville, US). Curcumin in powder, purity about 95%, was purchased from <https://supplementsyou.com/> (Jersey, United Kingdom). The ionic liquid 1-ethyl-3-methylimidazolium diethyl phosphate (EMIM DEP, >95%) was obtained from Io-li-tec, and used without further purification.

5.2.1 Cellulose/curcumin fibres formation

This process was first established by Marta Gina Coscia as described below and has been reproduced in this thesis by the author for further characterization.

The cellulose pulp sheets were finely chopped into ($1 \times 1 \text{ cm}^2$) small pieces using scissors and grinded into filaments using a Bosch MMB43G3BGB Glass Jug Blender. To prepare cellulose/curcumin composite fibres, 4 % of cellulose (with respect to the mass of the ionic liquid) was dissolved in EMIM DEP. The solution preparation was carried out in a fume hood using a magnetic stirrer hotplate from Fisher Scientific (Loughborough, UK) with an oil bath heated at 80 °C. The viscous solution was stirred for 6 h until there was a complete dissolution of cellulose. When the cellulose was dissolved 0 wt.%, 1 wt.%, 5 wt.% and 10 wt.% of curcumin (with respect to the mass of cellulose) was added to the 4 wt.% cellulose/EMIM DEP solutions. The cellulose/EMIM DEP

with 0 wt.%, 1 wt.%, 5 wt.% and 10 wt.% of curcumin was transferred into a 20-ml Luer lock syringe (Terumo, UK). The solution in the syringe was degassed in a vacuum oven at 60 °C overnight to remove any bubbles before spinning. A lab-built spinning facility, which consists of a syringe pump, a deionized water bath and a winding drum with a monitor, was used for the dry-jet wet fibre spinning of cellulose (Figure 1). The cellulose/curcumin/EMIM DEP solution was injected into the water bath at a fixed extrusion velocity ($V1 = 2.9 \times 10^{-2}$ m/s), while the winding drum and electric motor were continuously winding the fibres at varying winding velocities ($V2$) of 1.5×10^{-1} m/s, 2.9×10^{-1} m/s and 4.8×10^{-1} m/s downstream. After spinning, the fibres were immersed in deionized water for 2 days, with a change of water every 24 h, and then rolled and dried in a fume hood for a further 48 h. According to [27], the fibres spun under high extension rate within the air gap tends to align better and shows high crystallinity. Following the similar trend, here we have investigated the fibres spun with the higher draw ratio.

In the fibre spinning process, the air gap between the die and the roller was maintained at $d = 3$ cm. Here, the draw ratio, $DR = V2/V1$ is the degree of stretching applied to the fluid filament within the air gap. Here, $V1$ is the average velocity at which fluid is ejected from the die. $V2$ is the velocity at which fibre is taken up on the spool. $V1 = Q/\pi r^2$, where Q is the volume flow rate and r is the die radius.[27].

$$f = \langle P_2(\cos \theta) \rangle = \frac{(3\langle \cos^2 \theta \rangle - 1)}{2} = (-2) \frac{\int_0^\pi \rho(\theta) P_2(\cos \theta) \sin \theta d\theta}{\int_0^\pi \rho(\theta) \sin \theta d\theta} \quad \text{Eq. 1}$$

Here, P_2 is the second order Legendre function. θ is the average polar disorientation angle of a crystallite w.r.t the fibre axis. Φ is the azimuthal angle, the angle of the scattering in the diffraction pattern. $f = -0.5$ and $f = 1$, indicates the perfect orientation of cellulose crystallites would have in the perpendicular and a perfect orientation parallel to fibre axis respectively.

By Segal's law [32, 33], the following equation was used to calculate the crystallinity index of the fibres:

$$\text{CrI (\%)} = [(I_{002} - I_{\text{am}}) / I_{002}] \times 100\%$$

Where, I_{002} = peak intensities of crystalline region. And I_{am} = Peak intensity for the amorphous region.

5.2.2 Statistical analysis

All data obtained after measuring the fibre diameter was analyzed using Prism software version 7. Two-way ANOVA with Bonferroni post-tests was carried out; p value less than 0.0100 were considered significant. Mechanical testing was subjected to the same analysis.

5.3 Results

5.3.1 Surface Morphology

The surface morphology of dry cellulose/curcumin fibres were investigated using the optical microscope. All the fibres maintained their continuity without any visible cracks.

5.3.2 Scanning electron microscopy

Cross-section Observation of Cellulose Fibres

To determine the true cross section of cellulose fibres, the cross-sections of regenerated cellulose-curcumin fibres were imaged using optical microscope. Six to seven randomly picked filaments of cellulose fibres with 0 %, 1 %, 5 % and 10 % curcumin were mounted vertically and parallel to each other into a cylindrical resin mold. A combination of PRIME™ 20LV epoxy resin and PRIME™ 20 slow hardener purchased from Gurit (Newport, UK) with a mix ratio (weight) of 100:26 was used for the moulds. After filament mounting, the moulds were cured at room temperature for 2 days. They were then polished perpendicular to the filament axis direction using a Buehler Beta™ grinder polisher and a Vector™ power head (Esslingen am Neckar, Germany).

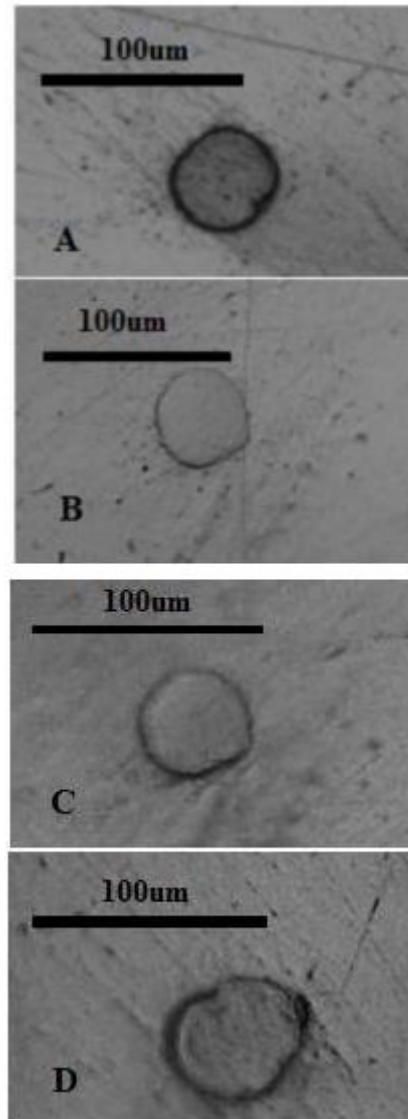


Figure 19: Microscopic image for cross-sections of the cellulose fibres with (A) 0% curcumin fibres. (B) 1% curcumin fibres. (C) 5% curcumin fibres. (D) 10% curcumin fibres.

The cross-sectional shapes of fibre filaments mounted in resin moulds for cellulose fibres with 0 %, 1 %, 5 % and 10 % curcumin were observed using a ZEISS Axio Imager 2 microscope (Cambridge, UK). It is clear from the cross-sectional images in figure 19 that the neat cellulose fibres and cellulose curcumin composite fibres (with 1wt %, 5wt % and 10wt % curcumin) has almost circular cross-section. Although there are impurities on the surface of the

fibres that can be seen clearly from the figure 20, but doesn't have major contribution towards the diameter variations of the fibres. Following the work that has previously been done by our group [57], the diameter was measured from the fibres surface. Hence, it supports the calculated diameter values for the cellulose fibres with neat cellulose and cellulose/curcumin fibres composites (1 wt.%, 5wt % and 10 wt.% curcumin).

10% Curcumin Cellulose fibres

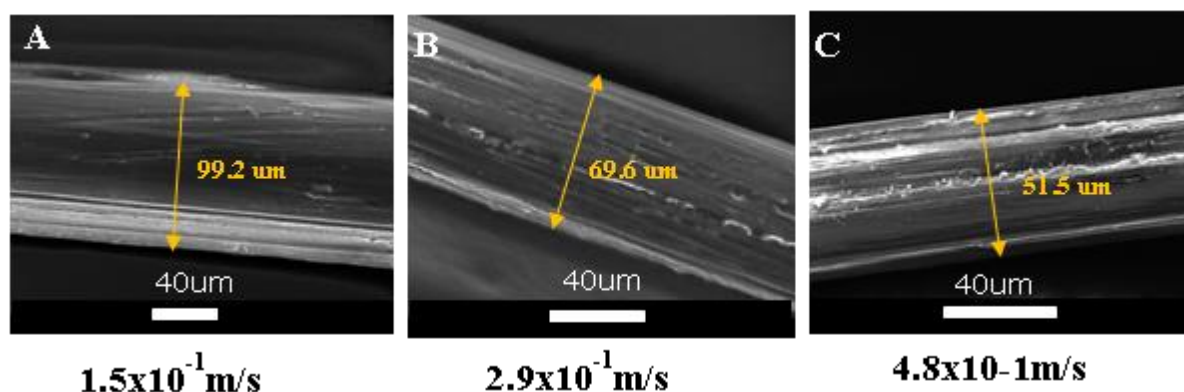


Figure 20: SEM images for the Cellulose fibres with 10% curcumin representing the decrease in diameter with increase in the winding speed from 1.5×10^{-1} m/s, 2.9×10^{-1} m/s and 4.8×10^{-1} m/s.

SEM images shown in Figure 20 and Figure 21 show the morphological observation to greater extent. No sign of large clumps of curcumin particles or sign of fibre breakage was observed in the samples with increasing concentration of curcumin. Figure 20 shows the variation in the diameter of 10 wt.% cellulose/curcumin composite fibres spun at three different winding speeds i.e. 0.15 m/s, 0.29 m/s and 0.48 m/s. As seen from figure 20 the diameter of the cellulose/curcumin fibre decreases with increase in the winding speed. Similar trend in reduction in fibre diameter with increase in winding speed was observed for other set of fibres with difference curcumin concentration.

Additional experiments were carried out to check if the cross section of the fibres is circular.

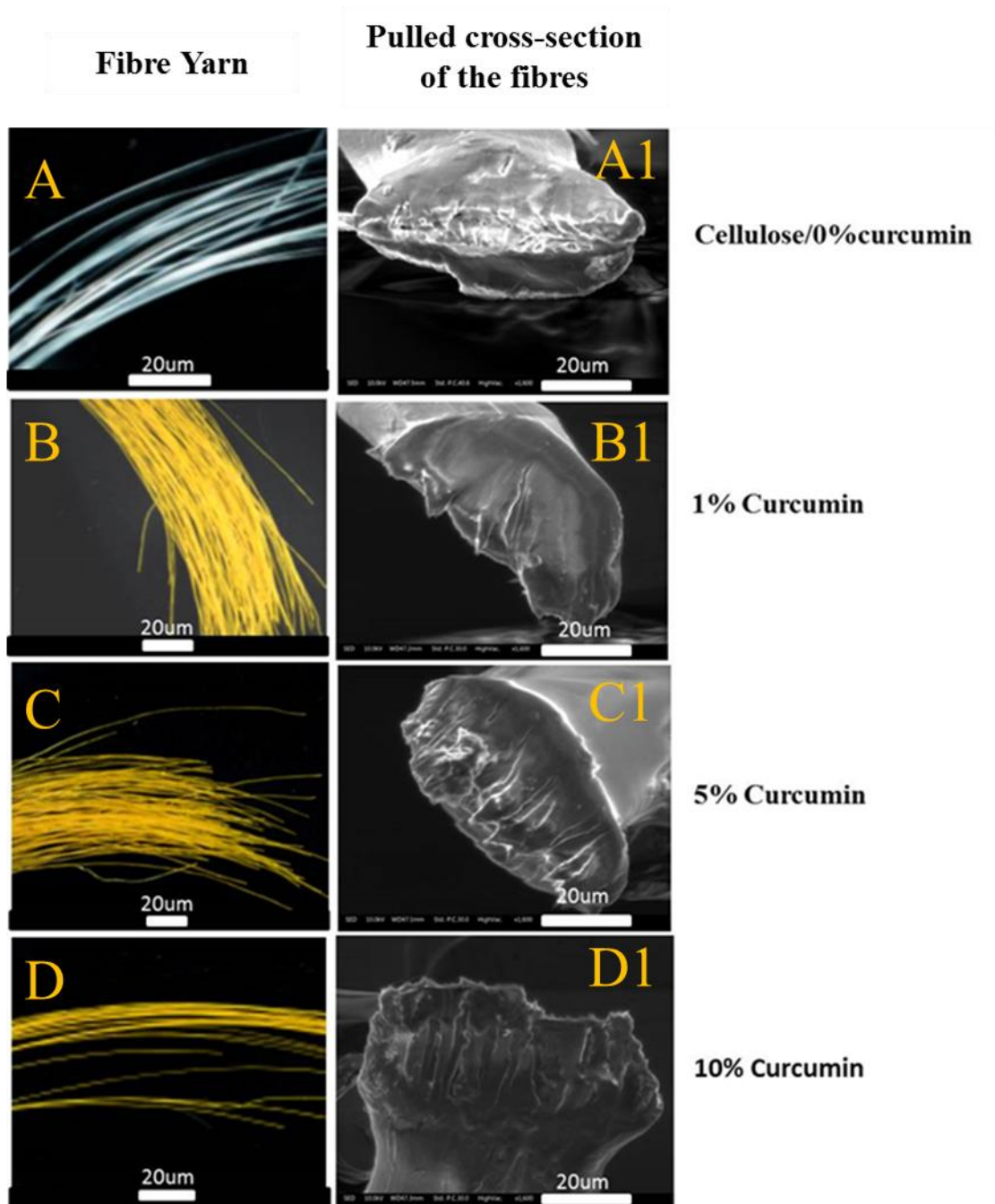


Figure 21: A, B, C, D represents (macro-level) images of the fibres of the bundle of cellulose fibres with 0%, 1%, 5% and 10% curcumin respectively- Indicating the colour change with increase in curcumin concentration.

A1, B1, C1, D1 represents (micro-level) images of the pulled out cross-section of a single cellulose fibre with 0%, 1%, 5% and 10% curcumin respectively.

The average diameters of the fibres at three different winding velocities (V2) of 0.15 m/s, 0.29 m/s and 0.48 m/s and different concentration of curcumin are shown in Figure 20. Figure 20 showed no effect of increase of curcumin concentration on the fibre diameter in various groups represented in clusters of increasing curcumin concentration. However different winding showed significant decrease in fibre diameter in similar groups in all concentrations of curcumin studied. Hence the average diameter of the fibres decreases with the increase in the winding velocities but had no effect on it with increasing curcumin concentration. (Figure 22).

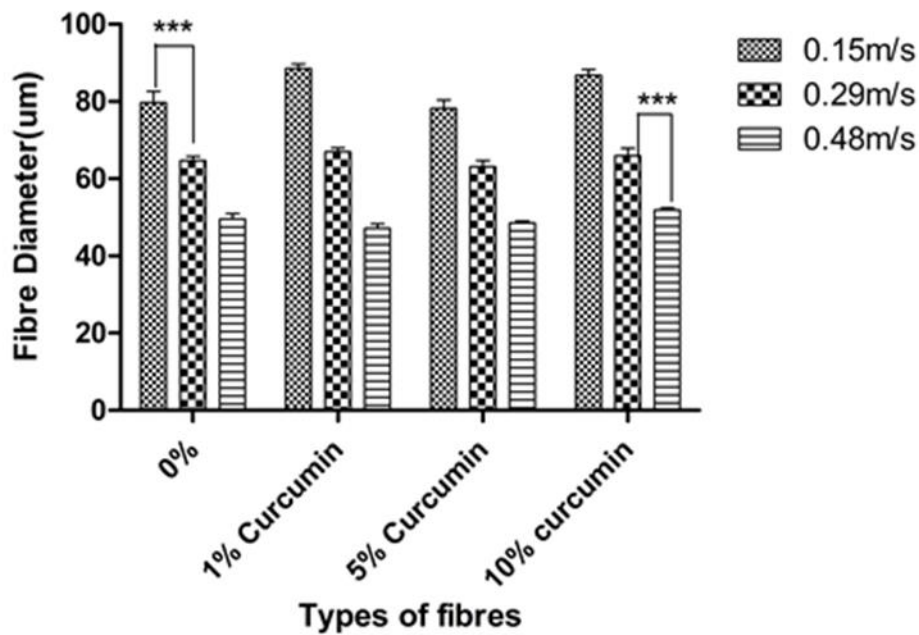


Figure 22: Graphic representation of fibre diameter at different winding velocities: 1.5×10^{-1} m/s, 2.9×10^{-1} m/s and 4.8×10^{-1} m/s. significant statistical variation was seen in the fibre diameter with different winding speed.

5.3.3 Mechanical properties

This testing was done by Marta Gina Coscia and myself. The fibres spun with maximum stable winding speed 0.48 m/s were used to do the mechanical testing and further fibres characterization.

As with tensile strength, the largest and the smallest values of the Young's modulus were measured in 1% curcumin fibres (16.2GPa) and 10% curcumin fibres (13.06 GPa), respectively[63]. However, statistically no significant variation in the tensile strength was observed with the increase of curcumin concentration.

5.3.4 FTIR spectroscopy

The FTIR spectrum of the fibres without curcumin was compared with those of as-received EMIM DEP and cellulose (Figure 23). In the FTIR spectrum of regenerated cellulose and cellulose/curcumin fibres (Figure 23A) the peaks associated with the functional groups of solvent EMIM DEP, namely P=O (1250 cm^{-1}) [35] is not present which indicates that the EMIM DEP solvent is completely removed from the regenerated fibre.

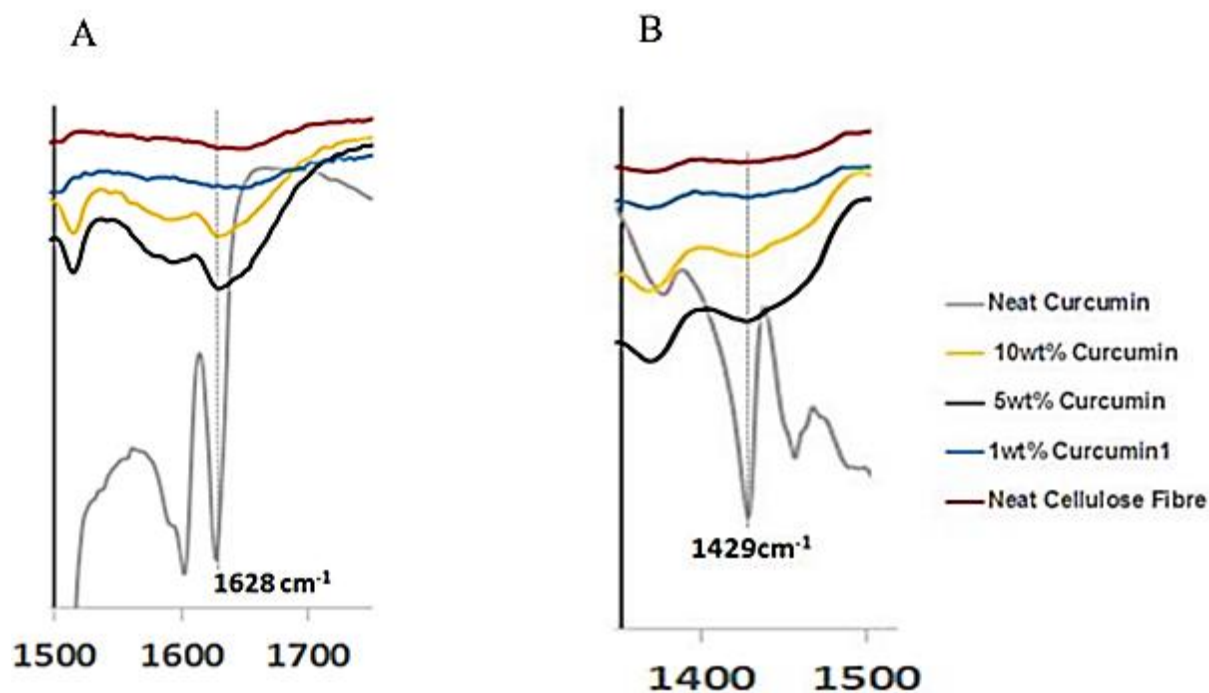


Figure 23: FTIR spectra of EMIM DEP solvent and the regenerated cellulose and cellulose/curcumin fibres.

Furthermore, the FTIR was used to confirm the presence of curcumin inside the cellulose/curcumin fibres (Figure 23A and 23B). The peak at 1628 cm^{-1} present in pure curcumin and the curcumin/cellulose fibres is from curcumin mixed stretching vibrations of C=O and C=C bonds [36, 37]. The peaks at 1429 cm^{-1} , found in pure curcumin and cellulose/curcumin fibres are assigned to in plane bending of aromatic (CCC, CCH)[38, 39].

FTIR Spectroscopy for studying removal of EMIM DEP from cellulose fibres is shown in figure 24.

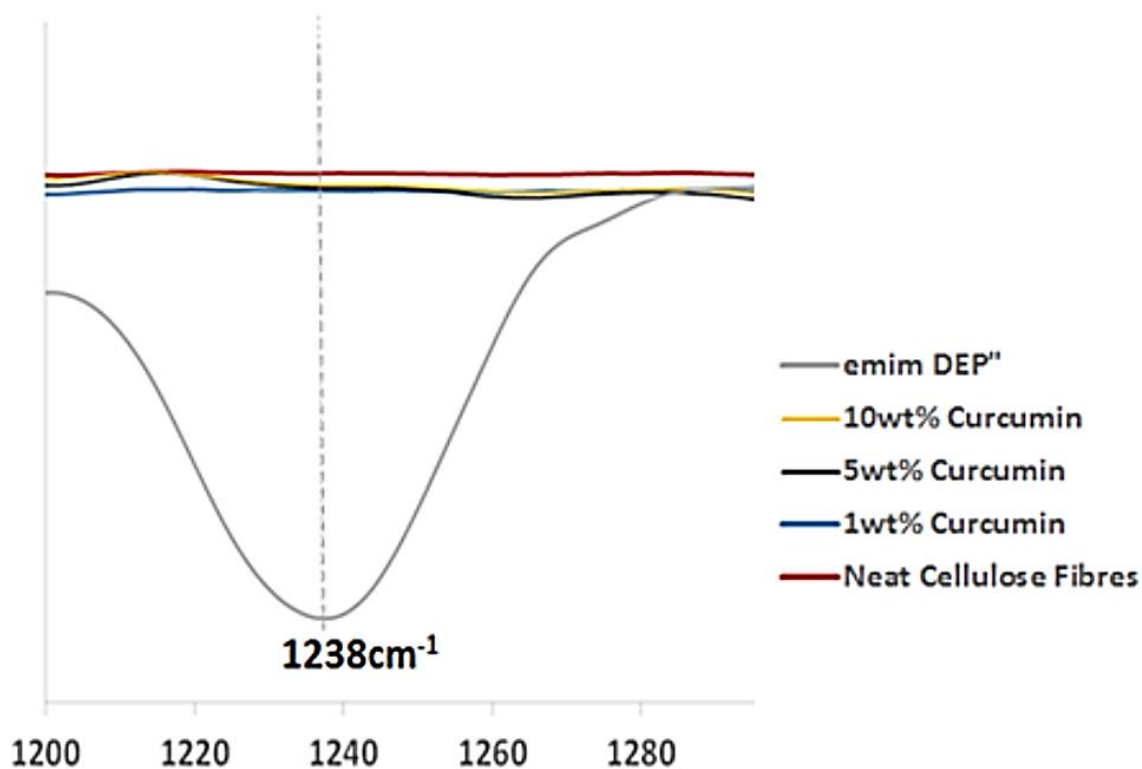


Figure 24: FTIR spectra of EMIM DEP solvent and the regenerated cellulose and cellulose/curcumin fibres; none of the regenerated cellulose fibres show the P=O bond peak at 1238 cm^{-1} indicating that the solvent is completely removed from the fibres.

5.3.5 Wide Angle X-ray Diffraction (WAXD) of the Fibres

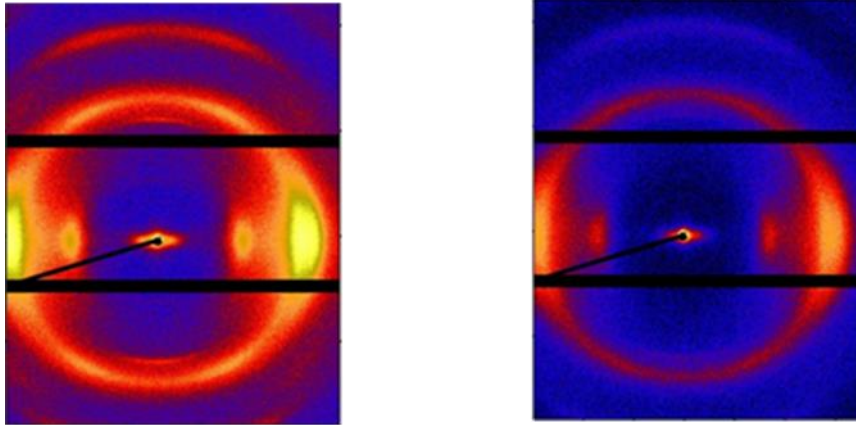


Figure 25: WAXD image of (a) pure cellulose fibre (b) 10% curcumin/cellulose fibre.

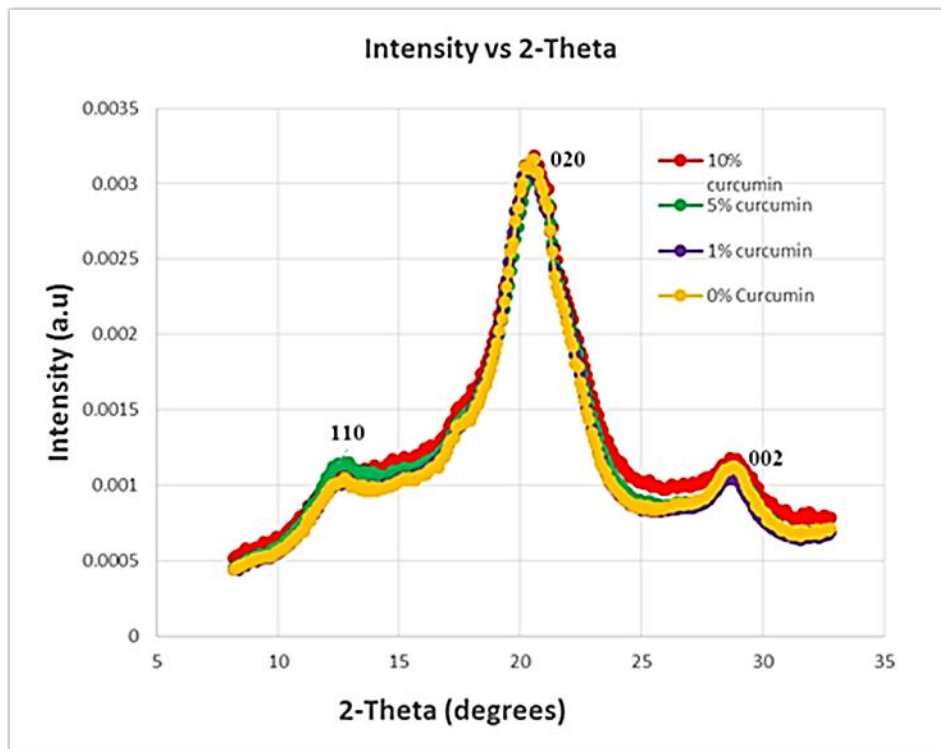


Figure 26: Radial Scan of WAXD of (a) pure cellulose fibre (b) 10% curcumin/cellulose fibre.

Figure 25 shows the 2D diffraction pattern of cellulose and cellulose curcumin composite fibres. The radial scanning data of cellulose (with varying curcumin percentage) is shown in the Figure 26. The intensity and 2-theta graph in Figure 26 clearly shows the diffraction pattern of the fibres which is similar to that of the cellulose II crystal structure according to previously reported work on cellulose fibres[33].The peak at two theta 12 degrees shows the 110 crystal plane, at 22 degrees corresponds to 020 plane and at 28 degrees corresponds to the 002 crystal plane in cellulose.

5.3.6 Orientation Factor

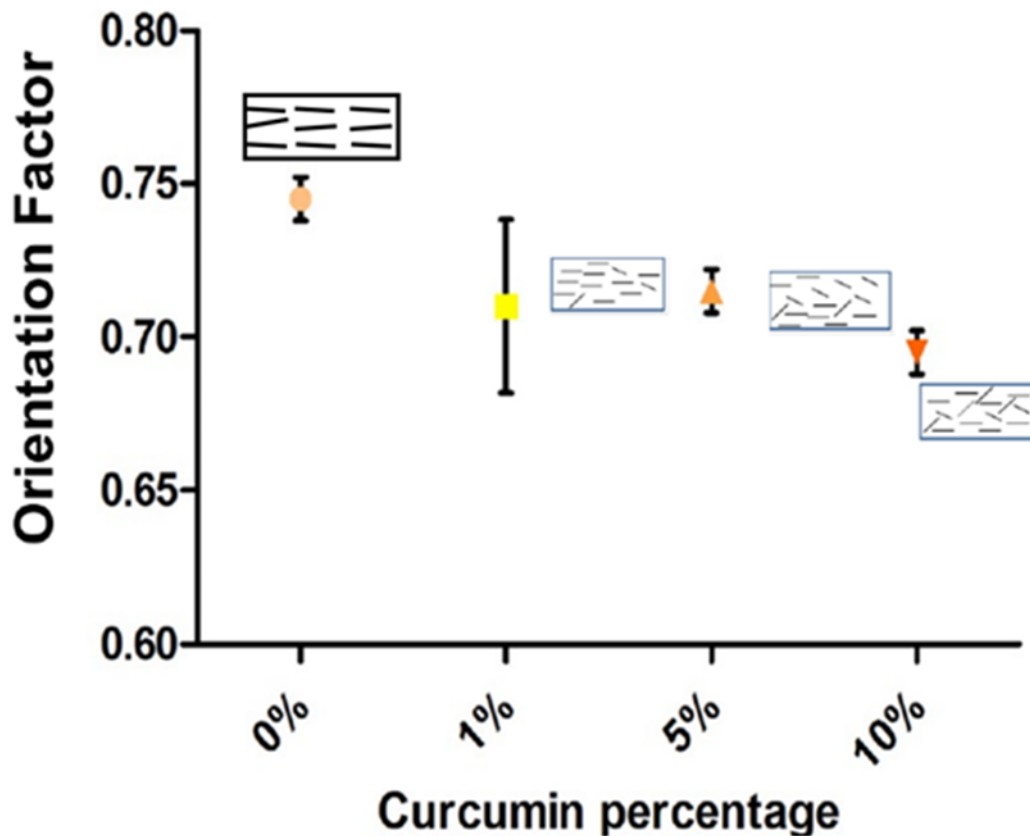


Figure 27: Variation of orientation factor of the fibres while processing in ionic liquid with the increase of curcumin.

Figure 27 represents the effect of curcumin on cellulose fibre alignment which is measured in terms of the orientation factor (refer to section 5.5.2.4). The

orientation factor of 1 represents complete alignment of polymer chains in the direction of the fibre axis and the orientation factor 0 represents completely random orientation of polymer chains in a given sample/fibre. Figure 27 shows that with the increment in curcumin percentage from 0wt% to 10wt%, the orientation factor of cellulose fibres decreases from 0.74 to a lower value 0.69. Hence, the addition of curcumin partly disturbs the orientation of cellulose chains in the fibres. Diagrammatic representation of the same has been shown in Figure 30 in the boxes below the actual graph.

5.3.7 Crystallinity Index

The crystallinity of cellulose and cellulose curcumin fibres were calculated using the Segal's equation as explained in section 5.5.2.4, the crystallinity index of the fibres with curcumin concentration 0wt%, 1wt%, 5wt% and 10wt% was found to be 63%, 67%, 66% and 65% respectively.

5.4 Discussion

In this thesis, we have successfully manufactured curcumin /cellulose based fibres using ionic liquid as a solvent. The fibres have the potential to be used in drug, cosmetic and food industry. Curcumin, a pharmacological product which is obtained from a rhizome has been found to have anti-inflammation, anti-oxidation and anti-cancer activities[40-42]. In the past, various methods have to been used to entrap curcumin to harness its medicinal benefits. Success has been obtained in the form of membranes/ films [40] fibrous mats[43]nanoparticles[44], Nano fibres[32, 45] and electro spun fibres[34]. Due to its low solubility, alkaline nature and high degradation rate as well as use of various synthetic carriers have however rendered its potential unexplored.

On the other hand cellulose is widely used in drug [31, 32],cosmetic and food packaging industry[46, 47]. Here we have manufactured curcumin based cellulose fibres in various concentrations and at different winding speed. The fibres showed good dispersion of curcumin as evident by the following set of

experiments conducted, with SEM, showing non-porous cross-sectional surface, FTIR- reflecting similar curcumin peaks for all the tested samples and wide angle, X-ray diffraction results confirming the consistency of results for each sample when compared with the pure cellulose diffraction pattern.

Dispersion of curcumin in cellulose however renders its use in medical science. Curcumin although has low solubility in water[48, 49] but was found to be easily dispersed in ionic liquid solution with cellulose. This entrapment of curcumin in fibre form with cellulose which is highly biocompatible [31, 43] thus renders it highly versatile in food packaging industry.

The fibres thus obtained showed a decrease in the diameter with increase in the winding speed (Figure 20). Similar results were obtained by Rahatekar[50]. This is due to the fact because in dry wet jet spinning, there is a 3 cm air gap between the spinneret and the water bath where the water get stretched before entering in the coagulation process. This stretch helps in better alignment of the fibre [33]. On increasing the winding speed, the stretch in the fibre in the air gap as well as in the water bath increases. This results in better alignment of the cellulose chains in the fibre hence increasing the orientation parameter as shown in figure 27.

From SEM images, figure 20, 21, no aggregated curcumin clumps were found on the surface neither there was any evidence of breakage in fibre surface due to aggregations.

The mechanical properties of our cellulose/curcumin composite fibres showed no significant increase with the addition of more curcumin to cellulose. According to Zainuddin[32], the addition of curcumin improves the mechanical properties of the fibres moderately. But it starts decreasing with increase in curcumin concentration due to the binding tendency of curcumin on the matrix surface, which can be further improved by cross-linking process. Dai also observed the improvement in the Young's modulus after adding the modified

curcumin particles in the fibre matrix, but there was no significant changes when he analyzed the fibres dispersed with unmodified curcumin particles[34]. The tensile strength of the fibres obtained in our studies were still higher than many viscose fibres being produced [51 , 52-54].

FTIR results corresponding from figure 24 also showed that the solvent peak corresponding to EMIM DEP was not present in any of the regenerated cellulose fibres which strongly indicated that the solvent EMIM DEP is removed from the fibres. We also confirmed the presence of curcumin with its characteristic peaks in cellulose/curcumin composites. Similar characteristic peaks [36] were observed by other researchers in gelatin and curcumin composites [34] where they manufactured electro spun curcumin gelatin blended Nano fibrous mats and water soluble complexes of curcumin with cyclodextrins[55].

The orientation factor of our fibres was found to be reduced with increase of curcumin concentration as shown in figure 27. This is due to the limited tendency of curcumin molecules to dissolve in the matrix. Up to certain percentage curcumin supports the fibre crystal structure which has been reported by (Dai, 2016), with further increase in concentration it acts as impurity in the matrix and hinders the hydrogen bonding in the cellulose matrix. This effect the alignment of the fibre as evident from results been reported by (Norhidayu Zainuddin, 2017a), where Norhidayu found the decrease in mechanical properties with increasing concentration of the curcumin in the polymer matrix. Here when we relate the orientation factor with mechanical properties of the fibres, it is clear that better aligned fibres with good orientation factor shows improved mechanical properties and vice versa (C. Zhu1, 2013; L.V. Haule, 2016).

X-ray analysis, corresponding to figure 25 and 26, however showed that addition of curcumin [56] in cellulose fibres doesn't have significant difference

on the degree of crystallization for all cellulose/curcumin fibres compared with the neat cellulose fibres. These values are similar to what earlier been reported by Rahatekar in [33, 50], where the cellulose fibres were spun using wet spinning technique. As evident from Marcela's results where they worked on the methylcellulose-based films containing graphenes and curcumin[56], it is clear that the curcumin has no significant effect on the crystallinity index of the fibre matrix.

In this work, we have significantly improved the art of manufacturing cellulose fibres reinforced with curcumin while working with different concentration and winding speed. These fibres has the potential applications in cosmetics, food industry, packaging and many other biomedical applications as well.

5.5 Summary

In this thesis, we have manufactured strong regenerated cellulose and cellulose/curcumin composite fibres (ranging from 1wt% to 10wt% curcumin) with use of EMIM DEP as a solvent. The increase in curcumin concentration in cellulose fibres did not affect the fibre diameter. However increased winding speed significantly reduced in the diameters of cellulose and cellulose/curcumin composite fibres. Curcumin was found to be uniformly dispersed in cellulose fibres as evident by SEM and optical microscopy analysis. The tensile strength of regenerated cellulose/curcumin fibres were found to be ranging from 223 to 336 MPa and Young's modulus ranging from 13 to 14.9 GPa. The high winding speed resulted in efficient alignment of cellulose chains as confirmed by X-ray diffraction, orientation factor ranging from 0.69 to 0.74. However, increase in the curcumin concentration caused small reduction in degree of alignment of cellulose chains, no major change was observed in the crystallinity index of the fibres due to addition of curcumin. In this work, we have successfully managed to entrap curcumin in cellulose fibres which can have potential applications in medical and food packaging industry.

5.7 References:

1. Eichhorn, S.J., et al., Review: current international research into cellulose nanofibres and nanocomposites. M. et al. *J Mater Sci*, 2010. **45**(1): p. 1-33.
2. Kontturi, E., T. Tammelin, and M. Österberg, Cellulose—model films and the fundamental approach. *Chemical Society Reviews*, 2006. **35**(12): p. 1287-1304.
3. Sidhu, G.S., et al., Enhancement of wound healing by curcumin in animals. *Wound Repair and Regeneration*, 1998. **6**(2): p. 167-177.
4. Martson, M., et al., Is cellulose sponge degradable or stable as implantation material? An in vivo subcutaneous study in the rat. *Biomaterials*, 1999. **20**(21): p. 1989-1995.
5. Granja, P., et al., Mineralization of regenerated cellulose hydrogels induced by human bone marrow stromal cells. *Eur Cell Mater*, 2005. **10**(1): p. 31-37.
6. Miyamoto, T., et al., Tissue biocompatibility of cellulose and its derivatives. *Journal of biomedical materials research*, 1989. **23**(1): p. 125-133.
7. Müller, F.A., et al., Cellulose-based scaffold materials for cartilage tissue engineering. *Biomaterials*, 2006. **27**(21): p. 3955-3963.
8. Czaja, W.K., et al., The future prospects of microbial cellulose in biomedical applications. *Biomacromolecules*, 2007. **8**(1): p. 1-12.
9. Poustis, J., C. Baquey, and D. Chauveaux, Mechanical properties of cellulose in orthopaedic devices and related environments. *Clinical Materials*, 1994. **16**(2): p. 119-124.
10. Granja, P.L., et al., Cellulose phosphates as biomaterials. Mineralization of chemically modified regenerated cellulose hydrogels. *J. Mater. Sci.*, 2001. **36**(9): p. 2163-2172.

11. Svensson, A., et al., Bacterial cellulose as a potential scaffold for tissue engineering of cartilage. *Biomaterials*, 2005. **26**(4): p. 419-431.
12. de Moura, M.R., L.H.C. Mattoso, and V. Zucolotto, Development of cellulose-based bactericidal nanocomposites containing silver nanoparticles and their use as active food packaging. *Journal of Food Engineering*, 2012. **109**(3): p. 520-524.
13. Imran, M., et al., Cellulose derivative based active coatings: Effects of nisin and plasticizer on physico-chemical and antimicrobial properties of hydroxypropyl methylcellulose films. *Carbohydr. Polym.*, 2010. **81**(2): p. 219-225.
14. Aggarwal, B.B., et al., Potential of spice-derived phytochemicals for cancer prevention. *Planta medica*, 2008. **74**(13): p. 1560.
15. Kaefer, C.M. and J.A. Milner, The role of herbs and spices in cancer prevention. *The Journal of Nutritional Biochemistry*, 2008. **19**(6): p. 347-361.
16. Mahmood, K., et al., Recent developments in curcumin and curcumin based polymeric materials for biomedical applications: A review. *International journal of biological macromolecules*, 2015. **81**: p. 877-890.
17. Ramsewak, R.S., D.L. DeWitt, and M.G. Nair, Cytotoxicity, antioxidant and anti-inflammatory activities of Curcumins I–III from *Curcuma longa*. *Phytomedicine*, 2000. **7**(4): p. 303-308.
18. Ruby, A.J., et al., Anti-tumour and antioxidant activity of natural curcuminoids. *Cancer Letters*, 1995. **94**(1): p. 79-83.
19. Sidhu, G.S., et al., Curcumin enhances wound healing in streptozotocin induced diabetic rats and genetically diabetic mice. *Wound Repair and Regeneration*, 1999. **7**(5): p. 362-374.
20. Sonkaew, P., A. Sane, and P. Suppakul, Antioxidant activities of curcumin and ascorbyl dipalmitate nanoparticles and their activities after

- incorporation into cellulose-based packaging films. *Journal of agricultural and food chemistry*, 2012. **60**(21): p. 5388-5399.
21. Vimala, K., et al., Fabrication of curcumin encapsulated chitosan-PVA silver nanocomposite films for improved antimicrobial activity. *Journal of Biomaterials and Nanobiotechnology*, 2011. **2**(01): p. 55.
 22. Holbrey, J. and R. Rogers, *Ionic liquids in synthesis*. Wiley VCH Verlag GmbH and Co. KGaA, 2002.
 23. Silva, S.S., et al., Green processing of porous chitin structures for biomedical applications combining ionic liquids and supercritical fluid technology. *Acta biomaterialia*, 2011. **7**(3): p. 1166-1172.
 24. Pu, Y., N. Jiang, and A.J. Ragauskas, Ionic liquid as a green solvent for lignin. *Journal of Wood Chemistry and Technology*, 2007. **27**(1): p. 23-33.
 25. Wu, R.-L., et al., Green composite films prepared from cellulose, starch and lignin in room-temperature ionic liquid. *Bioresource Technology*, 2009. **100**(9): p. 2569-2574.
 26. Wang, H., G. Gurau, and R.D. Rogers, Ionic liquid processing of cellulose. *Chemical Society Reviews*, 2012. **41**(4): p. 1519-1537.
 27. Haward, S.J., et al., Shear and extensional rheology of cellulose/ionic liquid solutions. *Biomacromolecules*, 2012. **13**(5): p. 1688-1699.
 28. Stoimenovski, J., et al., Crystalline vs. Ionic Liquid Salt Forms of Active Pharmaceutical Ingredients: A Position Paper. *Pharmaceutical Research*, 2010. **27**(4): p. 521-526.
 29. Moniruzzaman, M., et al., Ionic liquid-assisted transdermal delivery of sparingly soluble drugs. *Chem. Commun.*, 2010. **46**(9): p. 1452-1454.
 30. Foster, S.M.C.R.M.J.G.P.E.J., Mechanically switchable polymer fibres for sensing in biological conditions. *J. Biomed. Opt*, 22(2):27001, 2017. **22**(2).

31. Rramaswamy Ravikumar, M.G., Udumansha Ubaidulla, Eun Young Choi, Hyun Tae Jang, Preparation, characterization, and in vitro diffusion study of nonwoven electrospun nanofibre of curcumin-loaded cellulose acetate phthalate polymer. *Saudi Pharm J.* 2017 Sep; 25(6): 921–926..
32. Norhidayu Zainuddin, I.A., Hanieh Kargarzadeh, Suria Ramli, Hydrophobic kenaf nanocrystalline cellulose for the binding of curcumin. *Carbohydrate Polymers*, 2017. **163**: p. 261-269.
33. Sameer S. Rahatekar, A.R., Rahul Jain, Mauro Zammarano, Krzysztof K. Koziol, Alan H. Windle, Jeffrey W. Gilman, Satish Kumar, Solution spinning of cellulose carbon nanotube composites using room temperature ionic liquids. *Polym. J.*, 2009. **50**(19).
34. Dai, X., Electrospun curcumin gelatin blended Nano-formulated curcumin accelerates acute wound healing through Dkk-1-mediated fibroblast mobilization and MCP-1-mediated anti-inflammation, *NPG Asia Materials* volume 9, e368 (2017).
35. FitzPatrick, M., P. Champagne, and M.F. Cunningham, Quantitative determination of cellulose dissolved in 1-ethyl-3-methylimidazolium acetate using partial least squares regression on FTIR spectra. *Carbohydrate Polymers*, 2012. **87**(2): p. 1124-1130.
36. Alfin Kurniawana, F.G., Adi Tama Nugrahaa, Suryadi Ismadjib, Meng-Jiy Wang, Biocompatibility and drug release behavior of curcumin conjugated gold nanoparticles from aminosilane-functionalized electrospun poly (N-vinyl-2-pyrrolidone) fibres. *Int. J. Pharm.*, 2017.
37. Mohanty, C. and S.K. Sahoo, The in vitro stability and in vivo pharmacokinetics of curcumin prepared as an aqueous nanoparticulate formulation. *Biomaterials*, 2010. **31**(25): p. 6597-6611.

38. Mohan, P.K., et al., Water soluble complexes of curcumin with cyclodextrins: Characterization by FT-Raman spectroscopy. *Vibrational Spectroscopy*, 2012. **62**: p. 77-84.
39. Pan, C., et al., Improved blood compatibility of rapamycin-eluting stent by incorporating curcumin. *Colloids and surfaces B: Biointerfaces*, 2007. **59**(1): p. 105-111.
40. Qianyun Maa, Y.R., Lijuan Wang, Investigation of antioxidant activity and release kinetics of curcumin from tara gum/ polyvinyl alcohol active film. *Food Hydrocoll.*, 2017. **70**, 286-292.
41. Hualin Wang , L.H., Peng Wang, Minmin Chen, Suwei Jiang, Shaotong Jiang, Release kinetics and antibacterial activity of curcumin loaded zein fibres. *Food Hydrocoll.*, 2017. **63**: p. 437-446.
42. Jialing Pan, T.X., Fengli Xu, Yali Zhang, Zhiguo Liu, Wenbo Chen, Weitao Fu, Yuanrong Dai, Yunjie Zhao, Jianpeng Feng, Guang Liang, Development of resveratrol-curcumin hybrids as potential therapeutic agents for inflammatory lung diseases. *Eur. J. Med. Chem.*, 2017. **125**.
43. Tsekova, P.B., et al., Electrospun curcumin-loaded cellulose acetate/polyvinylpyrrolidone fibrous materials with complex architecture and antibacterial activity. *Mater Sci Eng C Mater Biol Appl*, 2017. **73**: p. 206-214.
44. Sara Perteghella, B.C., Laura Catenacci, Milena Sorrenti, Giovanna Brunib, Vittorio Necchi, Barbara Vigani, Marzio Sorlini, Maria Luisa Torre, Theodora Chlapanidas, Stem cell-extracellular vesicles as drug delivery systems: New frontiers for silk/curcumin nanoparticles. *Int J Pharm.* 2017 Mar 30;520(1-2):86-97.
45. Norhidayu Zainuddin, I.A., Hanieh Kargarzadeh, Suria Ramli, Hydrophobic kenaf nanocrystalline cellulose for the binding of curcumin. *Carbohydr Polym.* 2017 May 1;163:261-269..

46. Prodyut Dhar, S.S.G., Narendren Soundararajan, Arvind Gupta, Siddharth Mohan Bhasney, Medha Milli, Amit Kumar, and Vimal Katiyar, Reactive Extrusion of Polylactic Acid/Cellulose Nanocrystal Films for Food Packaging Applications: Influence of Filler Type on Thermomechanical, Rheological, and Barrier Properties. *Ind. Eng. Chem. Res.*, 2017. **56**(16).
47. Nooshin Noshirvani, B.G., Reza Rezaei Mokarram, Mahdi Hashemi, Véronique Coma, Preparation and characterization of active emulsified films based on chitosan-carboxymethyl cellulose containing zinc oxide nano particles. *Int. J. Biol. Macromolec, Int J Biol Macromol.* 2017 Jun;99:530-538.
48. Hongying Liang, J.M.F., Parimala Nacharaju, Fabrication of biodegradable PEG–PLA nanospheres for solubility, stabilization, and delivery of curcumin. *Artif Cells Nanomed Biotechnol.* 2017 Mar;45(2):297-304.
49. Zeynep Aytac, T.U., Core-shell nanofibres of curcumin/cyclodextrin inclusion complex and polylactic acid: Enhanced water solubility and slow release of curcumin. *Int J Pharm.* 2017 Feb 25;518(1-2):177-184.
50. C. Zhu¹, J.C., K. K. Koziol², J. W. Gilman³, P. C. Trulove⁴, S. S. Rahatekar¹, Effect of fibre spinning conditions on the electrical properties of cellulose and carbon nanotube composite fibres spun using ionic liquid as a benign solvent. *Express Polym Lett*, 2013. **8**(3): p. 154-163.
51. Mouthuy, P.-A.S.Š., Maja; Čipak Gašparović, Ana; Milković, Lidija; Carr, Andrew, Physico-chemical and biological characterisation of the use of curcumin-loaded electrospun filaments for soft tissue repair applications. *FULIR*, 2017.
52. Shao-Zhi Fu, X.-H.M., Juan Fan, Ling-Lin Yang, Qing-Lian Wen, Su-Juan Ye, Sheng Lin, Bi-Qiong Wang, Lan-Lan Chen, Jing-Bo Wu, Yue

- Chen, Jun-Ming Fan, Zhi Li, Acceleration of dermal wound healing by using electrospun curcumin-loaded poly(ϵ -caprolactone)-poly(ethylene glycol)-poly(ϵ -caprolactone) fibrous mats. *J Biomed Mater Res B Appl Biomater*, 2014. **102**.
53. Marziyeh Ranjbar-Mohammadi, S.R., S. Hajir Bahrami, M.T. Joghataei, F. Moayer, Antibacterial performance and in vivo diabetic wound healing of curcumin loaded gum tragacanth/poly(ϵ -caprolactone) electrospun nanofibres. *Mater Sci Eng C Mater Biol Appl*. 2016 Dec 1;69:1183-91.
54. Alejandro Costoya, A.C.a.C.A.-L., Electrospun Fibres of Cyclodextrins and Poly(cyclodextrins). *Molecules*, 2017. **22**(2) 230.
55. P.R. Krishna Mohan, G.S., C.V. Muraleedharan, Roy Joseph, Water soluble complexes of curcumin with cyclodextrins: Characterization by FT-Raman spectroscopy. *Vib Spectrosc*, 2012(62), 77-84.
56. Marcela-Corina Roşu, E.P., Crina Socaci, Lidia Măgeruşan, Florina Pogăcean, Maria Coroş, Alexandru Turza, Stela Pruneanu, Cytotoxicity of methylcellulose-based films containing graphenes and curcumin on human lung fibroblasts. *Process biochemistry* 2017 v.52, pp. 7-249.
57. C. Zhu, J.C., K. K. Koziol, J. W. Gilman, P. C. Trulove, S. S. Rahatekar, 2013. Effect of fibre spinning conditions on the electrical properties of cellulose and carbon nanotube composite fibres spun using ionic liquid as a benign solvent. *Express Polym Lett* 8, 154-163.

Chapter 6

Conclusion and Future Work

In this thesis, cellulose composite fibres are manufactured for engineering and bio-medical studies. Considering the main aim of the thesis, to manufacture strong and stiff, 4% DP890 fibres were manufactured and tested for mechanical properties. On wet stretching, it was observed that the tensile strength and the stiffness was improved, although there was a drop in the strain range. This is due to the fact that the fibrils in the fibres were highly aligned to its maximum possible optimized limit, hence stronger and stiffer than the un-stretched fibres. At the same time, as the fibres were already been stretched to its limit, hence, the strain value was decreased.

At this stage, the mechanical properties of the fibres manufactured were found to be moderate while considering to be used as pre-cursor for carbon fibres. and there was a huge scope for its improvement. Cellulose Nano crystals has always been a keen interest of the researcher working in the field of cellulose due to their extra-ordinary mechanical properties. Depending on the source and the technique followed for its extraction, the aspect ratio of the fibres varies, and hence the mechanical properties. Tunicate CNC show better mechanical properties among the others due to their high aspect ratio. Therefore, at this stage, cellulose composites fibres were manufactured by marrying, DP890 cellulose matrix with tunicate CNC and was wet stretched to improve the alignment of the fibres and hence the stiffness from 32GPa to 43GPa. Where the CNC provides the mechanical strength, the wet stretching/drawing improves the orientation of the structure, making it stronger. This is the first time when CNC dispersed cellulose fibres are manufactured using ionic liquid and have shown reasonably good results.

The orientation factor and the improvement in degree of alignment after stretching was confirmed by X-ray diffraction. For composite fibres, the

complete removal of the ionic liquid is significant. Washing the fibres with water twice for two days completely removed the solvent from the fibres which can be recycled. The high resolution images of the pulled out cross-section of the fibres re-enforced with CNC shows longer fibrils sticking out of the surface than the ones without CNC re-enforcement. It could be due to the high aspect ratio of the CNC in the matrix. Hence, confirms the uniform dispersion of CNC in the DP890 cellulose matrix. The properties achieved from these fibres are close enough to the best ever been reported. Not only properties, also the manufacturing method been established during this work is novel and the solvent is less harmful for the environment and can be recycled as well.

On carbonization, the properties of these fibres are comparable with glass fibre. Considering the density, the carbonized fibres (1.56g/cm³) produced in this study are lighter than that of E-glass fibers (2.60g/cm³) and similar tensile strength and stiffness behavior from Table 3, page 39. Hence a potential replacement for glass fibres and can also be used as pre-cursor for carbon fibres. These fibres can potentially be used in sports applications, racing cars, helmets[1], mobile and laptop covers, automotive and wind- turbine applications by replacing the glass fibres.

The cellulose composite fibres were also studied for bio-medical applications. Here, the curcumin based cellulose nanoparticles were manufactured successfully with moderate mechanical properties. The potential applications for these fibres can be for food packaging, bandages, and drug delivery applications, successfully.

Future Work:

Although the fibres spun in this study show reasonably good mechanical properties, still there is a potential to improve the strain range as well as tensile strength for these to be used as carbon fibres precursor. This can be done by further increasing the concentration of cellulose as well as by optimizing the

diameter of the fibres while considering the alignment as well. As the end results for the cellulose composite fibres could potentially be carbon fibres after graphitization or carbonization, it is significant to have enough thickness of the cellulose composite fibres before carbonization in order to attain enough yield and hence the properties.

Dispersion of Nano-crystals is also a significant area in this study which can be further studied and optimized by controlling the pre or post processing of CNC's for dispersion. It would also be interesting to work on manufacturing the cellulose composite fibres using CNC's from various sources as well as extracted using various techniques. The degree of polymerization of the cellulose also plays an important role in the strain range. Hence, this could be an interesting area to look at in future. It is critical to analyse whether the CNC's are actually dispersing or diluting to confirm the visual results from high resolution SEM images in this study. It is suggested to study the dispersion and dilution process to understand the rheology of the material.

Although, ionic liquids can be re-cycled, but this has not been done during this study. It would be interesting to find out the ways to recycle the ionic liquids while working at small or lab scale projects.

Curcumin based cellulose composite fibres show the presence of curcumin after washing the ionic-liquid off from the fibres. For these type of fibres, it would be interesting to see their impact from the prospect of cell study. These fibres were manufactured only by using DP890 cellulose. It is well known that CNC are highly potential for drug delivery. Hence, manufacturing curcumin based fibres using CNC would be an interesting area to look at while considering the life of the product, delivery and the impact.

Dispersion of curcumin and cellulose Nano-crystals is a challenging subject. A very little work has been done in this sector. And the majority used the Viscose process which leaves very harmful impact on the environment. Here in this

MSc. R. Aerospace Engineering

study, we have established a process where we are not only using natural resources also the solvent that is less hazardous to the environment and can be recycled. We have succeeded in dissolving and dispersing cellulose, cellulose Nano-crystals. In this thesis, full characterization of curcumin dispersed cellulose fibres has been done, which is completely novel. These newly developed fibres (Nano-cellulose crystals and curcumin dispersed) will find potential applications in engineering and the bio-medical applications.

References:

1. https://depts.washington.edu/matseed/mse_resources/Webpage/Bicycle/Bicycle%20Materials%20Case%20Study.htm
-