STRUCTURE AND PROPERTIES OF LIGNIN-BASED COMPOSITE CARBON NANOFIBRES

by

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Abstract

This research investigates the feasibility of developing value-added products from lignin in nanofibre form for structural and functional applications. Specifically, softwood Kraft lignin (SKL) was used as the precursor to fabricate nanofibres via the electrospinning process and then converted into carbon nanofibres (CNF). The mechanical properties of SKL nanofibres were characterized for structural applications at the nanofibre mat level and the single nanofibre level. The electrochemical performance of SKL CNFs was characterized for functional applications at the nanofibre mat level.

This research harnessed different processing methods through hierarchical improvements of the mechanical properties of SKL CNF. The mechanical properties of SKL nanofibre mats were improved by the reduction of nanofibre diameter through the optimization of electrospinning process. The mechanical properties of SKL nanofibres gained an order of magnitude improvement through heat treatment processes of thermo-stabilization and carbonization. Aligned nanofibre mats were successfully fabricated via the rotating drum method resulting in further enhancement of the mechanical properties of SKL CNF. Single-walled carbon nanotube (SWNT)-SKL core-shell composite nanofibres were successfully fabricated via the emulsion electrospinning process. The mechanical properties of the SWNT/SKL composite nanofibres were found to increase as the percent of SWNT increases.

This research also investigated the mechanical properties translation between SKL single nanofibres and their fibre assemblies. The mechanical properties of the SKL single nanofibres were characterized and then analyzed by the statistical Weibull distribution. The experimental results were in good agreement with the analytical values.

A prototype supercapacitor (SC) cell using SKL-based CNF as binder-free electrodes was constructed to demonstrate the feasibility of the SKL CNF for functional applications. The electrochemical performance of the SC cell was characterized and the energy density and power density of the SC cell were found to meet the requirement for commercial products.

In summary, this research sheds light on our understanding of the mechanism of the mechanical properties improvement of SKL CNF, which helps guide the tailoring of the mechanical performance of SKL CNF. Moreover, the electrochemical performance of SKL-based CNFs demonstrated that they are promising candidates as electrode materials for SC and a wide range of energy storage devices.

Lay Summary

Taking advantage of the abundant availability and renewable nature of lignin, the goal of this research is to investigate the feasibility of developing value-added products from ligninbased carbon nanofibre (LCNF) for structural composites and functional applications. To assess the potential of LCNF for structural applications, the mechanical properties of lignin-based nanofibres were characterized at the single nanofibre and the fibre mat level. Using the electrospinning method, the effect of molecular order and fibre orientation on the tensile stress-strain behavior of the LCNF was investigated. The potential of LCNF for functional applications was demonstrated by the electrochemical performance characterization of a prototype supercapacitor cell.

This research helps to understand the mechanism of the mechanical properties improvement of LCNFs, and to identify determining factors that can be used to enhance their mechanical performance. Moreover, the electrochemical performance of LCNF demonstrates that they are promising candidates as electrode materials for functional applications.

Preface

Part of chapter 5, 6, and 7 have been published in the Journal of Fiber Bioengineering and Informatics (Fabrication and Properties of Lignin Based Carbon Nanofiber, 2013, 6(4), 335-347), Journal of Nanotechnology in Engineering and Medicine (X-Ray Diffraction Analysis of Kraft Lignins and Lignin-Derived Carbon Nanofibers, 2014, 5(2), 021006-1-5), a conference paper in SAMPE conference and proceeding (Mechanical and Electrical Properties of Electrospun Random and Aligned Lignin Based Carbon Fiber Mats, 2013), and a book chapter in Lignin in Polymer Composites (Lignin-based Composite Carbon Nanofibers, 2016, 167-194)

In chapter 5, Mr. Wilhelm Tsai and Ms. Mina Vafaei helped conduct some of the tensile testing experimental work and Dr. Azadeh Goudarzi generated part of X-RD results. I conducted all of the rest of the experimental work, data analysis, and wrote the manuscript. Professor Frank Ko and Dr. John Kadla suggested corrections to improve the manuscript.

Chapter 8 includes some analysis that was collected by Dr. Seyed Hosseini. He helped conduct model analysis and draft part of the sections in section 8.2 and 8.4. I wrote everything else and conducted all of the other experimental work. A version of chapter 8 has been submitted for publication for Textile Research Journal and is under review.

Chapter 7 includes TEM images that were collected by Dr. Yingjie (Phoebe) Li (Figure 7.1 (d)) and Dr. Junyeon Hwang (7.2 ((a)-(d)). I wrote everything else in chapter 7 and conducted all of the experimental work.

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List of Symbols

- CF = carbon fibre
- CFRP = carbon fibre reinforcement composite
- PAN = polyacrylonitrile
- CNF = carbon nanofibre
- SC = supercapacitors
- EDLC = electric double-layer capacitor
- CNT = carbon nanotube
- SKL = softwood Kraft lignin
- SWNT = single-walled carbon nanotube
- PEO = poly-(ethylene oxide)
- HKL = hardwood Kraft lignin
- PET = poly-(ethylene terephthalate)
- PP = polypropylene
- RSM = response surface methodology
- MEMS = micro-electro-mechanical system
- BET = Brunaer-Emmett-Teller specific surface area
- AFM = atomic force microscopy
- MWNT = multi-walled carbon nanotube
- ECNF = electrospun carbon nanofibre mat
- DMF = N,N'-dimethylformamide
- $F_{1-3}SKL$ = methanol-soluble fraction softwood Kraft lignin
- F₄SKL = methanol/methylene chloride soluble softwood Kraft lignin

- SEM = scanning electron microscope
- QNM = quantitative nano-mechanical test
- TEM = transmission electron microscopy
- FT-IR = Fourier transform infrared spectroscopy
- XRD = X-ray diffraction
- FWHM = full-width at half-maximum
- I_D/I_G = Ratio of the intensities of the D- and G- band measured with Raman spectroscopy
- CV = cyclic voltammetry curve
- ESR = equivalent series resistance
- EIS = electrical impedance spectroscopy
- RMSE = root mean square error
- APS = angular power spectrum
- σ = electrical conductivity
- η = intrinsic viscosity
- ξ_i = natural variables

.

 $T_g =$ glass transition temperature

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Dedication

This dissertation is dedicated to my parents and my sister who have supported me in many ways. I would also like to thank the rest of my family who has encouraged me to overcome many difficult challenges and hard times.

Chapter 1: Introduction and Motivation

Canada stands to be a major producer in renewable resources, as it is rich in forest resources. Canada possesses 347 million hectares (ha) of forest, representing nearly 9% of the world's forests [1]. The forestry industry in Canada accounts for \$60 billion per year, contributing 3% of the Gross National Product (GNP) and 8-10% of the Gross Domestic Product (GDP) [2]. However, it faces competition with low-cost forest sources from other countries and declining demand for products in North American. The industry must change, and the development of new and high-value products as a complement to its traditional commodity products is one sustainable path for the future.

Canada's forests are tremendously abundant sources of biomass, which is a significant advantage for Canada in the rapidly burgeoning global "bio-economy" market. This new market requires the use of renewable and environmentally-friendly alternatives to replace products derived from fossil fuels, and the projected global market size for emerging renewable bioproducts could reach \$195 billion [3]. Making good use of these bio-resources from forests could also help ease the entire society's dependence on petro-chemicals and reduce net greenhouse gas (GHG) emissions.

These benefits can come from converting the low-value by-products of traditional forestry processes to create new high value-added bio-products ranging from industrial chemicals to advanced materials. With its vast forest resources, Canada could become a major exporter of bio-products. These products have the potential to generate high-value returns and also represent a huge economic opportunity for Canada. The development of innovative products and technologies from the by-products of traditional forestry processes can not only offer a significant path to maximize revenues and profits along the entire forest industry value chain, but

can also boost the economic sustainability of the forest industry in Canada. It is the key to maintaining Canada's international competitiveness.

This research was funded by Canada NSERC Biomaterials and Chemicals Strategic Research Network (Lignoworks). The goal of Lignoworks is to generate new knowledge for developing innovative and value-added products from lignin. It aims to create technology platforms for lignin-based materials and chemicals that can provide alternatives to fossil fuel feedstock. At the same time, it will also provide benefits to traditional pulp mills by diversifying the range of products portfolio they can offer.

Lignin is one of the three main components of the plant cell walls and is the second most abundant biopolymer on Earth after cellulose [4]. Lignin represents a substantial, low-cost source of forest-based raw material that is a major by-product of the pulp- and paper-making processes, as well as from cellulosic ethanol production. Kraft pulping is one of the most common pulping processes, generating approximately 40 to 50 million tons of Kraft lignin yearly [5]. The process uses substantial amounts of chemicals (NaOH and Na₂S) to dissolve and separate cellulose from the lignin [6–10], which is then concentrated and dried to recover so-called Kraft lignin. Kraft lignin is a poly-dispersed, branched, and hydrophobic biopolymer with a molecular mass lower than that of native lignin [6]. Owing to the complex structure of lignin macromolecules and their key role in the chemical recovery and energy requirements for pulp and paper mills, producing products from lignin has been challenging and hence limited. The current market value of lignin is low that it is commonly burned as fuel to heat processing plants with a value of ~ 400 \$/ton. Less than 2% (w/w) of total estimated lignin is currently being used for commercial products, such as dispersants, adhesives and surfactants (Figure 1.1) [10–13]. One of the promising potential applications for lignin is the production of advanced materials such as lignin-based

carbon fibre (CF), which has an estimated value of 21,000-800,000 \$/ton [9]. The low cost of lignin and the fact that it is a renewable resource make it an attractive precursor for CF to enhance the value of lignin.



Figure 1.1: Lignin products and their market price.

CF is one of the most advanced lightweight engineering materials, with high strength, high modulus, and excellent electrical and thermal conductivity [8,9,14–18]. CF is used for a variety of purposes and is extensively used in carbon fibre reinforcement composites (CFRP) in sports equipment, the automotive industry, and the aircraft and aerospace industries. More specific applications can be found in energy storage devices, including as electrodes and catalyst substrates [8,9,14–19]. Modern CF was developed in the late 1950s, and early researchers made use of precursors such as polyacrylonitrile (PAN), petroleum pitch, and rayon [18]. The production of CF involves fibre spinning, thermo-stabilization, carbonization, and graphitization.

Polymeric materials that have a high carbon content and do not melt during the carbonization process, such as lignin, are also considered to be suitable candidates for CF precursors [17].

The market and the demand for CF have undergone rapid growth in recent years, but the cost of CF is still an issue for more widespread applications [19]. Low-cost and high carbon content precursors such as polyethylene or poly-acrylic fibre are also used in CFs, but they are still petroleum-based materials. To develop a low-cost CF for the automotive sector, the aim is to reach a manufacturing cost between \$10 and \$15/kg [13]. Currently, the manufacturing cost of commercial grade PAN-based CF is approximately \$20/kg or higher, and the precursor cost is over 50%. With the precursor cost as low as \$400/ton, the manufacturing cost of lignin-based CF could be reduced to less than \$10/kg [8,9,13–15]. Figure 1.2 illustrates the cost of manufacturing PAN-based CF compared to the estimated cost for lignin-based CF.



Figure 1.2: Comparison of the manufacturing cost of (a) polyacrylonitrile-based carbon fibre and (b) lignin-based carbon fibre.

The anticipated demand for CF in the automotive industry provides a great incentive for the development of lignin-based CF. However, adapting lignin-based CF for automotive applications is hindered by the insufficient mechanical properties of lignin-based CF compared to PAN- and pitch-based CFs. The strength and Young's modulus requirements of CF for automotive structural applications are 1.72 GPa and 172 GPa, respectively [13]. An examination of the CF performance map (Figure 1.3) shows that the strength of typical lignin-based CF is in the range of 300 to 700 MPa, which is only approximately one-tenth of the commercial PAN-based CF strength (3-7 GPa). This poses a significant challenge to the application of lignin-based CF.



Figure 1.3: Mechanical performance map of carbon fibres (CF) with different precursors.

To address the issue of the low mechanical properties of lignin CF, considerable efforts have been devoted to exploring strategies to improve the strength and modulus of lignin CF. It is well known that the tensile strength of fibres increases with decreasing fibre diameter due to the reduction of the number and size of defects and the enhancement of molecular orientation along the fibre axis [20]. It is difficult to reduce the diameter of lignin fibre via traditional spinning methods, but there exists several modern methods for producing nano-sized fibres. Among these methods, the electrospinning technique is the most popular process being used to produce ligninbased carbon nanofibres (CNF). Due to its other superior and unique properties such as high surface area and high aspect ratio, CNF is also suitable for many functional applications, such as electrodes for energy storage devices.

Batteries and supercapacitors (SC) are ubiquitous in personal electronics and in a myriad of other daily applications. SCs are an emerging energy storage technology that provides higher power density, but relatively lower energy density, compared to traditional chemical batteries. Other key characteristics of SCs include the ability for fast charge-discharge rates, long lifetime cycles, and stable operation at various temperatures. SCs can fill the gap between capacitors and batteries (Figure 1.4), and these properties make SCs suitable for applications that require instantaneous power [21]. Current applications of SCs include portable electronics, power backups, LED signs, medical devices, and transportation uses. SCs can also be combined with batteries to make hybrid devices with higher power density and longer life cycles. The electric double-layer capacitor (EDLC) is the major form of SC manufacturing and has seen increasing demand. Areas of growth for the SC market include wind turbine power generators, gridconnected solutions, and the electric vehicles market. According to market research, the global SC market size was \$400 million in 2015. This market is expected to have an 18% growth rate to reach annual revenues of \$836 million in 2018 and \$6 billion in 2024. The EDLC market will grow even faster, with expectations of 30% growth from 2018-2024 [22].



Figure 1.4: Ragone plot of the power density against energy density for various energy storage devices.

Activated carbon powders are widely used to fabricate carbon electrodes for SC, and other types of carbon-based materials such as carbon aerogels and carbon nanotubes (CNT) have also been developed [23]. Lignin-based CNF is a suitable candidate material because of its high surface area and low production cost. Moreover, it can be used as binder-free and free-standing electrodes for SC with low resistivity, whereas other materials require additional adhesive binding agents that result in higher internal resistance [24].

This thesis aims to develop methods to prepare lignin-based electrospun CNFs and to assess the mechanical properties of these CNFs for structural applications, as well as assessing their suitability for energy storage devices in the form of SCs for functional applications.

Chapter 2: Literature Review

2.1 Lignin Structure and Chemistry

Lignin is one of the three major constituents of plant cell walls. It occurs at higher concentrations in the cell walls of woody plants such as softwood and hardwood trees [7,25]. It is a high molecular weight aromatic-containing polymer possessing a random, three-dimensional, and heterogeneous structure [9,10,13,15]. Lignin composition and structure can vary among plant species and the processes required to extract it. In softwood species, lignin represents approximately 30% of the total plant mass, whereas in hardwoods, lignin comprises 20-25% [25]. Plant lignin is synthesized via the peroxidase-mediated dehydrogenation of three types of phenyl propane monomers (monolignols), followed by the formation of carbon-carbon and aryl-ether linkages at random through radical-coupling reactions between phenolic radicals [8,25]. Figure 2.1 shows the three classifications of monolignols: guaiacyl, syringyl, and 4-hydroxyl-phenyl propane structures [8].



Figure 2.1: Lignin biosynthesis precursors: (a) p-Coumaryl alcohol (4-hydroxyl-phenyl propane); (b) coniferyl alcohol (guaiacyl); and (c) sinapyl alcohol (syringyl).

Several types of C–O and C–C inter-unit linkages occur in lignin, giving rise to its heterogeneous, 3-D structure [25]. No known method can isolate lignin from plants in an unaltered, native state [26]. Chemical processes include alkaline, acidic, and organic solvent processing, whereas physical processes involve "steam-exploding" lignin [27]. Both approaches result in the fragmentation and degradation of native lignin structures [7,9]. The treatment process can affect the resulting average molecular weight, functional groups present, degree of condensation, types of inter-unit linkages, and types and ratios of monomeric units [7,10,13–15].

2.2 Lignin-Based Carbon Fibres

Lignin-based CF has several advantages over PAN and pitch-based CFs, such as lower cost and higher carbon content. The high oxygen content of lignin will likely require shorter stabilization time than other precursors. The various hydroxyl and ether groups will help cross-linking to occur within lignin CF. One major challenge that remains, however, is the complex and variable molecular structure of lignin that differs among tree species [6,10,13,19,28].

Several studies have been conducted concerning the production of lignin-based CF, and the results and mechanical properties are summarized in Table 2.1. One of the earliest studies of lignin-based CF dates back to 1969, when Otani et al. [29] used thiolignin, alkali lignin, and lignosulphonates as precursors, with the carbonization temperature between 600 and 1000 °C. The resultant CF had a tensile strength of ~300 MPa. Mansmann et al. [30] also manufactured CF from lignosulphonates, with the addition of small amounts of poly-(ethylene oxide) (PEO) or acrylic acid-acrylamide (AAc-AAm) copolymers. The tensile strength and Young's modulus of the resultant lignin CF were 600-800 MPa and 33 GPa, respectively. The first commercial ligninbased CF pioneer plant was then developed in 1970s by Nippon Kayaku Co. to make a product

called "Kayacarbon" [31]. This CF was also made from lignosulphonate with polyvinyl alcohol (PVA) as a plasticizer; however, the CF had microvoids and a lack of homogeneity between crystalline planes [32,33]. Thus, it was abandoned because of its low tensile strength (~200 MPa) and low modulus (27 GPa) caused by flaws.

Afterwards, several research groups attempted to improve the mechanical properties of lignin-based CF by applying different pre-treatment methods for lignin precursors. Sudo et al. applied a steam-explosion method to extract hardwood lignin and then convert it into CF. The fibre diameter of this CF was relatively fine (7.6 μm), and its tensile strength (660 MPa) and Young's modulus (40.7 GPa) were improved; however, the CF yield was only 20.7% [34]. To increase yield, phenolation was used to modify the lignin structure. As a result, the yield was increased to 40-49%, but the tensile strength and Young's modulus were reduced to 460 MPa and 32.5 GPa, respectively [35]. Softwood lignin from an acetic acid-based pulping extraction process was also used in an attempt to make CF, but the tensile strength (0.150 MPa) and Young's modulus (19.5 GPa) were lower than those obtained using other methods [36].

The studies reviewed above all required a complicated process for lignin treatment, and therefore the proposed processes were unsuitable for commercial lignin-based CF manufacturing. Several groups have investigated the production of CF directly from lignin by improving the spinn-ability of lignin fibres and their conversion to CF. Kadla et al. [28] first reported melt-spun CF from commercialized hardwood kraft lignin (HKL) by blending it with PEO. In this process, HKL did not require modification, but had to be purified or desalted by washing with distilled water and HCl. When PEO was added in a range of 3-5% (w/w), the lignin-PEO blends could be melt-spun into fibre. The resulting HKL CF had a 40-46% yield with a diameter of 31-63 µm, and the tensile strength and modulus were 400-550 MPa and 30-60 GPa,

respectively. The tensile strength was found to increase with decreasing fibre diameter. Subsequent elaboration of this method involved blending HKL with either poly-(ethylene terephthalate) (PET) or polypropylene to enhance its spinnability and chain flexibility, resulting in reduction of the fibre's brittleness [37]. In particular, the mechanical properties of the resultant CF were enhanced by blending with PET. A HKL:PET (3:1) ratio CF had a diameter of 31 µm and considerably higher tensile strength (~3-fold, 660 MPa) than that of Kayacarbon.

Other CF manufacturing methods used a more purified form of lignin (Alcell lignin), but the use of Alcell lignin did not significantly improved CF strength (520 MPa) [13]. In addition, a thermal pre-treatment did improve tensile strength (710 MPa), but this pre-treatment required a very slow heating rate. Baker demonstrated that purified HKL could be melt-spun into fibre and then thermo-stabilized at a low temperature in a relatively cost-effective manner [13]. Softwood Kraft lignin (SKL) can also be melt-spun into fibre by blending it with plasticizers or HKL. The resulting CF had a diameter of 10 μ m, the tensile strength of 1.1 GPa, and a yield approaching 50%. Heat stretching during the thermal treatment was expected to lead to further improvements in the mechanical properties of SKL CF [38]. Lignin has also been blended with PAN to make CF. Zoltek and Weyerhaeuser developed a pilot-scale PAN/lignin CF containing up to 45 wt % of lignin. The reported PAN/lignin (65/35 w/w) CF strength could reach 1.68 GPa, with a Young's modulus of 201 GPa, which reaches the U.S. Department of Energy's automotive targets [38].

In summary, lignin-based CF typically have larger diameters and relatively low tensile strength and modulus than PAN- and pitch-based CFs. The strength of lignin-based CF is approximately one-tenth that of commercial PAN-based CF (3-7 GPa), and the highest strength of pure lignin-based CF achieved to date is 1.1 GPa [38]. According to previous research, the

mechanical properties of lignin-based CFs are dependent upon the source and properties of the lignin, including lignin monomer proportions, molecular weight, degree of branching, functional groups, and purity. Moreover, non-lignin impurities or constituents incorporated during lignin processing are also important [13,15,28,39]. To manufacture CFs with greater strength, it is clear that lignin should be pre-processed and purified. Furthermore, the lignin should have a narrow molecular weight distribution to ensure uniform increases in molecular weight throughout the material during oxidative thermo-stabilization, to provide for a more uniform structure during carbonization. Softwood lignin has a better potential than hardwood lignin for CF production because of its higher alkoxy and carbon content; however, softwood lignin requires greater modification because of its higher degree of branching [8,13,28,36,37,40–42].

It is proposed to produce nanofibres from lignin via electrospinning process to address the issue of low mechanical properties of lignin-based CF. By reducing the fibre diameter down to the nanoscale size, the probability of the structural flaws and defects will be reduced to improve the mechanical properties.

Table 2.1: Mechanical properties of previously-synthesized lignin-based carbon fibre.

HW = hardwood, HAc = acetic acid, PEO = poly-(ethylene oxide), PET = poly-(ethylene

Lignin type	Fibre diameter	Tensile Strength	Young's Modulus	Elongation	Reference
	(µm)	(MPa)	(GPa)	of Break	
				(%)	
lignosuphofonates	Х	300	Х	Х	[43]
Kayacarbon	Х	250	27.0	1.0	[31]
Steam explosion	7.6±2.7	660±230	40.7±6.3	1.63±0.29	[34]
HW lignin					
Steam explosion	Х	455	32.5	1.4	[35]
phenolated HW lignin					
HW lignin	14±1.0	355±3.1	39.1±13.3	0.98±0.25	[40]
HAc pulping					
Softwood lignin	84±15	26.4±3.1	3.59±0.43	0.71±0.14	[41]
HAc pulping					
HW Alcell lignin	31±3	388±123	40.0±14	1.00±0.23	[28]
HW lignin	46±8	422±80	40±11	1.12±0.22	[28]
Lignin-PEO (97:3)	34±4	448±70	51±13	0.92±0.21	[15]
Lignin-PEO (95:5)	46±3	396±47	38±5	1.06±0.14	[15]
Lignin	Х	422	39.6	1.07	[36]
Lignin-PET	Х	511	66.3	0.77	[36]
Lignin-PP	Х	113	22.8	0.50	[36]
Lignin-PET (95:5)	31 ± 5	669	84	1.10	[37]
Purified organic HKL	11	520	28.6	Х	[38]
Alcell HKL	Х	1100	69-83	Х	[38]
	1				

terephthalate)	PP = nol	vpropylene	HKL =	hardwood	kraft	lign	in
tereprinatate),	ii poi	ypropytene,	TINL	naruwoou	Man	ngn	III.

2.3 Electrospinning

In this research, the electrospinning process is selected for the fabrication of lignin-based nanofibre. Electrospinning is a cost-effective method of producing submicron fibres. It uses electrostatic force to generate ultra-fine fibres, and has been refined since its invention in the 1930s [44]. Figure 2.2 shows a typical electrospinning set-up: a polymer solution is placed in a syringe with a metal tip that is charged with high voltage, and an electric field is generated between the metallic collector and the needle tip. A uniform jet of polymer forms when the voltage reaches a critical value and overcomes the surface tension of the deformed droplet (the Taylor Cone) of the polymer solution [45]. The jet diameter can be modified via electrically induced bending instability, which results in hyper stretching and rapid evaporation of the solvent [46]. Random (non-woven) fibrous mats can accumulate on the collector surface [47], or aligned fibrous mats can be produced through proper control of the electrodes and the use of rotating drums [48].



Figure 2.2: Electrospinning set-up for producing submicron fibres.

There are many processing parameters can influence the spinnability and physical properties of electrospun nanofibres [48–50]. In spinning lignin CNFs, the main objective is to reduce the fibre diameter to increase tensile strength. According to Rutledge et al. [49], the diameter of electrospun fibres can be controlled by adjusting certain process parameters and is governed by the following equation:

$$d = \left[\gamma \varepsilon \frac{Q^2}{I^2} \frac{2}{\pi (2 \ln X - 3)}\right]^{1/3}$$
(2-1)

Where d is the fibre diameter, γ is the surface tension, ε is the dielectric constant of the solution, Q is the flow rate, I is the current carried by the fibre, and X is the ratio of the initial jet length to the nozzle diameter.

The quantitative study and optimization of nanofibre diameter through the electrospinning process can be performed using response surface methodology (RSM). A fully factorial experimental design and polynomial regression analysis can be applied to establish the relationship between nanofibre diameter and different variables, such as solution concentration and applied voltage [51].

2.4 Electrospun Carbon Nanofibres

Electrospun nanofibres can be converted into carbon nanofibres (CNF), giving rise to unique mechanical and electrical properties. The typical process of preparing CNFs involves electrospinning, followed by subsequent heating steps for thermo-stabilization and carbonization [52,53]. After spinning, the as-spun nanofibre is then heated under tension at 200-300 °C in an oxygenated atmosphere for thermo-stabilization. Thermo-stabilization causes cross-linking of the fibre surface to prevent the fibre from melting or fusing at higher carbonization temperatures. Carbonization involves further heating of the fibre at 1000-2000 °C in an inert atmosphere [9,16–19]. Graphitization, at 3000 °C, can be used to attain further increases in tensile modulus, electrical conductivity, and thermal conductivity of CNFs [54].

Potential applications of electrospun CNFs include supercapacitors, filters, catalyst supports for rechargeable batteries, and the reinforcement of nanocomposites [55]. The mechanical properties of electrospun CNFs have been assessed [52,53,56–59], and because PAN is the dominant precursor for CF, the majority of CNF research has been devoted to PAN.

Most electrospun PAN-based CNFs do not demonstrate such high tensile strength and modulus. Zussman et al. [60] reported that single PAN CNFs had tensile strength between 0.4-0.9 GPa and Young's modulus of 63 ± 7 GPa. Zhou et al. produced PAN nanofibre bundles with 0.3-0.6 GPa strength and 40-60 GPa Young's modulus [53], approximately six times lower than those of microscale CFs. Stronger PAN-based CNFs were manufactured by optimizing the thermo-stabilization and carbonization processes to produce smooth surface CNFs with homogeneous nanofibre cross-sections [61]. The single CNF tensile testing using micro-electromechanical systems (MEMS) showed that the tensile strength reached 3.52 GPa with a 1400 °C carbonization temperature, whereas the elastic modulus increased monotonically until 1700 °C (max: 172 GPa) [61]. This method produced CNFs with tensile strength and modulus three to six times higher than previously reported. Chae et al. [62] developed a CNF bundle with tensile strength and modulus of 3.2 GPa and 337 GPa, respectively. They also electrospun a CNT
reinforced composite CNF with tensile strength and modulus of 4.5 GPa and 463 GPa, respectively [59].

For lignin-based electrospun CNFs, several different kinds of technical lignins have been used as precursors. Ruiz-Rosas et al. [63] were the first to report the manufacture of CNF using organosolv lignin (Alcell). By dissolving it in ethanol at 1:1 w/w, this lignin could be coaxially electrospun, producing nanofibres with diameters in the range of 400 nm. The research further converted the nanofibre into CNF with a 200 nm diameter and a surface area up to $1200 \text{ m}^2 \text{ g}^{-1}$ (BET, N₂). The heating rate of thermo-stabilization in this process was slow (0.25 $^{\circ}$ C min⁻¹), however, and the CNF yield was relatively low (31.6%). Experimentation with seven technical lignins, including SKL, and the addition of PEO demonstrated that the fibre spinnability and uniformity could be improved [39]. After converting to CNF, the diameter of SKL CNF was 635 nm, and the tensile strength and Young's modulus of CNF mats were 32 MPa and 4.8 GPa, respectively. Baker and Hosseinaei [64] purified commercial SKL using a solvent extraction (75/25 DMF/methanol) and electrospun fibre in the range of 35-50% SKL concentration. The rate of thermo-stabilization was relatively fast and a comparable fibre diameter was achieved (300 nm). Unfortunately, the mechanical strength of this CNF was not reported. Although electrospun lignin-based CNF has been successfully fabricated, its mechanical properties have not been rigorously tested. This research is dedicated to performing detailed investigations of the mechanical properties of electrospun lignin-based CNF at various structural levels, from the single nanofibre level to the fibrous mat level.

2.5 Mechanical Properties of Single Nanofibres and Fibrous Mats

The mechanical properties of electrospun nanofibres have been studied in both random and aligned nanofibre mats. Electrospun nanofibre mats were typically cut into rectangular or dumbbell shapes before testing [65–71]. Relevant previous research concerning the mechanical properties of nanofibre mats is summarized in Table 2.2.

Material	Fibre Diameter	Modulus	Strength	Reference
	(nm)	(MPa)	(MPa)	
Bombyx mori	200-400	0.6	15	[70]
Poly(lactic-glycolic)	500-800	323	23	[65]
acid				
Gelatin	100-1900	117 (100 nm)	2.9 (100 nm)	[67]
		123 (1900 nm)	3.4 (1900 nm)	
Poly-(ethylene oxide)	100-150	7	0.09	[69]
Peptide Polymer	450	1800	35	[68]
Polyurhthane	100-500	3.7	10	[71]

Table 2.2: Tensile properties of electrospun nanofibre membranes.

Because the electrospun fibre mats are inherently porous (usually 80 – 90% porosity), the accurate assessment of stress is difficult [70]. A number of variables can affect the tensile properties of fibrous mats, including the volume density of fibres in the mat, the fibre diameter, the mechanical properties of individual nanofibres, and interactions within the fibre network [72]. Equation 2-2 below can be used to correct for the effects of these variables on the tensile strength, where the areal density is the measured mass of the test piece divided by its area [70].

Stress
$$\binom{g}{\text{tex}} = \frac{\text{Force (g)}}{\text{Width (mm)} \times \text{Areal density } \binom{g}{\text{sq} \cdot \text{m}}}$$
 (2-2)

To gain a fundamental understanding of the mechanical properties of electrospun fibres, the stress-strain behaviour of single nanofibres has been evaluated. Although mechanical tests of fibre mats provide basic parameters that can be useful in predicting the mechanical properties of single nanofibres, other factors such as the fibre architecture can also affect the final strength of fibre mats [73]. Therefore single nanofibres need to be tested to examine the effects in assemblies such as mats or yarns. There are three main challenges must be overcome in single nanofibre tensile testing. The first challenge is the sample preparation and collection of single nanofibres on test templates without slippage or breakage. The second challenge is measuring the diameter of a single nanofibre without incurring damage. The third challenge is building a sensitive, high-resolution force transducer and actuator that can measure the load applied at the pico-Newton force ranges [74 – 78].

Single electrospun nanofibres can now be mechanically characterized using technological advances in MEMS, atomic force microscopy (AFM), and other sensitive mechanical testing systems for pico-Newton load measurements [79]. Several methods have been developed to characterize the mechanical properties of single electrospun nanofibres [60,80 – 83], and these are summarized in Table 2.3.

Method	Materials	Fibre Diameter	Modulus	Strength	Break of	Reference
		(nm)	(GPa)	(MPa)	Elongation	
					(%)	
Nano tensile tester	PCL	1000 - 1700	0.12	40	200	[75]
	PLLA	610 - 890	1 – 2.9	89 - 183	0.45 - 1.54	[76]
	PCL	200 - 5000	0.3 - 3.2	20 - 200	20 - 300	[78]
	PCL	400 - 2600	0.35	Х	Х	[77]
	PHBV	1750 - 520	0.15 - 2.67	23 - 268	0.57 - 2.83	[79]
AFM cantilever	PAN	1250	Х	302	Х	[80]
	PAN carbon fibre	70 - 500	Х	350 - 1000	Х	[60]
	PA 6/6	550	0.45 - 0.95	110 - 150	61 - 66	[81]
	PEO	700	Х	45	Х	[83]
	Nylon 6/6	400 - 900	1 – 3.25	Х	Х	[82]
AFM	PAN/SWNT carbon fibre	50 - 200	60 - 130	Х	Х	[84]
	B. Mori silk/PEO	800	0.75 - 8.0	Х	Х	[85]
	Fe ₃ O ₄ /PEO	400	0.66 - 1.04	Х	Х	[86]
AFM bending	Polypyrrole nanotubes	35 - 160	1.2 - 60	Х	Х	[87]
	PLLA	260 - 410	0.1 – 1.0	Х	Х	[88]
	TiO ₂ /PVP	68 - 148	0.33 - 2.33	Х	Х	[89]
	PAMPS	60 - 250	0.3 – 2.1	Х	Х	[90]
	PVA	10 - 160	20 - 500	Х	Х	[91]
Deflection detect	PEO	70 - 450	7	Х	Х	[92]
	Nylon 6	70 - 150	15 - 30	Х	Х	[93]
	PAN	179 – 408	3.79 - 47.79	Х	Х	[94]
MEMS	PLLA	150 - 2000	1 - 7	Х	Х	[95]
	PAN		172±40	3500 ± 600		[96]
Mechanical	PAN carbon fibre	100 - 200	57 – 75	Х	Х	[60]
resonance	Silica glass	120	266			[97]

 Table 2.3: Mechanical characterization of single electrospun nanofibres.

The most direct way to measure the mechanical properties of nanofibres is using a nano tensile tester, which can measure yield stress, ultimate tensile strength, Young's modulus, and elongation at failure. The major issues in conducting a reliable tensile test are handling of the nanofibre and gripping the sample, since a single nanofibre sometimes cannot be readily observed with the naked eye. Other challenges include gripping the nanofibre on the template without stress concentration or slippage, and aligning the fibre without inducing off-axis loading, such as torsion. The noise levels during the measurement must also be carefully controlled. All these challenges can be surmounted, however, by the aid of a laser confocal microscopy and a nano manipulator.

It has been observed that Young's modulus of nanofibres increases with decreasing fibre diameter, and it increases significantly when fibres are spun below a critical fibre diameter. Arinstein et al. [82] found that the Young's modulus of electrospun nylon 6,6 nanofibres increased rapidly below 300 nm. Pai et al. [98] found that the Young's modulus of individual poly-(trimethyl hexamethylene terephthalamide) electrospun fibres increased for diameters smaller than 500 nm. The modulus could reach 6 GPa for 170 nm nanofibres, which is three times higher than that of the bulk material. Naraghi et al. [99] also reported that the PAN electrospun nanofibre showed a three-fold increase in Young's modulus when the fibre diameter decreased from 300 to 100 nm. Papkov et al. [100] reported that both the strength and toughness of individual PAN electrospun nanofibres increased when the fibre diameter was smaller than 150 nm, whereas the Young's modulus and tensile strength can reach 48 GPa and 1.75 GPa, respectively.

This fibre diameter-dependent phenomenon is largely due to confinement effects, as polymer chains are forced to align more strongly along the fibre axis in a smaller diameter fibre than in a larger diameter fibre. The increase of Young's modulus is not due to the increase of crystallite orientation, but can be attributed to the orientation of smaller amorphous regions. For example, the Young's modulus of 150 nm electrospun PAN nanofibres was found to be 25 times

higher than that of bulk PAN as-spun fibres, exceeding that of super-drawn solution-spun ultrahigh molecular weight PAN, where fibres exhibit extremely high levels of chain orientation [100]. Because the crystallization of fibre was still restrained by the rapid solidification of nanofibres, the author assumed that the increase of mechanical properties could be attributed to the molecular orientation of amorphous regions with decreasing nanofibre diameter. This result is much higher than that of the previously report of electrospun PAN (100-200 nm). Differences in testing equipment (the nano tensile tester and the MEMS system) and gauge lengths could explain the differences among the results.

The polymer chain relaxation is also a crucial factor for the mechanical properties of the nanofibre. Research suggested that the lose in the mechanical properties of electrospun nanofibres can be attributed to the chain relaxation [101]. The residual solvent in collected nanofibre can cause the acceleration of chain relaxation and shorten the relaxation time; thus, the orientation induced by the electrospinning process disappears before solidification [101]. Post-processing, such as drawing, can prevent chain relaxation after orientation.

In summary, research studied on the influence of nanofibre diameter to the mechanical properties of electrospun nanofibres suggested that the mechanical properties of the nanofibre increased with decreasing of the nanofibre diameter. The reduction of the nanofibre diameter can be achieved through the optimization of electrospinning process. Other methods to improve the mechanical properties of the nanofibre include the addition of suitable fillers such as carbon nanotubes for the composite nanofibre fabrication to strengthen the nanofibre, and it will be reviewed in the next section.

2.6 Structure and Properties of Carbon Nanotubes

Carbon nanotubes (CNTs) were first discovered in 1991 by Ijima [102], and have since become an important construct for the materials science. Shaped by one or a few layers of sheets of graphene with *sp2*-orbitals, the periodically repeated hexagon patterns of carbon atoms are rolled into a cylinder, producing a lightweight material with exceptional mechanical and electrical properties [103]. The strong in-plane covalent bonds provide CNTs with their superior mechanical properties [104]. Advanced constructs of CNTs can be made beyond the singlewalled carbon nanotubes (SWNTs; Figure 2.3) to include multi-walled carbon nanotubes (MWNTs) [105]. MWNTs are composed of more than one layer of carbon held together by van der Waals forces. The diameters of SWNTs and MWNTs vary depending on the production method, but range between 0.4-3 nm and 10-100 nm, respectively. The length of CNTs is usually in the microscopic range and the aspect ratio (length to diameter) is typically between 100 and 10,000. The elastic modulus of SWNT could reach up to 1 TPa, and the tensile strength ranges from 30-50 GPa, with a break elongation of 6-30%, far surpassing what has been possible to date with CNF [104].



Figure 2.3: Three different types of single-walled carbon nanotubes.

2.7 Carbon Nanotube-Reinforced Nanofibres

CNTs have attracted the attention of many researchers hoping to translate their exceptional mechanical properties into reinforced composite fibres [106–116]. However, CNTs are prone to aggregation due to the van der Waals interactions among themselves that lowers their reinforcing capacity. Currently, key challenges for the effective reinforcement of fibres with CNTs are the homogenous dispersion of CNTs, good interfacial adhesion and stress transfer, and the orientation of CNTs along with the polymer matrix [108,115,116]. Electrospun composite nanofibres could yield better alignment with CNTs, as CNTs tend to orient along the fibre axis due to the flow of polymer solution. Moreover, the electrostatic charge applied during spinning can orient the CNT along the nanofibre axis, and the stretching of the polymer jet can induce molecular orientation [110–113]. Hence, electrospinning is a promising technique to produce CNT-reinforced nanofibres.

Research has been done into co-electrospinning of various CNT/polymer composite nanofibres [84,117–119]. A SWNT-reinforced electrospun polyurethane nanofibre has been fabricated, and mechanical properties tests have shown that the tensile strength was increased by 104%, while the elastic modulus was improved by 250% [113]. Another study concerning 7.5 wt% MWNT reinforced nylon 6,6 nanofibres also demonstrated a four-fold increase in tensile strength and a five-fold increase in modulus [106]. PAN/SWNT CNF [84,117–119] has been demonstrated to possess enhanced mechanical properties following the addition of SWNT up to 10 wt%. These improvements were attributed to the good dispersion and alignment of the MWNTs along the nanofibre axis.

2.8 Theories and Models of Mechanical Properties Translation with Different Nanofibre Assemblies

The applying of models to assess how the properties of a single fibre translate to different fibre assemblies can help us to realize a broad spectrum of applications for electrospun nanofibres [120]. In traditional textile fibres, several models have been proposed to predict the mechanical properties of non-woven fabrics and were focused on the elastic behavior of fibre networks or mats [98,121–124]. Cox proposed the model to predict elastic modulus based on a paper fibre network [121] by assuming that an ideal fabric is a perfectly homogeneous plane of long, straight, and thin fibres oriented either at random or with some defined statistical distribution. Each fibre is also posited to extend from end to end and fibres could stretch, but not bend. The mechanical behavior of flexible, non-woven fabrics can be predicted using an orthotropic model developed for rigid materials, and the prediction of elastic modulus, proportional limit, and rupture stress were found to be reasonably good [123]. Planar fibre

networks deform via fibre bending, elongation, and contraction under external in-plane loading [124]. In contrast, models concerning the fibre orientation and distribution in electrospun nanofibres show that the fibre network, fibre curvature, intrinsic fibre properties, and fibre-fibre junctions are the main factors that affect the mechanical properties of non-woven mats [98,122].

Other studies concerning the mechanical properties of a single fibre and fibre assemblies, including fibre mats and yarns, were focused on investigating the statistical Weibull distribution of individual fibres [125–127]. Due to the nature of variation of the lignin material, a statistical Weibull distribution is suitable to apply to analysis the strength uniformity of lignin-based nanofibres. The experimental characterizations combine with the Weibull analysis of the mechanical behavior on lignin-based nanofibre will be considered in predicting and tuning the desired mechanical features of lignin-based nanofibres and their fibre assemblies.

2.9 Supercapacitors

Among all energy storage devices, supercapacitors (SC) provide one of the fastest charge/discharge cycles, as well as high energy and power density, long cycling durability, and superior reversibility [128–130]. SCs are categorized according to the electrolytes, materials, and configurations employed in their designs [24]. Depending on their charge and storage mechanism, SCs are categorized as electric double-layer capacitors (EDLC) or pseudo-capacitors [131]. EDLCs store energy by the physical adsorption of ions instead of a chemical reaction. EDLCs and pseudo-capacitors are the two main types of SCs, although a hybrid capacitor can be manufactured by combining the two into a single device. Because of the high surface area and low production cost, activated carbon powders are widely used in the fabrication of carbon electrodes, and other types of carbon-based materials, such as carbon aerogels and CNTs, have

also been developed. CNF is also a suitable candidate because it can be used as binder-free and free-standing electrodes for SCs with low resistivity, whereas other materials require additional adhesive binding agents that result in higher internal resistance [24].

A typical EDLC unit cell includes two electrodes, an electrolyte, and an insulating separator (Figure 2.4). Both electrodes can be manufactured from the same material. When charged, positive and negative ions are generated from the electrolyte via dissociation and combine with solvent molecules to form solvated ions. These ions accumulate on the interface of the electrode and the electrolyte, forming an 'electric double layer' [132]. The thickness of the double layer is usually in the range of 5-10 Å. After being discharged, the electrolyte ions return to solution and form re-bonds. Pseudo-capacitors rely on the surface or near-surface electron charge transfer between the electrode and electrolyte (Faradic charge-transfer mechanism) rather than on the typical charge separation mechanism used in EDLC. Several important parameters are used to characterize the electrochemical performance of SCs, including the specific capacitance, power density, and energy density [128–131,133]. Methods for performing these tests are described in Chapter 3.



Figure 2.4: Typical configuration of an electric double-layer capacitor cell.

Carbon materials are good candidates for electrochemical capacitor electrodes, since they have good electrical conductivity and electrolyte wettability. Carbon materials also have better mechanical stability and corrosion resistance than other electrode materials [134].Carbon materials can possess very porous structures and high surface area (1000-2000 m² g⁻¹), particularly after activation, which can be optimized to improve the capacitance. The capacitance of carbon-based capacitors increases linearly with surface area when surface area is low, but tends to plateau when surface area is further increased. Pore size distribution has a greater influence in carbon materials with high surface areas [135]. Electrode materials in EDLC must have high conductivity and electrochemical stability, which make carbon-based materials such as CF, activated carbons, graphene, and CNT good candidates. Their performances have been extensively tested [128,129,131,133,136,137].

CNTs have been found to be suitable materials for SC electrodes due to their high electrical conductivity, chemical stability, and large surface area. The performance varies with the type, morphology, and functional groups of the CNTs. MWNT- and SWNT-based SCs have been prepared and tested, with MWNT possessing more than twice the specific capacitance (80 F g^{-1}) of SWNT [138]. Research has also demonstrated that modifying the morphology and structure of CNTs by oxidation doubled the specific capacitance, from 25 to 50 F g^{-1} [139]. Electrodes manufactured from locally aligned CNT films had a specific power density as high as 30 kW kg⁻¹ because of their ordered structure and high packing density of CNT films [140]. Capacitance has been enhanced through a variety of approaches, including the deposition of coatings [141] and the impregnation of electro-activated metal particles [142]. Differences also exist in terms of which electrolytes are used [140].

This thesis will describe the manufacture of electrospun carbon nanofibre mats (ECNF) from lignin-based CNF. ECNF can be used as free-standing electrodes without any binders because of their relatively high specific surface area and superior mechanical properties [143]. Researchers have formulated procedures to fabricate ECNF with a more inter-connected structure or a more porous structure to improve the electrochemical capacitance by varying the heating parameter or adding catalysts during the carbonization/activation process, respectively [136,137,144].

PAN-based ECNFs have been fabricated with a charge density of 264 F g⁻¹ and capacitance of 100 mA g⁻¹ [145]. The addition of zinc chloride during carbonization increased the specific capacitance of PAN ECNF (140 F g⁻¹) [146], and nickel-embedded PAN ECNF also showed improvement in specific capacitance [147]. ECNF prepared with redox-active components such as metal oxides (e.g., Ruthenium or silver particles [148]) or conducting

materials (e.g., CNT [149]) bulk up the capacity of electrodes and can combine the chemistry of EDLCs and pseudo-capacitors. Ruthenium (Ru)-embedded PAN-based CNF increased capacitance from 140 F g^{-1} to 391 F g^{-1} with 7.31 wt% Ru, whereas the addition of CNTs simultaneously increased the BET surface area and electrical conductivity [150].

Research into the use of lignin in manufacturing ECNF-based SC electrodes shows promise, but lacks a comprehensive body of work. The advantages of lignin include its abundant functional groups for modification, its high porosity for easy access to electrolyte ions, and its heterogeneous nature for energy storage capacity enhancement. To date, research using functionalized lignin char-based electrodes has shown realistic pseudo-capacitor performance and energy storage capacity [131]. Functionalizing lignin ECNFs can enhance wettability and increase surface utilization and pore access [26]. The stability of pseudo-capacitor electrodes also improved because the lignin char matrix can prevent oxidation-reduction reactions [151].

Other successful examples of lignin-based electrodes include the manufacture of nanoporous SCs with specific capacitance as high as 87 F g⁻¹ [152]. Notably, increased graphitization has a negative effect on the non-Faradic charge storage capacity [153]. A mainly lignin-based ECNF (70/30 lignin and polyvinyl alcohol) was manufactured as a free-standing, binder-free, mechanically-flexible electrode [144] with high surface area (up to 1400 m² g⁻¹) and large-sized nanographites. The specific capacitance of this SC could reach 344 F g⁻¹ with 8.1 Wh kg⁻¹ energy density. After 5000 charge/discharge cycles, the electrode maintained 96% capacitance retention. Lignin-based pseudo-capacitors have also been fabricated with lignin-based, NiO-loaded mesoporous carbon [154], with similarly promising results and a capacitance retention of 93.7% after 1000 charge/discharge cycles.

Chapter 3: Objectives

Taking advantage of the abundant availability and renewable nature of lignin, the goal of this research is to investigate the feasibility of developing value-added products from lignin in nanofibre form for structural and functional applications.

For structural applications, lignin-based carbon fibres (CF) have been fabricated in previous research. However, the mechanical properties of lignin-based CF are still lower than that of commercial CF. To address the issue, we propose that the mechanical properties of ligninbased CF can be hierarchically improved by the reduction of fibre diameter, the increase of fibre alignment, the incorporation of single-walled nanotubes (SWNT), and the combination of proper heat treatment processes. Several processing methods will be harnessed to validate and to evaluate these effects.

Lignin-based nanofibres will be fabricated in this research. By reducing the fibre diameter to nanoscale size, it can reduce the probability of the structural flaws and defects in the fibre. The nanofibre will undergo through the aligning process to further increase the fibre alignment to enhance the molecular orientation in the nanofibre. The SWNT/lignin composite nanofibres will also be fabricated in this research. The addition of SWNT can reinforce the lignin nanofibre and also help the formation of more ordered carbon structures during the carbonization process. These methods combined with proper heat treatment processes can help the cross-linking and rearrangement of chemical structures of lignin-based nanofibres and can convert them into carbon nanofibres (CNF) with better mechanical properties.

A two-parameter Weibull distribution can be used to analyze the strength distribution of lignin nanofibres due to the structure variation of lignin. The parameters obtained from the Weibull analysis can also be applied to other existing models to validate and predict the

mechanical properties translation of SKL nanofibres from the single nanofibre level to different nanofibre assembly level.

Moreover, lignin-based CNF can have several different functional applications because of the unique structural and chemical properties of lignin. This research will also explore the potential of lignin-based CNF by making binder-free and free-standing carbon electrodes for energy storage devices.

Specifically, softwood Kraft lignin (SKL) will be used as the precursor to fabricate nanofibres via the electrospinning process and then converted into CNF (Figure 3.1). The objectives of this research are:

1. To optimize the electrospinning process to obtain finer fibre. A factorial experimental design at three levels of two electrospinning parameters (solution concentration and spinneret needle inner diameter) will be carried out using the response surface methodology (RSM) to establish the relationship between each parameter and the response (fibre diameter).

2. To characterize the mechanical properties improvements by harnessing different processing methods at the nanofibre mat level. Tensile tests will be conducted on random nanofibre mats under all optimization and heat treatment process conditions to evaluate the influence of the nanofibre diameter reduction and the heat treatment process on the mechanical properties improvement of SKL nanofibres. Chemical structural changes of SKL nanofibres during the heat treatment process will be studied via various characterization techniques, including scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (X-RD), and Raman spectroscopy. Aligned nanofibre mats will be fabricated through the rotating drum method and the effect of fibre alignment on the improvement of mechanical properties will be investigated. SWNT/SKL composite nanofibres will be fabricated

through the emulsion electrospinning process, and tensile tests of SWNT/SKL composite nanofibre mats will be characterized to determine the reinforcement of mechanical properties with the addition of SWNT. The chemical structure of SWNT/SKL nanofibres will be investigated via SEM, high resolution transmission electron microscopy (TEM), and Raman spectroscopy.

3. To investigate the mechanical properties translation between SKL single nanofibres and their fibre assemblies. The mechanical properties characterization will conduct at the single nanofibre level to examine the intrinsic properties of SKL nanofibres. A mechanical properties investigation of SKL nanofibres from the single nanofibre level to the nanofibre mat level will be constructed. Statistical Weibull distribution will be utilized to analyze the strength uniformity of SKL single nanofibres. The shape factor and scale factor obtained from Weibull analysis will be applied to different models to validate and predict the translation of mechanical properties from single nanofibres to different nanofibre assemblies.

4. To characterize the electrochemical performance of SKL CNF mats for functional applications. A prototype supercapacitor (SC) cell using SKL-based CNF mats as binder-free electrodes will be constructed. A series of characterizations of the electrochemical properties will be conducted and the performance of the proposed electrodes will be compared with commonly-used carbon-based materials.



Figure 3.1: Research goals for electospun lignin-based CNF.

Chapter 4: Materials and Experimental Methods

4.1 Materials

Softwood Kraft lignin (SKL, Indulin-AT) was obtained from MeadWestvaco (Glen Allen, VA, USA). Poly (ethylene oxide) (PEO) with an average molecular weight of 1×10^6 g mol⁻¹ was obtained from Sigma-Aldrich (Oakville, ON) and used as received. N.N-dimethylformamide (DMF), methanol, methylene chloride, and toluene were all ACS Reagent grade and obtained from Fisher Scientific (Ottawa, ON), and used as received.

4.2 Lignin Fractionation

SKL was fractionated according to methods described in previous research [155]. SKL was fractionated using different organic solvents and the fractionation 4 (F₄SKL) part was used as the precursor material (Figure 4.1) [155]. SKL was first acid-washed with dilute HCl (pH 2) to remove impurities and ash. In this process, 100 grams of SKL were suspended in 1 L HCl, stirred for 30 minutes, and then filtered five times. After the acid wash, SKL was dried in the oven at 105 °C overnight. [155]. The resultant SKL was then extracted with methanol (CH₃OH) in a ratio of 100 g L⁻¹ by vigorous stirring for 30 min. The mixture was then filtered, and the insoluble fraction was air-dried overnight. This process was repeated three times, and the methanol-soluble fraction (F₁₋₃ SKL) was discarded. The insoluble SKL part that remained after methanol extracted with a 70/30 (v/v) mixture of methanol/methylene chloride (CH₃OH/CH₂Cl₂). The insoluble material was air-dried and re-extracted three times. The soluble SKL part from the 70/30 methanol/methylene chloride washing (F₄SKL) was concentrated and dried as the precursor material.



Figure 4.1: Fractionation process of softwood Kraft lignin.

4.3 Electrospinning Process

An electrospinning solution of F_4 SKL was prepared by blending 99:1 with PEO (w/w) and dissolving in DMF. Solution vials were sealed and vortexed for one minute, then heated in an oil bath at 80 °C for two hours, during which time the solutions were vortexed for two minutes every 30 minutes. Three different gauges of needle, G18, G20, and G25 (corresponding to needle inner diameters of 1.27 mm, 0.89 mm, and 0.51 mm, respectively), were used in combination with solution concentrations of 25 wt%, 30 wt%, and 35 wt% to optimize the electrospinning process. An electrospinning distance of 15 cm was used, a voltage of 15 kV was applied, and the solution was pumped at a rate of 0.03 mL min⁻¹. All conditions were fully factorial, and RSM was used to construct a performance map to visualize the influence of all variables on fibre diameter. Random fibre mats were prepared using a static collector in a nanofibre electrospinning unit (NEU, Kato tech, Japan), whereas aligned fibre mats were prepared using a NANON-01A (MECC, Japan) rotating drum electrospinning setup (Figure 4.2) [101] at a collection speed of 2000 revolutions per minute (RPM).



Figure 4.2: Rotating drum electrospinning set-up for aligned nanofibre mats collection.

4.4 Emulsion Electrospinning Process

Composite nanofibres were prepared from water-in-oil emulsions of SWNT/F₄SKL using emulsion electrospinning process (Figure 4.3) modified from previous research [156], where the oil phase consisted of 25 wt% F₄SKL/PEO (99:1) with DMF/toluene (80/20), and the aqueous phase of SWNT was suspended in distilled water (0.2% w/v) via sonication (Sonicator 3000 by Misonix Inc.) for 2 hours. The SWNT suspension was mixed with a Span 80TM surfactant (10% w/w), then added to the toluene solution and sonicated in the bath sonicator (Branson 3510 by Industrial Automation) for one hour to form micelles. In the meantime, the appropriate amount of F₄SKL/DMF solution was kept at 80 °C in an oil bath for two hours and vortexed every half hour for 30 seconds. The SWNT solution was then added to the F₄SKL/DMF solution and further sonicated for 2 hours in the bath sonicator.



Figure 4.3: Schematic mechanism for the formation of a core-shell composite fibre during emulsion electrospinning.

4.5 Heat Treatment Process

The heat treatment process included the thermo-stabilization and carbonization. Thermostabilization was performed at three different heating rates (0.5 °C/min, 5 °C/min, and 20 ± 2 °C/min) combined with three different final heating temperatures (150 °C, 200 °C, and 250 °C), and held isothermally for one hour in a gas chromatography oven (Hewlett-Packard 5890 Series II) with an air atmosphere. The most suitable thermo-stabilization conditions were determined based on the tensile testing results of the thermo-stabilized fibre mats.

For the carbonization process, a 5 °C/min heating rate was used to reach a steady state temperature of 800 °C, 900 °C, and 1000 °C for one hour in a nitrogen atmosphere in a GSL-1100X tube furnace (MTI Corp, Richmond, CA) by clamping strips of electrospun fibre mats (~0.5 cm \times 6 cm) at each end between two stainless-steel plates.

4.6 Characterization

4.6.1 Morphological and Structural Characterization

 F_4 SKL electrospun fibre morphology was examined with a scanning electron microscope (SEM, Hitachi S3000N) under high vacuum with a 5 kV acceleration voltage and at a 15-mm working distance. Fibre diameter was measured using the ImageJ software (U.S. National Institutes of Health), and 100 random samples measurements were made for each fibre mat.

4.6.2 Mechanical Properties Characterization

4.6.2.1 Nanofibre Mats

The mechanical properties of fibre mats were assessed using the KES-G1 Kawabata micro-tensile testing system at an elongation rate of 0.01 cm/s. For fibre mats, a sample strip 5 cm long \times 0.5 cm wide was glued onto a paper frame and tested (Figure 4.4). The gauge length for the tensile test was 4 cm [157], and the load was recorded based on loading voltage and converted into grams. The specific stress (g tex⁻¹) was calculated using Equation 2-1. At least 30 samples were tested for each condition.



Figure 4.4: Specimen preparation for tensile test of fibre mats.

4.6.2.2 Single Nanofibres

During the electrospinning process, a U-shaped copper collector was placed in front of the spinning area to collect single nanofibres. Typically, 20 to 30 nanofibres were deposited onto the copper collector. A plastic template strip with epoxy glue was then used to transfer nanofibres from the copper collector. After the epoxy glue was fully solidified for 24 hours, excess fibres were removed with the help of a confocal microscope (LEXT OLS 4000, Olympus, USA) and a nanomanipulator (Kleindiek nanotechnik, GmbH, Germany) to visualize and trim excess fibres without disturbing the targeted nanofibre. Ten to fifteen measurements of the sample diameter were made using the laser scanning mode on the confocal microscope. The tensile strength of a single nanofibre was then conducted using the UTM T150 tensile testing system (*Agilent* Technologies). Figure 4.5 provides an overview of the single nanofibre preparation process. A single nanofibre specimen was mounted into the grips of the tensile tester with the aid of an intense light source. Once the grips were secured, the two edges of the template were cut with a knife to ensure that the machine would record only the mechanical strength of the single fibre (Figure 4.6). At least 25 samples were tested for each test.



Figure 4.5: Scheme of the single F₄SKL electrospun nanofibre tensile test.



Figure 4.6: Specimen mounted into the grips ((a) & (b)), and the high-speed camera image ((c)) of a single nanofibre tensile test.

4.6.2.3 Atomic Force Microscopy (AFM)

The PeakForce quantitative nano-mechanical (PeakForce QNM) mapping test was used to characterize the Young's modulus of the F_4SKL single CNF using an AFM (Veeco Instruments, Santa Barbara, CA, USA). A TAP150ATM probe with a nominal spring constant of 5 N/m was mounted on a cantilever. CNF samples were first sonicated using a bath sonicator in a water solution with 0.02 wt%, and a drop of solution was casted onto a magnetic disc with a mica substrate. The cantilever deflection sensitivity was calibrated on a sapphire calibration standard, and the cantilever spring constant was determined using the thermal tuning method. The applied force was fixed at 20 nN, with a 0.1-Hz scan rate, a 300 × 300 nm scan area, and a sampling 512 samples/line frequency. The AFM instrument sensitivity was estimated to be on the order of ~100–200 pN under the conditions used for imaging, based on the noise of the sample traces.

4.6.3 Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR was performed using a Spectrum One FT-IR Spectrometer (Perkin Elmer Instruments, Waltham, USA). Samples were analyzed using 32 scans collected over a scan range of 4000-600 cm⁻¹, with a resolution of 4 cm⁻¹. The spectra were normalized at 1600 cm⁻¹, which was assigned to the maximum absorbance peak of the aromatic skeletal vibrations and C=O stretch in the study samples.

4.6.4 X-Ray Diffraction (X-RD)

An X-ray diffractometer (MultiFlex, Rigaku Co., Tokyo, Japan) was used to measure the carbon structures of F_4SKL CNF across a scanning range of 5-60° (2 θ). The apparent crystallite thickness (L_c) and the average interlayer spacing (d) were calculated using the Bragg and Scherrer equations:

$$d = \frac{\lambda}{2\sin\theta} \quad (4-2)$$

$$Lc = \frac{\kappa\lambda}{\beta\cos\theta} (4-3)$$

Where θ is the Bragg angle of the peaks (°), λ is the wavelength of X-ray used (0.154 nm), β is the half-height width of the peaks (rad), and the L_c form factor K is 0.89.

4.6.5 Raman Spectroscopy

Raman spectra of CNFs were obtained with a RM1000 Raman microscope system (Renishaw, Gloucestershire, U.K) equipped with a 785 nm diode laser for 1% laser power (9-10 mW). Each sample was scanned four times from 900 to 1800 cm⁻¹ with baseline correction before curve fitting. The Raman spectra of carbonaceous materials have two separate characteristic bands: i) the defect-induced D-band peak (centered approximately at a wave-number of 1310 cm⁻¹) related to disordered turbostratic structures and ii) the crystalline graphite G-band peak (centered approximately at a wave-number of 1580 cm⁻¹) related to ordered graphitic structures [159,165-166]. In this study, the D-band was fitted with a Lorentizian line curve and the G-band was fitted with a Breit-Wigner-Fano line curve. The intensity ratios (I_D/I_G) were calculated based on the D-band and G-band intensity heights and are related to the degree of defects in CNF [155].

4.7 Preparation and Characterization of Electrospun Carbon Nanofibre Electrodes

4.7.1 Supercapacitor (SC) Unit Cell Preparation

Figure 4.7 shows the structure of a prototype SC constructed using two 1 cm \times 1 cm rectangular CNF mats as electrodes and a cellulose micro-porous filter paper as a separator. Three types of lignin-based random CNF mats were tested: F₄SKL, 0.5% SWNT/F₄SKL, and 1% SWNT/F₄SKL. Two stainless steel substrates were incorporated to act as current collectors. Electrodes and separators were put into a 6 M KOH electrolyte for at least 24 hours before electrochemical performance characterization. After assembly, the SC cell was connected to the AUTOLAB testing station through a connection port on each side of the current collector.



Figure 4.7: Construction of a symmetric supercapacitor cell.

4.7.2 Electrical Conductivity Measurement

The two-point probe method was applied to measure the resistance R (Ω) of the CNF mats using a multi-meter. Samples sized 3 cm × 0.5 cm were painted with silver paint at both ends and mounted onto glass slides. Electrical conductivity (σ) was calculated from the measurement of R by the following equation:

$$\sigma\left(\frac{s}{cm}\right) = \frac{L}{WtR} (4-4)$$

Where: L is the distance between the two probes, W is the sample width, and t is the thickness of the sample.

4.7.3 Electrochemical Performance Measurement

After being connected to the AUTOLAB testing station, a series of electrochemical performance tests was conducted on the prototype SC cell, including a cyclic voltammetry (CV) test, charge/discharge test, electrical impedance spectroscopy (EIS) test, and durability test. CV curves were derived for each CNF mat at a 30 mV S⁻¹ scan rate and with a potential range of 0-0.8 V. CNF mat samples were also scanned at four different voltage sweeping rates (5, 10, 30, and 50 mV s⁻¹) with a potential range of 0-0.8 V. The charge/discharge rate of CNF electrodes was tested using the galvanostatic method. In this test, the SC was charged at a constant current until a voltage of 0.8 V was achieved, at which point the SC was discharged to 0 V and the cycle was repeated. At the moment when the current switches direction, the sudden vertical drop (IR drop) in voltage is related to the internal resistance or equivalent series resistance (ESR) of the SC. Three different current densities (400, 1000, and 2000 mA g⁻¹) were applied to all custombuilt SCs. EIS was utilized to analyze the internal resistance of the electrode material, as well as the resistance between the interface of the electrode and the electrolyte. EIS was measured with a frequency response detector (263A, EG&G) over frequencies from 10 mHz to 100 kHz at room temperature.

Chapter 5: Electrospinning Process Optimization of Lignin Nanofibres

5.1 Introduction

An empirical model for the electrospinning process optimization is critical for the quantitative study of the influence of various parameters. The response surface methodology (RSM) has been successfully applied in numerous material and process optimization studies. This approach takes the combined effects of several parameters into account and uses statistical methods to fit an empirical model. The model can describe the influence of parameters and predict the results of various parameter combinations, and the surface contour plot of the parameters can also lead to the optimum processing condition.

Nanofibre diameter is one of the most important characteristics that can affect the mechanical properties of the final products, and it was chosen as the response variable for optimization in this study. The fibre diameter of electrospun nanofibres depends on various parameters, including solution properties (e.g., solution concentration, viscosity, and surface tension), processing conditions (e.g., applied voltage and needle diameter), and ambient conditions (e.g., temperature and humidity). Preliminary experimental results showed that the solution concentration and the needle diameter were influencing variables on the diameter of F₄SKL electrospun fibres. Hence, this chapter will characterize the relative contribution of these two electrospinning parameters to the average F₄SKL fibre diameter. In this contribution, the simultaneous effects of these two electrospinning parameters on the average F₄SKL fibre diameter were systematically investigated. An appropriate study range was determined for each parameter where dry, stable, and continuous fibres without beads or droplets could be obtained. The purpose of this study is to investigate the optimum combination of polymer concentration

and needle diameter for fabricating F₄SKL nanofibres with smaller diameters. This empirical model can guide further experiments concerning the mechanical properties of F₄SKL electrospun nanofibres for future applications.

5.2 Choice of Parameters and Experimental Design

5.2.1 Choice of Parameters and Range

Polymer solution viscosity is a major contributing factor to fibre diameter during the electrospinning process. Factors such as polymer molecular weight, solution concentration, and temperature can influence the solution viscosity. For a particular polymer solution at a fixed temperature, solution concentration is the major factor affecting the viscosity. Therefore, the solution concentration was selected for investigation in this study.

The Mark-Houwink-Sakurada equation shows the relationship between intrinsic viscosity (η) and molecular weight (M) and can be expressed as follows:

$$\left[\eta \right] = \mathrm{KM}^{\mathrm{a}} \left(5\text{-}1 \right)$$

Where K and a are constants for a particular polymer-solvent system at a given temperature. The constant $K = 1.89 \times 10^{-3}$ and a = 0.130 were previously determined for SKL in a DMF system [159]. By applying these constants in Equation 5-1, the intrinsic viscosity of F_4 SKL in this study (molecular weight of 36,000 g mol⁻¹) was calculated to be $[\eta] = 0.0739$.

The Berry number (B) is another parameter that indicates the degree of polymer chain entanglements in a solution and can be expressed as a product of intrinsic viscosity and solution concentration as:

$$B = [\eta] * C (5-2)$$

For a uniform electrospun nanofibre with a small diameter, the Berry number ranges from 1 < B < 2.7, which is equivalent to 15% < C < 35% in terms of F₄SKL concentration. In practice, although F₄SKL electrospun fibre formation could be observed with solution concentrations above 15%, the lower end of that concentration range resulted in fibre that contained droplets or beads due to polymer relaxation and low solution viscosity. Hence, in determining the solution range to test, three level of solution concentration were chosen: 25%, 30%, and 35% ('C25', 'C30', and 'C35').

A smaller spinneret needle diameter was found to generate electrospun nanofibre with a finer fibre diameter [160]. According to the model (Equation 2-1) proposed by Rutledge et al., the spinning jet velocity is related to the ratio between the flow rate and the cross-sectional area of the capillary, which is determined by the spinneret needle diameter [49]. For a smaller spinneret needle diameter, the Taylor cone formed at the needle tip is smaller, and the acceleration of the polymer jet is decreased. The flight time for the polymer jet becomes longer, leading to more stretching and elongation of the polymer jet and resulting in smaller fibre diameter [160]. Hence, the fibre diameter can be reduced by decreasing the spinneret needle diameter. In this study, three different needle gauges (G18, G20, and G25) corresponding to three different needle inner diameters (0.51 mm, 0.89 mm, and 1.27 mm, respectively) were chosen for investigation.

5.2.2 Experimental Design

RSM was used to predict the influence of the solution concentration (ξ_1) and the needle diameter (ξ_2) on fibre diameter (y). Three levels were employed for each factor, resulting in quadratic models with nine treatment combinations. The coded variables (x_j) were obtained from the natural variables (ξ_i) listed in Table 5.1 and were calculated from the input variables in the equation. Coded variables values of -1, 0, and 1 were used to represent low, intermediate, and high levels of each factor. Analyses were carried out with the Design Expert statistical software.

By using coded variables $(X_1, X_2, ..., X_K)$, the response function can be expressed as a second-ordered (quadratic) model in the following form:

$$y = \beta_0 + \sum_{j=1}^k \beta_j X_j + \sum_{j=1}^k \beta_{jj} X_j^2 + \sum_{i < j} \sum_{j=2}^k \beta_{ij} X_i X_j + \varepsilon$$
(5-3)

Where β s are numerical values for coefficients and ε is the error term in the model. The numerical coefficient values (β_i) can be found using the least-squares method, and contour plots are depicted as response surfaces to show the influence of the parameters and the relationship between the response and the variables. Table 5.1 presents the measured average diameters of F₄SKL as-spun fibres.

Experiment	Coded v	variables	Natural variables		Response
	X ₁	X ₂	Concentration	Needle	F ₄ SKL As-Spun
			(ξ1)	Diameter (ξ_2)	Fibre Diameter
			(wt %)	(mm)	(nm)
C25-G25	-1	-1	25	0.51	629 ± 31
C25-G20	-1	0	25	0.89	770 ± 46
C25-G18	-1	1	25	1.27	776 ± 24
C30-G25	0	-1	30	0.51	805 ± 43
C30-G20	0	0	30	0.89	935 ± 36
C30-G18	0	1	30	1.27	1184 ± 43
C35-G25	1	-1	35	0.51	1341 ± 59
C35-G20	1	0	35	0.89	1410 ± 38
C35-G18	1	1	35	1.27	1776 ± 60

Table 5.1: Design of experiments and related responses.

5.3 **Results and Discussion**

5.3.1 Fibre Morphology and Average Diameter

The average fibre diameters and morphology of the F_4SKL as-spun fibres were analyzed using SEM. The SEM images for all electrospinning conditions are shown in Figure 5.1. F_4SKL as-spun fibres tended to have beads and droplets when the solution concentration was below 25% due to the insufficient molecular entanglement in the lowest viscosity solution. F_4SKL solution concentrations of 25% and higher were sufficient for generating uniform, smooth fibres. Higher solution concentrations produced larger diameter fibres due to the increased solution viscosity. The average fibre diameter more than doubled when the F_4SKL concentration increased from 25 to 35 wt% (with the same needle gauge). As expected, the fibre diameter decreased with the smaller gauge needles. The smallest average nanofibre diameter was 629 ± 31 nm, obtained from the combination of G25-C25, whereas the largest fibre diameter was 1776 ± 60 nm obtained from the combination of G18–C35. The 35% solution produced average fibre diameters above 1 µm with all three needles, indicating that the effect of the solution concentration was greater than that of the spinneret needle diameter.

Gauge/Con	G18	G20	G25
C25	55 NO15, Smg 20 OUV v5 01 10m		
C30		55 ND15. 6mi 20' Čŕv' rásički 10mi	
C35	1015.5mm 201.0x* v4.0x 30un	85 NO18, 5m2 20 00V vi, 0X 100m	13 HULS and Solicit of the Solicit

Figure 5.1: SEM images of F₄SKL as-spun fibre morphology for different electrospinning

combinations.

5.3.2 Response Function

After the β s were estimated, the quadratic model for the average fibre diameter (AFD) in terms of coded variables could be written as:

$$AFD = 160.17*X_1 + 392.14*X_2 + 72.21*X_1*X_2 + 49.36*X_1^2 + 145.79*X_2^2 + 938.28 (5-4)$$

And in terms of natural variables as:

 $AFD = 4754.19 - 1339.94*(gauge inner diamter) - 305.58*(concentration) + 38.23*(gauge inner diamter)*(concentration) + 345.84*(gauge inner diamter)^2 + 5.83*(concentration)^2 (5-5)$

Table 5.2 shows the *F* statistics of this test along with the *p*-value for this model. The *p*-value of this model was very small, leading to the conclusion that the null hypothesis must be rejected, but suggesting that there are some significant terms in the model. R^2 is a measurement of the amount of response variation that can be explained by the variables, and R_{adj} is the R^2 adjusted for the number of terms in the model. The R^2 demonstrated that the model is 98% explained by the variables, and both R^2 and R^2_{adj} values indicated that the model fit the experimental data well. The slight difference between R^2 and R^2_{adj} suggested that there might be some insignificant terms in the model.
	F	p-value	R ²	\mathbf{R}^{2}_{adj}
Average fibre diameter	91.61	< 0.0001	0.9849	0.9742

Table 5.2: Significance probability (p-value) and correlation coefficients (R^2 and R^2_{adj}) for theresults from statistical analysis models.

A contour plot and a surface response plot of the effect of interactions between the spinneret needle diameter and the solution concentration on fibre diameter are shown in Figure 5.2 and Figure 5.3, respectively. In this study, the average F₄SKL as-spun fibre diameter increased monotonically with increasing solution concentration. Larger spinneret needles also increased the average fibre diameter, but to a lesser degree than the solution concentration. These observations suggest that the solution concentration is an important variable affecting the fibre diameter confirms that increased viscoelastic force from a higher solution concentration can cause a larger electrostatic stretching force resistance, leading to electrospun fibres with larger diameters. These observations are consistent with both theoretical expectations and previous research findings [49].



Needle Diameter

Figure 5.2: Contour plot for average fibre diameter in terms of solution concentration and needle

diameter.



Figure 5.3: Response surface plot for average fibre diameter in terms of solution concentration and needle diameter.

5.4 Concluding Remarks

In this study, RSM was employed to establish the relationships between two electrospinning parameters (solution concentration and spinning needle inner diameter) and one response (fibre diameter). A factorial experimental design at three levels of each parameter was carried out. A RSM quadratic model was developed, and the significance test of the coefficients demonstrated that the model fits the experimental data well. A Contour plot was generated to study the effects of variables on fibre diameter. It was found that fibre diameter was more sensitive to changes in solution concentration than in spinneret needle diameter. F_4SKL fibre diameter tended to decrease with decreasing of solution concentrations and needle diameters. Additionally, changes in fibre diameter were more pronounced at lower solution concentrations and smaller spinneret needle diameters. These observations suggest that solution concentration is an important variable affecting fibre diameter. The smallest fibre diameter (629 ± 31 nm) was achieved with a 25% solution concentration (C25) combined with a 0.51-mm needle inner diameter (G25). This combination was therefore used in all further electrospinning processes.

Chapter 6: Mechanical Properties of Electrospun Lignin Nanofibre Mats

6.1 Introduction

A fundamental understanding of the mechanical properties and behavior of F₄SKL electrospun nanofibre mats is critical for their structural applications. In the work described in this chapter, the mechanical properties characterization was first carried out on the random nanofibre mats formed of as-spun, thermo-stabilized, and carbonized F₄SKL nanofibres to determine the mechanical properties improvement achieved by fibre diameter reduction and heat treatment processes. Microstructure characterizations including SEM, FT-IR, X-RD, and Raman spectroscopy were used to analyze changes in F₄SKL nanofibre structure after heat treatment. Tensile tests on the aligned nanofibre mats were then carried out to evaluate the mechanical properties improvement achieved by fibre alignment.

6.2 Results and Discussion

6.2.1 Mechanical Properties of As-spun Nanofibre Mats

After electrospinning, all nine combinations of F_4SKL as-spun fibre were collected as random (non-woven) fibre mats. Mechanical properties characterization was carried out on 5 mm × 50 mm strips to investigate and analyze the effects of fibre diameter on the mechanical properties of fibre mats. Representative stress-strain curves are presented in Figure 6.1, and the average tensile strengths and Young's moduli under all conditions are summarized in Table 6.1.



Figure 6.1: Typical stress-strain curve of F₄SKL as-spun random fibre mats with different solution concentrations and needle gauges.

The stress-strain curves of F₄SKL as-spun random fibre mats exhibited an extensive plastic deformation through necking of the fibre mats prior to fracture, and all the curves demonstrated similar characteristics (Figure 6.1). It is known that the mechanical behavior of a fibre mat is determined not only by individual fibre properties, but also by the geometry and interaction between fibres in the mat [161]. The sliding friction among individual fibres could also contribute to an increase in resistance to fibre mat deformation. When the increasing stretch loading overcomes these interaction forces, the yielding occurs. After the yielding point is followed by a gradual decrease in Young's modulus caused by the fibre slippage. Once the fibre mat starts to deform plastically, the fibre stretches further, and the reduction of fibre cross attachment also decreases the resistance to deformation, eventually resulting in splitting of the

fibre mat. As a result, the slope decreases in the second region of the stress-strain curve [118,157].

Sample	Tensile Strength	Young's Modulus	Diameter (nm)
	(MPa)	(MPa)	
C25-G25	5.65 ± 0.61	579.11 ± 16.98	629 ± 31
C25-G20	4.41 ± 0.74	490.93 ± 42.90	805 ± 43
C25-G18	3.62 ± 0.11	312.10 ± 42.90	1341 ± 59
C30-G25	4.21 ± 0.23	436.59 ± 37.84	770 ± 46
C30-G20	3.84 ± 0.10	353.70 ± 36.43	935 ± 36
C30-G18	3.47 ± 0.41	343.03 ± 16.37	1410 ± 38
C35-G25	3.98 ± 0.55	415.24 ± 59.41	776 ± 24
C35-G20	3.32 ± 0.58	357.68 ± 43.47	1183 ± 43
C35-G18	3.13 ± 0.13	228.17 ± 30.70	1776 ± 60

Table 6.1: Tensile properties of F₄SKL as-spun random fibre mats.

The tensile strength and Young's modulus dependence of F_4SKL random as-spun fibre mats with the average fibre diameter are shown in Figure 6.2 (a) and (b), respectively. It is evident that both tensile strength and Young's modulus increased with decreasing fibre diameter. Random fibre mats with the smallest average fibre diameter (629 nm; C25-G25) had the highest tensile strength and Young's modulus (5.65 ± 0.61 MPa and 579.11 ± 16.98 MPa, respectively). Conversely, the G18-C35 combination with the largest average fibre diameter (1776 nm) had the lowest tensile strength and Young's modulus $(3.13 \pm 0.13 \text{ MPa} \text{ and } 228.17 \pm 30.70 \text{ MPa}, \text{respectively}).$

There are other considerations in interpreting the results derived from non-woven fabric mats. The calculation of specific stress is related to fibre density, which was not directly measured for individual mat samples in this experiment. The density was assumed to be uniform (~1.35 g cm⁻³) because of the difficulty in determining the actual density due to the highly porous and compressible nature of fibre mats. Studies on the modified non-woven fabric density determination have been proposed including by measuring the thickness of the fibre mats with a constant pressure or by using the mercumeter. However, the measurement results were still inconsistent. The measured tensile strength of these fibre mat samples could have been significantly higher if a more accurate measurement of density was possible [122]. Furthermore, the sliding friction between fibres and the fibre distribution in the testing samples may also have had impacts on testing results.

As anticipated, fibre mats made with larger fibres exhibited lower strength and elastic modulus. Another possible explanation could be that larger fibres have fewer fibre-to-fibre contact points due to the increase in fibre diameter in a given area. These results are in agreement with previous research concerning the mechanical properties of electrospun fibre mats [162–164]. With appropriate post-processing, the mechanical properties of F₄SKL electrospun fibres can be further improved.

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Figure 6.2: Dependence of (a) tensile strength and (b) Young's modulus of F₄SKL as-spun random nanofibre mats with the average fibre diameter.

6.2.2 Mechanical Properties of Thermo-stabilized Nanofibre Mats

The as-spun nanofibre mat (G25-C25) underwent further heat treatment to investigate the effects of the thermo-stabilization process on the mechanical properties of F₄SKL nanofibres. Thermo-stabilization process is critical for carbonization and greatly influences the mechanical properties of the resulting CFs and CNFs. Previous studies have shown that thermo-stabilization in an oxygen atmosphere prior to carbonization can promote the cross-linking reaction of chemical structures between molecular chains of lignin fibres, and can prevent fibres from fusing in further carbonization processes [13,15,42]. The thermo-stabilization process of lignin involves polymer condensation and dehydration, since the alkyl components of lignin are partially oxidized. During the thermo-stabilization process, water, methanol, and methane are released, and esters and anhydride groups are formed as the temperature rises [43]. Thermo-stabilization parameters, such as heating rate, stabilization temperature, and the ambient atmosphere, can all

affect chemical reactions and the final properties of the thermo-stabilized fibre. In this research, three different heating rates (0.5 °C/min, 5 °C/min, and 20 °C/min) combined with three different final thermo-stabilization temperatures (150 °C, 200 °C, and 250 °C) held for one hour were used to investigate the thermo-stabilization effect on the mechanical properties performance of F_4SKL electrospun nanofibres.

SEM images of thermo-stabilized (TS) F_4SKL nanofibres at different heating rates and temperatures revealed that the nanofibres maintained their shape and did not fuse even at the highest heating rate of 20 °C/min held at 250 °C (Figure 6.3). The resilience against fusing suggests that pure F_4SKL nanofibres possess a lower thermal activation energy and a higher thermal processing rate [165]. Moreover, F_4SKL has a higher molecular weight (36,000 g mol⁻¹), which results in a higher glass-transition temperature (T_g).

	150 °C	200 °C	250 °C
0.5 °C /min	viisk 0000 20kV 20mm	HISK 000 20KV 20M	11.5K 0000 20KV 20M
5 °C /min	11.5K 0800 20KV 200H	K1.5K 0800 ZOKV ZOPA	×1.5K 0000 20KV 2000
20±3 °C /min	11.5K 0800 28KV 29MK	икана кака кака кака кака кака кака кака	¥1.5К 0000 2014 200ж

Figure 6.3: SEM images of F₄SKL thermo-stabilized nanofibres at different heating rates and temperatures.

The stress-strain curves of random TS mats under all thermos-stabilization conditions are presented in Figure 6.4, and the average fibre diameter and mechanical properties for each condition are summarized in Table 6.2. A histogram of tensile strength and Young's modulus for all F₄SKL random TS mats indicates that both strength and Young's modulus increased with the heating temperature (Figure 6.5).

The results showed that 150 $^{\circ}$ C TS mats had more extensive stress-strain behavior with larger plastic deformation regions. In contrast, the 200 $^{\circ}$ C and 250 $^{\circ}$ C TS mats showed brittle

behavior, exhibiting a very narrow plastic deformation region and breaking shortly after reaching the yielding point. The immediate drop in stress after fracture is a clear indication of brittle fibre mats; similar behavior has been observed in amorphous nanofibre mats heated above a certain temperature [166]. Despite the increased brittleness, the 250 °C TS mats had higher tensile strength and Young's modulus than that of the 200 °C and 150 °C samples. The higher strength could be attributed to the formation of intermolecular cross-linking structures in F₄SKL TS nanofibre at 250 °C. The 250 °C TS sample exhibited low strain at break, indicating that the F₄SKL became very brittle, behaving like a porous film containing voids that act as stress concentrators to initiate crack formation [166,167].

The results showed that F_4SKL TS nanofibre diameters did not vary under all thermostabilization conditions. As for mechanical properties, the tensile strength and Young's modulus of random TS mats increased steadily with increasing thermo-stabilization temperature (Figure 6.4 and Table 6.2). At a heating rate of 5 °C/min, the tensile strength and Young's modulus of F_4SKL 150 °C random TS mats slightly increased to 9.40 ± 2.57 MPa and 1.11 ± 0.27 GPa, respectively, whereas the tensile strength and Young's modulus of F_4SKL 200 °C random TS mats further increased to 18.70 ± 2.58 MPa and 1.39 ± 0.19 GPa, respectively. Compared to asspun random nanofibre mats, the 250 °C TS samples increased in tensile strength and Young's modulus from 5.65 ± 0.61 MPa and 0.58 ± 0.02 GPa, to 25.54 ± 2.68 MPa and 1.35 ± 0.19 GPa, respectively. As for the effect of heating rate, the mechanical properties of F_4SKL random TS mats increased at the same final temperature with an increase of heating rate from 0.5 to 5 °C/min. The mechanical properties of F_4SKL random TS mats did not increase, however, and even declined when the heating rate was increased from 5 °C/min to 20 °C/min. To summarize, the heating rate and the final thermo-stabilization temperature were both correlated with the mechanical properties of F_4SKL nanofibre mats. Compared to as-spun nanofibre mats, the mechanical properties of random TS mats demonstrated a four-fold increase after being thermo-stabilized with a 5 °C/min heating rate at 250 °C for one hour.



Figure 6.4: Representative stress-strain curves of F₄SKL thermo-stabilized nanofibre mats under

varying heating rates and temperatures.



Figure 6.5: Plot of tensile strength and Young's modulus against thermo-stabilization temperature for F₄SKL nanofibre mats.

Sample		Tensile Strength	Elastic Modulus	Elongation	Average Fibre
		(MPa)	(MPa)	(%)	Diameter (nm)
0.5 °C/min	150 °C	8.02 ± 2.65	914.53 ± 193.96	8.72 ± 2.78	594 ± 79
0.5 °C/min	200 °C	14.63 ± 2.41	1031.12 ± 146.11	1.81 ± 0.26	540 ± 76
0.5 °C/min	250 °C	18.84 ± 3.88	1073.91 ± 204.21	2.26 ± 0.01	579 ± 73
5 °C/min	150 °C	9.40 ± 2.57	1111.41 ± 270.94	8.22 ± 3.44	568 ± 67
5 °C/min	200 °C	18.70 ± 2.58	1347.24 ± 188.28	1.56 ± 0.24	544 ± 87
5 °C/min	250 °C	25.54 ± 2.68	1387.76 ± 138.45	2.60 ± 0.51	548 ± 79
20 °C/min	150 °C	6.57 ± 1.82	597.82 ± 143.04	8.10 ± 0.02	591 ± 79
20 °C/min	200 °C	11.21 ± 1.96	888.65 ± 105.5	1.53 ± 0.22	563 ± 85
20 °C/min	250 °C	22.09 ± 3.66	1131.4 ± 149.9	2.15 ± 0.40	567 ± 67

Table 6.2: Mechanical properties of thermo-stabilized F₄SKL random nanofibre mats.

FT-IR revealed changes in the chemical structure of F_4SKL nanofibres under different thermo-stabilization temperatures at the same heating rate (5 °C/min). The FT-IR spectrum showed characteristic absorption bands of the at 1267 – 1266 cm⁻¹, 1126 – 1140 cm⁻¹, 1033 – 1031 cm⁻¹, 856 – 854 cm⁻¹, and 816 – 814 cm⁻¹, which were consistent with softwood lignin [168,169] (Figure 6.6). F₄SKL samples also demonstrated the absorption band characteristics of aromatic structures with the O–H stretching band (3380 – 3365 cm⁻¹), the C–H stretching band (2840 – 2940 cm⁻¹), and the aromatic skeleton stretching bands (~1600, 1152 – 1151 and 1425 – 1422 cm⁻¹). Table 6.3 gives the complete list of spectral bandwidths assigned to bond structures.

The FT-IR spectroscopy of F₄SKL nanofibres oxidized at 250 °C showed a reduction in sharpness for all band peaks compared to the 200 °C and 150 °C samples. At the highest thermostabilization temperature, a strong increase in peak intensity was detected at 1720 - 1750 cm⁻¹, corresponding to the non-conjugated C=O stretching, indicating the formation of esters, ketones, aldehydes, and carboxyl groups. This can be attributed to the cleaved β -O-4 bond that introduced the rearrangement of the F₄SKL structure [170]. Additionally, a reduction in absorbance was observed in the region from $1000 - 1400 \text{ cm}^{-1}$ in the 250 °C treated TS nanofibres. In this region, the bands at 1200 cm⁻¹ and 1033 cm⁻¹ correspond with C–O stretching and deformation of the methoxyl group, which indicate that the methoxyl group at the C3 position may be cleaved at 250 °C. The decreased band peak at 1041 cm⁻¹ corresponds to β -O-4 alkyl ether vibration, indicating the cleavage of β -O-4 linkages. Collectively, the evidence suggests a general breakdown of the lignin chemical structure at 250 °C. The cleavage of alkyl-aryl ether linkages at earlier stages of the thermo-stabilization process could produce the bond formation of ketones, phenols, and carboxyl groups, resulting in a series of structural rearrangements and cross-linking reactions that transform lignin into a thermo-set polymer [170]. The shift of aromatic out-of-

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plane C–H stretching (780 – 860 cm⁻¹) indicates cross-linking reactions at the C5 position on the aromatic structure and changes in aromatic substitutions. Overall, the results showed that anhydrides, esters, and aromatic carbon-carbon bonds were formed at 250 $^{\circ}$ C.

Elemental analysis showed that the carbon content of the F₄SKL nanofibre first increased from 73.94% to 75.62% after thermo-stabilization at 150 °C, then gradually decreased to 75.29% and 72.96% at 200 °C and 250 °C, respectively. A possible reaction mechanism for the eventual loss of carbon at higher temperatures could be due to the hemolytic cleavage and structural rearrangement of β -O-4 alkyl-aryl ethers [170]. Braun *et al.* [42] developed a continuous heating transformation diagram, showing that carbon and hydrogen content decreased while oxygen content increased when thermo-stabilization temperatures rose up to 200-250 °C, and oxygen content decreased at higher treatment temperatures. The present F₄SKL nanofibres experimental results showed similar trends [42,171].



Figure 6.6: FT-IR of F₄SKL nanofibres at different thermo-stabilization temperatures: 150 °C, 200 °C, and 250 °C.

Id.	Band assignment	Peak wavenumber (cm^{-1})
1	O-H stretch	3412-3460
2	C-H stretch in methyl and methylene groups	2842-3000
3	C=O stretch in un-conjugated ketones, carbonyls and	1695-1720
	ester groups	
4	Aromatic skeletal vibrations and C=O stretch	1600
5	Aromatic skeletal vibrations	1505-1515
6	C-H deformation; asymmetry in –CH ₃ and –CH ₂ -	1450-1465
7	Aromatic skeletal vibrations combined with C-H in	1430
	plane deformation	
8	Aliphatic C-H stretch in CH ₃	1384
9	G ring plus C=O stretch	1270
10	C-C, C-O, C=O stretch	1210-1220
11	C-O deformation in secondary alcohols and aliphatic	1080
	ethers	
12	Aromatic C-H in-plane deformation, C-O stretch in	1030-1035
	primary alcohols, un-conjugated C=O stretch	
13	HC=CH- out-of-plane deformation	966
14	C-H out-of-plane deformation in position 5 and 6 of G-	822
	units	
15	C-H out-of-plane deformation in position 2 of G-units	855

Table 6.3: FT-IR band assignments for F4SKL nanofibres[170,171].

6.2.3 Mechanical Properties of Random Carbon Nanofibre Mats

6.2.3.1 Tensile Test of Random Carbon Nanofibre Mats

Previous results showed that thermo-stabilization with a 5 °C/min heating rate at 250 °C for one hour can achieve the highest mechanical properties for F₄SKL random nanofibre mats. This condition was therefore used for thermo-stabilization. The carbonization process was then carried out at a 5 °C/min heating rate to 800 °C, 900 °C, and 1000 °C in a tube furnace in nitrogen atmosphere for one hour. SEM images of F₄SKL CNF morphology showed that the CNF maintained the fibre shape and did not fuse (Figure 6.7). The F₄SKL CNF average diameter decreased with increasing carbonization temperature (Table 6.4). Compared with the F₄SKL asspun nanofibre, the average fibre diameter of 1000 °C CNF showed 24.64% shrinkage, from 629 to 474 nm. Elemental analysis showed that the carbon content of the F₄SKL CNF increased to 86 wt% or higher after carbonization at 1000 °C.

Mechanical properties of the electrospun F₄SKL random CNF mats carbonized at 800 °C, 900 °C, and 1000 °C were characterized (Figure 6.8). The tensile test results indicate that both tensile strength and Young's modulus increased with increasing carbonization temperature. Strain at break of the CNF mats occurred around 1% for all conditions. The tensile strength and Young's modulus of 800°C CNF mats were 35.60 ± 4.78 MPa and 5.03 ± 0.45 GPa, respectively, whereas the tensile strength and Young's modulus of 1000 °C random CNF mats increased to 50.73 ± 7.31 MPa and 6.33 ± 1.23 GPa, respectively. Hence, the tensile strength was improved by ~42 % and Young's modulus was improved by ~25 % when raising the carbonization temperature from 800 to 1000 °C. The 1000 °C CNF mats had an order of magnitude increase in tensile strength compared to the as-spun nanofibre mats (5 to 50 MPa). The mechanical properties of 1000 °C CNF mats were higher than those reported in previous research using the

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same material with larger fibre diameter [155], but lower than those of lignin-PAN CNF mats [172] and PAN-based CNF mats [157,173].



Figure 6.7: Scanning electron microscopy images of F₄SKL carbon nanofibres carbonized at (a)

800 °C, (b) 900 °C, and (c) 1000 °C.



Figure 6.8: Plot of tensile strength and Young's modulus vs. carbonization temperature for F_4SKL carbon nanofibre mats.

Temperature (°C)	Tensile Strength (MPa)	Elastic Modulus (GPa)	Strain at Break (%)	Average Fibre Diameter (nm)
800	35.60 ± 4.78	5.03 ± 0.45	1.15 ± 0.31	564 ± 56
900	45.31 ± 3.51	5.80 ± 0.79	1.03 ± 0.42	515 ± 72
1000	50.73 ± 7.31	6.33 ± 1.23	0.98 ± 0.31	475 ± 81

Table 6.4: Mechanical properties and average fibre diameter of F₄SKL carbon nanofibres at different carbonization temperatures.

6.2.3.2 X-Ray Diffraction (X-RD) Analysis of Carbon Nanofibres

The microstructure of F₄SKL CNFs was characterized by X-RD and Raman spectroscopy. X-RD patterns and structure parameters of F₄SKL nanofibres carbonized at various temperatures can be seen in Figure 6.9 and Table 6.5. The carbonized samples had broad peaks around 22° and 44° that can be attributed to the (002) and (100) crystallographic planes in the disordered carbon structures [174–176]. When the carbonization temperature increased from 800 to 1000 °C, the peak intensity and sharpness also increased, and the (002) peak position shifted to a higher 20 angle, from 21.30° to 23.04°. The average inter-planar spacing ($d_{(002)}$) and crystallite size parameter (L_c) could be determined according to the Bragg equation and the Scherrer equation using the Gaussian distribution adoption [174]. The decrease in average interlayer spacing ($d_{(002)}$) from 0.4166 to 0.3855 nm and the increase in crystallite size (L_c) from 0.9807 to 1.187 nm could be attributed to the structural development from disordered carbon to short-range ordered carbon structures (Table 6.5). The results indicated that the increase in carbonization temperature led to the formation of graphitic crystallites and structural rearrangements that created larger and more

ordered structures. Nevertheless, the average interlayer spacing ($d_{(002)}$) of 1000 °C F₄SKL was significantly greater than that of pure graphite (0.3354 nm), suggesting a turbostratic carbon structure of F₄SKL CNF. Similar results have been reported with 1000 °C lignin-based melt-spun carbon fibres ($d_{(002)} = 0.3878$ nm and $L_c = 0.900$) [177]. Previous research showed that the average inter-planar spacing distance reduced with increasing final carbonization temperature, and the $d_{(002)}$ of 1500 °C and 2000 °C lignin-based CFs were found to be 0.345 nm and 0.342 nm, respectively [177]. Compared with PAN-based CNFs, the graphitic structure of lignin-based CFs is comparable to that of the 'T-300' Grade PAN-based CNF when carbonized at 2100 °C [177]. It is clear from the results that the F₄SKL carbonization process is more complicated than that of PAN-based CFs, due to the complexity of lignin structures.



Figure 6.9: X-ray diffraction patterns of F₄SKL carbon nanofibres at different temperatures.

Temperature (°C)	2θ ₍₀₀₂₎ (°)	d ₍₀₀₂₎ (nm)	$L_{c}(nm)$
800	21.3031	0.4166	0.9807
900	22.2304	0.3994	1.110
1000	23.0410	0.3855	1.187

Table 6.5: Structural parameters of X-ray diffraction patterns of F₄SKL carbon nanofibres.

6.2.3.3 Raman Spectroscopy Analysis of Carbon Nanofibres

Raman spectroscopy is an advanced method of investigating micro-structural changes during the carbonization process. Typical Raman spectra of carbonaceous materials (Figure 6.10) have two separate characteristic bands: the disordered carbon D-band peak (centered at a wavenumber of approximately 1310 cm⁻¹) and the crystalline graphite G-band peak (centered at a wave-number of approximately 1580 cm⁻¹). The intensity ratio (I_D/I_G), peak position change, and full width at half maximum (FWHM) of the D-band and the G-band can indicate the structural change and the development of ordered graphitic crystallites in the carbonaceous materials [178] The FWHM of the D-band is related to the graphitization degree of the carbonaceous material, whereas the FWHM of the G-band is related to the degree of ordered carbon structures. The Dband FWHM decreases as the degree of graphitization increases, and the G-band FWHM decreases when the degree of ordered carbon structure increases [179].

The results indicated that the I_D/I_G of F₄SKL CNF increased from 1.71 to 1.86 as carbonization temperatures increased from 800 to 1000 °C (Table 6.6). In terms of peak position, both the D-band and G-band peak positions shifted to higher frequencies with increasing carbonization temperature. According to the Raman spectra three-stage model of amorphous and disordered carbon formation proposed by Ferrari and Robertson [180,181], the trend of the I_D/I_G

ratio for graphitic/amorphous carbons depends on the degree of graphitization. An amorphization trajectory reveals that when an amorphous carbon gradually forms a more ordered graphitic structure, it will first increase the I_D/I_G ratio and the G-band will shift to a higher frequency. When it is in the stage of the formation of nano-crystallized graphitic structures, the I_D/I_G ratio then decreases and the G-band peak position shifts to a lower frequency due to the decrease in the number of ordered rings [180,181]. Since lignin is an amorphous polymer, it begins from the amorphous state during carbonization. As the temperature increases, the amorphous carbon becomes more ordered with the formation of nano-crystalline graphitic structure due to the nucleation growth and clustering of aromatic rings [180]. The shift towards a higher frequency G-band peak of F₄SKL CNF is also in agreement with the three-stage model of amorphization [180]. The trend towards increased ordering of aromatic rings is supported by the decrease in Dband FWHM with increasing carbonization temperature. The decrease of D-band FWHM is related to the increasing number of six-carbon aromatic rings in F₄SKL CNF, whereas the increase of the G-band FWHM can be attributed to the increased distribution of non-aromatic conjugated sp^2 carbon chain structures in F₄SKL CNF. Previous research concerning the carbonization of wood, cellulose, and organosolv lignin showed similar results [182] and indicated that lignin graphitization increased with increasing carbonization temperature [183]. These previous studies also concluded, however, that the long-range graphitic ordered structures had no preferential orientation along the carbon fibre axis. To utilize F₄SKL as a more suitable precursor for CNF production, methods to enhance the crystallinity of lignin must be applied to the F₄SKL precursor. In contrast, PAN is considered to be a semi-crystal polymer and the I_D/I_G ratio of PAN-based CF decreases with increasing temperature in a similar carbonization temperature range [173,184–187].

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Temperature	D-band	G-band	R-value	FWHM of D	FWHM of G
(°C)	position	position	(I_D/I_G)	$(W_{\rm D})$	$(W_{\rm G})$
800	1309.54	1582.33	1.71 ± 0.05	235.97 ± 4.88	63.37 ± 3.90
900	1310.15	1583.52	1.77 ± 0.09	229.45 ± 0.50	65.31 ± 2.56
1000	1311.86	1583.96	1.86 ± 0.03	210.65 ± 4.38	68.18 ± 1.97

Table 6.6: F_4SKL carbon nanofibres peak positions, intensity ratios (I_D/I_G), and full width at half maximum (FWHM) of the D-band and the G-band at different carbonization temperatures.



Figure 6.10: Typical Raman spectrum of F_4SKL carbon nanofibres in the wave number region of 900 – 1800 cm⁻¹, and the fitting curve for the D-band (~1310 cm⁻¹) and the G-band (~1580

cm⁻¹).

6.2.4 Mechanical Properties of Aligned Nanofibre Mats

Due to equipment limitations, methods such as post-drawing to induce high molecular orientation in traditional fibres are often not feasible for single nanofibres. Research has shown that electrospinning can induce molecule chain orientation of nanofibres during the electrospinning process [188], and further stretching of the nanofibres using a high-speed rotating collector can significantly increase the molecular orientation and crystallinity of nanofibres [189] to improve mechanical properties [190]. Lignin is an amorphous polymer, and the structure of which could hinder the alignment of macromolecular chains during electrospinning. The stretching of as-spun F₄SKL precursor nanofibres can therefore improve molecular structural orientation [191]. After the mechanical properties and microstructure characterization of random nanofibre mats, aligned nanofibre mats were collected and characterized in order to study the effect of fibre alignment on the mechanical properties improvement of F₄SKL nanofibres. A rotating drum device (NANON) was used during the electrospinning process to collect F₄SKL aligned nanofibre mats at different numbers of revolutions per minute (RPM). The results showed that fibre alignment increased with increasing collector RPM from 500 to 2000 RPM, whereas discontinuous and short nanofibres were produced at higher rotating speeds. SEM images indicated that F₄SKL aligned nanofibres formed uniform fibres that maintained their shape and did not fuse before or after thermo-stabilization and carbonization (Figure 6.11).

The average diameter of the as-spun randomly distributed nanofibres was 629 ± 31 nm, whereas the average diameters of the 250 °C TS fibres and 1000 °C CNF were 548 ± 79 and 475 ± 81 nm, respectively. In comparison, the as-spun aligned nanofibres had an average diameter of 499 ± 71 nm, whereas the 250°C TS and the 1000°C CNF had average diameters of 420 ± 60 nm

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and 368 ± 62 nm respectively. The average diameter of the aligned nanofibres showed a 25% reduction compared to that of the randomly distributed nanofibres under the same conditions. This can be attributed to the polymer chain stretching of the nanofibre in the rotating drum electrospinning process [173].



Figure 6.11: Morphology of F₄SKL aligned (a) as-spun and (b) carbon nanofibre.

The degree of alignment of nanofibre mats can be determined using the Angular Power Spectrum (APS) based on SEM images. The APS can obtained according to the following equation [192]:

$$A(\theta) = \sum_{r=1}^{R} p_r(\theta) \quad (6-3)$$

Where P is a two-dimensional Fourier Power Spectrum (FPS) from a SEM image (N*N pixels), and *r* and θ are the elements of the polar coordinate. The variables *r* and θ range from 1

to N/2 and 0 to 2π , respectively. The intensity of the APS is normalized by the corresponding mean intensity of the FPS, and the normalized APS versus θ shows the degree of alignment of nanofibre mats. The APS analyses of random and aligned nanofibre mats with corresponding SEM images are demonstrated in Figures 6.12 and 6.13, respectively. The results show that aligned nanofibre mats have a prominent peak around 90 ± 6 degrees (Figure 6.12), whereas random nanofibre mats (Figure 6.13) form broad peaks around 90 ± 30 degrees and 18 degrees. In the aligned nanofibre mats, most of the fibres were aligned in the fibre length direction.



Figure 6.12: Aligned nanofibre mats and their corresponding Aligned Power Spectra (APS).



Figure 6.13: Random nanofibre mats and their corresponding Aligned Power Spectra (APS).

The tensile strength of F₄SKL as-spun random nanofibre mats (5.5 MPa) was lower than that of the aligned nanofibre mats (11.1 MPa; Figure 6.14). After carbonization at 1000 °C, the tensile strength of the random nanofibre mat increased by one order of magnitude from 5.5 MPa to 50 MPa, whereas that of the aligned nanofibre mats increased six-fold from 11 MPa to 66 MPa. The Young's moduli of 1000 °C random and aligned CNF mats were 6.33 ± 1.23 GPa and 17.40 ± 0.55 GPa, respectively, and the strains at break of random and aligned CNF mats were 1.0 ± 0.2 % and 0.8 ± 0.2 %, respectively. In comparison to random CNF mats, the tensile strength of aligned CNF mats improved by 32%, whereas the Young's modulus improved by 175%. These results demonstrated that the mechanical properties of electrospun nanofibre mats can be enhanced by performing a proper fibre alignment. Fibre alignment improves the molecular orientation along the fibre axis, resulting in significant increases in nanofibre mechanical properties. Applying a tension force during the stabilization and carbonization process of aligned nanofibres may further improve mechanical properties. Development and optimization of post-processing on the aligned F₄SKL nanofibre mats is the goal of future work.



Figure 6.14: Comparison of the tensile strengths (a) and Young's moduli (b) of F₄SKL random and aligned nanofibre mats.

6.3 Concluding Remarks

The mechanical properties characterization of as-spun, thermo-stabilized, and carbonized nanofibre mats indicated that the reduction of fibre diameter, a proper heat treatment process, and the fibre alignment could all improve the mechanical properties of F_4SKL nanofibre. The mechanical properties of thermo-stabilized nanofibre mats were affected by the heating rate and the holding temperature. FT-IR showed that F_4SKL had β -O-4 linkages cleavage and structure rearrangement reactions during 200-250 °C, indicating the cross-linking reaction and the structure change during thermo-stabilization process.

The mechanical strength of random nanofibre mats increased by an order of magnitude from 5 MPa to 50 MPa after carbonization at 1000 $^{\circ}$ C, whereas the strength of the corresponding aligned CNF mats increased from 11 MPa to 66 MPa. X-RD and Raman spectra analysis showed that the carbon structure of the 1000 $^{\circ}$ C F₄SKL CNF begins in the amorphous carbon stage and then gradually forms a nano-crystalline graphitic structure. Hence, a higher carbonization temperature is necessary to obtain better graphitic structures and improved mechanical performance

Chapter 7: Single-Walled Carbon Nanotube-Reinforced Lignin Composite Nanofibres

7.1 Introduction

The tensile test results and analysis showed that the mechanical properties of F₄SKL CNF need to be further improved. One method to enhance the mechanical properties of electrospun nanofibres is to add strong reinforcing materials into the electrospinning polymer solution to form composite nanofibres. Carbon nanotubes (CNT) are one of the promising fillers that can provide reinforcement for electrospun nanofibres, as evidenced in previous research indicating that the mechanical properties of nanofibres could be increased by adding CNTs [112–114]. CNT have also been found to increase the crystallinity of the polymer matrix by acting as nucleating agents. The graphitic structure and crystal orientation of CNF showed significant improvement, especially at lower carbonization temperatures [193]. However, increasing the amount of CNT could cause the formation of agglomerates and a non-uniform distribution of CNT in the nanofibres [113–115]. To avoid these issues, emulsion electrospinning was used in this research to prepare composite nanofibres [111]. Single-walled carbon nanotubes (SWNT) were added into the F₄SKL solution to fabricate SWNT/F₄SKL composite nanofibres where SWNT was embedded inside as the core and F₄SKL as the shell.

Core-shell composite nanofibres were prepared using a water-in-oil emulsion electrospinning system in which the aqueous phase consisted of SWNT in suspension and the oil phase made use of the F₄SKL solution. The resulting morphology and mechanical properties of as-spun and carbon nanofibres were characterized. Tensile tests were conducted at the nanofibre

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mat level and compared with the existing micromechanics model to assess the reinforcement effect on the mechanical properties of F_4 SKL nanofibres. The changes in carbon structure with and without SWNT were analyzed by Raman spectra. Electrochemical performance tests were also conducted on the CNF mats to investigate potential applications as carbon electrodes for supercapacitors, and the results will be discussed in Chapter 9.

7.2 Results and Discussion

7.2.1 Morphology and Mechanical Properties of SWNT/F₄SKL Composite Nanofibres

SWNT-reinforced F₄SKL composite nanofibres were fabricated using an emulsion electrospinning technique by introducing a SWNT aqueous solution into a 25 wt% F₄SKL solution. 0.5 wt% and 1 wt% SWNT on weight of F₄SKL were used, and the solution preparation was as described in Section 4.4. Figure 7.1 shows typical SEM images of 1 wt% SWNT/F₄SKL as-spun (a), 250 °C thermo-stabilized (b), and 1000 °C (c) carbon nanofibres. These SEM images show that continuous and uniform SWNT/F₄SKL composite nanofibres can be obtained via emulsion electrospinning while maintaining the fibre shape after carbonization at 1000 °C. The nanofibre diameter decreased from 900 to 500 nm after carbonization at 1000 °C. The TEM image shows that these SWNT/F₄SKL nanofibres have the core-shell structure with the SWNT embedded inside the core and the F₄SKL matrix as the shell (Figure 7.1d).



Figure 7.1: Scanning electron microscopy images of SWNT/F₄SKL (a) as-spun, (b) thermostabilized, and (c) carbon nanofibres as well as (d) a transmission electron microscopy image of the core-shell structure of the SWNT/F₄SKL nanofibre.

A cross-sectional TEM image of an SWNT/F₄SKL composite CNF indicates that it has a core-shell structure (Figure 7.2 (a)). TEM images also reveal the amorphous carbon nature of F₄SKL CNF. As shown in Figures 7.2 (b) and 7.2 (c), SWNT/F₄SKL CNF exhibits short-range parallel stacking of thin graphitic layers with an interlayer spacing of 0.33 nm around the SWNT.

These results suggest that SWNT can act as nucleation sites for the formation of ordered carbon structures.



Figure 7.2: Transmission electron microscopy images of SWNT/F₄SKL carbon nanofibre, showing (a) a cross-section of nanofibre, (b) a single-walled nanotube, (c) a graphitic layer, and (d) the interlayer spacing.

After the SWNT/F₄SKL composite nanofibres were collected, mechanical property tests were performed on the as-spun and 1000 °C CNF random nanofibre mats to evaluate the reinforcement effect of SWNT. The average tensile stress-strain curves of the SWNT/F₄SKL as-spun random nanofibre mats are shown in Figure 7.3, and mechanical property test results are summarized in Table 7.1. These results showed that the mechanical properties of random nanofibre mats increased with increasing amount of SWNT. The tensile strength of F_4 SKL random as-spun nanofibre mats showed a 25% increase from 5.65 to 7.18 MPa, whereas the Young's modulus showed a 28% increase from 0.58 to 0.76 GPa with the addition of 1 wt% SWNT. Similarly to the pure F_4 SKL as-spun random nanofibre mats, the tensile test results for SWNT/F₄SKL as-spun random nanofibre mats before fracture.

The average tensile stress-strain curves of the SWNT/F₄SKL random CNF mats are shown in Figure 7.4, and the testing results are detailed in Table 7.2. It was found that the tensile strength of CNF mats increased with the increase of SWNT content. The average stress-strain curve and tensile strength of 1 wt% SWNT/F₄SKL random CNF mats were similar to those of 0.5 wt% SWNT/F₄SKL random CNF mats, whereas the 0.5 wt% SWNT/F₄SKL random CNF mats exhibited a lower tensile modulus. Compared to the pure F₄SKL random CNF mats, the 1 wt% SWNT/F₄SKL random CNF mats showed a 50% increase in tensile strength and an 82% increase in Young's modulus.


Figure 7.3: Average stress-strain curves of F₄SKL and SWNT/F₄SKL random as-spun nanofibre mats incorporating different concentrations of single-walled carbon nanotubes.

 Table 7.1: Mechanical properties of F4SKL as-spun random nanofibre mats incorporating different concentrations of single-walled carbon nanotubes.

Sample	Tensile Strength (MPa)	Young's Modulus (MPa)	Strain at Break (%)	Average Diameter (nm)
F ₄ SKL	5.65 ± 0.61	579.11 ± 16.98	1.85 ± 0.81	629 ± 31
0.5% SWNT/F ₄ SKL	5.99 ± 1.24	589.68 ± 199.16	2.26 ± 0.53	734 ± 76
1% SWNT/F ₄ SKL	6.61 ± 1.05	733.11 ± 124.55	2.02 ± 0.32	746 ± 75



Figure 7.4: Average stress–strain curves of F₄SKL and SWNT/F₄SKL random carbon nanofibre mats incorporating different concentrations of single-walled carbon nanotubes.

 Table 7.2: Mechanical properties of F4SKL random carbon nanofibre mats incorporating different concentrations of single-walled carbon nanotubes.

Tensile	Young's Modulus	Strain at	Average
Strength	(GPa)	Break (%)	Diameter (nm)
(MPa)			
50.73 ± 7.31	6.33 ± 1.23	0.98 ± 0.31	475 ± 81
66.04 ± 12.08	10.46 ± 1.48	0.89 ± 0.38	546 ± 76
75.61 ± 8.51	11.58 ± 1.11	0.94 ± 0.40	525 ± 71
	Tensile Strength (MPa) 50.73 ± 7.31 66.04 ± 12.08 75.61 ± 8.51	Tensile Young's ModulusStrength (MPa) 50.73 ± 7.31 6.33 ± 1.23 66.04 ± 12.08 10.46 ± 1.48 75.61 ± 8.51 11.58 ± 1.11	Tensile Young's ModulusStrain at Strength (GPa)Strain at Break (%) (MPa) (GPa) $Break (\%)$ 50.73 ± 7.31 6.33 ± 1.23 0.98 ± 0.31 66.04 ± 12.08 10.46 ± 1.48 0.89 ± 0.38 75.61 ± 8.51 11.58 ± 1.11 0.94 ± 0.40

In this study, SWNT/F₄SKL random CNF mats exhibited brittle failure, and 1 wt% SWNT/F₄SKL random CNF mats had the highest mechanical properties. This can be attributed to the stress transfer effect of SWNT enhancing the mechanical properties of the F₄SKL CNF matrix. During the tensile testing process, the applied force can cause strain hardening of the nanofibre. SWNT oriented in the loading direction can strengthen the fibre matrix until it reaches its weakest point with highest stress concentration before the fracture occurs. Previous results have shown that if CNTs were dispersed uniformly into the matrix without obvious agglomerations, the mechanical properties of CNT-reinforced composite nanofibres can be improved. Higher CNT contents may reduce the mechanical properties of composite nanofibres, however, due to the poor CNTs dispersion [157]. The optimum SWNT content in F₄SKL nanofibres needs to be further investigated.

The SWNT/F₄SKL aligned CNF mats were also fabricated and collected using the rotating drum method described in Section 4.3, after which the samples were tensile-tested. Figure 7.5 illustrates the mechanical properties comparison of random and aligned CNF mats at various levels of SWNT content, and the average tensile stress-strain curves of the SWNT/F₄SKL aligned CNF mats are shown in Figure 7.6. It can be seen that fibre alignment further improves the mechanical properties of composite nanofibre mats. An approximately 30% increase in tensile strength and a 100% increase in Young's modulus were observed in the aligned composite nanofibre mats compared to the random nanofibre mats, indicating the reinforcement effect by fibre alignment. The influence of SWNT content on the random and aligned nanofibre assemblies is similar.

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Figure 7.5: Comparison of the tensile strength (a) and Young's modulus (b) of F₄SKL and SWNT/F₄SKL random and aligned carbon nanofibre mats.



Figure 7.6: Average stress-strain curves of F₄SKL and SWNT/F₄SKL aligned carbon nanofibre mats incorporating different concentrations of single-walled carbon nanotubes.

The results showed similar trends in the mechanical property reinforcement as those found in previous research. Baker [13] investigated the mechanical property enhancement of CNTs by adding MWNT into different types of lignin precursors and then melt-spinning them into fibre. The results showed that 15 wt% MWNT enhanced the mechanical properties of lignin-based melt-spun fibres, and the resulting CF exhibited a 20% increase in tensile strength and a 50% increase in modulus.

Several factors such as interfacial bonding between the SWNTs and the F_4 SKL matrix can also affect the mechanical reinforcement provided by SWNT. Furthermore, these fibres were tested without any post-treatment. Post-processing methods such as mechanical drawing would further align the F_4 SKL molecules and the SWNTs within the fibres as well. This drawing effect has been observed in micrometer filaments with a significant improvement in tensile properties [194]. Following up with the heat treatment of the fibres might generate better interactions between SWNT and F_4 SKL, hence improving the mechanical properties.

The addition of strong carbon nanomaterials such as CNTs to reinforce the mechanical properties of polymer fibres has been studied for decades, and one model for CNT-reinforced composites can be express as [121]:

$$\rho_{\min(p)} = \mu_1 \mu_2 \rho_r f_r + \rho_m f_m$$
 (7-1)

Where μ_1 is the length efficiency factor, μ_2 represents the orientation efficiency factor of CNT, ρ_{mix} denotes the mechanical properties of a composite fibre, and ρ_r and ρ_m represent the mechanical properties of the reinforcement and the matrix, respectively. For SWNT, μ_1 can be

set to one because the length and diameter ratio of SWNT is larger than 10, and if the SWNT is aligned through the matrix, then μ_2 can be set to one [137].

After the mechanical properties of SWNT/F₄SKL composite nanofibres were calculated, the Young's modulus of SWNT/F₄SKL random CNF mats (E_c) with the addition of SWNT can be calculated using the modified rule of mixture equation and can be expressed as follows [195]:

$$E_{c} = \left(\left(E_{1} \phi_{1} + E_{2} (1 - \phi_{1}) \right) a \right)^{b} \quad (7-2)$$

Where E_1 is the modulus of SWNT, E_2 is the modulus of F₄SKL, ϕ_1 is the volume fraction of SWNT, *a* is the coefficient factor of the composite nanofibre, and *b* is the power coefficient of the composite nanofibre.

The volume fraction of SWNT can be calculated from the following equation:

$$FVF = \frac{1}{1 + \frac{\rho_F}{\rho_m} \left(\frac{1}{FWF} - 1\right)} (7-3)$$

Where FVF is the SWNT volume fraction, FWF is the SWNT weight fraction, ρ_F is the density of SWNT (0.8 g cm⁻³), and ρ_m is the density of F₄SKL CNF (1.5 g cm⁻³).

For a random nanofibre mat, the coefficient factor a = 3/8, and the power coefficient can be obtained using the best-fit method. Figure 7.7 shows the fitting result of the model equation and the experimental data, and the boundary condition was set-up from 0.5 wt% of SWNT content. It demonstrates that the model equation and the experimental data fits well when the SWNT volume fraction is in the 0.5-2% range (a = 3/8 and b = 0.675).



Figure 7.7: Model for the Young's moduli of SWNT/F₄SKL random carbon nanofibre mats, plotting Young's modulus against single-walled carbon nanotubes content.

7.2.2 Raman Spectroscopy of SWNT/F₄SKL Carbon Nanofibres

Raman spectroscopy was used to analyze the carbon structural changes that occurred in the SWNT/F₄SKL composite CNF during the carbonization process. The full width at half maximum (FWHM) of both the graphitic band peak (G-band) and the disordered carbon band peak (D-band) along with the intensity ratio (I_D/I_G), were also applied for characterization (Table 7.3; Figure 7.8 (a) and (b)). The D-band and G-band FWHM line plots are shown in Figure 7.8 (c) and (d). It is evident that the intensity ratio I_D/I_G of 1000 °C SWNT/F₄SKL composite CNF decreased with increasing SWNT content, indicating that the incorporation of SWNT could act as a nucleation site to induce the transformation of the amorphous carbon to form a more ordered

nano-size graphitic crystallite structure. This trend is also similar to that found in previous research on CNT/PAN-based electrospun composite CNF [193]. The D-band FWHM decreased with increasing SWNT concentration, indicating the ordering of poly-aromatic carbons and the breakage of cross-links between aliphatic carbons and small aromatic carbons. SWNT could further promote reordering of disordered aromatic rings in the composite CNF. The SWNT/F₄SKL composite CNF showed a significantly narrower G-band FWHM compared to that of pure F₄SKL CNF, and the G-band FWHM also decreased and become sharper with increasing SWNT concentration. These results suggest that low a SWNT content can enhance the ordering of carbon crystallites during the carbonization process [193].

Table 7.3: SWNT/F₄SKL carbon nanofibres peak positions, intensity ratios (I_D/I_G), and the fullwidth at half-maximum (FWHM) of the D-band and G-band in relation to different single-walled carbon nanotube (SWNT) contents.

CNF	D-band	G-band	R-value	FWHM of D	FWHM of G
	position	position	(I_D/I_G)	$(W_{\rm D})$	$(W_{\rm G})$
F ₄ SKL	1311.86	1583.96	1.86 ± 0.03	228.65 ± 1.56	68.18 ± 0.91
0.5% SWNT/F ₄ SKL	1310.56	1581.13	1.65 ± 0.08	210.22 ± 5.62	62.05 ± 1.20
1% SWNT/F ₄ SKL	1308.81	1582.78	1.42 ± 0.02	190.86 ± 6.68	49.42 ± 3.51



Figure 7.8: Typical Raman Spectrum of SWNT/F₄SKL carbon nanofibres (a), as well as the intensity ratio (b), and the full-width at half-maximum (FWHM) of the D-band (c) and G-band (d) as a function of single-walled nanotube (SWNT) concentration (wt%).

7.3 Concluding Remarks

In this study, SWNT/ F_4 SKL composite nanofibres were fabricated using the emulsion electrospinning process, and the nanofibre morphology and mechanical properties were examined. SEM and TEM images showed that SWNT/F₄SKL composite nanofibres have the core-shell structure, with SWNT embedded as the core and the F_4 SKL matrix as the shell. The SWNT/F₄SKL composite nanofibres maintained their shape after carbonization at 1000 °C, and TEM images revealed that SWNT/F₄SKL CNFs exhibit short-ranged parallel stacking of small graphitic layers around the SWNT. Raman spectroscopy of 1000 °C SWNT/F₄SKL composite CNFs showed that the intensity ratio (I_D/I_G) , D-band FWHM, and G-band FWHM decreased with increasing SWNT concentration. These results also support the conclusion from the TEM images that the incorporation of SWNT could provide the nucleation site to form a more ordered nano-crystallite graphitic structure. Tensile tests were performed on F_4SKL , 0.5 wt% SWNT/F₄SKL, and 1 wt% SWNT/F₄SKL random and aligned CNF mats to evaluate the reinforcing effect of SWNT on mechanical properties. The tensile strength and Young's modulus increased consistently as the concentration of SWNT increased to 1 wt%. By adding 1 wt% of SWNT, the tensile strength and Young's modulus of CNF mats were increased by 50%. Fibre alignment can further enhance the mechanical properties by providing a 30% increase in tensile strength and a 100% increase in Young's modulus. The Young's modulus of SWNT/F₄SKL random CNF mats also fitted well with the modified rule of mixture model. These results suggest that the presence of SWNT can improve the mechanical properties of F₄SKL nanofibres. With appropriate post-processing, SWNT/F₄SKL composite nanofibres are expected to have higher mechanical properties.

Chapter 8: Mechanical Properties from Single Nanofibres to Fibre Assemblies

8.1 Introduction

A fundamental understanding of the estimation and prediction of the mechanical properties of F₄SKL electrospun single nanofibres in relation to various nanofibre assemblies is important for designing devices for structural and functional applications. Furthermore, the mechanical properties of single nanofibres must be studied in greater detail to achieve further mechanical properties improvements of. Previous research has been conducted on the mechanical behaviour of electrospun nanofibre assemblies [122,161,196–199], yet there remains a lack of data concerning the contribution of individual nanofibres to the mechanical properties of nanofibre mats or yarns. In this study, single nanofibre tensile tests were performed to characterize the mechanical properties of F₄SKL electrospun nanofibres, and the results were analyzed using a Weibull distribution. The translation of mechanical properties from single nanofibres to random and aligned nanofibre mats was investigated by correlating single nanofibre tensile test results with nanofibre mat tensile test results. Various models were applied to validate and predict the mechanical properties translation from single nanofibres to different nanofibre assemblies. The results are critical for validation and modification of the electrospun F₄SKL nanofibres and of other assemblies for potential commercial products

8.2 Theoretical Analysis

Classical and early studies concerning the mechanical properties of fibres and fibre assemblies including fibre mats and yarns were focussed on investigating the statistical Weibull distribution of individual fibres based on the weakest link model [125–127]. Daniels [127] developed the model to investigate the relationship between the statistical strength of an aligned fibre bundle and its constituent fibres, and the results showed that the fibre strength tends to have a normal distribution. In addition, the results of several important mathematical studies on breaking kinetics have been reported based on a statistical theory of mechanical breakdown in time-dependent systems, in which the strength of classical fibres was found to be independent of the rate of loading [200–202]. For a parallel fibre twisted yarn, Daniels' model was modified by directly applying the twisting angle effects of yarns [127].

8.2.1 Weibull Distribution for Single Nanofibres

A single F₄SKL nanofibre can be considered as a polymer chain with several different types of linkages. According to the weakest link theory or size effect on failure, if a fibre is gradually stretched, it breaks at its weakest cross-section [203]. For Weibull-type fibres, the cumulative distribution function of tensile strength provides the probability that fibres break before the strength reaches the value of σ . A two-parameter Weibull distribution can be expressed as follows [125]:

$$F_{l}(\sigma) = 1 - \exp\left[-\frac{1}{l_{0}}\left(\frac{\sigma}{\eta}\right)^{\beta}\right]$$
 (8-1)

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Where σ is the fibre tensile strength, η is the scale parameter, and β is the shape factor for a given fibre gauge length (l₀). The shape factor β shows the strength distribution of fibres, with a higher value of β indicating higher fibre strength uniformity. This probability is a continuous function of l and σ , and the expected mean value of the fibre strength ($\hat{\sigma}_{f}$) with length l can be calculated as [204]:

$$\widehat{\sigma}_{f} = \eta \left(\frac{1}{l_{0}}\right)^{-1/\beta} \Gamma \left(1 + \frac{1}{\beta}\right) \quad (8-2)$$

Where Γ is the gamma function, and the coefficient of variation of $\widehat{\sigma_f}$ is:

C. V. =
$$\left(\frac{\Gamma\left(1+\frac{2}{\beta}\right)}{\Gamma^2\left(1+\frac{1}{\beta}\right)}-1\right)^2$$
 (8-3)

8.2.2 Tensile Strength of Aligned Nanofibre Mats and Twisted Nanofibre Yarns

The tensile strength of an aligned nanofibre mat has a normal distribution [127] and is also related to the scale parameter (η) and shape factor (β). The expected mean strength ($\hat{\sigma}_b$) of the aligned nanofibre mat is:

$$\hat{\sigma}_{\rm b} = \eta \left(\frac{1}{l_0}\beta\right)^{-1/\beta} \exp\left(-\frac{1}{\beta}\right) \quad (8-4)$$

The tensile strength of a twisted nanofibre yarn has a normal distribution as well [127]. Previous research has shown that several parameters can influence the tensile properties of a yarn. The scale parameter (η) and the shape factor (β) are two important factors, as previously described for the strengths of single nanofibres and aligned nanofibre mats. The other factor that could be considered is the critical fibre length (l_c) of the yarn, and the expected mean value of yarn strength $\hat{\sigma}_v$ is [205]:

$$\hat{\sigma}_{y} = K_{\alpha} K_{l} V_{F} \eta (l_{c} \beta)^{-1/\beta} \exp\left(-\frac{1}{\beta}\right) \quad (8-5)$$

Where K_{α} is the orientation efficiency factor due to the fibre obliquity and K_{l} is the fibre length efficiency factor, which is related to the fibre aspect ratio. K_{α} depends on the twist angle at the yarn surface (α) and the Poisson's ratio (V_{LT}) of the yarn, and can be defined as follows [206]:

$$K_{\alpha} = \frac{2\alpha(1 - V_{LT}) + (1 + V_{LT})\sin 2\alpha}{4\alpha} \quad (8-6)$$

Cox showed that the value of length efficiency factor K_1 can approach unity if the fibre length or fibre aspect ratio is large [121]. Another factor that must be taken into consideration is the fragmentation phenomenon. Fragmentation phenomenon in a yarn is a process in which the constituent fibres continuously break during increasing yarn elongation before the rupture of the yarn, and those fibres are again involved in the build up of the yarn's strength. For composites, critical fibre length (l_c) can be obtained according to the following equation [207]:

$$l_{c} = \frac{r_{f}\sigma_{f}}{\mu g} (8-7)$$

Where r_f is the fibre diameter, σ_f is the fibre tensile strength, g is the shear strength (the local lateral pressure) and μ is the friction coefficient between fibres.

The mean lateral pressure on the fibres in the yarn can be calculated as [205]:

$$g = \frac{n}{2\mu} E_f \epsilon_y K_\alpha \quad (8-8)$$

Where E_f is the Young's modulus of the fibre, ϵ_y is the yarn strain, and n is the yarn cohesion factor that indicates how yarn fibres grip and can be calculated according to the twist angle at the yarn surface [205].

For a twisted yarn, l_c can be calculated as [206]:

$$l_{c} = \frac{2r_{f}\sigma_{f}}{nE_{f}\epsilon_{y}K_{\alpha}} (8-9)$$

To calculate the surface angle of a twisted yarn, the following equation can be used [208]:

$$\alpha = \arctan\left[10^{-3}\tau \left(\frac{40\pi}{\rho_{\rm f}V_{\rm f}}\right)^{1/2}\right] \quad (8-10)$$

Where α is twist angle at the yarn surface, τ is the twist factor (tex^{1/2}. twist per cm), ρ_f is fibre specific density, and V_f is fibre-volume fraction ($\rho_{bundle}/\rho_{polymer}$). The yarn strain can be obtained according to the following equation [208]:

$$\epsilon_{\rm f} = \epsilon_{\rm v} (\cos^2 \alpha - V_{\rm LT} \sin^2 \alpha)$$
 (8-11)

8.3 Mechanical Properties of Single F₄SKL Nanofibres

 F_4 SKL single nanofibres were collected during the electrospinning process. After the nanofibre diameters were measured under a laser confocal microscope, samples were mounted on the Agilent UTM T150 system to conduct mechanical properties testing. As-spun nanofibres (ANF), 250 °C thermo-stabilized nanofibres (TNF), and 1000 °C carbon nanofibres (CNF) were tested, as described in Section 4.6.6.2. Representative laser confocal images of a single nanofibre are presented in Figure 8.1. Engineering stress-strain curves from uni-axial tensile tests for representative single nanofibres are shown in Figure 8.2, and detailed testing results are listed in Table 8.1. The calculation of the Young's modulus for the F₄SKL single nanofibre was performed in the linear region of the stress-strain curve for all samples so that only the elastic deformation was included.



Figure 8.1: Representative laser confocal microscope images of F₄SKL single (a) as-spun and (b)

carbon nanofibres.



Figure 8.2: Representative stress-strain curves of single F₄SKL nanofibres.

Sample	Tensile Strength	Young's	Strain at Break	Average
	(MPa)	Modulus (GPa)	(%)	Diameter (nm)
As-Spun	37.47 ± 10.76	2.43 ± 0.89	1.85 ± 0.41	885 ± 105
Thermostabilized	103.65 ± 16.74	7.12 ± 1.55	6.92 ± 2.80	714 ± 75
Carbon	309.35 ± 39.18	33.83 ± 7.98	1.01 ± 0.32	646 ± 71

Table 8.1: Mechanical properties and the average fibre diameter of F₄SKL nanofibres.

The results of single nanofibre mechanical properties tests showed that the average tensile strength and Young's modulus of F_4SKL ANF were 37.47 ± 10.76 MPa and 2.43 ± 0.89 GPa, respectively. The fibre diameters of testing samples ranged from 700 to 990 nm, and the mechanical properties were found to vary with the fibre diameter. Both tensile strength and Young's modulus tended to increase with decreasing fibre diameter, whereas the strain at break decreased with decreasing fibre diameter. These results are in agreement with previous studies reporting that smaller-diameter electrospun fibres exhibited higher strength and stiffness [73,75,98].

Extensive research has investigated the influence of nanofibre diameter on the mechanical properties of electrospun nanofibres, and most studies have shown that the Young's modulus of the nanofibre increases with decreasing nanofibre diameter, and it increases significantly when the nanofibre is smaller than a critical nanofibre diameter [61,82,98,100]. One of the main reasons for this is the confinement effects that force the polymer chains to align along the fibre axis during the electrospinning process. As a result, improvements in the polymer chain orientation were also observed in electrospun nanofibres with smaller fibre diameters [209]. For

semi-crystalline or amorphous polymers, the increase in Young's modulus can be attributed to the orientation of amorphous regions smaller than the nanofibre diameter [101].

Previous research on the mechanical properties investigation of lignin materials with different characterization methods, including nano-indentation and quantum mechanical molecular determination, showed that the Young's moduli of lignin are in the range of 1.8 to 6.7 GPa [197–204]. These values are in good agreement with the tensile test results of F_4SKL asspun single nanofibres (Table 8.2). The test results showed that the F_4SKL ANF has similar mechanical properties to those of its bulk materials. There are some methods that can improve the mechanical properties of the F_4SKL ANF. Post-processing such as drawing can prevent chain relaxation after the polymer chain orientation. An annealing process is another option to enhance the mechanical properties of electrospun nanofibres which can bring about more than a two-fold increase in tensile strength and modulus [162].

Method	Туре	Modulus (GPa)	Reference
Nano-indentation	Middle lamella (native lignin)	3.1-6.7	[213,215]
Quantum chemical determination	β-O-4 model compound	2.3-4.7	[214]
Molecular mechanics calculation	Lignin model compound	6.2	[212]
Single nanofire tensile test	SKL	2.4	[216]

Table 8.2: Young's Modulus of lignin obtained from different characterization methods.

After thermo-stabilization at 250 °C, both the tensile strength and Young's modulus of F₄SKL single TNF experienced a two- to three-fold increase, to 103.65 ± 16.74 MPa and $7.12 \pm$ 1.55 GPa, respectively. After carbonization at 1000 °C, the tensile strength and Young's modulus of F₄SKL single CNF experienced a one order of magnitude increase, to 309.35 ± 39.18 MPa and 33.83 ± 7.98 GPa, respectively. ANF and CNF showed brittle stress-strain behavior with small strain at break (1.6% and 1.0%, respectively), whereas TNF exhibited a larger strain at break (6.9%). The tensile testing results of F_4 SKL single CNF demonstrated higher mechanical properties than that of previous research on the thermal spinning of softwood acetic acid lignin CF (~147 MPa tensile strength and ~20 GPa Young's modulus) [217], and are comparable to those of melt-spun softwood kraft lignin CF from the LignoBoost process (~300 MPa tensile strength and 30 GPa modulus) [218]. Because the F₄SKL precursor nanofibre did not have tension applied to it during the heat treatment process, the F₄SKL single CNF can be considered similar to the isotropic fibres. The Young's modulus of the F₄SKL single CNF varies within the range of 25-40 GPa, which is near the value of isotropic pitch CF (33 GPa) [219]. However, the strength of F₄SKL single CNF is lower than that of isotropic pitch-based CFs (700-800 MPa) [219]. For most F_4SKL single CNFs, the strain at failure is 0.7-1.2%, which is also in the range of typical commercial CFs [219,220]. The Young's modulus scatter range was larger in F₄SKL single CNF than it is in the electrospun PAN-based single CNF at the same carbonization temperature [61], indicating a lower uniformity of the modulus distribution in F₄SKL-based CNF.

The tensile strength of F₄SKL single CNF is inferior to that of commercial PAN-based CFs (3-7 GPa). The applied tension force in the heat treatment process is critical for stretching the fibre precursor molecular chain and for achieving high mechanical properties after carbonization. The additional stretching of the lignin precursor during the heat treatment process

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may increase the properties of the CNFs, and close the gap between the properties of commercial and lignin-based CFs. Final carbonization temperature is another factor that could significantly affect the mechanical properties of F_4SKL single CNF. The carbonization and graphitization temperatures for commercial CF usually range from 1000 to 2500 °C. In this temperature range, the higher-strength and higher-stiffness CF with a more ordered crystal structure can be obtained. Baker et al. demonstrated that the SKL melt-spun CF could form more ordered crystal structures after carbonization above 1400 °C; therefore, F_4SKL CNF can be expected to have better mechanical properties with increasing final carbonization temperature [13].

The PeakForce quantitative nano-mechanical (PeakForce QNM) mapping test method was applied to characterize the Young's modulus of the F_4SKL single CNF and to validate the F_4SKL single CNF tensile test results. The relative modulus of QNM scanning indicated that the average Young's modulus of F_4SKL CNF in the scanning area (300 nm × 300 nm) was 21.76 GPa, and the maximum value could reach 45.40 GPa. The test results from the PeakForce QNM mapping were consistent and in agreement with the F_4SKL single CNF tensile test results.

The surface morphology (Figure 8.3(a)) and the cross-sectional microstructure (Figure 8.3(b)) of 1000 °C F₄SKL single CNF were further examined via field emission scanning electron microscopy. The surface morphology displayed some imperfections and flaws, which could be caused by the release of volatiles on the fibre surface during the carbonization process. As mentioned previously, the type, size, and distribution of defects could affect the overall fibre strength distribution. Previous research suggested that carbonization heating rates have a major effect on the surface structure of lignin-based CFs [13,42,171]. A slow heating rate during carbonization could result in poor structural development of the lignin-based CF because of the formation of H₂O and CO₂ gases, whereas relatively rapid heating rates (3-5 °C/min) can lead to

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better carbon fibre surface structures [13]. The fractured cross-sectional micrographs demonstrated the structural heterogeneity of the F_4SKL CNF, as the F_4SKL CNF formed a random granular-like structure in the core (Figure 8.3b). The Young's modulus of CF is related to the crystallinity and orientation of the carbon chain along the fibre axis, whereas the strength of CF is affected by its defects and crystalline morphologies [218]. For commercial CF, the Young's modulus increases monotonically with increasing carbonization temperature due to the development of a larger and better-aligned graphitic structure, whereas the tensile strength can be improved by removing the flaws and defects from CF. Tensile failure begins from disorienting crystals under a localized shear force where the crystallites are weakest in shear on basal planes. A higher carbonization temperature is necessary for F_4SKL CNF to achieve a more homogeneous structure.



Figure 8.3: Field emission scanning electron microscope images of (a) the surface morphology and (b) a fractured cross-section of 1000 \degree C F₄SKL carbon nanofibres.

8.4 Elastic Modulus Estimation of F₄SKL Nanofibres via Statistical Modeling

8.4.1 F₄SKL As-spun Single Nanofibres to Nanofibre Assemblies

After mechanical properties characterization of F_4SKL single nanofibres, these results were applied to different models for further examination and validation of the mechanical properties translation from the single nanofibre level to different nanofibre assembly levels. Representative stress-strain curves of F_4SKL as-spun single nanofibres, random nanofibre mats, and aligned nanofibre mats are presented in Figure 8.4. These curves indicate that the failures of the single F_4SKL nanofibre and aligned nanofibre mats are brittle and occur simultaneously at the ultimate tensile strength, whereas random nanofibre mats exhibit a ductile stress-strain behavior due to the stress transfer capability of nanofibres in the mats [221]. The mechanical properties of as-spun single nanofibres were five to eight times higher than those of random nanofibre mats, which are also consistent with the non-woven fabric mechanical properties transition theories and models developed in previous research [60,77–80,82]. Although the tensile strength of aligned nanofibre mats is expected to equal or be near to that of the single nanofibres, the strength and extension dispersion of single nanofibres in the aligned nanofibre mats cause the strength of aligned nanofibre mats to obey the normal distribution [127].



Figure 8.4: Representative stress-strain curves of F₄SKL single as-spun nanofibres (ANF), random nanofibre mats, and aligned nanofibre mats.

The Weibull distribution of the failure probability of the F₄SKL as-spun single nanofibre strength is shown in Figure 8.5. The Pearson's chi-squared test with df = 3 gives χ^2 = 1.835 and a *p*-value = 0.607, which shows that the model is significant at the level of α = 0.05. Considering $1/I_0$ = 1 and using maximum likelihood estimation, the scale parameter (η) for the value of strength with a failure probability of 63% and the shape factor (β) obtained from the slope of the best-fit line of the Weibull distribution are η = 41.48 MPa and β = 3.65, respectively. The results indicate that the F₄SKL nanofibre has a more uniform stress distribution than that of wood (β = 0.9) or tunicate nanofibrils (β = 1) [222]. Using Equations 8-2 and 8-3, the expected mean nanofibre strength ($\widehat{\sigma}_{f}$) and its coefficient of variance (CV%) were 37.40 MPa and 30.47%, respectively. These values are in good agreement with the experimental strength (37.47 ± 10.76)

MPa) and CV% (28.72 %), respectively. The average fibre diameter of F_4SKL single nanofibres was 885 ± 105 nm. Additionally, the Young's modulus and strain at break of F_4SKL single nanofibres were 2.43 ± 0.89 GPa and $1.85 \pm 0.41\%$, respectively.



Figure 8.5: Weibull probability of failure distribution in relation to the strength of F₄SKL single as-spun nanofibres.

The length-dependent Weibull function also shows that the expected strength of the F_4SKL as-spun nanofibre increases with decreasing nanofibre length (Figure 8.6). It also demonstrates that with a nanofibre length lower than 300 nm, the F_4SKL as-spun nanofibre strength significantly increases. The estimated mean strength of F_4SKL aligned nanofibre mats is calculated to be 12.50 MPa using Equation 6-4, and this value shows reasonable agreement with the experimental mean tensile strength of aligned nanofibre mats (14.21 ± 0.66 MPa).

The strength of a twisted nanofibre yarn depends on several parameters including the F₄SKL nanofibre specific density (1.35 g cm⁻³ [159]) and volume fraction ($V_f = 0.9$ [223]). Parameters such as K_{α} , fibre critical length (l_c), and yarn cohesion factor (n) also depend on the yarn surface helix angle (α) obtained via Equation 8-6 and 8-9. Among these, l_c is the key parameter affecting the yarn strength. The estimated yarn strength can be calculated using Equation 8-5 by assuming a constant yarn Poisson's ratio of $V_{LT} = 0.5$ when the twist factor is changed from 30 to 125. When the lateral pressure is low, the fragmentation phenomenon does not occur completely. With the increase of the lateral pressure, the fragmentation phenomenon becomes more prominent, and l_c decreases due to the increase in yarn strain (Figure 8.7). The decrease in l_c has a major effect on the increase of yarn strength. The estimated yarn strength can increase to 189.55 MPa when l_c decreases to 213.95 nm (Figure 8.8). The results are comparable to the strength of the PAN-based nanofibre twisted yarn, which ranged from 50 to 350 MPa [224,225]. The high ratio of $\hat{\sigma}_v/\hat{\sigma}_f$ obtained for the F₄SKL nanofibre yarn in this study can be attributed to the high values of nanofibre aspect ratio, fibre specific volume, and twist value of nanofibre yarns. These factors lead to higher lateral pressure in the yarn, and the effect of fibre interaction, especially for brittle fibres such as lignin, leads to a smaller value of l_c than conventional fibres [226]. These results indicate that the strength of a nanofibre yarn can be greater than that of its constituent fibres.



Figure 8.6: Relationship between the expected strength and fibre length of F₄SKL single

nanofibres.



Figure 8.7: Relationship between fibre critical length and yarn strain during the yarn fragmentation process.



Figure 8.8: Yarn strength as a function of fibre critical length.

8.4.2 Strength and Weibull Distribution of F₄SKL Carbon Nanofibres

The mechanical properties of F_4 SKL single CNF were also analyzed by the two-parameter Weibull distribution. The probability of failure was calculated according to Equation 8-1 and plotted in Figure 8.9. The experimental data were then approximated, and Weibull parameters were obtained through Equation 8-2 and 8-3 as the reference length (l_0) was set to 5 mm for all analyses.



Figure 8.9: Weibull probability of failure distribution in relation to the strength of F₄SKL single carbon nanofibres.

The diameter of the F_4SKL single CNF samples measured by the confocal microscope ranged from 500 to 900 nm, and the tensile strength of the F_4SKL single CNF followed the theory of brittle materials that the smaller the fibre diameter, the higher the strength. The strength of the F_4SKL single CNF increased from 280 MPa to 400 MPa when the CNF diameter was reduced from 919 to 556 mm.

Once the parameters of the Weibull distribution have been determined, the strength distribution of the nanofibre can be predicted. The strength prediction of the F₄SKL single CNF was performed using the Weibull parameters obtained from the F₄SKL single CNF tensile test. The expected average strength ($\hat{\sigma}_f$) of the F₄SKL single CNF (361 MPa) is close to, but slightly

higher than that of the experimental data (309.35 ± 39.18 MPa). The result indicates that the experimental strength distribution fits the Weibull distribution fairly well.

The value of the shape factor reflects the flaw distribution of the material. A high value of shape factor could be obtained from a material with a homogeneous flaw distribution, whereas a low shape factor indicates an uneven flaw distribution in the material with a much more significant scatter of strength values observed. The test results showed that the F₄SKL single CNF has a lower shape factor value (4.9) than that found for the electrospun PAN-based single CNF in previous research, which means that the strength uniformity of the F₄SKL single CNF is more scattered than that of the PAN-based single CNF (5.9 - 6.4) [61]. Nevertheless, the Weibull modulus value obtained from the F₄SKL single CNF is within the interval found for commercial CFs (4 to 10) [227,228].

8.5 Concluding Remarks

In this chapter, tensile tests were conducted on F_4SKL single nanofibres and their mechanical properties were systematically characterized by employing the two-parameter Weibull statistical distribution. The average tensile strength and Young's modulus of the F_4SKL as-spun single nanofibres were 37.47 MPa and 2.43 GPa, respectively. The mechanical properties increased by one order of magnitude after carbonization at 1000 °C. The strength of the F_4SKL single CNF (~300 MPa) is lower than that of commercial CF, whereas the Young's modulus of the tested F_4SKL single CNF (~30 GPa) is comparable to values reported for isotropic CFs. The strain at failure of the single CNF ranged between 0.7 and 1.2%, which is also similar to that of commercial CFs. The surface structure of the 1000 °C F_4SKL CNF displayed imperfections and flaws on the cross-section. Together, these results suggest that the postprocessing and a higher carbonization temperature are necessary for manufacturing F_4SKL CNF with higher mechanical properties.

For F₄SKL nanofibres, the experimental results and the predictions based on Weibull statistics fitted well. The two important mechanical indices of scale parameters and shape factors were obtained and further used to estimate the single F_4SKL nanofibres strength. These parameters were also used to estimate the strength of aligned nanofibre mats and the twisted yarn by applying different models. The shape factor value obtained for F_4SKL indicates that the individual fibres have higher strength dispersion and brittle behavior at rupture. These findings were verified by direct observation of individual nanofibre stress-strain curves and the CV% calculation of the nanofibre strength in practice. The estimated strength values of single nanofibres and aligned nanofibre mats were in good agreement with experimental results. At low twist level, when the fibre critical length is on the same order as the gauge length, the varn strength is approximately one-half the strength of its constituent fibres. As a fibre's critical length decreases to $0.05 l_0$, the yarn strength increases from one-half to three-quarters of the strength of its constituent fibres. This observation is in agreement with classical yarn behavior during the fracturing process. With increasing yarn strain, the fibre critical length can reach a minimum value of the nano-scale size, and the yarn strength increases rapidly. These results indicate that a fibre critical length with a nano-scale size value will significantly reinforce and enhance the mechanical properties of nanofibrous assemblies, leading to a stronger yarn. To verify the validity of the estimated strength of F₄SKL nanofibre yarn and to consider any necessary correction factors, the yarn strength must be measured in practice for future work.

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Chapter 9: Lignin-Based Carbon Nanofibre Electrodes for Supercapacitors

9.1 Introduction

Supercapacitors (SC) have advantages of the high power density, rapid charge/discharge rates, and a long cycle life among energy storage devices. The electrode materials of SC can be made from carbonaceous materials, including activated porous carbons, carbon aerogels, graphene sheets, CNTs, and CNFs [133,136,140–142,229–235]. Electrospun lignin-based CNF mats are promising candidates as electrode materials because unlike the aforementioned materials, there is no need to add binding agents, which could reduce the overall performance, to create mechanically flexible and free-standing electrodes for SC [144]. In this chapter, a prototype symmetric SC unit cell was constructed using F₄SKL and SWNT/F₄SKL CNF mats as electrodes, and the electrochemical performance properties of the SC were assessed

9.2 Results and Discussion

9.2.1 Electrical Conductivity

Electrical conductivity is one of the key performance parameters for a high-performance SC electrode material, as it governs the rate of charge transportation. In this study, the electrical conductivity was characterized via the two-point probe method and the results showed that the electrical conductivity of F₄SKL CNF mats increased with increasing SWNT content (Figure 9.1). F₄SKL CNF mats had an electrical conductivity of 5.31 ± 0.42 S cm⁻¹, whereas 1% SWNT/F₄SKL composite CNF mats had an electrical conductivity of 27.82 ± 1.97 S cm⁻¹. The electrical conductivity achieved by 1% SWNT/F₄SKL CNF mats was higher than that of PAN-based CNF mats (9.60 S cm⁻¹), PAN/cellulose acetate-based CNF mats (8.20 S cm⁻¹), and

phenolic resin-based (5.29 S cm⁻¹) CNF mats [155,236,237]. It is worth noting that the electrical conductivity of a CNF mat cannot be directly interpreted as the electrical conductivity of the individual CNF in the mat because the electrical conductivity of a CNF mat is determined not only based on the conductivity of individual nanofibres in the mat, but also based on the interactions among the nanofibres.



Figure 9.1: Electrical conductivity of three different carbon nanofibre (CNF) mats.

9.2.2 Cyclic Voltammetry Test

The electrochemical performance of the CNF mats was investigated via the cyclic voltammetry (CV) test. The CV test is usually a measurement of the electrode capacity. A continuous current with a fixed scan rate is applied to reach a given upper limit of voltage, and then the voltage returns to the lower limit to complete a cycle. By integrating the area under the

CV curve and dividing by the voltage and the sample mass (m), the specific capacitance (C_{c-v} , F g⁻¹) and energy density (E) of the SC cell can be obtained using the following equations:

$$C_{c-v} = \frac{\int_0^v I dv}{m \,\Delta V} \ (9-1)$$

$$E = \frac{C_{c-v} \times V^2}{8}$$
 (9-2)

Where ΔV is the potential range (0.8 V)

The CV curve of an ideal SC has a rectangular shape in the sweeping voltage range. In practice, most CV curves show a quasi-rectangular shape due to the internal resistance of the sample or other effects. The results showed that all samples had a quasi-rectangular CV curve (Figure 9.2). The 1% SWNT/F₄SKL CNF mat exhibited a better quasi-rectangular shape than that of the pure F₄SKL CNF mat. It also exhibited the largest loop area, which indicates the highest gravimetric capacitance.



Figure 9.2: Cyclic voltammograms of different carbon nanofibre mat samples at a 30 mV s⁻¹ scan rate.

The increase of the voltage sweep rate did not affect the shape of the CV curves (Figure 9.3). The specific capacitances of all samples were found to decrease with increasing scan rate (Table 9.1 and Figure 9.4) due to the shorter ion migration time allowed at a faster scan rate [238]. The highest specific capacitance was 162 F g⁻¹ for the 1% SWNT/F₄SKL CNF mat, which is higher than that of the lignin-PVA CNF (67 F g⁻¹) [144] and the lignin-based mesoporous carbon (102.3 F g⁻¹) [133], but lower than that of the activated lignin-based CNF (344 F g⁻¹) [154]. The energy densities of F₄SKL and 1% SWNT/F₄SKL at 50 mV s⁻¹ were 4.61 Wh kg⁻¹ and 10.48 Wh kg⁻¹, respectively, showing comparable or higher energy density than commercialized carbon materials (3-5 Wh kg⁻¹) [239]. These results indicate that lignin-based CNF mats can serve as electrode materials in SCs.

Sample	5 mV s ⁻¹	10 mV s ⁻¹	30 mV s ⁻¹	50 mV s ⁻¹
F ₄ SKL	83	78	67	52
0.5% SWNT/F ₄ SKL	123	119	90	76
1% SWNT/F ₄ SKL	162	160	155	131

 Table 9.1: Gravimetric capacitance (F g⁻¹) of carbon nanofibre mats calculated from cyclic

 voltammetry curves at four different scanning rates.



Figure 9.3: Cyclic voltammograms of the 1% SWNT/F₄SKL carbon nanofibre mat at different scan rates in 6 M KOH aqueous electrolyte at room temperature.


Figure 9.4: Specific capacitance as a function of the scan rate.

9.2.3 Galvanostatic Charge/Discharge Test

The galvanostatic charge/discharge method was conducted to perform further analysis of the electrochemical performance of F_4SKL and 1% SWNT/ F_4SKL CNF mats. In this test, SC samples were charged with a constant current until they reached the target voltage (0.8 V). Once the target voltage was attained, the current was discharged to 0 V, and then another cycle was repeated. During the switch in current direction, the curve typically showed a vertical drop (IR drop) in voltage, which was related to the internal resistance or equivalent series resistance (ESR) of the SC. A linear triangle shape with a small discharge IR drop is desired for an ideal SC. In this test, three different current densities (400, 1000, and 2000 mA g⁻¹) were applied to the CNF samples, and the charge/discharge curves of the 1% SWNT/ F_4SKL CNF mats under different current density,

the charge/discharge triangles became much more linear, indicating better and more promising reversible SC behaviors.



Figure 9.5: Galvanostatic charge/discharge curves of 1% SWNT/SKL carbon nanofibre mats at current densities of 2000, 1000, and 400 mA g⁻¹.

Specific capacitance (Ci-v) can also calculated from the discharge curve via Equation 9-3

$$C_{i-v} = \frac{2 \times I_m \times dt}{dV} (9-3)$$

Where dV/dt can be obtained from the slope of the discharge curve.

The specific capacitance of F_4SKL and 1% SWNT/ F_4SKL CNF mats were 86 and 175 F g⁻¹, respectively. These values were in agreement with the specific capacitance values derived

from the CV curves. As the current density rose from 400 to 1000 to 2000 mA g^{-1} , the IR drop of the initial onset point of the charging curve increased for both F₄SKL CNF and 1% SWNT/F₄SKL CNF mats. The relatively linear increase in the drop voltage suggests that the R_{ESR} of the mats remained constant, indicating that the high current density did not change the structure or chemistry of the mats. The R_{ESR} were estimated following Equation 9-4:

$$R_{ESR} = \frac{\Delta V_{initial}}{I_m} (9-4)$$

Where $\Delta V_{\text{initial}}$ is the initial potential drop from the galvanostatic discharge curve, and I_m is the discharge current normalized by the mass of an single electrode.

The R_{ESR} of F₄SKL and 1% SWNT/F₄SKL CNF at 2000 mA g⁻¹ were 28.9 and 11.3 Ω , respectively. The lower resistance of the 1% SWNT/F₄SKL CNF mat was consistent with the better rectangular shape of its CV curve. Based on these R_{ESR} from the discharge curves, the power densities for F₄SKL and 1% SWNT/F₄SKL CNF cells at 1000 mA g⁻¹ were calculated to be 2.22 and 10.09 kW kg⁻¹, respectively, using the following equation:

$$P = \frac{V^2}{4 \times R_{ESR} \times \overline{m}} (9-5)$$

9.2.4 Electrochemical Impedance Spectroscopy

A sinusoidal AC current was applied to the SC, and the corresponding voltage was measured via EIS. The frequency-dependent impedance (Z_w) can be calculated from the following equation:

$$Z_w = \frac{E_w}{I_w} \quad (9.6)$$

Where E_w and I_w are frequency-dependant voltage and current, and Z_w is the Warburg impedance associated with 1-D linear semi-infinite diffusion of electrolytes to the flat electrode planes. Z_w can be separated into a low-frequency real impedance (Z') related to the series resistance behavior of the system and a high-frequency imaginary impedance (Z'') related to the capacitive behavior of the system [240]. A Nyquist plot can be obtained by drawing the imaginary impedance as a function of the real impedance.

The lignin-based SC produced a semicircular Nyquist plot in the high-frequency range with a linear tail in the low-frequency range (Figure 9.6). Randle's model was used to calculate the R_{ct} , namely the charge-transfer resistance from electrolytes moving through the electrodes during kinetically controlled electrochemical reactions. The x-intercept of the Nyquist curve represents the R_{ESR} of the SC, and the semi-circle diameter represents the R_{ct} . A smaller semicircle indicates higher ion migration rates, and a vertical line in the low-frequency part shows better ion accessibility in the SC. The R_{ESR} of F_4SKL and 1% SWNT/ F_4SKL CNF were 0.89 and 0.66 Ω , respectively, and the plain F_4SKL CNF had a larger semi-circle than did the composite fibre mat. Although the R_{ESR} of both samples were similarly located in the narrow range of 0.60.9 Ω , the R_{ct} for the 1% SWNT/F₄SKL CNF electrode was much smaller than that of the pure F-₄SKL CNF SC. The knee frequencies of 1% SWNT/F₄SKL CNF mats were also considerably higher than those of F₄SKL CNF mats, suggesting increasing ion diffusion ability to the carbon planes. Overall, these observations suggest a decreased resistivity in composite SWNT/F₄SKL CNF mats compared to that of F₄SKL CNF mats.



Figure 9.6: Nyquist plots based on electrical impedance spectroscopy analysis of SKL and 1% SWNT/SKL carbon nanofibre mats.

9.2.5 Cycling Durability and Stability Test

Cycling durability and stability are important parameters affecting the lifespan of electrode materials and the SCs. After 1000 charge/discharge cycles at a constant exposure to high current density (2000 mA g⁻¹), the gravimetric capacitance of the 1% SWNT/F₄SKL CNF electrode was

reduced by only about 5% (Figure 9.7), indicating that the electrode was electrochemically stable and durable. The slight decrease in capacitance with the increase of cycle numbers could be due to the loss of a small amount of electrode materials, which is a common phenomenon with carbonaceous materials [126,130,138]



Figure 9.7: Cyclic stability of 1% SWNT/SKL carbon nanofibre mats after 1000 cycles in 6 M KOH.

9.3 Concluding Remarks

The electrochemical performance characterization presented in this chapter suggests that lignin-based CNFs are suitable candidates as the electrode material in SCs. The relatively high specific capacitance and good electrochemical performance of lignin-based CNF mats could be attributed to the complex nanofibre network in CNF mats that shortens the transport pathway of electrons. Moreover, the nano-size crystalline domains surrounded by a continuous disordered carbon matrix can enhance the electrochemical performance because amorphous regions enable electron transportation throughout the fibre structures and provide access to charge storage sites within the nano-scale graphitic domains [217]. The energy density and power density plot shows that the F₄SKL-based CNF mats are promising to meet the requirements for commercial products (Figure 9.8). Overall, these results indicate that the F₄SKL-based CNF mats possess the potential to serve as electrode materials for the SC and energy storage devices applications.



Figure 9.8: Ragone plot of the power density against energy density for various energy storage devices.

Chapter 10: Conclusions and Future Work

10.1 Conclusion

This research explored the feasibility of developing value-added products from lignin in nanofibre form for structural composites and functional applications. Specifically, fractionated softwood Kraft lignin (SKL) was used as the precursor to fabricate nanofibres by using the electrospinning process and then converting into carbon nanofibres (CNF). Subsequently, the mechanical properties of the SKL nanofibres for structural applications at the nanofibre mats level and the single nanofibre level were characterized. Moreover, several different processing methods to hierarchically improve the mechanical properties of SKL CNF, including the reduction of fibre diameter, the heat treatment process, the increase of fibre alignment, and the incorporation of single-walled carbon nanotubes (SWNT) were harnessed. Furthermore, the statistical Weibull distribution was applied to analyze the strength distribution of SKL single nanofibres and the scale parameter and shape factor obtained from Weibull analysis were applied to different models to validate and predict the mechanical properties translation from a single nanofibre to various nanofibre assemblies. Finally, the electrochemical performance of SKL CNF for functional applications at the nanofibre mats level was characterized.

The findings of this research can be summarized as follows:

A systematic study on the optimization of SKL nanofibre diameter in the electrospinning process was successfully conducted. A quadratic model equation to establish the relationship between fibre diameter with the solution concentration and spinneret needle diameter was constructed by using the response surface methodology. It was found that the random as-spun nanofibre mats comprising smaller fibres demonstrated higher mechanical properties compared

to larger fibres. The results indicated mechanical property can be improved by reducing the fibre diameter.

The influence of the heat treatment process on the mechanical properties of SKL nanofibres was investigated. It was identified that both heating rate and final heating temperature of the thermo-stabilization process can affect the chemical structure and mechanical properties of the resulting SKL nanofibre. The mechanical properties of SKL random nanofibre mats gained an order of magnitude increase after carbonization at 1000 $^{\circ}$ C. Aligned nanofibre mats were successfully fabricated by using the rotating drum method, and the fibre alignment can improve the tensile strength and Young's modulus by ~30% and ~100%, respectively.

This research also demonstrated that the SWNT/SKL core-shelled composite nanofibres can be successfully fabricated using the emulsion electrospinning process by embedding the SWNT as the core and the SKL matrix as the shell. The tensile test results showed that the mechanical properties of SWNT/SKL nanofibre mats increased as the amount of SWNT increased. TEM images and Raman spectra revealed that the incorporation of SWNT could act as the nucleation site to form more ordered nano-crystallite graphitic structures. These results indicate that mechanical properties are reinforced by SWNT

This research further characterized the mechanical properties of SKL single nanofibres. The results showed that the tensile strength of the SKL single CNF could reach up to 300 MPa, which is higher than previous research of softwood melt-spun carbon fibre [217]. A statistical Weibull distribution was utilized to analyze the strength uniformity of the SKL single nanofibres, and the scale parameter and shape factor obtained from the Weibull analysis were applied to different models to validate and predict the mechanical properties translation from single

nanofibres to various nanofibre assemblies. The estimated strength of single nanofibres and aligned nanofibre mats were in good agreement with experimental results.

A prototype SC was constructed as an illustration for functional applications by using SKL-based CNF mats as binder-free electrodes. The electrochemical performance of the SC cell demonstrated a relatively good specific capacitance, a low equivalent series resistance, and an outstanding cycling stability. The energy density and power density calculated from the results shows that the SKL-based CNF mats are promising candidates as the electrode materials to meet the requirement for commercial products. The collective results indicated that the SKL-based CNF mats can be used as carbon electrode materials for the SC and other energy storage devices.

In summary, this research demonstrated the potential of lignin-based CNF for advanced applications. For structural applications, this research harnessed different processing methods to hierarchically improve the mechanical properties of the SKL CNF and also investigated the effect of molecular order and fibre orientation on the tensile stress-strain behavior of the SKL CNF. It demonstrated that the mechanical properties of SKL CNF can be improved by the reduction of nanofibre diameter, by proper heat treatment processes, by the increase of the fibre alignment, and by the incorporation with SWNT. This research also investigated the intrinsic properties of SKL single nanofibres and their fibre assemblies by using the statistical Weibull distribution. For functional applications, this research also demonstrated the feasibility of SKL-based CNF as binder-free electrodes for supercapacitors.

This research sheds light to our understanding of the mechanism of the mechanical properties improvement of SKL CNF, and to identify determining factors that can be used to enhance its mechanical performance. Moreover, the electrochemical performance of SKL-based

CNF mats demonstrates that they are promising candidates as electrode materials for the SC and other energy storage devices for functional applications.

10.2 Future work

This study investigated the mechanical properties and electrochemical properties of SKLbased CNF for structural and functional applications. On the other hand, there still has room for further research related to the area discussed herein. Some suggestions for future research are provided here:

The mechanical properties of the SKL nanofibre and CNF can be improved by applying post-processing methods such as mechanical drawing. Hence, the implementation and optimization of suitable post-processing methods for SKL nanofibres need to be further investigated.

Microstructure characterization in this study suggested that the carbon structure of the 1000 °C SKL CNF was in the amorphous carbon stage to the formation of the nano-crystalline graphitic structure stage. Higher carbonization temperature is necessary for manufacturing SKL CNF with more ordered carbon structure and higher mechanical properties. The optimized carbonization temperature and the carbon structure changes during higher carbonization temperature need to be explored for future work.

The highly complex and heterogeneous chemical structure of lignin is one of the main challenges to improve the mechanical properties of the lignin-based CF. The structure modification of lignin precursor and the investigation of structural-mechanical properties of lignin nanofibres at the molecular level with advanced equipments such as the AFM-IR, it could help to realize the potential of lignin-based CNF for structural application in the future.

SWNT/SKL composite nanofibres with core-shell structure were successfully fabricated by employing emulsion electrospinning method in this study, and the mechanical properties increased with the increasing amount of SWNT. For future work, SKL with optimized SWNT contents needs to be further investigated. The interfacial bonding between the SWNT and SKL matrix can affect the mechanical properties reinforcement of SWNT and it needs further study. The failure mechanism is also important for the strengthening and toughening of the fibre. It also needs to be examined to elucidate the mechanism for the stress transfer and to provide guidance for further improvement of the translation of the SWNT properties to the SKL CNF.

The mechanical properties of the SKL single nanofibres were analyzed by employing a two-parameter Weibull statistical distribution. The scale parameter and shape factor were also utilized to estimate the aligned nanofibre mats and the twisted yarn strength by applying different models. The estimated single nanofibre and aligned nanofibre mat strengths were in good agreement with experimental results. To verify the validity of the estimated SKL nanofibre yarn strength and to consider any correction factors if needed, the SKL nanofibre yarns need to be fabricated and the yarn strength needs to be measured in practice for future work.

The electrochemical properties characterized on the SKL-based SC cell suggested that it is a promising candidate for electrode materials to meet the energy density and power density requirements for commercial SC. In the future, the integrated design for scaling up the manufacturing of SC will be established. Other treatment processes such as activation that can further increase the surface area of CNF can also be applied to enhance the overall performance of CNF electrodes. The flexibility of CNF can also be improved by the incorporation of SKL CNF with other materials. Flexible electrodes are suitable for wearable electronics, which can further expand the applications of SKL CNF.

Bibliography

- [1] How much forest does Canada have?, Nat. Resour. Canada. (2016).
 http://www.nrcan.gc.ca/forests/report/area/17601 (accessed April 30, 2017).
- [2] Forestry statistical data, Nat. Resour. Canada. (2016). https://cfs.nrcan.gc.ca/statsprofile (accessed April 10, 2017).
- [3] Forest bioeconomy, bioenergy and bioproducts, Nat. Resour. Canada. (2016).
 http://www.nrcan.gc.ca/forests/industry/bioproducts/13315 (accessed May 7, 2017).
- [4] A.J. Ragauskas, G.T. Beckham, M.J. Biddy, R. Chandra, F. Chen, M.F. Davis, et al.,
 Lignin valorization: improving lignin processing in the biorefinery., Science. 344 (2014)
 1246843. doi:10.1126/science.1246843.
- [5] Global Lignin Products Market Segmented By Product Type, Source, Application, And Geography Trends And Forecasts (2016 2021), Mordor Intell. (2016).
 http://www.researchandmarkets.com/research/x27phs/global_lignin (accessed May 5, 2017).
- [6] I. Norberg, Carbon fibres from kraft lignin, KTH Royal Institute of Technology, 2012.
- [7] A.J. Ragauskas, C.K. Williams, B.H. Davison, G. Britovsek, J. Cairney, C.A. Eckert, et al., The Path Forward for Biofuels and Biomaterials, Science (80-.). 311 (2006) 484–489. doi:10.1126/science.1114736.
- [8] S. Kubo, J.F. Kadla, Carbon Fibers from Lignin-Recyclable Plastic Blends, in: Encycl. Chem. Process., 1st ed., Taylor & Francis, 2007: pp. 317–331. doi:10.1081/E-ECHP-120039775.

- J.F. Kadla, S. Kubo, R.A. Venditti, R.D. Gilbert, A.L. Compere, W. Griffith, Lignin-based carbon fibers for composite fiber applications, Carbon N. Y. 40 (2002) 2913–2920.
 doi:10.1016/S0008-6223(02)00248-8.
- G. Gellerstedt, E. Sjöholm, I. Brodin, The Wood-Based Biorefinery: A Source of Carbon Fiber?, Open Agric. J. 3 (2010) 119–124. doi:10.2174/1874331501004010119.
- [11] I. Brodin, E. Sjoholm, G. Gellerstedt, Kraft lignin as feedstock for chemical products: The effects of membrane filtration, Holzforschung. 63 (2009) 290–297.
 doi:10.1515/HF.2009.049.
- J.D. Gargulak, S.E. Lebo, Commercial Use of Lignin-Based Materials, in: Lignin Hist.
 Biol. Mater. Perspect., American Chemical Society, 1999: pp. 15–304.
 doi:doi:10.1021/bk-2000-0742.ch015.
- [13] D.A. Baker, T.G. Rials, Recent advances in low-cost carbon fiber manufacture from lignin, J. Appl. Polym. Sci. 130 (2013) 713–728.
- [14] D.A. Baker, N.C. Gallego, F.S. Baker, On the characterization and spinning of an organic-purified lignin toward the manufacture of low-cost carbon fiber, J. Appl. Polym. Sci. 124 (2012) 227–234. doi:10.1002/app.33596.
- [15] J.F. Kadla, S. Kubo, R.D. Gilbert, R.A. Venditti, Lignin-Based Carbon Fibers, in: Chem.
 Modif. Prop. Usage Lignin, 2002: pp. 121–137. doi:10.1007/978-1-4615-0643-0
- [16] J. Melorose, R. Perroy, S. Careas, Carbon fibres filaments and composites, 2015. doi:10.1017/CBO9781107415324.004.
- [17] M.L. Minus, S. Kumar, The processing, properties, and structure of carbon fibers, J.
 Miner. Met. Mater. Soc. 57 (2005) 52–58. doi:10.1007/s11837-005-0217-8.

- [18] P. Morgan, History and Early Development of Carbon Fibers, in: Carbon Fibers Their Compos., CRC Press, 2005: pp. 65–120. doi:10.1201/9781420028744.ch3.
- [19] E. Frank, F. Hermanutz, M.R. Buchmeiser, Carbon fibers: Precursors, manufacturing, and properties, Macromol. Mater. Eng. 297 (2012) 493–501. doi:10.1002/mame.201100406.
- [20] K.L. Pickering, M.G.A. Efendy, T.M. Le, A review of recent developments in natural fibre composites and their mechanical performance, Compos. Part A Appl. Sci. Manuf. 83 (2016) 98–112. doi:10.1016/j.compositesa.2015.08.038.
- [21] Electrochemical Double Layer Capacitors (Supercapacitors), (2016).
 http://large.stanford.edu/courses/2012/ph240/aslani1/ (accessed April 3, 2017).
- [22] Market for Supercapacitors, (2017). http://www.luxresearchinc.com/news-andevents/press-releases/read/market-supercapacitors-grow-128-836-million-2018 (accessed April 12, 2017).
- [23] M. Winter, R.J. Brodd, What are batteries, fuel cells, and supercapacitors?, Chem. Rev. 104 (2004) 4245–4269. doi:10.1021/cr020730k.
- [24] R.B. Berenguer, Trends and research challenges in supercapacitors, Boletín Del Grup.
 Español Del Carbón. 37 (2015) 9–13.
 http://www.gecarbon.org/boletines/articulos/BoletinGEC_037_art3.pdf (accessed April 5, 2017).
- [25] T. Koshijima, T. Watanabe, F. Yaku, Structure and Properties of the Lignin—
 Carbohydrate Complex Polymer as an Amphipathic Substance, in: Lignin, American
 Chemical Society, 1989: pp. 2–11. doi:doi:10.1021/bk-1989-0397.ch002.

- [26] W.-J. Liu, H. Jiang, H.-Q. Yu, Thermochemical conversion of lignin to functional materials: a review and future directions, Green Chem. (2015) 4888–4907.
 doi:10.1039/C5GC01054C.
- [27] J. Ralph, K. Lundquist, G. Brunow, F. Lu, H. Kim, P.F. Schatz, et al., Lignins: Natural polymers from oxidative coupling of 4-hydroxyphenyl- propanoids, Phytochem. Rev. 3 (2004) 29–60. doi:10.1023/B:PHYT.0000047809.65444.a4.
- [28] J.F. Kadla, S. Kubo, R.A. Venditti, R.D. Gilbert, A.L. Compere, W. Griffith, Lignin-based carbon fibers for composite fiber applications, Carbon N. Y. 40 (2002) 2913–2920. doi:10.1016/S0008-6223(02)00248-8.
- [29] S. Otani, Y. Fukuoka, B. Igarashi, K. Sasaki, Method for producing carbonized lignin fiber, 3.461,082, 1969.
- [30] M. Mansmann, G. Winter, G. Pampus, H. Schnoring, N. Schon, W. Elbergeld, Process for the production of carbon fibers, 3,723,609, 1998.
- [31] K.C. Nippon Ltd., "Kayacarbon" Manufacturer's brochure, 1970.
- [32] I. Tomizuka, D.J. Johnson, Microvoids in pitch-based and lignin-based carbon fibres as observed by X-ray.pdf, Yogyo-Kyokai-Shi. 86 (1978) 187–192.
 doi:http://doi.org/10.2109/jcersj1950.86.992 186.
- [33] D.J. Johnson, I. Tomizuka, O. Watanabe, The fine structure of lignin-based carbon fibres, Carbon N. Y. 13 (1975) 321–325. doi:10.1016/0008-6223(75)90037-8.
- [34] K. Sudo, K. Shimizu, A new carbon fiber from lignin, J. Appl. Polym. Sci. 44 (1992) 127–
 134. doi:10.1002/app.1992.070440113.

- [35] K. Sudo, K. Shimizu, N. Nakashima, A. Yokoyama, A new modification method of exploded lignin for the preparation of a carbon fiber precursor, J. Appl. Polym. Sci. 48 (1993) 1485–1491. doi:10.1002/app.1993.070480817.
- [36] S. Kubo, Y. Uraki, Y. Sano, Preparation of carbon fibers from softwood lignin by atmospheric acetic acid pulping, Carbon N. Y. 36 (1998) 1119–1124. doi:10.1016/S0008-6223(98)00086-4.
- [37] S. Kubo, J.F. Kadla, Lignin-based Carbon Fibers: Effect of Synthetic Polymer Blending on Fiber Properties, J. Polym. Environ. 13 (2005) 97–105. doi:10.1007/s10924-005-2941-0.
- [38] G. Husman, Development and Commercialization of a Novel Low-Cost Carbon Fiber,
 2014. http://energy.gov/sites/prod/files/2014/07/f17/lm048_husman_2014_o.pdf (accessed July 7, 2016).
- [39] I. Dallmeyer, F. Ko, J.F. Kadla, Electrospinning of Technical Lignins for the Production of Fibrous Networks, J. Wood Chem. Technol. 30 (2010) 315–329. doi:10.1080/02773813.2010.527782.
- [40] S. Kubo, Y. Uraki, Y. Sano, Thermomechanical analysis of isolated lignins, Holzforschung. 50 (1996) 144–150. doi:10.1515/hfsg.1996.50.2.144.
- [41] Y. Uraki, S. Kubo, N. Nigo, Y. Sano, T. Sasaya, Preparation of Carbon Fibers from Organosolv Lignin Obtained by Aqueous Acetic Acid Pulping, Holzforschung. 49 (1995) 343–350. doi:10.1515/hfsg.1995.49.4.343.
- [42] J.L. Braun, K.M. Holtman, J.F. Kadla, Lignin-based carbon fibers: Oxidative thermostabilization of kraft lignin, Carbon N. Y. 43 (2005) 385–394.
 doi:10.1016/j.carbon.2004.09.027.

- Y. Li, A.J. Ragauskas, Kraft Lignin-Based Rigid Polyurethane Foam, J. Wood Chem.
 Technol. 32 (2012) 210–224. doi:10.1080/02773813.2011.652795.
- [44] A. Formhals, Process and apparatus for preparing artificial threads, 1934. doi:D01D5/00.
- [45] P.K. Baumgarten, Electrostatic spinning of acrylic microfibers, J. Colloid Interface Sci. 36 (1971) 71–79. doi:10.1016/0021-9797(71)90241-4.
- [46] A.K. S., P. Sanpui, K. Chatterjee, Fabrication of Poly(Caprolactone) Nanofibers by
 Electrospinning, J. Polym. Biopolym. Phys. Chem. 2 (2014) 62–66. doi:10.12691/jpbpc-2 4-1.
- [47] D.H. Reneker, A.L. Yarin, Electrospinning jets and polymer nanofibers, Polymer (Guildf).
 49 (2008) 2387–2425. doi:10.1016/j.polymer.2008.02.002.
- [48] F. Ko, Nanofiber Technology, in: Nanomater. Handb., CRC Press, 2006. doi:10.1201/9781420004014.ch19.
- [49] G.C. Rutledge, S. V. Fridrikh, Formation of fibers by electrospinning, Adv. Drug Deliv. Rev. 59 (2007) 1384–1391. doi:10.1016/j.addr.2007.04.020.
- [50] S.R. Bhattarai, N. Bhattarai, H.K. Yi, P.H. Hwang, D. Il Cha, H.Y. Kim, Novel biodegradable electrospun membrane: scaffold for tissue engineering, Biomaterials. 25 (2004) 2595–2602. doi:10.1016/j.biomaterials.2003.09.043.
- [51] S. Sukigara, M. Gandhi, J. Ayutsede, M. Micklus, F. Ko, Regeneration of Bombyx mori silk by electrospinning. Part 2. Process optimization and empirical modeling using response surface methodology, Polymer (Guildf). 45 (2004) 3701–3708. doi:10.1016/j.polymer.2004.03.059.

- [52] M.S.A. Rahaman, A.F. Ismail, A. Mustafa, A review of heat treatment on polyacrylonitrile fiber, Polym. Degrad. Stab. 92 (2007) 1421–1432.
 doi:10.1016/j.polymdegradstab.2007.03.023.
- [53] Z. Zhou, C. Lai, L. Zhang, Y. Qian, H. Hou, D.H. Reneker, et al., Development of carbon nanofibers from aligned electrospun polyacrylonitrile nanofiber bundles and characterization of their microstructural, electrical, and mechanical properties, Polymer (Guildf). 50 (2009) 2999–3006. doi:10.1016/j.polymer.2009.04.058.
- [54] F. Liu, H. Wang, L. Xue, L. Fan, Z. Zhu, Effect of microstructure on the mechanical properties of PAN-based carbon fibers during high-temperature graphitization, J. Mater. Sci. 43 (2008) 4316–4322. doi:10.1007/s10853-008-2633-y.
- [55] I. Chun, D.H. Reneker, H. Fong, X. Fang, J. Deitzel, N.B. Tan, et al., Carbon nanofibers from polyacrylonitrile and mesophase pitch, J. Adv. Mater. 31 (1999) 36–41. http://cat.inist.fr/?aModele=afficheN&cpsidt=1869343 (accessed July 11, 2016).
- [56] T. Wang, S. Kumar, Electrospinning of polyacrylonitrile nanofibers, J. Appl. Polym. Sci. 102 (2006) 1023–1029. doi:10.1002/app.24123.
- [57] S.Y. Gu, J. Ren, G.J. Vancso, Process optimization and empirical modeling for electrospun polyacrylonitrile (PAN) nanofiber precursor of carbon nanofibers, Eur. Polym. J. 41 (2005) 2559–2568. doi:10.1016/j.eurpolymj.2005.05.008.
- [58] J. Liu, Z. Yue, H. Fong, Continuous Nanoscale Carbon Fibers with Superior Mechanical Strength, Small. 5 (2009) 536–542. doi:10.1002/smll.200801440.
- [59] H.G. Chae, Y.H. Choi, M.L. Minus, S. Kumar, Carbon nanotube reinforced small diameter polyacrylonitrile based carbon fiber, Compos. Sci. Technol. 69 (2009) 406–413. doi:10.1016/j.compscitech.2008.11.008.

- [60] E. Zussman, X. Chen, W. Ding, L. Calabri, D.A. Dikin, J.P. Quintana, et al., Mechanical and structural characterization of electrospun PAN-derived carbon nanofibers, Carbon N. Y. 43 (2005) 2175–2185. doi:10.1016/j.carbon.2005.03.031.
- [61] S.N. Arshad, M. Naraghi, I. Chasiotis, Strong carbon nanofibers from electrospun polyacrylonitrile, Carbon N. Y. 49 (2011) 1710–1719. doi:10.1016/j.carbon.2010.12.056.
- [62] H.G. Chae, M.L. Minus, A. Rasheed, S. Kumar, Stabilization and carbonization of gel spun polyacrylonitrile/single wall carbon nanotube composite fibers, Polymer (Guildf). 48 (2007) 3781–3789. doi:10.1016/j.polymer.2007.04.072.
- [63] R. Ruiz-Rosas, J. Bedia, M. Lallave, I.G. Loscertales, A. Barrero, J. Rodríguez-Mirasol, et al., The production of submicron diameter carbon fibers by the electrospinning of lignin, Carbon N. Y. 48 (2010) 696–705. doi:10.1016/j.carbon.2009.10.014.
- [64] D.A. Baker, O. Hosseinaei, High Glass Transition Lignins and Lignin Derivatives for the Manufacture of Carbon and Graphite Fibers, US 20140271443 A1, 2014.
- [65] W.-J. Li, C.T. Laurencin, E.J. Caterson, R.S. Tuan, F.K. Ko, Electrospun nanofibrous structure: A novel scaffold for tissue engineering, J. Biomed. Mater. Res. 60 (2002) 613– 621. doi:10.1002/jbm.10167.
- [66] K. Ohgo, C. Zhao, M. Kobayashi, T. Asakura, Preparation of non-woven nanofibers of Bombyx mori silk, Samia cynthia ricini silk and recombinant hybrid silk with electrospinning method, Polymer (Guildf). 44 (2003) 841–846. doi:10.1016/S0032-3861(02)00819-4.
- [67] Z.-M. Huang, Y.Z. Zhang, S. Ramakrishna, C.T. Lim, Electrospinning and mechanical characterization of gelatin nanofibers, Polymer (Guildf). 45 (2004) 5361–5368.
 doi:10.1016/j.polymer.2004.04.005.

- [68] L. Huang, R.A. Mcmillan, R.P. Apkarian, B. Pourdeyhimi, V.P. Conticello, E.L. Chaikof, Generation of Synthetic Elastin-Mimetic Small Diameter Fibers and Fiber Networks, Macromolecules. 33 (2000) 2989–2997. doi:10.1021/ma991858f.
- [69] L. Huang, K. Nagapudi, R.P. Apkarian, E.L. Chaikof, Engineered collagen-PEO nano bers and fabrics, J. Biomater. Sci. Polym. Edn. 12 (2001) 979–993.
 doi:10.1163/156856201753252516.
- [70] J. Ayutsede, M. Gandhi, S. Sukigara, M. Micklus, H.-E. Chen, F. Ko, Regeneration of Bombyx mori silk by electrospinning. Part 3: characterization of electrospun nonwoven mat, Polymer (Guildf). 46 (2005) 1625–1634. doi:10.1016/j.polymer.2004.11.029.
- [71] A. Pedicini, R.J. Farris, Mechanical behavior of electrospun polyurethane, Polymer (Guildf). 44 (2003) 6857–6862. doi:10.1016/j.polymer.2003.08.040.
- [72] M.G. McKee, J.M. Layman, M.P. Cashion, T.E. Long, Phospholipid nonwoven electrospun membranes., Science. 311 (2006) 353–5. doi:10.1126/science.1119790.
- [73] E.P.S. Tan, C.T. Lim, Mechanical characterization of nanofibers A review, Compos.
 Sci. Technol. 66 (2006) 1102–1111. doi:10.1016/j.compscitech.2005.10.003.
- [74] E.P.S. Tan, C.T. Lim, Nanoindentation study of nanofibers, Appl. Phys. Lett. 87 (2005) 1–
 3. doi:10.1063/1.2051802.
- [75] E.P.S. Tan, S.Y. Ng, C.T. Lim, Tensile testing of a single ultrafine polymeric fiber, 2005. doi:10.1016/j.biomaterials.2004.05.021.
- [76] R. Inai, M. Kotaki, S. Ramakrishna, Structure and properties of electrospun PLLA single nanofibres, Nanotechnology. 16 (2005) 208–213. doi:10.1088/0957-4484/16/2/005.

- [77] S.-C. Wong, A. Baji, S. Leng, Effect of fiber diameter on tensile properties of electrospun poly(ε-caprolactone), Polymer (Guildf). 49 (2008) 4713–4722.
 doi:10.1016/j.polymer.2008.08.022.
- S.Y. Chew, T.C. Hufnagel, C.T. Lim, K.W. Leong, Mechanical properties of single electrospun drug-encapsulated nanofibres, Nanotechnology. 17 (2006) 3880–3891. doi:10.1088/0957-4484/17/15/045.
- [79] K.H.K. Chan, S.Y. Wong, X. Li, Y.Z. Zhang, P.C. Lim, C.T. Lim, et al., Effect of Molecular Orientation on Mechanical Property of Single Electrospun Fiber of Poly[(R)-3hydroxybutyrate-co-(R)-3-hydroxyvalerate], J. Phys. Chem. B. 40 (2009) 13179–13185. doi:10.1021/jp905820h.
- [80] A. Buer, S.C. Ugbolue, S.B. Warner, Electrospinning and Properties of Some Nanofibers, Text. Res. J. 71 (2001) 323–328. doi:10.1177/004051750107100408.
- [81] E. Zussman, M. Burman, A.L. Yarin, R. Khalfin, Y. Cohen, Tensile deformation of electrospun nylon-6,6 nanofibers, J. Polym. Sci. Part B Polym. Phys. 44 (2006) 1482– 1489. doi:10.1002/polb.20803.
- [82] A. Arinstein, M. Burman, O. Gendelman, E. Zussman, Effect of supramolecular structure on polymer nanofibre elasticity, Nat. Nanotechnol. 2 (2007) 59–62.
 doi:10.1038/nnano.2006.172.
- [83] E.P.S. Tan, C.N. Goh, C.H. Sow, C.T. Lim, Tensile test of a single nanofiber using an atomic force microscope tip, Appl. Phys. Lett. 86 (2005) 1–3. doi:10.1063/1.1862337.
- [84] F. Ko, Y. Gogotsi, A. Ali, N. Naguib, H. Ye, G.L. Yang, et al., Electrospinning of Continuous Carbon Nanotube-Filled Nanofiber Yarns, Adv. Mater. 15 (2003) 1161–1165. doi:10.1002/adma.200304955.

- [85] M. Wang, H.-J. Jin, D.L. Kaplan, G.C. Rutledge, Mechanical Properties of Electrospun Silk Fibers, Macromolecules. 37 (2004) 6856–6864. doi:10.1021/ma048988v.
- [86] M. Wang, H. Singh, T.A. Hatton, G.C. Rutledge, Field-responsive superparamagnetic composite nanofibers by electrospinning, Polymer (Guildf). 45 (2004) 5505–5514. doi:10.1016/j.polymer.2004.06.013.
- [87] S. Cuenot, S. Demoustier-Champagne, B. Nysten, Elastic Modulus of Polypyrrole
 Nanotubes, Phys. Rev. Lett. 85 (2000) 1690–1693. doi:10.1103/PhysRevLett.85.1690.
- [88] E.P.S. Tan, C.T. Lim, Physical properties of a single polymeric nanofiber, Appl. Phys. Lett. 84 (2004) 1603–1605. doi:10.1063/1.1651643.
- [89] S.-H. Lee, C. Tekmen, W.M. Sigmund, Three-point bending of electrospun TiO2 nanofibers, Mater. Sci. Eng. A. 398 (2005) 77–81. doi:10.1016/j.msea.2005.03.014.
- [90] M.K. Shin, S.I. Kim, S.J. Kim, S.K. Kim, H. Lee, G.M. Spinks, Size-dependent elastic modulus of single electroactive polymer nanofibers, Appl. Phys. Lett. 89 (2006) 2004– 2007. doi:10.1063/1.2402941.
- [91] Q. Fu, Y. Jin, X. Song, J. Gao, X. Han, X. Jiang, et al., Size-dependent mechanical properties of PVA nanofibers reduced via air plasma treatment., Nanotechnology. 21 (2010) 95703. doi:10.1088/0957-4484/21/9/095703.
- [92] L.M. Bellan, J. Kameoka, H.G. Craighead, Measurement of the Young's moduli of individual polyethylene oxide and glass nanofibres, Nanotechnology. 16 (2005) 1095– 1099. doi:10.1088/0957-4484/16/8/017.
- [93] L. Li, L.M. Bellan, H.G. Craighead, M.W. Frey, Formation and properties of nylon-6 and nylon-6/montmorillonite composite nanofibers, Polymer (Guildf). 47 (2006) 6208–6217. doi:10.1016/j.polymer.2006.06.049.

- [94] S.Y. Gu, Q.L. Wu, J. Ren, G.J. Vancso, Mechanical properties of a single electrospun fiber and its structures, Macromol. Rapid Commun. 26 (2005) 716–720. doi:10.1002/marc.200400667.
- [95] D. Jaeger, J. Schischka, J. Bagdahn, R. Jaeger, Tensile testing of individual ultrathin electrospun poly(L-lactic acid) fibers, J. Appl. Polym. Sci. 114 (2009) 3774–3779. doi:10.1002/app.30959.
- [96] P.A. Yuya, Y. Wen, J.A. Turner, Y.A. Dzenis, Z. Li, Determination of Young's modulus of individual electrospun nanofibers by microcantilever vibration method, Appl. Phys. Lett. 90 (2007). doi:10.1063/1.2713128.
- [97] J. Kameoka, S.S. Verbridge, H. Liu, D.A. Czaplewski, H.G. Craighead, Fabrication of suspended silica glass nanofibers from polymeric materials using a scanned electrospinning source, Nano Lett. 4 (2004) 2105–2108. doi:10.1021/nl048840p.
- [98] C.-L. Pai, M.C. Boyce, G.C. Rutledge, Mechanical properties of individual electrospun PA 6(3)T fibers and their variation with fiber diameter, Polymer (Guildf). 52 (2011) 2295–2301. doi:10.1016/j.polymer.2011.03.041.
- [99] M. Naraghi, S.N. Arshad, I. Chasiotis, Molecular orientation and mechanical property size effects in electrospun polyacrylonitrile nanofibers, Polymer (Guildf). 52 (2011) 1612–1618. doi:10.1016/j.polymer.2011.02.013.
- [100] D. Papkov, Y. Zou, M.N. Andalib, A. Goponenko, S.Z.D. Cheng, Y.A. Dzenis, Simultaneously Strong and Tough Ultrafine Continuous Nano fibers, ACSNano. 7 (2013)
 3324–3331. doi:10.1021/nn400028p.
- [101] J. Yao, C. Bastiaansen, T. Peijs, High Strength and High Modulus Electrospun Nanofibers, Fibers. 2 (2014) 158–186. doi:10.3390/fib2020158.

- [102] S. Iijima, Helical microtubules of graphitic carbon, Nature. 354 (1991) 56–58.doi:10.1038/354056a0.
- [103] M. Terrones, Science and Technology of the Twenty-First Century: Synthesis, Properties, and Applications of Carbon Nanotubes, Annu. Rev. Mater. Res. 33 (2003) 419–501. doi:10.1146/annurev.matsci.33.012802.100255.
- [104] R.S. Ruoff, D. Qian, W. Kam, Mechanical properties of carbon nanotubes : theoretical predictions and experimental measurements, Comptes Rendus Phys. 4 (2003) 993–1008. doi:10.1016/j.crhy.2003.08.001.
- [105] K. Balasubramanian, M. Burghard, Chemically functionalized carbon nanotubes, Small. 1 (2005) 180–192. doi:10.1002/smll.200400118.
- [106] A. Baji, Y.W. Mai, S.C. Wong, M. Abtahi, X. Du, Mechanical behavior of self-assembled carbon nanotube reinforced nylon 6,6 fibers, Compos. Sci. Technol. 70 (2010) 1401– 1409. doi:10.1016/j.compscitech.2010.04.020.
- [107] R.H. Baughman, A. a Zakhidov, W. a de Heer, Carbon nanotubes --- the route toward applications, Science (80-.). 297 (2002) 787–92. doi:10.1126/science.1060928.
- [108] M.J. Biercuk, M.C. Llaguno, M. Radosavljevic, J.K. Hyun, A.T. Johnson, J.E. Fischer, Carbon nanotube composites for thermal management, Appl. Phys. Lett. 80 (2002) 2767– 2769. doi:10.1063/1.1469696.
- [109] F. Hussain, Polymer-matrix Nanocomposites, Processing, Manufacturing, and Application: An Overview, J. Compos. Mater. 40 (2006) 1511–1575.
 doi:10.1177/0021998306067321.

- [110] P. Kannan, S.J. Eichhorn, R.J. Young, Deformation of isolated single-wall carbon nanotubes in electrospun polymer nanofibres, Nanotechnology. 18 (2007) 235707. doi:10.1088/0957-4484/18/23/235707.
- [111] Y. Qin, Alginate fibers: an overwiew of the production processes and applications in wound management, Polym. Int. 57 (2008) 171–180. doi:10.1002/pi.
- [112] W. Salalha, Y. Dror, R.L. Khalfin, Y. Cohen, A.L. Yarin, E. Zussman, Single-walled carbon nanotubes embedded in oriented polymeric nanofibers by electrospinning, Langmuir. 20 (2004) 9852–9855. doi:10.1021/la048536b.
- [113] R. Sen, B. Zhao, D. Perea, M.E. Itkis, H. Hu, J. Love, et al., Preparation of single-walled carbon nanotube reinforced polystyrene and polyurethane nanofibers and membranes by electrospinning, Nano Lett. 4 (2004) 459–464. doi:10.1021/nl035135s.
- [114] E.T. Thostenson, Z. Ren, T.-W. Chou, Advances in the science and technology of carbon nanotubes and their composites: a review, Compos. Sci. Technol. 61 (2001) 1899–1912. doi:10.1016/S0266-3538(01)00094-X.
- [115] X.L. Xie, Y.W. Mai, X.P. Zhou, Dispersion and alignment of carbon nanotubes in polymer matrix: A review, Mater. Sci. Eng. R Reports. 49 (2005) 89–112. doi:10.1016/j.mser.2005.04.002.
- [116] N. Grossiord, J. Loos, O. Regev, C.E. Koning, Toolbox for dispersing carbon nanotubes into polymers to get conductive nanocomposites, Chem. Mater. 18 (2006) 1089–1099. doi:10.1021/cm051881h.
- [117] N. Titchenal, H. Lam, H. Ye, Y. Gogosti, F. Ko, J. Liu, et al., SWNT and MWNT Reinforced Carbon Nanocomposite Fibrils, in: 45th AIAA/ASME/ASCE/AHS/ASC

Struct. Struct. Dyn. Mater. Conf., American Institute of Aeronautics and Astronautics, 2004. doi:doi:10.2514/6.2004-1608.

- [118] H. Lam, N. Titchenal, N. Naguib, H. Ye, Y. Gogotsi, F. Ko, Electrospinning of Carbon Nanotube Reinforced Nanocomposite Fibrils and Yarns, MRS Proc. 791 (2003). doi:10.1557/PROC-791-Q10.5.
- [119] F. Ko, S. Khan, A. Ali, Y. Gogotsi, Structure and properties of carbon nanotube reinforced nanocomposites, Proc. 43rd Struct. Struct. Dyn. Mater. Conf. (2002). http://arc.aiaa.org/doi/pdf/10.2514/6.2002-1426 (accessed March 7, 2017).
- [120] M.N. Silberstein, C.-L. Pai, G.C. Rutledge, M.C. Boyce, Elastic–plastic behavior of non-woven fibrous mats, J. Mech. Phys. Solids. 60 (2012) 295–318.
 doi:10.1016/j.jmps.2011.10.007.
- [121] H.L. Cox, The elasticity and strength of paper and other fibrous materials, Br. J. Appl. Phys. 3 (2002) 72–79. doi:10.1088/0508-3443/3/3/302.
- [122] C.-L. Pai, M.C. Boyce, G.C. Rutledge, On the importance of fiber curvature to the elastic moduli of electrospun nonwoven fiber meshes, Polymer (Guildf). 52 (2011) 6126–6133. doi:10.1016/j.polymer.2011.10.055.
- [123] D.R. Petterson, Mechanics of Nowoven Fabrics, Ind. Eng. Chem. 51 (1959) 902–903. doi:10.1021/ie50596a024.
- [124] X.F. Wu, Y.A. Dzenis, Elasticity of planar fiber networks, J. Appl. Phys. 98 (2005)93501-1–9. doi:10.1063/1.2123369.
- [125] W. Weibull, A statistical theory of the strength of materials, R. Swedish Inst. Eng. Res.151 (1939) 1–45.

- [126] F.T. Peirce, Tensile Tests for Cotton Yarns–"The Weakest Link" Theorems on the Strength of Long and of Composite Specimens, J. Text. Inst. 17 (1926) T355-368. doi:10.1080/19447027.1926.10599953.
- [127] H.E. Daniels, The statistical theory of the strength of bundles of threads. I, in: Proc. R.
 Soc. London A Math. Phys. Eng. Sci., The Royal Society, 1945: pp. 405–435.
 doi:10.1098/rspa.1945.0011.
- [128] J.R. Miller, P. Simon, Electrochemical Capacitors for, Science (80-.). 321 (2008) 651–
 652. doi:10.1126/science.1158736.
- [129] L.L. Zhang, R. Zhou, X.S. Zhao, Carbon-based materials as supercapacitor electrodes, J.
 Mater. Chem. 38 (2009) 2520–2531. doi:10.1039/c000417k.
- [130] A.S. Aricò, P. Bruce, B. Scrosati, J.-M. Tarascon, W. van Schalkwijk, Nanostructured materials for advanced energy conversion and storage devices, Nat. Mater. 4 (2005) 366– 377. doi:10.1038/nmat1368.
- [131] P. Simon, Y. Gogotsi, Materials for electrochemical capacitors., Nat. Mater. 7 (2008) 845–854. doi:10.1038/nmat2297.
- [132] M. Jayalakshmi, K. Balasubramanian, Simple capacitors to supercapacitors An overview, Int. J. Electrochem. Sci. 3 (2008) 1196–1217.
- [133] D. Saha, Y. Li, Z. Bi, J. Chen, J.K. Keum, D.K. Hensley, et al., Studies on Supercapacitor Electrode Material from Activated Lignin- Derived Mesoporous Carbon, Langmuir. 30 (2014) 900–910. doi:10.1021/la404112m.
- [134] N. Blomquist, T. Wells, B. Andres, J. Bäckström, S. Forsberg, H. Olin, Metal-free supercapacitor with aqueous electrolyte and low-cost carbon materials, Sci. Rep. 7 (2017) 39836. doi:10.1038/srep39836.

- [135] P. Simon, A. Burke, Nanostructured carbons: Double-layer capacitance and more, Electrochem. Soc. Interface. 17 (2008) 38–43. doi:10.1016/j.carbon.2005.06.046.
- [136] Z. Chang, B. Yu, C. Wang, Lignin-derived hierarchical porous carbon for high-performance supercapacitors, J. Solid State Electrochem. (2016) 1405–1412. doi:10.1007/s10008-016-3146-2.
- [137] L. Feng, N. Xie, J. Zhong, Carbon nanofibers and their composites: A review of synthesizing, properties and applications, Materials (Basel). 7 (2014) 3919–3945. doi:10.3390/ma7053919.
- [138] E. Frackowiak, V. Khomenko, K. Jurewicz, K. Lota, F. Béguin, Supercapacitors based on conducting polymers/nanotubes composites, J. Power Sources. 153 (2006) 413–418. doi:10.1016/j.jpowsour.2005.05.030.
- [139] C. Li, D. Wang, T. Liang, X. Wang, J. Wu, X. Hu, et al., Oxidation of multiwalled carbon nanotubes by air: Benefits for electric double layer capacitors, Powder Technol. 142 (2004) 175–179. doi:10.1016/j.powtec.2004.04.037.
- [140] C. Du, J. Yeh, N. Pan, High power density supercapacitors using locally aligned carbon nanotube electrodes, Nanotechnology. 16 (2005) 350–353. doi:10.1088/0957-4484/16/4/003.
- [141] C. Liu, Electrochemical Characterization of Films of Single-Walled Carbon Nanotubes and Their Possible Application in Supercapacitors, Electrochem. Solid-State Lett. 2 (1999) 577. doi:10.1149/1.1390910.
- [142] C. Zhou, S. Kumar, C.D. Doyle, J.M. Tour, N. Science, R.U. V, et al., Functionalized Single Wall Carbon Nanotubes Treated with Pyrrole for Electrochemical Supercapacitor Membranes, Chem. Mater. (2005) 1997–2002. doi:10.1021/cm047882b.

- [143] M. Hughes, G.Z. Chen, M.S.P. Shaffer, D.J. Fray, A.H. Windle, Controlling the nanostructure of electrochemically grown nanoporous composites of carbon nanotubes and conducting polymers, Compos. Sci. Technol. 64 (2004) 2325–2331. doi:10.1016/j.compscitech.2004.01.026.
- [144] C. Lai, Z. Zhou, L. Zhang, X. Wang, Q. Zhou, Y. Zhao, et al., Free-standing and mechanically flexible mats consisting of electrospun carbon nanofibers made from a natural product of alkali lignin as binder-free electrodes for high-performance supercapacitors, J. Power Sources. 247 (2014) 134–141. doi:10.1016/j.jpowsour.2013.08.082.
- [145] Z. Zhou, X.F. Wu, Graphene-beaded carbon nanofibers for use in supercapacitor electrodes: Synthesis and electrochemical characterization, J. Power Sources. 222 (2013) 410–416. doi:10.1016/jjpowsour.2012.09.004.
- [146] C. Kim, B.T.N. Ngoc, K.S. Yang, M. Kojima, Y.A. Kim, Y.J. Kim, et al., Self-sustained thin Webs consisting of porous carbon nanofibers for supercapacitors via the electrospinning of polyacrylonitrile solutions containing zinc chloride, Adv. Mater. 19 (2007) 2341–2346. doi:10.1002/adma.200602184.
- [147] J. Li, E. hui Liu, W. Li, X. yun Meng, S. ting Tan, Nickel/carbon nanofibers composite electrodes as supercapacitors prepared by electrospinning, J. Alloys Compd. 478 (2009) 371–374. doi:10.1016/j.jallcom.2008.11.024.
- [148] Y.-W. Ju, G.-R. Choi, H.-R. Jung, C. Kim, K.-S. Yang, W.-J. Lee, A Hydrous Ruthenium Oxide-Carbon Nanofibers Composite Electrodes Prepared by Electrospinning, J. Electrochem. Soc. 154 (2007) A192. doi:10.1149/1.2426898.

- [149] X.W. Mao, T.A. Hatton, G.C. Rutledge, A Review of Electrospun Carbon Fibers as Electrode Materials for Energy Storage, Curr. Org. Chem. 17 (2013) 1390–1401. doi:10.2174/1385272811317130006.
- [150] Y.W. Ju, G.R. Choi, H.R. Jung, W.J. Lee, Electrochemical properties of electrospun PAN/MWCNT carbon nanofibers electrodes coated with polypyrrole, Electrochim. Acta.
 53 (2008) 5796–5803. doi:10.1016/j.electacta.2008.03.028.
- [151] R. Mysyk, E. Raymundo-Pi??ero, M. Anouti, D. Lemordant, F. B??guin, Pseudocapacitance of nanoporous carbons in pyrrolidinium-based protic ionic liquids, Electrochem. Commun. 12 (2010) 414–417. doi:10.1016/j.elecom.2010.01.007.
- [152] A.M. Navarro-Suárez, J. Carretero-González, V. Roddatis, E. Goikolea, J. Ségalini, E. Redondo, et al., Nanoporous carbons from natural lignin: study of structural–textural properties and application to organic-based supercapacitors, RSC Adv. 4 (2014) 48336–48343. doi:10.1039/C4RA08218D.
- [153] J.W. Jeon, L. Zhang, J.L. Lutkenhaus, D.D. Laskar, J.P. Lemmon, D. Choi, et al., Controlling porosity in lignin-derived nanoporous carbon for supercapacitor applications, ChemSusChem. 8 (2015) 428–432. doi:10.1002/cssc.201402621.
- [154] S. Hu, S. Zhang, N. Pan, Y. Lo Hsieh, High energy density supercapacitors from lignin derived submicron activated carbon fibers in aqueous electrolytes, J. Power Sources. 270 (2014) 106–112. doi:10.1016/j.jpowsour.2014.07.063.
- [155] I. Dallmeyer, L.T. Lin, Y. Li, F. Ko, J.F. Kadla, Preparation and characterization of interconnected, Kraft lignin-based carbon fibrous materials by electrospinning, Macromol. Mater. Eng. 299 (2014) 540–551. doi:10.1002/mame.201300148.

- [156] Y. Li, F.K. Ko, W.Y. Hamad, Effects of Emulsion Droplet Size on the Structure of Electrospun Ultrafine Biocomposite Fibers with Cellulose Nanocrystals, Biomacromolecules. 14 (2013) 3801–3807. doi:10.1021/bm400540v.
- [157] H. Lam, Electrospinning of Single Wall Carbon Nanotube Reinforced Aligned Fibrils and Yarns, Drexel, 2004.
- [158] D.A. Stevens, J.R. Dahn, An in situ small-angle X-ray scattering study of sodium insertion into a nanoporous carbon anode material within an operating electrochemical cell, J. Electrochem. Soc. 147 (2000) 4428–4431. doi:10.1149/1.1394081.
- [159] D. Dong, A. Fricke, Intrinsic viscosity and the molecular weight of kraft lignin, Polymer (Guildf). 36 (1995) 2075–2078. doi:10.1016/0032-3861(95)91455-G.
- [160] S. Ramakrishna, K. Fujihara, W.-E. Teo, T.-C. Lim, Z. Ma, Modeling of the Electrospinning Process, in: An Introd. to Electrospinning Nanofibers, World Scientific, 2005: pp. 155–191. doi:10.1142/9789812567611 0004.
- [161] S. Backer, D.R. Petterson, Some Principles of Nonwoven Fabrics1, Text. Res. J. 30 (1960)704–711. doi:10.1177/004051756003000912.
- [162] F. Chen, X. Peng, T. Li, S. Chen, X.-F. Wu, D.H. Reneker, et al., Mechanical characterization of single high-strength electrospun polyimide nanofibres, J. Phys. D. Appl. Phys. 41 (2008) 25308. doi:10.1088/0022-3727/41/2/025308.
- [163] X. Wei, Z. Xia, S.C. Wong, A. Baji, Modelling of mechanical properties of electrospun nanofibre network, Int. J. Exp. Comput. Biomech. 1 (2009) 45.
 doi:10.1504/IJECB.2009.022858.

- [164] F. Croisier, A.S. Duwez, C. Jérôme, A.F. Léonard, K.O. Van Der Werf, P.J. Dijkstra, et al., Mechanical testing of electrospun PCL fibers, Acta Biomater. 8 (2012) 218–224. doi:10.1016/j.actbio.2011.08.015.
- [165] S.M. Pourmortazavi, M. Sadri, M. Rahimi-Nasrabadi, M. Shamsipur, Y. Jabbarzade, M.S. Khalaki, et al., Thermal decomposition kinetics of electrospun azidodeoxy cellulose nitrate and polyurethane nanofibers, J. Therm. Anal. Calorim. 119 (2015) 281–290. doi:10.1007/s10973-014-4064-0.
- [166] M.M. Mannarino, G.C. Rutledge, Mechanical and tribological properties of electrospun PA 6(3)T fiber mats, Polym. (United Kingdom). 53 (2012) 3017–3025. doi:10.1016/j.polymer.2012.04.039.
- [167] G.H. Michler, H.H.K.B. Von Schmeling, The physics and micro-mechanics of nano-voids and nano-particles in polymer combinations, Polym. (United Kingdom). 54 (2013) 3131– 3144. doi:10.1016/j.polymer.2013.03.035.
- [168] D. Schorr, P.N. Diouf, T. Stevanovic, Evaluation of industrial lignins for biocomposites production, Ind. Crops Prod. 52 (2014) 65–73. doi:10.1016/j.indcrop.2013.10.014.
- [169] C.G. Boeriu, D. Bravo, R.J. a Gosselink, J.E.G. Van Dam, Characterisation of structuredependent functional properties of lignin with infrared spectroscopy, Ind. Crops Prod. 20 (2004) 205–218. doi:10.1016/j.indcrop.2004.04.022.
- [170] I. Norberg, Y. Nordström, R. Drougge, G. Gellerstedt, E. Sjöholm, A new method for stabilizing softwood kraft lignin fibers for carbon fiber production, J. Appl. Polym. Sci. 128 (2013) 3824–3830. doi:10.1002/app.38588.

- [171] I. Brodin, M. Ernstsson, G. Gellerstedt, E. Sjöholm, Oxidative stabilisation of kraft lignin for carbon fibre production, Holzforschung. 66 (2012) 141–147. doi:10.1515/HF.2011.133.
- [172] W.J. Youe, S.M. Lee, S.S. Lee, S.H. Lee, Y.S. Kim, Characterization of carbon nanofiber mats produced from electrospun lignin-g-polyacrylonitrile copolymer, Int. J. Biol. Macromol. 82 (2016) 497–504. doi:10.1016/j.ijbiomac.2015.10.022.
- [173] Z. Zhou, C. Lai, L. Zhang, Y. Qian, H. Hou, D.H. Reneker, et al., Development of carbon nanofibers from aligned electrospun polyacrylonitrile nanofiber bundles and characterization of their microstructural, electrical, and mechanical properties, Polymer (Guildf). 50 (2009) 2999–3006. doi:10.1016/j.polymer.2009.04.058.
- [174] J. Mittal, O.P. Bahl, R.B. Mathur, Single step carbonization and graphitization of highly stabilized PAN fibers, Carbon N. Y. 35 (1997) 1196–1197. doi:10.1016/S0008-6223(97)84653-2.
- [175] H. Hou, J.J. Gc, J. Zeng, Q. Li, D.H. Reneker, A. Greiner, et al., Electrospun
 Polyacrylonitrile Nanofibers Containing a High Concentration of Well-Aligned Multiwall
 Carbon Nanotubes, Chem. Mater. 17 (2005) 967–973. doi:10.1021/cm0484955.
- [176] Y. Li, Y.-S. Hu, H. Li, L. Chen, X. Huang, A superior low-cost amorphous carbon anode made from pitch and lignin for sodium-ion batteries, J. Mater. Chem. A. 4 (2015) 96–104. doi:10.1039/C5TA08601A.
- [177] F.S. Baker, Low cost carbon fiber from renewable resources, (2010) 1–28.
 https://www.energy.gov/sites/prod/files/2014/03/f11/lm005_baker_2010_o.pdf (accessed October 10, 2016).

- [178] T. Jawhari, A. Roid, J. Casado, Raman spectroscopic characterization of some commercially available carbon black materials, Carbon N. Y. 33 (1995) 1561–1565. doi:10.1016/0008-6223(95)00117-V.
- [179] R.M. Yadav, P.S. Dobal, T. Shripathi, R.S. Katiyar, O.N. Srivastava, Effect of growth temperature on bamboo-shaped carbon-nitrogen (C-N) nanotubes synthesized using ferrocene acetonitrile precursor, Nanoscale Res. Lett. 4 (2009) 197–203. doi:10.1007/s11671-008-9225-2.
- [180] A. Ferrari, J. Robertson, Interpretation of Raman spectra of disordered and amorphous carbon, Phys. Rev. B. 61 (2000) 14095–14107. doi:10.1103/PhysRevB.61.14095.
- [181] A. Ferrari, J. Robertson, Resonant Raman spectroscopy of disordered, amorphous, and diamondlike carbon, Phys. Rev. B. 64 (2001) 1–13. doi:10.1103/PhysRevB.64.075414.
- [182] K. Ishimaru, T. Hata, P. Bronsveld, D. Meier, Y. Imamura, Spectroscopic analysis of carbonization behavior of wood, cellulose and lignin, J. Mater. Sci. 42 (2007) 122–129. doi:10.1007/s10853-006-1042-3.
- [183] E. Frank, L.M. Steudle, D. Ingildeev, J.M. Spörl, M.R. Buchmeiser, Carbon fibers: Precursor systems, processing, structure, and properties, Angew. Chemie - Int. Ed. 53 (2014) 5262–5298. doi:10.1002/anie.201306129.
- [184] C. Kim, S.H. Park, J.I. Cho, D.Y. Lee, T.J. Park, W.J. Lee, et al., Raman spectroscopic evaluation of polyacrylonitrile-based carbon nanofibers prepared by electrospinning, J. Raman Spectrosc. 35 (2004) 928–933. doi:10.1002/jrs.1233.
- [185] S. Lee, J. Kim, B.-C. Ku, J. Kim, H.-I. Joh, Structural Evolution of Polyacrylonitrile Fibers in Stabilization and Carbonization, Adv. Chem. Eng. Sci. 2 (2012) 275–282. doi:10.4236/aces.2012.22032.

- [186] C. Kim, K.S. Yang, M. Kojima, K. Yoshida, Y.J. Kim, Y.A. Kim, et al., Fabrication of electrospinning-derived carbon nanofiber webs for the anode material of lithium-ion secondary batteries, Adv. Funct. Mater. 16 (2006) 2393–2397. doi:10.1002/adfm.200500911.
- [187] M. Bayat, H. Yang, F. Ko, Electromagnetic properties of electrospun Fe3O4/carbon composite nanofibers, Polymer (Guildf). 52 (2011) 1645–1653.
 doi:10.1016/j.polymer.2011.01.057.
- [188] S.D. Mohan, G.R. Mitchell, F.J. Davis, Chain extension in electrospun polystyrene fibres: a SANS study, Soft Matter. (2011) 4397–4404. doi:10.1039/c0sm01442g.
- [189] S.Z. Wu, F. Zhang, X.X. Hou, X.P. Yang, Stretching-Induced Orientation for Improving the Mechanical Properties of Electrospun Polyacrylonitrile Nanofiber Sheet, Adv. Mater. Res. 47–50 (2008) 1169–1172. doi:10.4028/www.scientific.net/AMR.47-50.1169.
- [190] T. Kongkhlang, K. Tashiro, M. Kotaki, S. Chirachanchai, Electrospinning as a New Technique To Control the Crystal Morphology and Molecular Orientation of Polyoxymethylene Nanofibers, (2008) 15460–15466. doi:10.1021/ja804185s.
- [191] H. Fong, Electrospun polymer, ceramic, carbon / graphite nanofibers and their applications, in: H. Nalwa (Ed.), American Scientific Publishers, 11, 2007: pp. 451–474.
- [192] S.A.H. Ravandi, K. Toriumi, Fourier transform analysis of plain weave fabric appearance, Text. Res. J. 65 (1995) 676–683. doi:10.1177/004051759506501108.
- [193] D. Papkov, A.M. Beese, A. Goponenko, Y. Zou, M. Naraghi, H.D. Espinosa, et al., Extraordinary improvement of the graphitic structure of continuous carbon nanofibers templated with double wall carbon nanotubes, ACS Nano. 7 (2013) 126–142. doi:10.1021/nn303423x.
- [194] L. Fambri, I. Dabrowska, R. Ceccato, A. Pegoretti, Effects of Fumed Silica and Draw Ratio on Nanocomposite Polypropylene Fibers, Polymers (Basel). 9 (2017) 41. doi:10.3390/polym9020041.
- [195] Y. Yamashita, F. Ko, A. Tanaka, H. Miyake, Characteristics of Elastomeric Nanofiber Membranes Produced by Electrospinning, J. Text. Eng. 53 (2007) 137–142. doi:10.4188/jte.53.137.
- [196] M. Arslan, M.C. Boyce, Constitutive modeling of the finite deformation behavior of membranes possessing a triangulated network microstructure, J. Appl. Mech. Asme. 73 (2006) 536–543. doi:Doi 10.1115/1.2130360.
- [197] A. Rawal, A Modified Micromechanical Model for the Prediction of Tensile Behavior of Nonwoven Structures, J. Ind. Text. 36 (2006) 133–149. doi:10.1177/1528083706067691.
- [198] A. Ridruejo, C. González, J. Llorca, A constitutive model for the in-plane mechanical behavior of nonwoven fabrics, Int. J. Solids Struct. 49 (2012) 2215–2229. doi:10.1016/j.ijsolstr.2012.04.014.
- [199] P. Jearanaisilawong, A Continuum Model for Needlepunched Nonwoven Fabrics, Massachusetts Institute of Technology, 2008.
- [200] B.D. Coleman, On the strength of classical fibres and fibre bundles, J. Mech. Phys. Solids.
 7 (1958) 60–70. doi:10.1016/0022-5096(58)90039-5.
- [201] B.D. Coleman, Statistics and time dependence of mechanical breakdown in fibers, J. Appl. Phys. 29 (1958) 968–983. doi:10.1063/1.1723343.
- [202] B.D. Coleman, D.W. Marquardt, Time dependence of mechanical breakdown in bundles of fibers. II. the infinite ideal bundle under linearly increasing loads, J. Appl. Phys. 28 (1957) 1065–1067. doi:10.1063/1.1722908.

- [203] F. Thomas, 32—X.—Tensile Tests for Cotton Yarns v.—"The Weakest Link" Theorems on the Strength of Long and of Composite Specimens, J. Text. Inst. Trans. 17 (1926) T355–T368. doi:10.1080/19447027.1926.10599953.
- [204] B.D.Coleman, On the strength of classical fibres and fibre bundles, J. Mech. Phys. Solids.
 7 (1958) 60–70. doi:10.1016/0022-5096(58)90039-5.
- [205] N. Pan, Prediction of statistical strengths of twisted fibre structures, J. Mater. Sci. 28 (1993) 6107–6114. doi:10.1007/BF00365030.
- [206] N. Pan, Develpment of a Constitutive Theory for short fiber yarns: Part I. Mechanics of staple yarn without slippage effect, Text. Res. J. 62 (1992) 749–765.
 doi:10.1177/004051759306301002.
- [207] A. Kelly, W.R. Tyson, Tensile properties of fibre-reinforced metals: Copper/tungsten and copper/molybdenum, J. Mech. Phys. Solids. 13 (1965) 329–350. doi:10.1016/0022-5096(65)90035-9.
- [208] J.W.S. Hearle, P. Grosberg, S. Backer, Structural mechanics of fibers, yarns, and fabrics, (1969).
- [209] U. Stachewicz, R.J. Bailey, W. Wang, A.H. Barber, Size dependent mechanical properties of electrospun polymer fibers from a composite structure, Polymer (Guildf). 53 (2012) 5132–5137. doi:10.1016/j.polymer.2012.08.064.
- [210] L. Salmén, Micromechanical understanding of the cell-wall structure, Comptes Rendus -Biol. 327 (2004) 873–880. doi:10.1016/j.crvi.2004.03.010.
- [211] K.W.M. Davy, M. Braden, Study of polymeric systems based on 2,2 bis-4(2-hydroxy-3-methacryloyl-oxypropoxy) phenyl propane, Biomaterials. 12 (1991) 406–410. doi:10.1016/0142-9612(91)90009-Y.

- [212] L. Petridis, J.C. Smith, A Molecular Mechanics Force Field for Lignin, J. Comput. Chem.31 (2010) 2967–2970. doi:10.1002/jcc.21075.
- [213] W.J. Cousins, Elastic modulus of lignin as related to moisture content, Wood Sci. Technol. 10 (1976) 9–17. doi:10.1007/BF00376380.
- [214] T. Elder, Quantum chemical determination of Young's modulus of lignin. Calculations on a beta-O-4' model compound., Biomacromolecules. 8 (2007) 3619–3627. doi:10.1021/bm700663y.
- [215] W.J. Cousins, R.W. Armstrong, W.H. Robinson, Young's modulus of lignin from a continuous indentation test, J. Mater. Sci. 10 (1975) 1655–1658.
 doi:10.1007/BF00554925.
- [216] L. Lin, Y. Li, F.K. Ko, Fabrication and Properties of Lignin Based Carbon Nanofiber, J.
 Fiber Bioeng. Informatics. 6 (2013) 335–347. doi:10.3993/jfbi12201301.
- [217] S. Kubo, Y. Uraki, Y. Sano, Preparation of carbon fibers from softwood lignin by atmospheric acetic acid pulping, Carbon N. Y. 36 (1998) 1119–1124. doi:10.1016/S0008-6223(98)00086-4.
- [218] Y. Nordström, R. Joffe, E. Sjöholm, Mechanical characterization and application of Weibull statistics to the strength of softwood lignin-based carbon fibers, J. Appl. Polym. Sci. 130 (2013) 3689–3697. doi:10.1002/app.39627.
- [219] R.J. Diefendorf, Pitch Precursor Carbon Fibers, in: A. Kelly, C. Zweben (Eds.), Compr. Compos. Mater., Pergamon, Oxford, 2000: pp. 35–83. doi:10.1016/B0-08-042993-9/00041-3.

- [220] A. Shindo, Polyacrylonitrile (PAN)-based Carbon Fibers, in: A. Kelly, C. Zweben (Eds.),
 Compr. Compos. Mater., Pergamon, Oxford, 2000: pp. 1–33. doi:10.1016/B0-08-042993-9/00040-1.
- [221] H.C. Wu, V.C. Li, Trade-off between strength and ductility of random discontinuous fiber reinforced cementitious composites, Cem. Concr. Compos. 16 (1994) 23–29. doi:10.1016/0958-9465(94)90027-2.
- [222] T. Saito, R. Kuramae, J. Wohlert, L.A. Berglund, A. Isogai, An ultrastrong nanofibrillar biomaterial: The strength of single cellulose nanofibrils revealed via sonication-induced fragmentation, Biomacromolecules. 14 (2013) 248–253. doi:10.1021/bm301674e.
- [223] S.A.H. Ravandi, R.B. Tork, F. Dabirian, A.A. Gharehaghaji, A. Sajjadi, Characteristics of Yarn and Fabric Made out of Nanofibers, Mater. Sci. Appl. 6 (2015) 103–110. doi:10.4236/msa.2015.61013.
- [224] F. Dabirian, Y. Hosseini, S.A.H. Ravandi, Manipulation of the electric field of electrospinning system to produce polyacrylonitrile nanofiber yarn, J. Text. Inst. 98
 (2007) 237–241. doi:10.1080/00405000701463979.
- [225] S.A. Hosseini Ravandi, E. Hassanabadi, H. Tavanai, R.A. Abuzade, Mechanical properties and morphology of hot drawn polyacrylonitrile nanofibrous yarn, J. Appl. Polym. Sci. 124 (2012) 5002–5009. doi:10.1002/app.35602.
- [226] A.S. Watson, R.L. Smith, An examination of statistical theories for fibrous materials in the light of experimental data, J. Mater. Sci. 20 (1985) 3260–3270. doi:10.1007/BF00545193.
- [227] J.W. Hitchon, D.C. Phillips, The dependence of the strength of carbon fibres on length, Fibre Sci. Technol. 12 (1979) 217–233. doi:10.1016/0015-0568(79)90032-0.

- [228] K. Naito, Y. Tanaka, J.M. Yang, Y. Kagawa, Tensile properties of ultrahigh strength PAN-based, ultrahigh modulus pitch-based and high ductility pitch-based carbon fibers, Carbon N. Y. 46 (2008) 189–195. doi:10.1016/j.carbon.2007.11.001.
- [229] C. Moreno-Castilla, M.B. Dawidziuk, F. Carrasco-Marín, Z. Zapata-Benabithe, Surface characteristics and electrochemical capacitances of carbon aerogels obtained from resorcinol and pyrocatechol using boric and oxalic acids as polymerization catalysts, Carbon N. Y. 49 (2011) 3808–3819. doi:10.1016/j.carbon.2011.05.013.
- [230] E.J. Ra, E. Raymundo-Piñero, Y.H. Lee, F. Béguin, High power supercapacitors using polyacrylonitrile-based carbon nanofiber paper, Carbon N. Y. 47 (2009) 2984–2992.
 doi:10.1016/j.carbon.2009.06.051.
- [231] C. Emmenegger, P. Mauron, P. Sudan, P. Wenger, V. Hermann, R. Gallay, et al., Investigation of electrochemical double-layer (ECDL) capacitors electrodes based on carbon nanotubes and activated carbon materials, J. Power Sources. 124 (2003) 321–329. doi:10.1016/S0378-7753(03)00590-1.
- [232] X. Lu, H. Dou, B. Gao, C. Yuan, S. Yang, L. Hao, et al., A flexible graphene/multiwalled carbon nanotube film as a high performance electrode material for supercapacitors, Electrochim. Acta. 56 (2011) 5115–5121. doi:10.1016/j.electacta.2011.03.066.
- [233] R.B. Rakhi, W. Chen, D. Cha, H.N. Alshareef, Nanostructured ternary electrodes for energy-storage applications, Adv. Energy Mater. 2 (2012) 381–389.
 doi:10.1002/aenm.201100609.
- [234] V. Presser, L. Zhang, J.J. Niu, J. McDonough, C. Perez, H. Fong, et al., Flexible nanofelts of carbide-derived carbon with ultra-high power handling capability, Adv. Energy Mater. 1 (2011) 423–430. doi:10.1002/aenm.201100047.

- [235] L. Zhang, T. You, T. Zhou, X. Zhou, F. Xu, Interconnected Hierarchical Porous Carbon from Lignin-Derived Byproducts of Bioethanol Production for Ultra-High Performance Supercapacitors, ACS Appl. Mater. Interfaces. 8 (2016) 13918–13925. doi:10.1021/acsami.6b02774.
- [236] S. Imaizumi, H. Matsumoto, K. Suzuki, M. Minagawa, M. Kimura, A. Tanioka, Phenolic Resin-Based Carbon Thin Fibers Prepared by Electrospinning: Additive Effects of Poly(vinyl butyral) and Electrolytes, Polym. J. 41 (2009) 1124–1128. doi:10.1295/polymj.PJ2009160.
- [237] Y.-W. Ju, S.-H. Park, H.-R. Jung, W.-J. Lee, Electrospun Activated Carbon Nanofibers Electrodes Based on Polymer Blends, J. Electrochem. Soc. 156 (2009) A489. doi:10.1149/1.3116245.
- [238] S. Zhang, N. Pan, Supercapacitor performance of crumpled and planar graphene materials produced by hydrogen gas reduction of graphene oxide, J. Mater. Chem. A. 1 (2013)
 7957. doi:10.1039/c3ta11006k.
- [239] A. Burke, M. Miller, The power capability of ultracapacitors and lithium batteries for electric and hybrid vehicle applications, J. Power Sources. 196 (2011) 514–522.
 doi:10.1016/j.jpowsour.2010.06.092.
- [240] Y. Gawli, A. Banerjee, D. Dhakras, M. Deo, D. Bulani, P. Wadgaonkar, et al., 3D
 Polyaniline Architecture by Concurrent Inorganic and Organic Acid Doping for Superior
 and Robust High Rate Supercapacitor Performance., Sci. Rep. 6 (2016) 21002.
 doi:10.1038/srep21002.
- [241] M. Ago, M. Borghei, O.J. Rojas, Free-standing electrospun carbon network from lignin as a conductive electrode for high - performance supercapacitors, 2016.