Polyacrylonitrile nanofibre yarn; electrospinning and their post-drawing behaviour

by

Zhigang Xie

(B. Eng)

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CANDIDATE DECLARATION

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Xie Zaigang

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12 Aug 2013
Dedication

This work is dedicated to my son, Christopher Xie, for the joy he brought to me.
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It became enlightened at once when this master research journey approaching the end, that it is not only about acquiring new knowledge, investigating things in a scientific way and elaborating research findings, but also essentially a phenomenal tough training and a self-examination experience which surely has remarkably benefited to my life and my future career. Hereby I would like to express my gratitude to those who shared their insights and experiences, and provided support to my research.

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Other Contribution

A prototype of the nanofiber yarn spinner that I have built based on this research has been commercialized and one machine has been installed in University of Wollongong.
Abstract

Electrospinning is an effective method to produce nanofibres; however it is still challenging to directly electrospin continuous nanofibre yarn which is essential for preparing complex fabrics rather than nonwoven. Polyacrylonitrile (PAN) is the exclusive precursor of high performance carbon fibre. Carbon nanofibre with diameters an order of magnitude smaller than those of commercial carbon fibres are expected to tremendously increase the mechanical properties. Electrospun PAN nanofibre yarn made it possible to continuously produce carbon nanofibre. This research focused on electrospinning continuous PAN nanofibre yarns and their post drawing effects. The whole experimental work is divided into two parts.

The first part of this master of philosophy research was to establish an effective way to produce continuous nanofibre yarn. By using a back disc aided electrospinning setup to deposit positively and negatively charged nanofibres onto the large open end of a rotating funnel and subsequently stretching the fibre deposition off the funnel to form a cone shape nanofibre web, a twisted continuous nanofibre yarn was easily produced from the vertices of the cone.

The second part of this research was to understand the drawing performance of PAN nanofibre yarns and the influence of drawing parameters on yarn and fibre morphology, molecular orientation and mechanical properties in order to make the yarn suitable for carbon nanofibre precursor. The optimum drawing temperature and drawing force for PAN nanofibre yarn has been experimentally examined. Although the jet has been elongated many times during electrospinning, the molecular orientation in the nanofibre yarn was not
high, however was found remarkably improved under small drawing ratio. The significantly improved fibre alignment, molecular orientation and mechanical properties suggesting such post drawing PAN nanofibre yarn a possible carbon nanofibre precursor.
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Chapter 1

Introduction

1.1 Significance of research

Electrospinning is an efficient method to produce continuous polymeric fibres of diameter controllable in the range from tens of nanometers to several micrometres (1). Electrospun nanofibres show high surface-to-mass ratio, reasonable mechanical strength, ability to be incorporated with various materials through electrospinning and novel second fibrous structure have attracted extensive interests in both scientific and industrial sectors. Electrospun nanofibres are conventionally produced in the form of nonwoven mats which have been used in diverse areas including filtration, wound dressing, catalyst and some of composite structure applications. Challenges remains for nanofibres to be electrospun in the form of yarns. Since yarns are the key building blocks for constructing complex fibrous structures, making nanofibre yarns has received extensive attention.

Polyacrylonitrile (PAN) fibres have been widely used in textile and for industrial applications. PAN is also used as precursor for making carbon fibres. Worldwide carbon fibre production was over 40,000 metric tons and valued over one billion US dollar in 2010 (2). Global demand for carbon fibre has been continuously increasing, especially for aerospace, wind energy and automotive applications (Figure 1.1). High performance carbon fibres are exclusively derived from PAN precursor. Commercial PAN precursor fibres
made from wet-spin or dry-jet wet spin methods have a diameter around tens of microns. The carbon fibres produced from those PAN precursors have a diameter of a few micro meters. When the diameter reduced from 7.7 μm (T-300) to 5.0 μm (T-1000), the tensile strength of carbon fibre increased by 60% from 4.60 GPa to 7.37 GPa [1]. Electrospinning can produce much fine PAN fibre, hence the carbon nanofibre. Carbon fibres with diameters an order of magnitude smaller than the commercial carbon fibres are expected to tremendously increase the mechanical properties [2].

![Figure 1.1](image.png)

**Figure 1.1, Growth in demand of carbon fibre over 50 years from 1970 - 2020**

(2)

### 1.2 Research problems and specific aims

Woven fabrics prepared from electrospun nanofibres have rarely been reported. To prepare woven fabrics needs yarns. However it is still challenging to make continuous yarns directly from electrospinning.
Recently, Ali et al (3) in our group has reported a method to electrospin nanofibre yarns. The technique involves simultaneous electrospinning of oppositely-charged nanofibres onto a funnel collector. However this method showed difficulty in controlling the fibre deposition. It was difficult to use this setup to produce continuous PAN nanofibres yarns.

Electrospun PAN nanofibre yarns contain randomly orientated fibres. The randomly orientated fibres fracture during heating processes of carbon fibre production as cannot withhold the substantial shrinkage force. Carbon nanofibres made directly from electrospun PAN fibres were reported to have low mechanical properties. Thus the precursor fibres have to be uniaxial orientated to allow shrinking along the fibre axis to avoid the fibre breakage during the processes. Commercial PAN carbon fibre precursors are drawn to several tens of times in hot water to improve the fibre alignment. The molecular orientation, crystallinity and mechanical properties of the precursor fibre are also improved after the drawing.

Thus here comes the research question: **How to produce continuous PAN nanofibre yarns and whether they can be drawn in a similar way as PAN carbon fibre precursor?**

To address this research question, two specific aims have been proposed:

**Specific Aim 1: Develop an effective method to electrospin continuous PAN nanofibres yarns.**
Specific Aim 2: Understand the drawing performance of PAN nanofibre yarns and the influence of drawing parameters on yarn and fibre morphology, molecular orientation and mechanical properties.

1.3 Thesis outline

Besides this chapter, the thesis includes 5 more chapters as described below:

Chapter 2 is a literature review of electrospinning theory, parameters effecting on fibre morphology, and various collection methods for electrospun fibre bundles or yarns. The applications of PAN, the limitation in existing carbon fibre precursor and carbon fibre manufacturing processes, and recent development in making electrospun PAN based carbon nanofibres are also reviewed.

Chapter 3 describes all materials, electrospinning setups, experiment processes, characterisation instruments and methods that were used in this research.

Chapter 4 is the experiment section of making electrospinning PAN nanofibre yarns. The effect of disc-aided electrospinning for making continuous PAN nanofibre yarn were studied and compared with those of conventional electrospinning.

Chapter 5 is an experiment section on drawing PAN nanofibre yarns. The effect of hot wet or hot dry on the morphology and mechanical properties of nanofibre yarns were examined.
Chapter 6 summarises the conclusions obtained from this master of philosophy research. Suggestions for future works are also provided.
Chapter 2

Literature Review

In this chapter, several methods for preparing nanofibres are briefly introduced. Among these methods, electrospinning technique for its easiness in making nanofibres as well as its simple setup has attracted lots of attention recently. The electrospinning mechanism and fundamental parameters that influence the resulted nanofibre as well as methods of collecting the electrospun nanofibre bundle and yarn has been elaborated on. Polyacrylonitrile (PAN) has been widely used in textile and as a carbon fibre precursor. PAN precursor fibres of commercially available carbon fibres have diameter in micrometre size. A PAN precursor fibre that has diameter of nanofibre scale is expected to tremendously improve the mechanical strength of its derived carbon fibre. The carbon fibre manufacturing process and recent development of carbon nanofibres derived from electrospun PAN nanofibres have been reviewed.

2.1 Electrospinning of nanofibres and yarns

2.1.1 Introduction to nanofibres

Definition of nanofibre and its applications

A nanofibre is defined as a one dimensional material with a diameter less than 1 μm and length-to-diameter aspect ratio larger than 100:1. Nanofibres can have up to six orders of magnitude surface-to-volume-ratio greater than micro size fibres. This extraordinary high surface-to-volume-ratio has made
nanofibres superior to other fibres and has been applied in diverse areas, such as filtration (4, 5), wound treatment (6-8), scaffold and tissue engineering (9-12), drug delivery (13, 14), catalyst and enzyme carriers, energy conversion and storage (15-20), sensors (21) and composite reinforcement (22-24). Between 2001 and 2012, 7823 papers have reported the applications of electrospun nanofibres. Figure 2.1 shows the publications of nanofibres in diverse areas.

Figure 2.1, Statistics on the literature published about the applications of electrospun fibres in the period of 2001-2012 (25).

**Nanofibre preparation technology**

Several techniques can be used to prepare polymeric nanofibres, such as directly drawing, melt blown, template synthesis, through islands-in-a-sea fibres, phase separation, self-assembly and electrospinning (26). "Drawing" can produce a nanofibre as a long monofilament, but it is only applied to
viscoelastic materials which are able to bear large amounts of deformation without breaking.

The "Template Synthesis" technique uses nano-porous membranes as the template to produce nano-sized fibrils within the pores of the membranes. However it is not possible to prepare long and distinct nano-filaments (27).

The "Islands-in-a-sea" method uses a special extrusion process to produce island-in-a-sea bicomponent fibres, with islands dispersing in the sea matrix. By splitting the island polymer from the matrix, nanofibres can be obtained (28).

The "Melt blown" technique is commonly used for producing nonwoven fibres. During the process, a polymer melt is extruded from one or multiple orifice dies and drawn down by hot air jets. Due to complicated interactive actions between air and jets, submicron fibres obtained by the melt blown process are in the form of nonwoven mats.

"Electrospinning" is a method that uses electrostatic forces to stretch a viscous polymer solution into nanofibres. Figure 2.2 illustrates a typical electrospinning setup. From 1992 to 2012, 10573 papers have been published on the preparation of nanofibres using electrospinning.

The statistic results of the papers based on the nanofibre-making technology are shown in Figure 2.3. It appears that nanofibres prepared from electrospinning are the most commonly used in literatures.
Figure 2.2, A typical setup of electrospinning includes a syringe pump with polymer solution, a high voltage power supply and a grounded collector.

Figure 2.3, Statistics of papers published on nanofibre preparation from 1992 to 2012 (search made through Scifinder: Keywords nanofibre + electrospinning, self-assembly, template synthesis, phase separation, drawing, melt blown).

2.1.2 Electrospinning technique

Fundamentals of electrospinning
Reports of the electrospinning technique can be traced back to the 1930s where Formhals patented his inventions of apparatus for spinning artificial filaments using electric charges (29, 30). However, his apparatus was only able to produce micro size fibres and due to low production rate, this electrospinning technique didn’t attract attention for a long time. It was only until the 1990s, when US Professor Reneker published a series of papers (1, 31-33) on using electrospinning to prepare nanofibres. Because electrospinning easily forms nanofibres, this method soon brought lots of attention. The number of publications in the electrospinning field has been increasing exponentially over the last few years (Figure 2.4).

![Figure 2.4](image_url)

**Figure 2.4.** Statistics of annual literature based on electrospinning through the period of 1992-2012 (search made through Scopus by keyword Electrospinning).

Lots of scientific works have been concentrated on experimental methodologies to prepare nanofibres through electrospinning and understanding the process through mathematical methods. It is generally agreed that electrospinning involves competitive interactions between viscosity,
surface tension, and charge repulsion of polymer solution (33, 34). When a high voltage is applied to a polymer solution, the solution is electrified and attracted by the opposite electrode (35, 36). As a result, a droplet of polymer solution at the orifice forms a conical shape. When the electric potential is above a critical value, the electrostatic force overcomes surface tension of the polymer solution, the solution ejects from the vertex of the cone and results in a charged jet. In as early as the 1960s, Taylor (37) systematically studied the formation of the jet from the electrically charged viscous liquid. He concluded that the semi-vertical angle of the conical shape droplet shall be close to 49.3° before a stable and continuous jet can be obtained. The conical shape is now commonly referred to as the ‘Taylor cone’. Yarin et al (38) amended this angle to be close to 33.5° by defining the conical shape as hyperboloid (Figure 2.5). After ejected from the Taylor cone, the jet is elongated, thinned and accelerated following the trajectory of a short tapered straight segment, and then a segment bends, spirals and loops in three dimensions. Reneker et al (39) dispersed a micron sized particle in polymer solution and used a high speed camera to photograph the motion of the particle in the straight segment of the electrospinning jet. They observed that the particle travelled in an accelerated velocity from 0.5 to 5 m/s in few millimetres within the straight segment. Comparing with this acceleration as high as 590 m/s², the gravity acceleration of 9.8 m/s² is negligible (40). A decrease in jet diameter occurs almost immediately after the jet ejects from the Taylor cone. Xu et al (41) electrospun 6 wt% PEO aqueous solution under electrostatic field 49 V/mm and recorded the jet diameter decreased from 15.99 μm at 6 mm from the vertex of Taylor cone to 2.88 μm at 19.5 mm within the straight segment of the jet. Jet elongation as corroborated by acceleration of jet travel and decreasing in jet
diameter is driven by the repulsion between the charged components of the jet. The elongation rate of the jet during electrospinning is commonly as high as 10,000 times, the kinetic energy would be much higher if the jet did not coil (39). The coiling began at a certain distance from the orifice by initial small perturbation, right after the straight segment, and the diameter of each turn of the coil grows larger when moved toward the collector, which is often referred as envelope cone as illustrated in Figure 2.6. Within the envelop cone, the jet exhibits violent bending, coiling and whipping while the diameter of jet continues to decrease until solidified by solvent evaporation. Liu et al (42) used glint to trace bending frequency during electrospinning a 6 wt% polyethylene oxide aqueous solution and recorded 450 – 1250 turns per second.

Figure 2.5, The development of the Taylor cone before and after the jet ejected. The conical shape of the Taylor cone has been suggested as a hyperboloid (39).
Figure 2.6. A diagram of the envelope cone of an electrospinning jet where the straight segment is transformed into a three-dimensional coil that was proposed by Reneker et al (33). The diameter of each turn in the coil increases as the jet moved toward the collector.

Low viscosity and high surface tension can result in beads or a ‘bead-on-string’ structure where smaller solution droplets stringed by fibre and solidified together. Bead formation has been explained as a process similar to capillary breakup in electrospray which uses a low viscous solution and the droplets are formed due to the domination of surface tension. By gradually increasing the viscosity of the solution, the beads become bigger. The spaces between beads become longer, and the shape of the beads changes from spherical to spindle and eventually disappear (25, 32). An additive agent in the solution that increases the net charge density or reduces the surface tension can help reduce
bead formation (43, 44). Some process parameters, such as high voltage, flow rate and spinning distance can also affect bead formation (34, 44-46).

Amongst the three important electrospinning process parameters, applied voltage, spinning distance and flow rate of the solution, the applied voltage has the greatest effect on the resulting fibre diameter. Generally, a higher applied voltage results in finer fibres. Fennessey et al (47) produced electrospun PAN fibres of diameter $1.53 \pm 0.1 \mu m$ at applied voltage $8 \, kV$. When increasing the voltage to $16 \, kV$, the fibre diameter was significantly decreased to $0.38 \pm 0.03 \mu m$. Deitzel et al (48) discriminated the jet whipping model suggested by Reneker (33). They implanted a macroscopic electric field to restrain the bending instability and attempted to lengthen the straight section of the jet (Figure 2.7a). The macroscopic electric field is composed of a positively charged spinneret, a negatively charged collector and a series of rings with positive charge but slightly lower in voltage (Figure 2.7b). The chaotic motion of the jet has been greatly dampened by using this macroscopic electric field. As a result, the straight section of the jet was increased to about 10 cm when electrospinning 7 % PEO/water solution. The macroscopic electric field also has demonstrated the advantage of constraining the fibre deposition to $\sim 1 \, cm$ in diameter and has decreased fibre diameter to $\sim 270 \, nm$. The diameter of the deposition area was $\sim 7 \, cm$ and the fibre diameter was $\sim 400 \, nm$ from conventional electrospinning in comparison. They explained that the 20 kV high electric potential applied between spinneret and collector contributed to the decreased fibre diameter.
Similarly, Bunyan et al (49) introduced a metal disc electrode to the spinneret to create a nearly parallel electric field between the spinneret and the collector (Figure 2.8). They reported that the fibre deposition area has been greatly constrained with this method.

The spinning distance along with the applied voltage is what makes up the electric field strength. Thus at a certain applied voltage, the smaller the spinning distance and the greater the electric repulsion is. However, if the spinning distance is too short, the inadequate evaporation of solvent resulted in wet and inter-bonded fibres. A longer spinning distance favours fibres to be fully stretched and solidified, thus helping with decreasing the fibre diameter and improving the fibre uniformity (46, 50).

**Figure 2.7**, (a) Schematic of Deitzel’s setup, (b) macroscopic electric field composed by the setup (48).
In a continuous and stable electrospinning setup, feed rate should be maintained in order to form an equilibrium Taylor cone. If the feed rate exceeds the delivery rate of polymer solution at a given applied electric force, solution will drip at the end of the spinneret. The dripping solution under the electrostatic force can fly to the target without fully elongating or solidifying, causing beads or defective patterns in the depositing fibres. In the case of insufficient feed rate, the Taylor cone shrinks back and eventually disappears, resulting in an unstable jet or discontinuation of electrospinning (34, 46).

Other parameters such as temperature and ambient humidity can influence fibre morphology to some degree (51, 52).

**Figure 2.8.** Diagram of electrospinning setup with a disc electrode on the spinneret (49).
**Aligned nanofibres and nanofibre bundles**

The chaotic oscillation of the electrospinning jet intrinsically results nanofibres in nonwoven structures. This is essential to many applications of electrospun nanofibres such as filtration, tissue scaffolds, wound dressing and drug delivery. However some applications such as electronic, optoelectronic, sensor and mechanical useful material (e.g., carbon nanofibres from electrospun PAN nanofibres precursor) require well-aligned and highly axially orientated nanofibres.

Many works have reported on obtaining aligned electrospun fibre bundles. One easy approach is called ‘gap alignment method’. Li et al (53) demonstrated a method of obtaining highly aligned nanofibres by electrospinning nanofibres between two strips of an electrical conductor separated by a small air gap (Table 2.1a). Polyvinylpyrrolidone (PVP) and PAN solutions were electrospun on two grounded conductive silicon strips. Highly aligned electrospun nanofibres were stretched across the gap from distances of hundreds of millimetres to a few centimetres. The nanofibres can be transferred onto other substrate. The stacking density of the nanofibre was reported to be dependent on the gap width and collection time. Narrower gaps and longer collection time led to a higher density fibre array. Jalili et al (54) tested the gap width influencing the morphology of resultant fibres prepared by the same technique. When increasing the gap width from 2 to 5 cm, aligned fibre were increased but the density of fibres drastically decreased from 20 mass% (2cm) to 9 mass% (5cm).
Li et al (55) reported a method of using multiple parallel electrodes as a collector to control the fibre orientation (Table 2.1b). By alternatively grounding the electrode in pair, multilayer nanofibres with each layer of different fibre alignment directions were prepared.

Teo et al (56) described a method to get nanofibres preferentially deposited between two negatively charged fixed points 3 cm apart (Table 2.1c). They placed two steel blades in line with a gap. To ensure only the knife edges of the steel blades were exposed to the electric field, insulating tape was used to cover other parts. Fibre bundles were found to bridge between the steel blades. By dipping it in water, a fibre bundle of a micrometre diameter was obtained. They stated that the negative voltage applied to steel blades encouraged fibre deposition. However when the negative voltage was increased to - 4 kV, no fibre was deposited.

Yang et al (57) used this gap alignment method to electrospin a Polyvinyl alcohol (PVA) solution containing magnetic nanoparticles (Table 2.1d). With the aid of two parallel positioned permanent magnets to form a magnetic field perpendicular to the electric field, the gap can be enlarged to 10 cm. As a result, 10 cm long nanofibre bundles were electrospun using this setup.

Yan et al (58) suggested that the relative permittivity of the material should be considered when electrospinning aligned fibres between the gap of paired collectors (Table 2.1e). They have proved that a low relative permittivity material, such as epoxy resin (relative permittivity is 4) can be used to electrospin aligned fibres only when the gap distance is below 4 cm. When
using ferrite, which has a relative permittivity triple higher than epoxy resin, aligned nanofibres were obtained even when the gap width was larger than 6 cm. They also experimentally proved that water, which has a relative permittivity of 81, can help to obtain aligned fibres.

Liu et al (59) obtained aligned nanofibres by electrospinning a non-magnetized polymer in a magnetic field (Table 2.1f). They called it magnetic-field-assisted electrospinning (MFAES). They used two insulated bar magnets as collectors for electrospinning. Aligned nanofibres were collected from the gap between the magnets by electrospinning a Polylactic-co-glycolic acid (PLGA) and PVP solution, respectively. They reported that the optimum range for the gap was 0.5 - 4 cm.

The gap alignment method is an easy method to directly obtain aligned nanofibre bundles. However, those bundles could only be bridged between small gaps. As a result, those bundles and yarns only had a very short length, in the range from millimetres to a few centimetres. The charges carried by fibres prevent fibres from further depositing into aligned fibrous structure. Consequently, the alignment of fibres gradually disappeared with increasing the layer thickness (59).
| (a) Pairs of electrode collectors, 2003 (53) | (b) Paired multiple electrodes, 2004 (55) |
| (c) Paired blade collectors, 2005 (56) | (d) Magnetized polymer solution in MFAES, 2007 (57) |
| (e) Dielectric material collectors, 2009 (58) | (f) Non-magnetized polymer in a magnetic field, 2010 (59) |
**Electrospinning short nanofibre yarns and bundles**

Dalton et al (60) reported obtaining nanofibre yarn from the gap alignment method. They used two 12.5 mm diameter grounded discs placed 8 cm apart in parallel to collect aligned fibres. By rotating one of the discs, a short yarn of diameter $4.7 \pm 0.4 \ \mu m$ was obtained (Table 2.2a). A 9 wt% PCL-chloroform/methanol (3:1 in volume) solution was electrospun to yarn. However, the yarn quality was poor if the collection time was either too long or too short. Yarn length was around 5 cm which was approximately 85% of the gap distance.

Liu et al (61) made yarns by twisting aligned nanofibres. They used a stationary grounded electrode and a needle tip to form a gap. Aligned fibres then were obtained in the gap. A twist was introduced to the fibre bundle by rotating the needle (Table 2.2b). The length of the yarn can be changed in the range of 30 - 40 cm by inducing horizontal translation to the needle. Similarly, Lotus et al (62) used a rotating hollow hemisphere shaped collector and a tapered needle to collect aligned electrospun fibre bundles. Twisted yarn was obtained by rotating the hemisphere collector. However, this method was not able to prepare continuous yarns and the yarn was not consistent even in diameter. The yarn section closer to the rotating collector was thicker than the needle side.
Table 2.2, Methods of collecting short electrospun yarn

(a) Paired ring collectors, 2005 (60); (b) Twisting and stretching aligned fibre bundles, 2007 (61); 2008 (62)

Compared with the ‘gap alignment method’ which uses a pair of static collectors, a dynamic collector uses rapidly moving parts to assist in nanofibre alignment. Theron et al (63) reported a setup that used a grounded rotating disc with a sharp edge as the collector (Table 2.3a). The disc was 200 mm in diameter and 5 mm in thickness. The edge of the disc was sharpened into a half angle of 26.6° in order to create a strong converging electrostatic field. They observed a spindle shape electrospinning jets contour as the jet firstly flying in an envelope cone and its looping diameter gradually decreased as it approaches the disc. When the disc was rotated to give a linear speed of 22 m/s on the disc
edge, highly aligned nanofibres were wound around the disc edge surface. Using this method to electrospin 4 wt% PEO-water/ethanol (6:4 in volume) solution for 60 seconds, a highly aligned nanofibre bundle was prepared.

Fennessey et al (47, 64) used a highly rotating drum as a collector (Table 2.3b). When the surface velocity of the drum was above 9.84 m/s, electrospinning fibres were deposited uniaxial along the drum rotation direction. The degree of alignment was reported to be affected by drum rotation speed. However, the alignment degree of the fibres was lower than that of the fibres using the ‘gap alignment method (65). Fennessey et al measured the dichroism of nitrile (C≡N) groups in polyacrylonitrile (PAN) nanofibres. The dichroic ratio increased monotonously from 1 to 1.33 (recalculated according to literature) with drum surface velocity increasing from 0 m/s to 9.8 m/s. Further increasing the rotational speed did not improve fibre alignment. A much higher dichroic ratio of about 2.5 was reported with the fibres prepared by the ‘gap alignment method (66). Katta et al (67) combined the rotating cylindrical and ‘gap alignment method’ by using a rotating copper wire drum. Many grounded copper wires with spacing 1 cm apart were arranged along the longitude of the drum. The drum was 12.7 cm in diameter and was rotating at only 1 rpm (Table 2.3c). When a 20 wt% nylon-6/formic acid solution was electrospun, the fibres collected showed good alignment when the electrospinning was performed from 5 min to 15 min. A longer electrospinning time led to reduction in fibre alignment degree, and the alignment eventually disappeared after 40 minutes.
Bhattarai et al (65) used a grounded copper ring which was wound on an insulated cylinder as a collector. They obtained highly aligned nanofibre bundles from the copper ring (Table 2.3d). The degree of fibre alignment increased initially with increasing the cylinder rotating speed, and it reached a plateau at a surface speed 7.3 m/s.

**Table 2.3**, Dynamic rotation collector methods

<table>
<thead>
<tr>
<th>Method Description</th>
<th>Year</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotating sharp edge wheel collector</td>
<td>2001 (63)</td>
<td>(a) Rotating sharp edge wheel collector, 2001 (63)</td>
</tr>
<tr>
<td>Rotating drum collector</td>
<td>2004 (47)</td>
<td>(b) Rotating drum collector, 2004 (47)</td>
</tr>
<tr>
<td>Wired drum collector</td>
<td>2004 (67)</td>
<td>(c) Wired drum collector, 2004 (67)</td>
</tr>
<tr>
<td>Rotating drum with copper wire</td>
<td>2005 (65)</td>
<td>(d) Rotating drum with copper wire, 2005 (65)</td>
</tr>
</tbody>
</table>
Aligned electrospun nanofibre bundles obtained from the ‘gap alignment method’ are acceptable for use in micro-devices which require only a few fibres or a very thin layer but limited length. The dynamic collector is able to extend the length of aligned nanofibres to several tens of centimetres. The degree of alignment using the dynamic collector is generally lower than that of the ‘gap alignment method’. The dynamic collector methods have the same problem as the ‘gap alignment method’, that is, fibres gradually lose orientation after prolonged electrospinning time (67). The electrospun fibre layers which carry residual charge, being electrostatically attracted to the grounded or negatively charged collector, were difficult to peel off. The length of aligned fibre mat or bundle is limited by the circumference of the drum or disc. To the best of our knowledge none has exceed over 1 metre.

**Electrospinning continuous nanofibre bundles**

Continuous electrospun nanofibre bundle were obtained by Smit et al (68) who used a liquid reservoir as a collector. When nanofibres were electrospun into the liquid reservoir, an initial nonwoven web was formed and suspended flexibly in the liquid. Guided by a glass rod, the web was be drawn to a thin and continuous bundle (**Table 2.4a**). By using this method, they have electrospun Polyvinylidene fluoride (PVDF), PVA and Polyacetylene (PAC) into continuous bundles at a linear speed of 180 m/h. However the bundle prepared in this manner exhibited poor strength. Khil et al (69) have obtained a continuous porous PCL filament at the rate of 25 - 30 m/min using a similar setup. Their PCL filament was strong enough to be woven into a fabric.
Compared to conventional electrospinning where a grounded electrode is used as the collector, nanofibres from oppositely charged electrospinning nozzles can attract each other and bond together without the electrode collector. Dabirian et al (70) patented a method of obtaining a continuous nanofibre bundle by pulling off a nanofibre deposition which was formed by electrospinning differently charged jets (Table 2.4b). Pan et al (71) reported that continuous highly aligned nanofibre bundles were collected using a highly rotating cylinder collector (Table 2.4c). In both cases, electrospinning setups were arranged in opposite direction. Electrospun fibres carrying different charge were encountered and discharged in between the two nozzles. By initially picking up the fibre deposition and introducing it to the rotating collector, a continuous nanofibre bundle could be obtained. Dabirian et al used a “take-up” unit that operated at 5.79 m/h to collect the fibre bundle, while Pan et al used rotating rod to collect the fibre bundle at a surface speed of 0.9 to 3.0 m/s. Pan et al reported that the high speed collection caused difficulties in obtaining a continuous bundle due to the influence of airflow.
Table 2.4, Methods of collecting continuous electrospun yarn

(a) Continuous electrospun fibre bundle from liquid reservoir collector, 2005 (68, 69)

(b) Continuous electrospun fibre bundle from two-nozzle-conjugated electrospinning, 2006 (70, 72, 73)

(c) Continuous fibre bundle from oppositely charged electrospinning, 2006 (71)

**Electrospinning continuous nanofibre yarn**

Obtaining continuous electrospun yarn using a dynamic liquid collecting system was reported by Teo et al (74) (Table 2.5a). They have induced a water vortex as a collector into the electrospinning setup. The vortex was formed when the water drains out from a basin through a hole at the bottom. Water level in the basin was maintained by recirculating the water back to the basin. Electrospinning was carried out downwards to the water surface. The
electrospun fibre was emerged and twisted into a yarn by the vortex. The yarn, along with the water flow, passed through the hole of the basin and collected by a rotating mandrel at the bottom of the basin. They have electrospun polyvinylidene fluoride-co-hexafluoropropylene (PVDF-co-HFP) at a linear speed 60 m/min. However they had to keep a high concentration and high feed rate of the polymer solution to avoid yarn breakage. The average fibre diameter of the yarn obtained was more than 1 μm.

An enhancement to Teo et al work was reported by Yousefzadeh et al (75) (Table 2.5b). Their setup was more complicated than the water circulating system reported by Teo et al. They electrospun PAN fibre at the side of the basin and took up the yarn at the centre of the vortex in order to add twist and drag force. A tackle has been applied between the yarn take-up point and the rotating drum. This setup also needs polymer solution of a high concentration and a high feed rate. However, the production rate was much lower than that of Teo’s method.

Dabirian et al (72) obtained a continuous yarn by inserting a twist to the nanofibre bundle that was pulled out from the nanofibre deposition (Table 2.5c). Two differently charged electrospinning spinnerets were placed in opposite direction to produce a nanofibre deposition in between. A neutral surface was placed between the spinnerets but slightly behind to help with fibre deposition. A specially designed winder has been used to insert a twist while stretching the nanofibre bundle from the nanofibre deposition. Their setup was able to produce yarn at a linear speed of 5.79 m/h.
In 2007, Dabirian et al (76) reported a method of directly obtaining twisted yarn. They introduced a negatively charged bar adjacent to a negatively charged collecting surface to manipulate the electrostatic field. A specially designed take-up device was used to pull and twist the fibres that bridged on the negative charged bar and negative charged collecting surface into yarn (Table 2.5d). In this way, they reported a yarn production rate 14 m/h with inserting a twist at 400 RPM. The yarn obtained has a diameter around 170 μm and a fibre diameter around 400 nm. The as-spun yarn has a tensile strength of 58.08 MPa and a modulus of 1.66 GPa. However, it was difficult to position the negative polarity bar which was used to control the discharge of the electrospinning fibres. Afifi et al (77) used a slowly rotating funnel as a collector. Electrospun fibres that covered the bigger opening of the funnel were pulled off from centre and wound on a rotating drum (Table 2.5e). By using this method they have electrospun a PLLA/DCM solution into a continuous twisted yarn at a drawing linear speed of 63 mm/min. The yarn has an average diameter 164 μm and an average fibre diameter 6.0 ± 1.9 μm.

Ali et al (3) developed a method of directly obtaining twisted continuous yarn by simultaneously electrospinning oppositely charged nanofibres onto a rotating funnel (Table 2.5f). The setup included a funnel (110 mm rim diameter, 30° angle, 64 mm depth), two differently charged nozzles placed on each side of the funnel and a yarn winder. During electrospinning, nanofibres from differently charged nozzles were encountered and deposited onto the funnel to form a web. By picking and pulling the centre of the web to form a hollow cone shape, a continuous yarn was produced from the vertex of the
cone which was subsequently drawn to a yarn winder. The funnel is rotated for inserting twists to the yarn.

Table 2.5, Methods of collecting continuous nanofibre yarns

<table>
<thead>
<tr>
<th>Method</th>
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<tbody>
<tr>
<td>(a) Continuous yarn by using the dynamic liquid support system, 2011</td>
<td>(74)</td>
</tr>
<tr>
<td>(b) Collection of continuous yarn using a water vortex, 2011 (75)</td>
<td></td>
</tr>
<tr>
<td>(c) Continuous yarn from conjugated electrospinning, 2006 (70, 72, 73)</td>
<td></td>
</tr>
<tr>
<td>(d) Manipulating the electrostatic field using a negatively charged bar for continuous PAN yarn, 2007 (76)</td>
<td></td>
</tr>
<tr>
<td>(e) Collecting continuous yarn suing a slowly rotating funnel target, 2010 (77)</td>
<td></td>
</tr>
<tr>
<td>(f) Direct electrospinning of highly twisted nanofibre yarn, 2011 (3)</td>
<td></td>
</tr>
</tbody>
</table>
2.2 Polyacrylonitrile as a carbon fibre precursor

2.2.1 PAN polymer

The polymerization of acrylonitrile has been known since the 1890s (78). The chemical structure of PAN is shown in Figure 2.9:

![Chemical structure of the PAN repeat unit.]

It is generally agreed that PAN is a semi-crystalline polymer with no distinct crystalline and amorphous phases, but does have high degree of lateral order (79-82). Orientated PAN fibres have a high tenacity and retain dimensional stability in boiling water like normal crystalline polymers of a similar melting point (83). Unlike normal crystalline polymers which have a three dimensional lattice structure, PAN does not have any longitudinal order no matter which synthesis method or crystallizing treatment is used (83, 84). The most accepted
molecule chain conformation of PAN in ordered region is the kinked helical with a rod like structure. The ‘rods’ are packed in hexagonal fashion to exhibit lateral order (Figure 2.10) (83, 85-87). When examined using XRD, the diffraction pattern of such lateral order structure shows only two strong equatorial peaks representing lattice d-spacing of about 5.2 Å and 3.0 Å, in the ratio \( \sqrt{3} : 1 \) and non-equatorial scattering is generally not present or is very diffuse (83, 84, 87, 88).

![Figure 2.10](image)

**Figure 2.10.** (a) Proposed PAN molecule chain conformation (86) and (b) proposed hexagonal packing of PAN molecule chain in an ordered region (89).

The ‘glass transition’ is a reversible transition that occurs in amorphous materials or in amorphous regions of semicrystalline materials between a glass like state and a viscoelastic state (90). Most literature indicates that the glass transition temperature \( (T_g) \) of PAN is about 100 °C. Some papers reported additional transition temperatures at around 140 °C (91-93). Bashir et al (89) observed only one glass transition temperature \( (T_g) \) at ~100 °C for orientated
PAN samples but two glass transitions with additional glass transition temperature \( (T_{g_1}) \) at \( \sim 150 \, ^\circ\text{C} \) for un-oriented samples. They suggested that the \( T_{g_1} \) at \( \sim 150 \, ^\circ\text{C} \) came from an amorphous region while \( T_{g_\parallel} \) was related to the ordered region of PAN. Frushour commented against Bashir’s observation about the classical two-phase mode since a glass transition in the amorphous phase should have little effect on the crystalline phase (94). Bohn et al (83) had the same observation and concluded that PAN has a single phase combined with both crystalline and amorphous phase characteristics. Andrews and Kimmel (95, 96) assigned two glass-transitions to two types of bonding interactions: Van der Waals and dipolar. The \( T_g \) at \( \sim 100 \, ^\circ\text{C} \) was associated with Van der Waals repulsion and \( T_g \) at \( \sim 140 \, ^\circ\text{C} \) was the result of an association-dissociation equilibrium between nitrile dipoles on adjacent chains.

The PAN infrared absorptions exhibit strong dichroism of the nitrile-stretching vibration at 2244 \( \text{cm}^{-1} \). The dichroism increased in response to the stretching of PAN (47, 83, 97, 98). That is because the nitriles can be orientated approximately perpendicular to the drawing direction and the absorption for the perpendicular polarisation is greater than that for the parallel polarisation (97). However, even with the highest drawing ratio, PAN molecular chains are not fully-extended due to the intramolecular nitrile-nitrile dipole repulsion. Soon after the molecules are fully aligned, the films splinter and fibrillate (99). The nitrile groups of PAN have large dipole moments and are in close proximity which leads to a very large intramolecular dipolar and steric repulsion. The polymer chain of PAN is reported to have an internally “braced” stiff structure with a kinked chain (83) which leads to difficulties in dyeing (100) and stretching (101). Allen et al (102) have concluded that the strong
intramolecular nitrile repulsions in PAN prevent an ultrahigh modulus PAN fibre from being made by using any technique possible.

2.2.2 Application of PAN fibres

PAN fibres are defined as fibres that contain a weight percentage of acrylonitrile (AN) more than 85% (Figure 2.11) (103). PAN fibres have a market share of about 5% in the worldwide production of synthetic fibres, which is around 41.4 million metric tons per year (104). PAN fibres with diverse compositions or processing have been widely used in a large variety of applications, e.g. textiles, industrial applications and specially, carbon fibre precursor.

![Acrylic copolymers](image)

**Figure 2.11**, Chemical structure of the PAN copolymer.

**Textile application**

The molecular weight of PAN in textile applications is generally in the range of 40,000-70,000 g/mol. This is much lower than what is required for a carbon fibre precursor. A typical molecular weight of 90,000-140,000 g/mol and narrow molecular weight distribution is required for carbon fibre precursors (105).
PAN fibres are compatible with natural fibres and are mostly utilized in textiles. Its low density ($\rho = 1170\text{-}1180 \text{ kg/m}^3$) and thermal conductivity values ($\chi = 1.113 \pm 0.117 \text{ W/(m.K)}$), which are much better than those of wool. This is the cause of the increased demand for PAN fibres being used in textiles that were previously dominated by wool.

Because PAN decomposes at around 300 °C before it melts, melt spinning of PAN fibres is not possible. The high dipole moment caused by the strong interaction of nitrile groups in a PAN molecule makes PAN insoluble in many conventional solvents (105). The commercial production of PAN fibres were delayed until a proper solvent – dimethylformide (DMF) was discovered in the 1940s, allowing ‘wet’ or ‘dry’ spinning of PAN (100). DuPont first manufactured PAN fibres in Camden (USA) with the capacity to produce approximately 3000 tons per year. DuPont selected the dry spinning method using DMF as a solvent and introduced Orlon as the trade name of their PAN fibre in 1950.

Early PAN fibres were difficult to dye. They needed to be coloured before being spun into a fibre. To improve the dyeing-ability, homo-, bi- and tercopolymers of acrylonitrile were produced. The wet spinning process was developed in later the 1950s by Courtaulds which involved the acrylonitrile/methyl acrylate/itaconic acid (AN / MA / ITA) tercopolymer and using NaSCN as the solvent. There were several patents of the melt spinning process of PAN fibres, however to the best of our knowledge, no commercial production was yet made available.
PAN fibres are only a fraction of natural fibres in price. Along with its soft look and feel, PAN fibres are perfectly suited to imitate expensive wool and cashmere. Nowadays PAN fibres have been functionalized to have high comfort, heat regulation, antistatic properties, deodorants, quick-dry fibres and antibacterial functions. It is widely used in sweaters, sports apparel, underwear, socks, blankets, carpets, and soft-toys.

Micro fibres are referred to those with a filament diameter of 10 µm or less. Courtelle® micro fibre has a linear density 0.093 tex which is much lower than cotton, 0.202 tex, and wool fibres, 0.303 tex. Courtelle micro fibres can be blended with cotton, wool and other synthetic fibres. Textiles made from these blends have a high comfort index. Courtelle micro fibres were rated 2 versus 5.5 for cotton, where comfort index from 0 to 6 indicates the comfort from best to worst (106).

Based on the thermodynamic characteristics of phase transitions, the transition from the crystalline to the amorphous state is endothermic and crystallization is exothermic. Outlast® produced by Acordis is embedded with phase changing material (PCM) microcapsules. The phase transition of this material occurs in a relatively narrow region: 28.5-33.5 °C. As the thermal conductivity of PAN is very low, Outlast fibres are characterized by the fact that PCM microcapsules are incorporated in its polymer matrix (Figure 2.12) (107).
The antibacterial properties of PAN fibres can be attained by incorporating a biologically active component in the polymer substrate. This is achieved through the solution or inclusion modification in the processing stage of the gel fibre. Mitsubishi Rayon Co., the company that produced the Newtafel Parclen® fibre has kneaded the natural antimicrobial agent "chitosan" into the fibre to suppress the growth of bacteria and thus exhibiting a superior deodorant ability (108). Acrodis PAN fibres marketing the textile stock with Amicor® which have antibacterial and antimold properties. The antibacterial and fungicidal effects persist within the fibres even after repeated laundering. Cotton-Amicor blend yarn fabrics have successfully found applications in hospital clothing and linens (106).

The pilling effect caused by the stiffness, surface morphology and cross-section morphology of PAN fibres could be addressed by chemically crosslinking or physically embrittled PAN fibre surface (109). The Vonnel H6® series PAN fibres produced by Mitsubishi Rayon Co. have soft touch and
superior anti-pilling functions, which found use for making apparels such as sweaters and lingerie.

**PAN fibres for industrial applications**

Apart from applications in the field of textiles, PAN fibres have found applications in many industries such as construction, composite materials, hollow ion exchange fibres and precursors for high strength carbon fibres.

Fibre formation in wet spinning involves phase decomposition of the spinning solution. The gel like fibre during coagulation contains a structural network where its skeleton is formed by swollen fibril structures and cells that are filled with a mixture of solvent and precipitator. After the solvent is removed from the fibre, the specific surface area could vary from 80-150 m²/g (110). The as-spun gel fibres are superbly absorbent and therefore have found wide applications in ultrafiltration and ion exchange (111-113). The ion exchange properties of PAN fibres are attained by adding monomers with ion-exchanging groups to the composition of the AN copolymer or by converting the nitrile groups to carboxyl or amide groups (109).

PAN fibres treated by a temperature of 200-250 °C under a controlled tension forms a cross-linked thermal stable ladder structure (109, 114). Thermally stabilized PAN fibres cannot burn, melt, soften or drip. They are ideal for applications in making fire-retardant fabrics for seating in aircraft, trains, buses and cars, or protective clothing for fire fighters, armed forces, police, racing drivers and steelworkers (115). Thermally stabilized short PAN fibres are used
for reinforcing thermosetting plastics, which are useful for making brakes to be installed in automobiles and aircraft (116).

**PAN fibres as carbon fibre precursors**

Shindo was first used PAN as a carbon fibre precursor by in 1959 (117). He claimed the method of producing carbon or graphite materials by heating a PAN polymer up to 350 °C in an oxygen-rich atmosphere followed by heating it to a temperature above 800 °C. He reported the PAN derived carbon fibres have high degree of oriented graphite layer planes parallel to the fibre axis, suggesting a high fibre strength and modulus (118). This almost immediately brought worldwide attention because at the time most of the carbon fibres were manufactured from cellulosic. Carbon fibres derived from cellulosic is poor in strength (119). In 1963, Courtaulds in Coventry introduced a Special Acrylic Fibre (SAF) to manufacture carbon fibres. In the 1960’s when carbon fibres were first commercialized, they were only used on defence aircraft (105, 120). Nowadays their applications have been extended to diverse fields from aircraft and aerospace, to automotive, wind energy, electricity transmission, infrastructure and sports. Carbon fibres can also be made from mesophase pitch (MP). The high performance carbon fibres which are exclusively made from PAN are able to meet the primary requirement in the high performance engineering design and manufacture that is the strain to failure has to be above 2% (121) (Figure 2.13).
Figure 2.13, Modulus and strain at break point of commercial carbon fibres (122-126).

The superiority of high strength-to-weight ratio of carbon fibres enables the possibility of building lighter aircraft with improved fuel efficiency. Carbon fibres have an ultimate tensile strength over 10 times higher than structural steel (127) but is 80% lighter. The Boeing 787 commercial aircraft has adopted 80% in volume Carbon Fibre Reinforced Plastics (CFRP), which amounts to 23 tons of carbon fibres. The use of this lightweight composite has successfully reduced fuel consumption by 20% compared with today's similarly sized airplanes (128, 129).

The trend of today’s wind turbines is towards larger blade size for increasing the wind capture efficiency. Those blades are often 40 m long for land-based wind turbines and 60 m long for offshore applications. Such big blades require its building material to be very stiff, have a low density and long structural lifetime against fatigue. Structural composite materials containing glass fibres
or carbon fibres are mostly used to make blades. Carbon fibre composites have a stiffness 4.6 times and a tensile strength 1.3 times greater than that of glass fibre composites and lower in density (130). Using carbon fibres in 60 metre turbine blades is estimated to reduce total blade mass by 38% and decrease the cost by 14% compared to using 100% fibreglass (131). Racing car manufacturers have been using carbon fibre reinforced materials in their cars for many years now. Its low weight and high strength is essential for high-performance automobile racing. Recently, several mainstream vehicle manufacturers have started to use CFRP in upmarket cars.

2.2.3 Manufacturing process of PAN fibres and carbon fibres

PAN polymerisation and PAN copolymers

PAN is a linear polymer containing approximately 68% carbon. Solution free radical polymerisation from AN is commonly used for PAN fibre spinning. The most commonly used solvents for PAN are DMF, dimethyl sulfoxide (DMSO), ZnCl₂ and NaSCN (105).

The PAN fibres used for making carbon fibres usually are made from the PAN copolymer (100, 101, 105). This is because homopolyacrylonitrile is rigid, brittle and difficult to be drawn. In addition, homopolyacrylonitrile requires a high oxidation temperature, which increases chances of a sudden heat surge. The acrylic precursor for carbon fibre production usually contains no more than 10% co-monomer, such as methyl acrylate (MA), methyl methacrylate
(MMA), PAN acid, itaconic acid (ITA) or vinyl acetate (VAC), in order to reduce the cyclization temperature during oxidation, which facilitates the cyclization reaction, increases molecular orientation and improves fibre processing-ability (105).

**The spinning process**

Dry spinning was first used by DuPont in the 1960s, but declined afterwards due to the high cost of solvent recycling. Wet spinning has been widely accepted in producing PAN fibres for textiles and carbon fibre manufacturing. ‘dry jet wet spinning’ has been attracting more attention recently because it can spin the PAN solution with higher concentrations than wet spinning. Carbon fibres produced by this method show better mechanical properties (Figure 2.14). Melt spinning of PAN is possible by using a hydrating agent to decrease the melting point, however due to the melt spun precursor containing more defects than those from wet spinning and dry jet wet spinning, it has not been pursued for commercial carbon fibre production (122).

Dry spinning uses DMF as the solvent. A high concentration polymer solution, typically 30-32 wt%, was extruded through spinnerets with 1500 - 2500 holes into a vertical 2 stage tower where the upper tower is preheated at 300 - 400 °C. Inert gas was blown from the top to the bottom. Solvent was removed by the hot gas and reused after distillation. PAN fibres continue traveling from the upper tower to the lower tower where cooling air is cyclized to remove residual solvent and PAN fibres are then solidified. Dry spinning tends to provide the fibre with less surface defects than wet spinning as no coagulation bath is required (109).
Wet spinning involves spinning the PAN solution into coagulation solution which is a mixture of solvent and water. PAN fibres are turned from a gel-like state into solid fibres through coagulation of different solvent concentrations. The spinning solution has typical concentration between 10 to 25%. The solution concentration and PAN molecular weight have to be chosen carefully to yield a solution viscosity that provides a compromise between fibre drawing ability and final fibre properties (122). The solution is then extruded through an array of spinnerets directly into a coagulation bath to form fine filaments of several tens of micrometres. The coagulation bath is a mixture of the same type of solvent and water, however having less solvent content than in the PAN solution. Coagulation initially forms a skin of filament and then the solvent diffuses into the centre of the filament. The rate of diffusion depends on the diameter of the filament, difference of solvent concentration in the filament and the solvent solution, and the solution temperature. A high concentration of the non-solvent in the coagulation bath and high temperature of the coagulation solution can speed up the coagulation process; however it can also result in internal pores, surface defects and skin-core structure in precursor fibres. During coagulation, while the fibre is still in the gel state, a small extent of stretching can be carried out to orient the molecular chain along the axis of the fibre. Stretching is limited by the rate of coagulation and the speed of fibre drawing.

Dry-jet wet spinning is similar to wet spinning except extruded filaments travel through about a 10 mm small air gap before going into the coagulation bath. Dry-jet wet spinning enables a higher spinning line speed than wet spinning, because a higher concentration of PAN solution and higher spin bath
temperature can be used. The process avoids the high stress caused by coagulation which reduces the effects of dye swelling and the formation of skin-core structure, which are the main factors affecting the wet spinning technique (132, 133). Less surface defects are likely seen in dry-jet wet spun fibres.

![Spinning Diagram](image)

**Figure 2.14.** Diagram of a) dry spinning; b) wet spinning; c) dry-jet wet spinning (122)

**Post treatment for the carbon fibre precursor**

The freshly-spun fibres need to go through a series of post treatments, such as washing, surface treatments (134) and drawing (135). Drawing is the most critical and efficient method to reduce fibre diameter, linear density and defects per unit length, and improve the fibre quality, molecular orientation and tenacity. Drawing is performed by stretching the fibres from a few to several
ten times of its original length. This is usually achieved by passing the as-spun filament tows through a set of rollers with different speeds (91, 93, 98, 105). Carbon fibre production usually has a higher drawing ratio than those for textile applications. It is well known that the mechanical properties of carbon fibres are highly dependent on the mechanical properties of its precursor fibres (88, 136). Studies showed that high quality precursor fibres should have characteristics such as small diameter, large crystallinity, low co-monomer contents, high strength and high modulus (137, 138).

PAN fibres break when elongated only a little bit at room temperature due to the strong repulsion forces of nitrile groups (83). It is preferred to draw PAN fibres above its glass transition temperature and in wet conditions which is able to increase the chain mobility. In wet conditions the $T_g$ of PAN has been reported around 65 ºC (83, 93). It is common to draw the PAN fibres in hot water or steam (93, 139). During drawing, the PAN molecules along the chain slide pass one another, align in parallel and orient in the direction along the fibre axis to form a two dimensional rod structure. As the result of drawing, the PAN fibres reduce the diameter from tens of microns to a few microns. The defects per unit length are greatly reduced.

The fibre quality after drawing is greatly improved with the benefits of a smaller diameter, optimized external and inner structure, improved molecular orientation and increased crystallinity.

**Oxidation and carbonization of carbon fibres**
Post-drawn precursor fibres are subject to be stabilized at 180 - 300 °C to form a heat infusible material before being carbonized at a higher temperature. Stabilization is also known as oxidation because the process is carried out in an oxidizing atmosphere, which is usually in air (140) (80). The mechanism of stabilization is complicated and still not very clear (141-145). During the stabilization process, cyclization, dehydrogenation and oxidation take place. The process starts with oxygen initiated cyclization where HCN, NH₃ and H₂ evolve as result of cyclization and dehydrogenation. Oxygen containing groups –OH, C=O, COOH form during the oxidation, resulting in a three-dimensional cross-linked structure, which is often called a ladder structure (Figure 2.15). Cyclization is an exothermic reaction controlled by heat flux and diffusion of the oxygen atom in the fibre. Stabilization usually takes tens of minutes but can even take hours in some cases. It is the most time-consuming step of the carbon fibre manufacturing process (146).

![Figure 2.15](image)

**Figure 2.15.** (a) Proposed ladder structure of PAN (147) and (b) proposed chemistry of PAN stabilization (148).

Fibres shrink in two steps during the stabilization process. Entropy shrinkage due to the relaxation of molecular chains from the stretched and aligned states...
completes below 200 °C. The reaction shrinkage that starts from 200 °C is due to cyclization and formation of oxygen-group. The volume of shrinkage can be from 13% to 33%, and is influenced by the chemical and physical properties of the precursor polymer, stabilization temperature, heating gradient and gas environment (105, 146, 149). Uniaxial tension is applied on the fibre throughout the stabilization process against shrinkage to maintain the molecular orientation within the fibre. Insufficient tension leads to loss of the chain orientation, while over tension could result in fibre rupture, which seriously reduces the mechanical properties of resulting carbon fibre. To get good quality carbon fibres, the tension applied has to be wisely optimised at different stages of stabilization (149). It is generally agreed that the fibre is stabilized when oxygen content is 8 - 12 wt% (105).

Stabilized PAN fibres have to be carbonized to remove non-carbon contents from the fibre. This process is performed at a high temperature, typically from 400 to 1500 °C (Figure 2.16) (105, 150). At the early stage of the carbonization process, it releases a large amount of gases such as water steam, ammonia, hydrogen cyanide, carbon monoxide, carbon dioxide, nitrogen, and hydrogen. Under 600 °C, heating has to be controlled at a slow rate, such as 5 °C/min to prevent the formation of pores or any surface defects due to gas emission. Over 600 °C, the heating rate is increased because of less by-products are generated (150). The carbonization process is complete when the carbon content is above 92 % (122).
Further heating at 1500 - 3000 °C in an inert atmosphere results in greater crystallite size and preferred orientation in the fibre. This process is called graphitization. Graphitized fibres have a higher modulus but degraded strength because the process increases crystallinity and graphite content, but decreases disorder carbon content (151).

![Proposed structural changes for PAN precursor during carbonization](image)

**Figure 2.16**, Proposed structural changes for PAN precursor during carbonization (152).

### 2.2.4 Current problems and possible solutions for PAN derived carbon fibres

The crystal structure in carbon fibres is generally the same as in graphite, where sp² hybridized carbon atoms are bound to equidistant 120° angle and composes a hexagonal form in the x-y layer, and inter layers are bound by Van Der Waals force. The sp² hybridization bond strength of 400 kJ/mol endows graphite with a very high modulus (1060 GPa) parallel to the layers, but those layers are easy to slide due to comparable weak bonding interlayers. Different to graphite, carbon fibres have an imperfect crystalline structure between neighbour layers, due to the existence of sp³ bonds between the layers. **Figure**
2.17 represents the crystal structure of graphite and proposed structure of a carbon fibre (122).

Figure 2.17, a) Crystal structure of graphite crystal (153), b) crystal structure of turbostratic carbon (153) and c) structure of turbostratic carbon (154).

Carbon fibres are available commercially in high modulus (HM) types and high tensile strength (HT) types. The HM carbon fibres have a high modulus but low strain at failure. The HM carbon fibres have high crystallinity, low density of in-plane defects, strong texture parallel to fibre axis but a weak texture perpendicular to the fibre axis. A modulus of $940 \pm 40$GPa pitch based carbon fibre (K13D by Nippon Graphite Fibre Corp.) is commercially available. It is not very necessary to further improve the modulus of HM type carbon fibre because the theoretical modulus parallel to the basal plane of graphite is about $1020$ GPa (105, 122, 155). The theoretical tensile strength of the carbon fibre is about 20 GPa, however, only 35 % of the theoretical strength is
achieved from commercially available HT type carbon fibres (156). Whenever there are structural defects present. According to Griffith’s fracture theory, the tensile strength of the carbon fibre is decisive to the degree of its defects. It is evident that the strength of a carbon fibre decreases exponentially with increasing the gauge length where more defects are present in the carbon fibre test unit (Figure 2.18). Carbon fibres generally contain defects such as cracks, voids, cavities and core-shell structure etc. (Figure 2.19). Those defects are likely derived from the precursor and stabilization process.

![Graph showing the carbon fibre strength drastically decrease with increasing gauge length](image)

**Figure 2.18**, Figure shows the carbon fibre strength drastically decrease with increasing gauge length

The core-shell structure is first formed during wet spinning (Figure 2.20). As the polymer solution is extruded into the coagulation bath which has lower solvent content than it in the solution, a counter diffusion of solvent occurs. This results in a polymer precipitation near the interface between the polymer filament and the coagulation bath to form a very thin, dense and homogenous skin (of 200-300 nm). The skin however hinders the counter diffusion process, thus resulting in a highly orientated, crystallized skin and amorphous,
disordered voids, called core-shell structure (157). The non-solvent (typically water) permeated through skin becomes microvoids or cavities after the precursor is washed and dried.

**Figure 2.19**, Various structure defects of a PAN based carbon fiber (158).

**Figure 2.20**, Core-shell structure of wet-spun PAN fibre (157).
The drawing force applied on the fibre during coagulation affects the skin formation. This allows the formation of a highly orientated and highly crystallized structure in the skin. However, some of the polymer molecular chains can rupture and cause transverse strips on the skin. Those strips can get deeper and further developing into flaws while the skin-core boundary slowly moved towards the core region (83, 159).

Post-spin drawing of fibres facilitates the improvement of the fibre modulus but doesn't greatly improve the strength (121, 160, 161). Drawing can significantly reduce the amount of defect per unit volume, but is unable to remove defects completely (162). The decreased precursor fibre diameter after drawing has a significant effect on the oxidation process.

The fibre diameter is an important parameter affecting both mass and heat transfers. A large diameter retards the oxidation process and hinders the heat and molecule transport, which is diffusion driven. Coarse precursor fibre often results in a stabilized shell with an incompletely oxidated core. The core shell structure often leads to 'blowing out' of the core portion in the later carbonization process, which significantly damages the carbon fibre quality. The as-spun fibres usually have a diameter of several tens of microns, which is limited by the spinnerets. The fibres post-drawn have a diameter of a few microns. A smaller diameter of the precursor fibre can reduce the chance of forming core-shell structure within the fibres which leads to a higher strength of carbon fibre (138, 163, 164).
2.2.5 Perspective and progress of electrospun PAN fibre based carbon nanofibres

Technology for carbon fibre manufacturing has remained stagnant for a dozen years. Fibres with diameter sub-micron to tens of nanometres seem to be a breakthrough for preparing carbon fibres with superior mechanical properties. The effect of size is of major consideration because when carbon fibre diameter reduced from $7.71 \pm 0.88 \mu m$ (T-300) down to $5.06 \pm 0.22 \mu m$ (T-1000), the strength increased from $4.60 \pm 0.56$ GPa to $7.37 \pm 0.34$ GPa (165). Carbon fibres derived from nanofibres with diameters approximately an order of magnitude smaller than those of conventional carbon fibres shall exhibit tremendous enhancement in mechanical properties (166).

The conventional methods to prepare carbon nanofibres include Physical vapour deposition (PVD) and Chemical vapour deposition (CVD). These methods are very complicated and costly. The electrospinning process offers a simple and inexpensive way to prepare polymer nanofibres. The surface of electrospinning fibres are smoother than that of carbon fibres produced by conventional wet-spinning or air-gap wet-spinning techniques (Figure 2.21) (98). The electrospinning process does not involve a coagulation bath. The small diameter and high surface-to-volume ratio enhance solvent evaporation from the surface (47). A small diameter is favoured for the diffusion of oxygen molecules and heat transfer during the stabilization process. This greatly shortens the processing time and reduces the formation of core shell structure (161, 166, 167).
For conventional carbon fibre precursor, commoners are added to the PAN homopolymer as initiator of cyclization. The commoners also moderate the exotherm in stabilization process. They also function like a plasticizer to increase spinning ability. However the commoner should be added in a minimal amount for good quality carbon fibres (101). The addition of commoners in electrospun carbon nanofibres can be avoided because the jets elongate millions of times during the electrospinning. In the stabilization process, cyclization can be easily initiated at a lower temperature due to the small diameter of the precursor fibres (166). Soon after the electrospinning method for preparing nanofibres was introduced, electrospun PAN nanofibres were prepared for making carbon fibres (168-170) (Figure 2.22).
Figure 2.22, Publication numbers of electrospun fibres derived from carbon nanofibres. Search made on Scopus from 1998 to 2012 by keyword ‘electrospinning + carbon nanofibre’.

To prepare carbon nanofibres from electrospun nanofibres, the commercial process of producing carbon fibres has been employed, which includes drawing, stabilization, carbonization, and sometimes graphitization.

Zussman et al (167) first reported the mechanical properties of single carbon nanofibres prepared from electrospun PAN nanofibres. The bending modulus of 63 GPa and fracture stress 0.64 GPa with a failure probability of 63% fitted using Weibull statistical distribution were reported. They attributed the low mechanical properties of the carbon nanofibres to that the polymer precursor morphology, molecular orientation and the carbonization process are far from optimized.

Efforts have been made to produce continuous carbon nanofibres with good mechanical properties. Fennessey and Farris et al (47, 123) used a rotating
wheel to collect electrospun PAN nanofibre bundles. The bundles were then drawn in boiling water at a crosshead speed of 10 mm/min to 1.5, 1.8 and 2 times of its original length. The tensile strength of the post drawn PAN nanofibre bundles increased with increasing the drawing ratio. The highest tensile strength was $253 \pm 47$ MPa from bundle post 2 times drawing. Because the stabilization and carbonization processes were not optimized, the carbon fibre derived from this bundle had poor mechanical properties.

Moon et al (171) tightly wrapped nanofibre bundles on a graphite sheet during stabilization and carbonization and obtained carbon nanofibre. The carbon nanofibre bundles appeared to have lower strength than carbonized undrawn bundles. The strength of carbonized bundles decreased with increasing the draw ratio. They explained that the fibres broke because of they couldn’t tolerate the shrinkage stresses that developed during the stabilization and carbonization process, and resulted in the impaired strength of carbon nanofibre bundles. The highest strength of the carbon nanofibre was $986 \pm 15$ MPa which was obtained from the carbonized undrawn electrospinning nanofibre bundle. However, the value was far below the strength of the conventional carbon fibre.

Zhou et al (172) electrospun PAN homopolymer nanofibres on a rotating metal disk and obtained aligned nanofibre bundles. The bundle was then tightly wrapped onto a glass rod and stabilized and carbonized. The tensile strength and modulus of carbon nanofibre bundles were $542 \pm 45$ MPa and $58 \pm 6$ GPa, respectively. Ribbon-shaped graphite structures were observed under Transmission Electron Microscope (TEM). However, the longitudinal
directions of the graphitic structures were neither parallel to each other, nor parallel to the fibre axis. They explained that the low mechanical properties of the carbon nanofibres were because the electrospun PAN nanofibre bundles were not drawn to have high molecular orientation.

Cuilin et al (98) examined the crystallinity of post drawn electrospun SAF 3K fibre bundle. Nanofibre bundles were drawn 2, 3 and 4 times of their original length in a moisturized environment at 100 °C. They concluded the macromolecules in the nanofibres could be effectively improved under a small extent drawing. The mechanical properties of the nanofibre bundles could be substantially improved by a post-spinning drawing process. For the 4 times drawn nanofibre bundle, the tensile strength and Young’s modulus were 275 ± 140 MPa and 1412 ± 461 MPa, respectively. In comparison, the tensile strength and Young’s modulus for the as-spun nanofibre bundle was only 15 ± 11 MPa and 65 ± 26 MPa, respectively. A similar result was also reported by Ravandi et al (73) who had drawn a continuous highly-twisted electrospun yarn in 95 °C hot water. The tensile strength of the 4 times drawn yarn increased to 350 MPa comparing with 80 MPa for undrawn yarn.

Arshad et al (173) performed optimised experiments on preparing single carbon nanofibres from electrospinning and post-treatments. The fibre showed the emblematic average tensile strength and elastic modulus of 3.5 ± 0.6 GPa and 172 ± 40 GPa, respectively.
Chapter 3

Experiment Part

In this chapter, all materials, electrospinning setups, characterization methods and instruments used in this study are presented in detail.

3.1 Materials

Polyacrylonitrile (PAN, Mw 150,000 g/mol, Sigma-Aldrich) and N, N’-dimethylformide (DMF, Sigma-Aldrich) were used as received.

3.2 Electrospinning

3.2.1 Preparation of polymer solutions

The PAN solution was prepared by dissolving PAN into DMF at 80 °C with continuous stirring for 6 hours. The solution was then cooled naturally down to room temperature. 6 wt%, 8 wt%, 10 wt% and 12 wt% PAN solutions were prepared for the electrospinning experiments.

3.2.2 Electrospinning

The conventional electrospinning setup includes a plastic syringe with a 21 G (OD 0.8 mm, ID 0.5 mm) blunt head needle, a syringe pump (Baoding Longer Precision Pump Co., Ltd), a high voltage DC power supplier (either ES40P-20W for positive polarity high voltage supply or ES40N-20W for negative
polarity high voltage supply, Gamma High Voltage Research) and a grounded metal plate as the collector, as shown in Figure 3.1a.

In disc-aided electrospinning setup, the back disc electrode was a copper disc of diameter 8 cm and thickness 2 mm. A 1 mm diameter central through hole was made on the disc. Syringe needle was plugged into the hole with the needle orifice about 0.5 cm off the disc surface (Figure 3.1b). The high voltage was directly connected to the disc electrode and the back disc electrode was in physical contact with the needle.

Figure 3.1 (a) Schematic of conventional electrospinning setup; (b) a close-up photo of the needle nozzle with a back disc electrode. The disc electrode was held with in a plastic stand.
3.2.3 Electrospinning of nanofibre yarns

The electrospinning nanofibre yarns setup is shown in Figure 3.2, which includes a metal funnel, 2 electrospinning nozzles and a yarn winder. The metal funnel (diameter 110 mm, angle 30 °, length 65 mm) was installed on the top centre of the workspace. The funnel was driven by an electrical motor so that the rotating speed can be adjusted from 113 rpm to 2150 rpm. Two syringe pumps equipped with disposable syringes were installed vertically apart on each side of the funnel. The spinnerets were mounted on top of the syringe pumps. For the disc-aided electrospinning, the disc electrodes were in 30 degree to the funnel axis. The needle orifices were 25 cm in distance to the edge of the funnel. A 15 cm chemical-resistant tubing (ID 3.175 mm, OD 6.25 mm) with Luer fitting (OD 3.175 mm) was used for transferring polymer solution from each syringe to spinneret.

A specially designed winder was used for yarn collecting. The winder is able to induce horizontal translation while rotating, so that yarn can be evenly winded on a roller (2 cm width, 3 cm diameter). The winding rate can be adjusted between 0.32 m/min to 1.55 m/min. The funnel rotating speed and the winding rate were adjusted with separate controllers, which were mounted in a compartment beneath the working space along with the high voltage controllers and the syringe pump controller.

During the experiment, positively and negatively charged electrospinning nanofibres were encountered and deposited on the bottom (large end) of the funnel to form a thin nanofibre web. A strand of cotton yarn (or anything fibrous in a form of strand or yarn) about 60 cm in length with one end wound
onto the yarn winder and another end manually attached to the centre of the nanofibre web was used as a lead to form the nanofibre yarn. By winding the cotton yarn, the nanofibre web that covered on the funnel was drawn into a 3D cone shape (Figure 3.3). Subsequently the nanofibres that electrospun onto the cone were stretched towards the vertex of the cone and twisted into a yarn. By properly control the electrospinning parameters, the funnel rotating speed and the winding rate, a highly twisted continuous yarn can be produced following up the cotton yarn and collected onto the yarn winder.

Figure 3.2, The photo of the disc-aided electrospinning yarn setup
3.3 Stretching of yarns

3.3.1 Stretching in hot water

Nanofibre yarns was stretched in a water bath composed of a cylindrical container filled with deionized hot water and coiling copper tube as illustrated in Figure 3.4. By adjusting the temperature of hot water circulating through the coiling copper tube, the temperature of water bath can be controlled. By using this setup, the influence of water flow turbulence on the stretching process was minimized. The water bath temperature was maintained at 96 ± 1 °C throughout the stretching process. A thermometer was used to monitor the water temperature.

Before stretching, yarn samples were cut into a short length and the shortened yarns were then held firmly with clips at both ends. A soft, thin rub mat was attached to nips of the clips to prevent yarn from slipping or being damaged. Special care was taken for the 20 mm gauge length between the two clamps.
Stretching was carried out in the way of constant load. During stretching, the yarn samples were vertically immersed in hot water with one of the clips hung on a fixed point and another clip added with a certain weight. The weight was pre-determined from stress-strain curve of stretching yarns in hot water. The upper clip was fixed at different height, where the desired stretch ratio was reached when the clamp stopped at the bottom of the water bath. Post stretching yarn samples were left dry in room temperature for 24 hours before further characterizations.

![Illustration of hot water stretching apparatus.](image)

**Figure 3.4.** Illustration of hot water stretching apparatus.

### 3.3.2 Stretching in dry hot air

Yarns were stretched under a constant load in a conventional oven at 140 °C. The oven temperature was calibrated using Infrared thermal gun and thermal meter before the experiments. Yarn samples were cut into short length and clamped at both ends using a special pair of grips. Soft and thin rub mats were attached to nips of the grips to prevent yarn from slipping or being damaged. Special care was taken for the 20 mm gauge length between the two grips. One
of the grips was hung on the top grate of the oven and the other was loaded with certain weight. The weight was pre-determined from the stress-strain curves of stretching the yarns by using DMA. Blocks of different heights were placed under the yarns so the desired drawing ratio was reached when the grip touched block. The post drawn yarn was left in the oven to cool down to room temperature before various characterizations.

3.4 Characterizations

3.4.1 Morphology

Digital single-lens reflex camera has been used for taking photos of electrospinning jet.

The morphology of the electrospun nanofibres and nanofibre yarns were examined using scanning electron microscopes (SEM, JEOL Neoscope). Electrospun PAN nanofibre or nanofibre yarn samples were bond to the SEM sample stub using carbon double sided tape. A thin layer of gold was sputter coated on the surface to increase electrical conductivity of the samples. All SEM images were taken at a voltage of 10 kV and the magnification varied between 500 and 20,000 times. Fibre and yarn diameters were measured directly based on SEM images using an image analysis software (ImagePro+4.5, Media Cybernetics Co.). The fibre diameter was measured based on the SEM images and 600 counts was taken for each average fibre diameter and standard deviation. The yarn diameter was measured based on the SEM images and 200 counts was taken for each average yarn diameter and standard deviation.
3.4.2 Glass transition temperatures

The wet glass transition temperature (wet $T_g$) of PAN nanofibre yarns was determined based on the change of stress-strain curve under different temperatures. The experiments were carried out in a specially designed hot water bath. The water bath is similar to what has described in section 3.3.1. During the test, one end of the test sample was clamped on a grip that was firmly attached the 100 N load cell of the mechanical tester, while the other end was clamped at bottom of water container (Figure 3.5a). Lloyd LR30K mechanical tester (Figure 3.5b) was used to stretch the yarn sample with a gauge length of 20 mm at a crosshead speed of 2 mm/min. The stress and strain were continuously recorded by the mechanical tester.

![Figure 3.5](image)

**Figure 3.5**, a) Illustration of the apparatus for determining the wet glass transition temperature of PAN nanofibre yarns, and b) photo of the Lloyd mechanical test machine.

Differential scanning calorimetry (DSC) (TA instruments) was used to examine the glass transition temperature ($T_g$) of PAN polymer powder and
PAN nanofibre yarns. The PAN samples were placed in DSC sample tray and heated from 50 °C to 200 °C with a 5 °C/min heating rate, followed by immediate cooling to 50 °C at 5 °C/min cooling rate. The sample was then heated again to 200 °C with a 10 °C/min heating rate. The glass transition temperature was found as the temperature point of the step shift in DSC curve.

The Q800 Dynamic Mechanical Analyser (DMA) (TA instruments) was used to measure viscoelastic moduli, storage and loss modulus of PAN nanofibre yarns (Figure 3.6). Glass transition temperature (Tg) of PAN nanofibre yarns was determined as the temperature at the onset of down slope of the storage modulus. Yarn sample was mounted on the tensile clamps of the DMA. The experiment was carried out under a vibration frequency of 10 Hz and heating from 40 °C to 200 °C with a heating rate of 5 °C/min.

![Photo of Q800 DMA with a yarn mounted on its tensile test clamps.](image)

**Figure 3.6.** Photo of Q800 DMA with a yarn mounted on its tensile test clamps.

### 3.4.3 Thermal mechanical properties

The thermal mechanical properties of the electrospun nanofibre yarns were investigated using DMA under constant displacement and constant force
modes separately. Yarn samples were mounted on tensile clamps of DMA, which allowed the distance of displacement between 4 mm to 25 mm. The constant displacement tests were carried out at crosshead speed of 400 μm/min under elevated temperatures. The constant force drawing was carried out under various forces by heating the sample from 40 °C to 300 °C with 1 °C/min heating rate.

3.4.4 Fourier Transform Infrared spectroscopy (FTIR)

Dichroic information of yarns before and after stretching were obtained by using polarized Brucker Vertex 70 FTIR at 64 scan rate from 600 – 4000 cm\(^{-1}\) with 4 cm\(^{-1}\) resolution. The nitrile bending absorbance of PAN at 2244 cm\(^{-1}\) was used as reference for dichroic information. Yarn samples were horizontally mounted on the IR sample holder. IR beam was passed a polarized IR lens and transmitted through the yarn sample. The FTIR spectra were recorded at angels of -90, -60, -30, 0, 30, 60, 90 degrees to the yarn mounting direction. The data was analysed using OPUS software attached to FTIR with background noise deducted.

3.4.5 Wide-angle X-ray Diffraction (WXRD)

WXRD were measured by Bruker GADDS X-ray micro-diffractometer equipped with Bruker pinhole collimator using CuK\(_\alpha\) radiation operating at 40 kV and 40 mA. Each sample was scanned with 2-theta angle between 2° to 25°. Azimuthal angle scans were carried out at 2-theta angle between 15.3° and 19.6°. Analyses were performed on the collected XRD data using the Bruker XRD search match program EVA™.
3.4.6 Mechanical properties

The tensile properties of yarns before and after stretching were examined using Sifan 3 single fibre mechanical tester (Figure 3.7). Yarn samples were clamped with 20 mm gauge length and tested with a crosshead speed of 2 mm/min. The ultimate tensile strength and strain at break were obtained directly from the tester. The cross-sectional area of the electrospun nanofibre yarns was calculated from denier of the yarns and density of PAN. The Young’s modulus was estimated at the 1% strain. Each ultimate tensile strength, Young’s modulus and strain at break were calculated from 5 repeated measurement results.

Figure 3.7, Photo of Sifan 3 single filament tensile tester.
Chapter 4

Electrospinning of PAN nanofibre yarns

In this chapter, parameters that affect the preparation of polyacrylonitrile nanofibre yarns using conventional electrospinning method have been examined. Failure modes in the yarn making process have been discussed. The effect of the back-disc electrode and high voltage polarity on nanofibre deposition and morphology has been examined. Highly-twisted continuous PAN nanofibre yarns have been obtained directly from an electrospinning technique when a back-disc electrode is used to aid fibre deposition. The influences of processing parameters on yarn morphology and mechanical properties have been investigated.

4.1 Experiment part

Nanofibre yarns were prepared using the method described in Chapter 3.2.3. The average diameter and standard deviation of yarns and fibres were measured based SEM images using processing software (ImagePro+6.0).

4.2 Parameters affecting fibre deposition during electrospinning

In conventional electrospinning, fibre deposition on a solid collector is usually in the form of randomly oriented fibrous mat. The fibre deposition area is mainly affected by spinning distance and high voltage. Figure 4.1 shows the
influence of the spinning distance on the deposition area. The deposition area increases and deposition density decreases with increasing the spinning distance. Figure 4.2 shows the fibre deposition profiles when the electrospinning distance changes from 15 cm and 25 cm. When the spinning distance was larger than 25 cm, the fibre deposition was diffuse. In this case, the edge of fibrous mat deposited was hard to justify after 1 minute electrospinning.

Figure 4.1, Effect of spinning distance on deposition area. The electrospinning was taken under 13 kV and flow rate of 1 ml/h.
**Figure 4.2.** Photos showing fibres electrospun at a distance of 15 cm and 25 cm. The electrospinning was carried out for 1 minute. The dotted line shows the edge of the fibrous mat.

The influence of the applied voltage on the deposition area is shown in **Figure 4.3.** The deposition area drastically decreased with increasing the applied voltages. It was worth to note that the jet was hardly formed when the applied voltage was lower than 10 kV. When the applied voltage was higher than 15 kV, the jet was formed easily. However the jet was unstable and its ejection was intermittent.

The flow rate did not directly affect the deposition area. However, it affected the applied voltage, and in turn, the deposition area. This is because, at a given spinning distance, the mass flow of polymer solution that can be processed is mainly determined by the applied voltage. For a stable electrospinning process,
the mass flow of the polymer solution fed to the needle orifice has to be equal to that of the solution spun into nanofibres.

![Graph showing the effect of applied voltage on fibre deposition area.](image)

**Figure 4.3.** Effect of applied voltage on fibre deposition area (spinning distance 20 cm).

When the flow rate was lower than the fibre generation rate, the Taylor cone shrunk and retracted back into the nozzle. The jet ejected from inside of the needle. The jet oscillates in a high frequency but discontinuously, as illustrated in **Figure 4.4.** This increased the fibre deposition area.

When the flow rate was higher than that of the polymer solution being ejected, un-spun droplet developed. When the flow rate was slightly higher, affected by the droplet on the nozzle, the jet only changed direction, as shown in **Figure 4.5a-c.** The fibre deposition area was expanded in accordance to the jet direction change. When further increased the applied voltage, the droplet was pulled off the nozzle and be stretched into smaller droplets by electrostatic force (**Figure 4.5d-f**) and resulted in beaded fibres.
**Figure 4.4.** Photos to show the jet direction change when the jet was generated from inside of the needle.
Figure 4.5, Photos (a ~ c) to show the jet direction change when an un-spun droplet was formed at the orifice, and (d ~ f) pulling off a droplet from the needle orifice and then stretched into smaller droplets.

Electrospinning using different polarity of applied voltages has been investigated. The deposition of electrospinning using negative voltage was much larger than that using positive voltage (Figure 4.6). At 15 cm spinning distance, the deposition area of electrospinning using a negative high voltage nozzle was 3 times larger than that using same voltage but positive polarity. Such a difference was gradually reduced with increasing the spinning distance.
Figure 4.6. Fibre deposition area of positively or negatively charged nozzle at different electrospinning distances.

Figure 4.7 shows the differences in jet movement between positive and negative high voltage driven electrospinning. For the positively charged electrospinning, the jet maintained a short straight section before the whipping started. The initial whipping burst into crest like shape and resulted in the truncated cone contour when jet traveled in a helix trajectory. When the jet was driven under a negative voltage, it bent to the side immediately after leaving the nozzle. The jet bent randomly in direction, and the bending behavior did not alter with the applied voltage, the spinning distance and the flow rate.

Figure 4.8a shows a moment when the downward bending jet degrades while the upward bending jet starts. Since the exposure time of photo was long enough, both bending movements were captured. Once the whipping started, the jet flew in a helix trajectory. Because of the random bending, fibre deposition circulated around on the collector, which resulted in a circular belt on the collector in the beginning (Figure 4.8b). The central area of this circular
belt was gradually filled up with fibres when electrospinning time was sufficient. This can be used to explain why electrospinning under a negative high voltage has a larger deposition area than that under a positive one. The fibre deposition drastically increased with increasing the spinning distance. The influence of voltage polarity was relatively smaller than that of the spinning distance. The effect of electrode polarity on fibre deposition area turned to be smaller with increasing the spinning distance.

Figure 4.7, Photos to show the trajectory of electrospinning jets under a positive (left) and a negative (right) voltage.

Figure 4.8, Photos of (a) the bending jet of electrospinning using the negative voltage and (b) a circular belt like fibre deposition initially formed on the collector.
4.3 Fibre morphology and diameter

Figure 4.9 shows the morphology of electrospun fibres produced from different polymer concentrations. When the polymer concentration was low, ‘Beads-on-string’ structure was formed. When the PAN concentration was 6%, lots of beads were found among the fibres. These beads had a spindle shape. When 8% or 10% PAN solutions were used, the beads were significantly decreased in number. Fewer beads were found when the PAN concentration was higher.

The diameter of electrospun fibre produced from different polymer concentrations is shown in Figure 4.10. When the polymer concentration was increased from 6% to 12%, the fibres electrospun under positive and negative voltage increased its diameter from 171.57 ± 35.49 nm and 203.17 ± 46.01 nm to 397.55 ± 63.44 nm and 503.53 ± 91.03 nm, respectively. Fibres produced under positive voltage overall were slightly finer than those produced under negative voltage.

The influence of spinning distance on fibre diameter is shown in Figure 4.11. The fibre diameter slightly decreased with increasing the spinning distance from 15 cm to 25 cm. When the spinning distance was shorter than 15 cm, the jet could not be completely elongated before arriving at the collector, thus leading to coarse fibres. With the increase in the spinning distance, the jet received more elongation before the jet hit the collector. When spinning distance was further increased to 30 cm, the electrostatic field was too weak that cannot provide enough force to elongate the jet. As a result coarse fibres with a wide diameter distribution were produced.
Figure 4.9, SEM images of PAN nanofibres electrospun from 6%, 8 %, 10 % and 12% PAN solutions.

Figure 4.10, Effect of polymer concentration on fibre diameter.
The polarity of applied voltage had little effect on the fibre diameter. The influence of applied voltage on fibre diameter is shown in Figure 4.12. The fibre diameter slightly increased with increasing the applied voltage from 11 kV to 15 kV, and then drastically increased at 17 kV. The fibres electrospun under negative voltage had similar diameter to those under positive voltage.

![Figure 4.11](image)
**Figure 4.11**, Effect of spinning distance on fibre diameter.

![Figure 4.12](image)
**Figure 4.12**, Effect of applied voltage on fibre diameter.
4.4 Making yarns from conventional needle electrospinning

Figure 4.13 shows the yarn electrospinning setup developed by Ali et al (3) in our group, which includes a positive polarity high voltage power supply, a spinning funnel, two syringe pumps and a yarn winder. During electrospinning, one of the syringe needles was connected with high voltage while another was grounded. The funnel was not grounded. The fibre under positive high voltage was electrospun onto the funnel. The electrostatic charge carried by the deposited fibres built on funnel created an electrical potential between the funnel and the grounded needle. Fibre was then electrospun from the grounded needle orifice. However the electrical potential was so low that the grounded needle has to be placed very close to the funnel to be able to electrospin. The fibre electrospun from both needle orifices formed a fibrous web covering the large edge of the funnel. By using a non-conductive rod, the nanofibre web was then pulled from centre to form a fibrous cone with its bottom connecting the large end of the funnel. By continuous electrospinning fibres on to the cone and rotating funnel, a twisted yarn was drawn from the apex of the cone and wondered to a yarn winder.

However some problems were encountered when it was used for producing PAN nanofibre yarns. The short spinning distance between the grounded needle and the funnel resulted in wet fibres which had strong bonding with each other thus hindering the formation of fibrous cone. To avoid the formation of wet fibres, higher polymer concentration was trialled. However fibre diameter drastically increased with increasing the polymer concentration. The
needle was often blocked by the polymer solution due to the quick solidification. The fibres electrospun from positively charged nozzle flew to both grounded needle and funnel. This offset the electrostatic potential, thus terminating the electrospinning process. It was very hard to position the electrospinning units to carry out yarn electrospinning. PAN nanofibre yarn cannot be produced using this setup.

![Photo of yarn electrospinning setup developed by Ali et al in our group.](image)

**Figure 4.13**, Photo of yarn electrospinning setup developed by Ali et al in our group.

To produce PAN nanofibre yarns, the yarn electrospinning setup was modified. A negatively charged needle was used to replace the grounded needle. The negatively and positively charged nozzles were placed on each side of the funnel. Because the fibre deposition under negative voltage is larger than that under positive voltage, the negatively charged spinneret was placed closer to the funnel than the positively one. So that fibres electrospun from both nozzles had a similar deposition area. During electrospinning, fibres with negative and
positive charge deposited to the funnel large end. A non-conductive rod was used to pick the fibrous web from centre to form a fibrous cone. By rotating the funnel, a yarn can be twisted and drawn from the apex of the cone.

Although obtaining continuous PAN nanofibre yarn using this method, it was difficult to get dry fibres of proper density. Dry fibre suitable for yarn electrospinning could be obtained when spinning distance longer than 25 cm. At such a spinning distance, only very limited fibres were deposited onto the funnel, resulted in a very thin and weak fibrous cone (Figure 4.2). By decreasing the spinning distance, the fibres was densely deposited, but the fibres turned wet. Wet fibres hindered the fibre slippage, and as a result a thick film was formed which strongly stuck to the funnel. The cone formed in that case was not stable and often led to breakage or yarn rupture.

A regular cone was found most stable. When the diameter of fibre deposition was larger than the chord of the regular cone, some fibres deposited directly onto the yarn formed bulky fluffy structure. Although it was possible to increase the winding rate to stretch the cone so that the chord of the cone equal to the diameter of fibre deposition, the cone became unstable and collapsed easily (Figure 4.14a and b). On the other hand, when more fibres were deposited close to the apex of the cone, fewer fibres would be deposited to the bottom of the cone. Only a very small number of fibres were connected to the funnel. Without sufficient fibres bonded to the funnel, cone was easily pulled off the funnel, as shown in Figure 4.14c. No effective twist could be introduced to the yarn unless enough fibres were deposited on the funnel. When more fibres were deposited on the bottom of the cone, more fibres also
attached to the outer surface of the funnel. Those fibres were strongly bonded to the funnel, leading to cone rupture and yarn breakage (Figure 4.14d).

Yarns produced in this way were either discontinuous or low in strength. It contained lots of defects and had poor uniformity due to lack of twist.

![Figure 4.14](image.png)

**Figure 4.14.** Photos to show (a) a long nanofibre cone with its chord in same length to the diameter of fibre deposition, (b) collapsed nanofibre cone; (c) a nanofibre cone was pulled apart the funnel when not enough fibres were connected to the funnel, (d) yarn was about to break near the apex of the fibrous cone when fibres were densely deposited on outer edge of the funnel.

### 4.5 Effect of back-disc electrode on electrospinning
To address the problems associated with the previous setups, an 8 cm diameter back-disc electrode was introduced to electrospinning to control the fibre deposition. The main difference between the conventional electrospinning and the one having a back-disc electrode is that the disc electrode can create a parallel electric field, which restrains the fibre deposition (49). The fibre deposition of the back-disc electrode aided electrospinning and a conventional electrospinning is shown in Figure 4.15. At the same spinning distance, the deposition area for the disc aided electrospinning was only 1 quarter of that from conventional electrospinning. The smaller deposition area suggests higher areal fibre density.

Figure 4.15, Photo showing the fibre deposition (left) from disc-aided electrospinning and (right) from conventional electrospinning (both spinning distance 20 cm, and spinning duration 1 minute).

Electrospinning with a back-disc electrode requires higher voltage to initiate the electrospinning process when compared with conventional electrospinning. When the disc diameter was 8 cm, the lowest applied voltage for initiating the electrospinning operation was 20 kV. When the voltage was below 20 kV, the
electrospinning became discontinued. The applied voltage in disc aided electrospinning can operate at a wider range between 20 kV to 40 kV when compared with that in conventional electrospinning which is in the range of 11 kV ~ 15 kV (Figure 4.16). For needle-based electrospinning, the applied voltage is often less than 30 kV. Corona discharge occurs when the voltage is above this critical value, and the discharge causes damages to surrounding electronic devices. In this study, the back and edge sides of the disc were covered with plastic to prevent corona discharge on those surfaces.

It is worth to note that the back electrode geometry, the relative location of the needle nozzle on back electrode and the distance between the needle nozzle and the back electrode are important factors influencing the electric field profile. To simplify, the needle nozzle was set only in the centre of the back-disc with 0.5 cm protrusion.

![Figure 4.16](image.png)

**Figure 4.16.** The applied voltage range that was used in conventional electrospinning and back-disc (diameter 8 cm) electrode-aided electrospinning.
Figure 4.17 shows photos of electrospinning jets in disc-aided electrospinning using different polarity voltages. The initial straight jet was apparently longer than that of the conventional electrospinning. For the disc-aided electrospinning, regardless of the high voltage polarity, the whipping jet was highly restrained in the electrospinning zone. The half angle of the cone shape whipping jet was similar between the negative and the positive high voltage driven electrospinning and was smaller than it in the conventional electrospinning.

Figure 4.17, Photos to show jets in disc-aided electrospinning using a negative high voltage (-30 kV) and a positive high voltage (+30 kV). Dot lines indicate jet propelling direction and dash lines show the contour of whipping cone.

Unlike in conventional electrospinning where the jet changes direction upon droplet developed, the jet of disc-aided electrospinning remained straight and maintained its direction even when it was ejected from the droplet hang below the nozzle, as show in Figure 4.18.
**Figure 4.19** shows the dependence of deposition area on the applied voltage. The deposition areas decreased with the increase in the applied voltage. The voltage polarity showed almost no influence on fibre deposition area.

**Figure 4.18**, Photo shows jet ejected from a droplet hanging below the nozzle tip of the disc aided electrospinning.

**Figure 4.19**, Effect of applied voltage on the fibre deposition area for disc aided electrospinning (spinning distance of 20 cm).
Photos of fibres deposited from the disc-aided electrospinning at different spinning distances are shown in **Figure 4.20.** A circular area was formed suggesting a high fibre areal density. When a short spinning distance (e.g. 15 cm) was used, a ring like fibre web was first formed. This could be related to the strong electric field formed between the disc and the collector. When the electrospinning time was longer than 1 minute, fibre deposition area expanded to a larger area. This was caused by repulsive effect of the residual charge brought by the fibres deposited, stopping the later spun fibres from depositing in the same area. Such a phenomenon was not observed when the spinning distance above 20 cm.

![Photos to show fibres deposited from the disc-aided electrospinning at a spinning distance of (a) 25 cm, (b) 20 cm, and (c) 15 cm.](image)

**Figure 4.20.** Photos to show fibres deposited from the disc-aided electrospinning at a spinning distance of (a) 25 cm, (b) 20 cm, and (c) 15 cm.

The dependency of deposition area on the spinning distance is shown in **Figure 4.21.** The deposition area decreases with increasing spinning distance. For the disc-aided electrospinning, the deposition area was always smaller than that of conventional electrospinning at same spinning distance. This difference in the
fibre deposition area got larger at longer spinning distance. The deposition area was around 50 cm$^2$ for disc-aided electrospinning and around 120 cm$^2$ for conventional electrospinning when the spinning distance was 20 cm. When the spinning distance was increased to 25 cm, the deposition area was increased to about 100 cm$^2$ for disc-aided electrospinning and more than 300 cm$^2$ for conventional electrospinning. Very little difference in deposition area was found between the positive and negative voltage driven electrospinning.

![Graph showing deposition area vs spin distance](image)

**Figure 4.21**, Effect of spinning distance on fibre deposition area (disc-aided electrospinning, spinning duration 1 minute).

### 4.6 Fibre diameter and morphology

**Figure 4.22** shows the morphology of fibres produced from the disc-aided electrospinning. ‘Beads on string’ structure was observed when the polymer concentration was low. Beads were found among the fibres from disc-aided electrospinning using 6% PAN solution. However, the beads were much smaller in both size and quantity when compared with those produced from the conventional electrospinning. When the solution concentration was above 8%,
bead free nanofibres resulted. The polarity of high voltage showed no effect on the bead formation.

![Figure 4.22](image)

**Figure 4.22**, SEM images of nanofibres electrospun from disc-aided electrospinning using different PAN concentrations.

As shown in **Figure 4.23**, the diameter of fibres from the disc-aided electrospinning is similar to those from conventional electrospinning. When the solution concentration was increased from 6% to 12%, the fibres produced from the disc-aided electrospinning with negative and positive polarity of high voltage increased from $182.40 \pm 26.37$ nm and $197.62 \pm 60.73$ nm to $483.25 \pm 97.83$ nm and $543.22 \pm 189.86$ nm, respectively.

![Figure 4.23](image)

The influence of applied voltage on fibre diameter is shown in **Figure 4.24**. When increasing the applied voltage from 25 kV to 35 kV, the fibre diameter
was almost unchanged. Fibre diameter distribution from the positively-charged nozzle was narrower than those from negatively-charged one. The diameter distribution gradually increased with increasing the applied voltage.

![Graph showing fibre diameter distribution](image)

**Figure 4.23**, Effect of polymer concentration on fibre diameter.

![Graph showing effect of applied voltage](image)

**Figure 4.24**, Effect of applied voltage on fibre diameter of the disc-aided electrospinning (PAN concentration, 10%; spinning distance, 20 cm).

The influence of spinning distance on fibre diameter is shown in **Figure 4.25**. The fibre diameter decreased with increasing the spinning distance from 15 cm to 25 cm, and then slightly increased when the distance was above 30 cm. The
fibre diameter decreased from 382.50 ± 23.32 nm and 415.07 ± 48.60 nm to 357.33 ± 55.24 nm and 373.08 ± 41.01 nm for positive and negative 25 kV applied voltage, respectively, when spinning distance was increased from 15 cm to 25 cm. When the spinning distance was increased to 30 cm, the fibre diameters increased to 401.17 ± 42.50 nm and 427.95 ± 82.21 nm for positive and negative 25 kV applied voltage, respectively. The fibres produced from disc-aided electrospinning using positive high voltage were more uniform than those from using negative high voltage. The diameter distribution of the fibres electrospun at a spinning distance in the range between 20 cm and 25 cm was narrower than that produced either at a spinning distance of 15 cm or 30 cm. When the spinning distance was shorter than 20 cm, the jet couldn’t completely elongate before arriving at the collector. The residual charges carried by deposited fibre could affect the electrostatic field hence affect the elongation of the later arriving jet. With the increase in the spinning distance, the jet received more elongation before hitting the collector. Because the deposition area increased with the increase in the spinning distance, the fibre areal density decreased. As a result, reduced charge density leads to smaller electrical interaction to later coming electrospinning fibres. When the spinning distance was further increased to 30 cm, the electrostatic force was too weak to elongate the jet effectively, thus resulting in increased fibre diameter and diameter distribution.
Figure 4.25, Effect of spinning distance on fibre diameter (applied voltage 25 kV).

4.7 Making PAN nanofibre yarns based on disc-aided electrospinning

The setup for electrospinning of nanofibre yarn is shown in Figure 4.26. By using disc-aided electrospinning setups to simultaneously electrospin positively and negatively charged PAN nanofibres onto a rotating funnel collector, a thin fibrous web was initially formed on the funnel large end. Pulling off the web from the central part of the funnel led to the formation of a hollow nanofibre cone. The cone rotated at the same speed to the funnel. At the apex of the cone, fibre bundle can be drawn into a twisted yarn. By continuously electrospinning and depositing nanofibres on the cone, and meanwhile continuously drawing nanofibres from cone apex, a twisted continuous nanofibre yarn was thus formed, which can be wound easily on a winder.
Figure 4.26, Diagram of yarn spinning setup based on disc-aided electrospinning.

Both the positive and negative nozzles were driven with 25 kV high voltage and 10% PAN solution were used for the yarn production. These conditions were chosen based on the fact that they can produce bead-free and uniform nanofibres with a small fibre diameter and narrow diameter distribution. 25 cm spinning distance was chosen to ensure fibre deposition of dry nanofibres with proper density. When a longer spinning distance was employed, the nanofibre web density was reduced while the deposition area increased. The nanofibre web became weak and easily torn due to insufficient fibre density and lack of fibre bonding (Figur 4.27a). Nanofibre webs of higher fibrous density produced from a smaller spinning distance hindered the slippage of fibres in the fibrous cone, which prevented elongation into yarn. Figure 4.27b shows a
highly condensed fibrous web sticking on the funnel when the spinning distance was 15 cm. Such a web cone couldn’t be stretched into yarn. When making yarn with spinning distance 25 cm, a right circular nanofibre cone could be formed. The right nanofibre cone was found structural stable when compared with cone of other shape which tended to collapse latitudinally or longitudinally.

Under the optimised condition, the setup could produce continuous yarns for hours without breaking. Figure 4.28 shows the rolls of nanofibre yarns produced from disc-aided electrospinning method.

**Figure 4.27**, Photos of (a) the fibrous cone tore due to the low fibrous density (spinning distance, 30 cm) and (b) the nanofibre web that stuck on the funnel and was hardly stretched off (spinning distance, 15 cm).
The yarn making process was also affected by the yarn winding rate and funnel rotating rate. The yarn winding rate was a controllable parameter, however it was highly dependent on the funnel rotating speed. **Figure 4.29a** shows a typical nanofibre cone when the yarn is continuously produced. When the funnel rotating speed was low, increasing the yarn winding rate would stretch the cone longer and thinner. The stretched cone had higher fibre density in the parts close to the apex than the bottom due to cone deformation. Higher fibre density resulted in stronger fibre bonding, less fibre slippage and higher strength in the part. The cone was eventually torn from the part close to the bottom of the cone as it couldn’t withstand the winding force and break from its weakest position (**Figure 4.29b**). At a high funnel rotating speed, decreased yarn winding rate could lead to a thick and short nanofibre cone. The decrease in the cone length increased the local fibre density. The condensed nanofibre web hindered the nanofibre slipage, less fibres could be stretched and twisted into yarn, and eventually resulted in the yarn ruptured at the apex of the nanofibre cone.
**Figure 4.29c** shows a scene when the yarn is about to break at the apex of the cone because of the low winding rate.

The influence of the funnel rotating speed on the yarn winding rate is shown in **Figure 4.30**. The grey area is the operatable range of the winding rate at a given funnel rotating speed. The highest winding rate in this setup was achieved at 1.33 m/min.

Based on the yarn winding rate \( W \) and the funnel rotating speed \( R \), the apparent twist level \( T \) can be calculated as

\[
T \text{(tpm)} = \frac{R \text{ (rpm)}}{W \text{ (m/min)}}
\]

where the units of \( W \), \( R \) and \( T \) are m/min, rpm and turns per meter (tpm), respectively. Low funnel rotating speed leads to less vibration and aerodynamics interference, resulting in stable nanofibre web cone. However the fibres were loosely packed in the yarn when the twist level was low, and the yarn had low strength as well. The yarn strength increased with increasing the twist level. If the twist level was too high, substantial twisting could cause yarn rupture. **Figure 4.31** shows the relationship between the twist level and the winding rate in making continuous yarn. The highest twist level of 3524 tpm was achieved by this method on PAN nanofibre yarns at the winding rate of 0.66 m/min. High twist level and high winding rate require very high funnel rotation speed. When the funnel rotation speed was high enough, the electrospun fibres could be blown away by the air flow surrounding the funnel. The loss of fibres reduced the yarn strength. The winding rate has to be
lowered to reduce the winding force. Thus the highest winding rate could not be achieved together with the highest twist level. The highest twist level obtained at the highest winding rate was 1538 tpm.

**Figure 4.29**, Photos showing (a) the fibrous cone is about to be tore at a high winding rate and (b) the yarn is about to break from the thick nanofibre cone which was resulted by the too low winding rate.
Figure 4.30, Dependency of winding rate on funnel rotating speed.

Figure 4.31, Relationship between the winding rate and the twist level.

4.8 Yarn morphology and diameter

SEM photos of nanofibre yarns are shown in Figure 4.32. The yarn produced at the winding rate of 0.32 m/min and the funnel rotating speed of 245 rpm had yarn diameter of $247.21 \pm 55.21 \, \mu m$ and fibre diameter of $562.47 \pm 13.41 \, nm$. The yarn was uniform but contained fluffy fibre clusters. Some of the fibres in
the yarn aligned along the twist direction and the others were randomly orientated (Figure 4.32a and b).

When the winding rate was kept low (0.66 m/min), but the funnel rotating speed was increased to 2326 rpm, the highest twist level of 3524 tpm was obtained and the yarn drastically decreased its diameter to 136.11 ± 11.62 nm. The yarn diameter distribution became narrower as well. The yarn looked highly-compact, with the majority of fibres aligning along the twist direction, except for a few fibres which stuck out of the yarn (Figure 4.32c and d). The fibre diameter was 582.22 ± 31.09 nm.

When yarn was drawn at the highest winding rate of 1.33 m/min and the funnel spinning speed of 2045 rpm, the yarn had a diameter of 137.30 ± 11.23 μm. Although the yarn diameter was close to that which was produced at the highest twist level, it had more fluffy structure. Fibres in the yarn show partially aligned morphology (Figure 4.32e and f), and the fibre diameter was 569.24 ± 25.86 nm.
Figure 4.32, SEM photos of yarns and fibres produced under different winding rates and funnel rotating speeds.
4.9 Summary

The back-disc electrode played a key role in the formation of stable fibrous cone during electrospinning PAN nanofibre yarn: the back-disc electrode leads to condensed fibre deposition on the collector; Compared to conventional electrospinning, the disc-aided electrospinning has wider adjustable range of the applied voltage which provides ease in controlling fibre deposition; The high voltage polarity of the disc-aided electrospinning had little influence on electrospinning process and fibre deposition area. The beaded fibres were greatly reduced when a back-disc electrode was added for electrospinning.

Continuous PAN nanofibre yarns could not be electrospun successfully using conventional electrospinning systems. However, when back-disc electrode electrospinning system employed, continuous PAN nanofibre yarns were easily produced. The disc-aided electrospinning system used two oppositely charged nozzles to deposit PAN nanofibre onto the funnel. The nanofibre web subsequently becomes a cone shape when initially stretched from the centre. A twisted yarn could be continuously wound from the apex of the cone. Funnel rotating speed and winding rate influence yarn morphologies. The highest twist level that could be achieved by this nanofibre yarn spinning system was 3524 tpm and the highest winding rate was 1.33 m/min. Yarn with finest diameter and best uniformity is obtained at 0.66 m/min winding rate and 2326 rpm funnel rotating speed.
Chapter 5

Hot drawing of PAN nanofibre yarns

Electrospun PAN nanofibre yarns have been drawn in wet or dry condition at an elevated temperature to improve the polymer molecular orientation, crystallinity and yarn mechanical properties. The wet and dry glass transition temperatures of PAN in the yarns have been measured.

5.1 Experiment part

Wet Tg was measured using the setup described in section 3.2.4.1. Dry Tg was measured using DMA and verified by DSC.

The drawing ratio and strain (engineering strain) was calculated using following equations:

\[ \lambda = \frac{l}{L} \]
\[ e = \frac{\Delta L}{L} = \frac{l - L}{L} \]

Where \( \lambda \) is the drawing ratio, \( l \) is the final length of the yarn and \( L \) is the original length of the yarn. The engineering strain \( e \) is defined as the change in length \( \Delta L \) per unit of the original length \( L \) of the material.

Yarn and fibre morphologies were observed under SEM. Their diameters were measured based on the SEM images using the software Image Pro+6.0.
Polarized FTIR was used to investigate the influence of drawing on the molecular orientation. WXRD was used to measure the crystal structure and molecular orientation of PAN within the yarns. The mechanical properties of the yarns were measured using Sifan 3 single filament mechanical tester.

5.2 Wet drawing of electrospun nanofibre yarns

5.2.1 Measurement of wet Tg

Conventional PAN fibres can be drawn into many times of their original length in hot water. This treatment improves the PAN molecular orientation and crystallinity within the fibres, but reduces defects per unit length. The glass transition temperature in wet condition could be 10 °C to 40 °C lower than that in dry condition [1, 2]. This is because wet environment facilitates the movement of PAN molecular chains during stretching.

The curves of drawing force to drawing ratio on drawing PAN nanofibre yarns in hot water is shown in Figure 5.1. PAN yarns show an initial elastic deformation followed by a large plastic deformation at higher drawing ratio. The fraction of elastic deformation was reduced with increasing the water temperature. When the yarn was drawn at 96 °C, the initial elastic deformation became too small to be noticed.

The breaking force of the yarns drawn in 40 °C water was about 30 cN. The breaking force of the yarns changed with the increase in the drawing temperature. When the temperature increased from 40 °C to 80 °C, a drastic decrease in the breaking force was measured. The breaking force of the yarns
drawn in 80 °C water was about 20 cN. However, the breaking force was kept at about 17 cN when the drawing temperature was higher (90 °C ~ 96 °C).

The maximum drawing ratio changed with the drawing temperature. Increasing the drawing temperature from 40 °C to 80 °C led to the maximum drawing ratio increases from about 230% to 280%. At a higher temperature, e.g. 90 °C or 96 °C, the maximum drawing ratio had a very small change. The maximum drawing ratio of about 300% was obtained when the drawing temperature was above 90 °C. These results indicate that the change of the drawing force and the maximum drawing ratio with drawing temperature happens mainly at a drawing temperature below 90 °C. Once the drawing temperature was above this critical value, the drawing force and maximum drawing ratio changed very little with the temperature.

Based on the result, the wet Tg of PAN nanofibre yarn was estimated at 90 °C, which is in agreement with literature reports [2]. To obtain larger drawing ratio and smaller drawing force, and meanwhile to avoid use of boiling water, PAN nanofibre yarns were drawn at a temperature below 96 °C. The as-spun nanofibre yarns were drawn up to 4 times of its original length in 96 °C water under 15 cN.
Figure 5.1. Drawing force ~ drawing ratio of electrospun PAN nanofibre yarns in water at temperatures 40 °C, 60 °C, 80 °C, 90 °C and 96 °C.

5.2.2 Morphology of wet drawn nanofibre yarns

Yarn and fibre morphology of undrawn, post 2 and 4 times drawn yarns were observed under SEM. As shown in Figure 5.2, the as-spun yarn looks coarse. The fibres in the yarns are loosely stacked without obvious orientation. The fluffy fibres around the circumference of the yarn have damped the yarn uniformity. When the yarn was drawn to 2 times, it became compact and fibres showed some alignment. Fibres in the yarn tend to be bundled to form a layered morphology. This is probably due to the effect of water surface tension. The water wetted fibres tended to bundle tightly together to minimize the surface area. When the bundled fibres oriented along the same direction, the yarn tended to be more compacted. After 4 times drawing, the yarns became highly compacted and the fibres within these yarns were highly aligned along the yarn axis.

Figure 5.3 shows the fibre alignment degree obtained directly from SEM images of as-spun, and 2, 3 and 4 times drawn yarns. The fibre alignment
degree was low in as-spun yarn. Fibres presented in all the angles to the yarn axis, although fibre counts were slightly higher in the angles within 0 to 30 degree than other angles. The fibre counts in the angles within 0 to 30 degree were slightly increased for 2 times drawn yarn. In 3 and 4 times drawn yarns, fibre counts in the angles within ±30 degree to the yarn axis were found drastically increased, while fibres in other angles were substantially decreased. The fibre alignment degrees in 3 and 4 times drawn yarn were close.

Figure 5.2, SEM images to show PAN nanofibre yarns (a) & (b) without drawing and post (c) & (d) 2 times and (e) & (f) 4 times drawing.
Figure 5.3, Percentage of fibre alignment angle to the axis of nanofibre yarns;

Table 5.1 lists the yarn and fibre diameters of electrospun PAN yarns before and after drawing treatment. Yarn decreased its diameter by 38.3 % and 52.6 % respectively after 2 and 3 times of drawing. Higher drawing ratio did not result in a further decrease in the yarn diameter. The diameter of 4 times drawn yarn was similar to 3 times drawn one. The fibre diameter decreased by 16.4 % after 2 times drawing, when compared to the fibre in as-spun yarn. With further increasing the drawing ratio, the diameter of fibres decreased monotonously.

At the initial drawing stage, fibres are straightened and orientated. From random to orientate structure, fibres become compacted, resulting in a large decrease in the yarn diameter. When the fibres are drawn to be straight, a further elongation of yarn becomes difficult. As a result, the drawing treatment has a small effect on yarn diameter. In the case of fibres, the PAN molecular chain in ordered regions has been proposed to be in an irregular helical
conformation with its nitrile groups pointing outwards against the helical axis fitting in about 0.6 nm diameter rods in hexagonal packing (89, 99). Accompanied with chain extending, the rod diameter decreases in response to the drawing (87), that contributes to a large proportion of fibre diameter decrease during the drawing.

Table 5.1, Yarn and fibre diameters of as-spun, and 2, 3 and 4 times drawn yarns

<table>
<thead>
<tr>
<th>Drawing Ratio</th>
<th>Yarn Average Diameter (µm)</th>
<th>Yarn Standard Deviation (nm)</th>
<th>Fibre Average Diameter (nm)</th>
<th>Fibre Standard Deviation (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-spun</td>
<td>278.83</td>
<td>30.39</td>
<td>812.20</td>
<td>312.72</td>
</tr>
<tr>
<td>2x</td>
<td>172.09</td>
<td>25.45</td>
<td>678.91</td>
<td>138.92</td>
</tr>
<tr>
<td>3x</td>
<td>99.81</td>
<td>23.29</td>
<td>637.43</td>
<td>144.61</td>
</tr>
<tr>
<td>4x</td>
<td>99.86</td>
<td>19.37</td>
<td>560.23</td>
<td>139.48</td>
</tr>
</tbody>
</table>

5.2.3 Mechanical properties of wet drawn yarns

Sifan-3 single fibre tester was used to examine the mechanical properties of PAN nanofibre yarns. As shown in Figure 5.4a, the tensile strength and Young’s modulus of the yarns after drawing increase with the increase in the drawing ratio. The maximum tensile strength (208.78 ± 6.05 MPa) and Young’s modulus (3.67 ± 0.37 GPa) were obtained from 4 times drawn yarn, which were respectively more than 4.6 times and 7 times larger than those of un-drawn yarns (44.48 ± 4.82 MPa and 0.52 ± 0.10 GPa, respectively).
The representative stress ~ strain curves of as-spun, and 2 ~ 4 times drawn yarns are shown in Figure 5.4b. The strain at break of un-drawn yarn was 96.8%, which was more than 5 times larger than that of drawn yarns. The strain at break of drawn yarns was all less than 20%. An initial elastic deformation can be found in the stress ~ strain curve of the as-spun yarn and 2 times drawn yarn. However the initial elastic deformation for the 3 and 4 times drawn yarns was too small to be noticed.

Figure 5.4, a) Tensile strength and Young’s modulus as the function of drawing ratio; b) Stress ~ strain curve of as-spun, and 2, 3 and 4 times drawn yarns
In summary, in as-spun yarns the fibres are curled, randomly distributed and loosely stacked. A little drawing could substantially straighten the fibre, improve the fibre orientation and decrease the yarn diameter. Drawing also decreases the fibre diameter. Consequently, the tensile strength and Young’s modulus after drawing treatment increase.

5.3 Dry drawing of PAN nanofibre yarns

5.3.1 Measurement of dry Tg

PAN fibres become viscoelastic above its glass transition temperature. Drawing of PAN fibres is preferably to be carried out at a temperature above the Tg. Generally, the molecular mobility increases with increase of the temperature. However PAN does not melt until it becomes degraded at 250 °C (143).

Figure 5.5 shows a typical DSC curve of PAN. The exothermal peak of PAN decomposition which starts at about 260 °C and reaches the maximum at 280 °C can be clearly observed. Therefore, the temperature for hot drawing of PAN fibres has to be performed at a temperature below this critical value.
Figure 5.5, DSC curve of PAN fibres with heating rate 5 °C/min in nitrogen environment.

DMA is considered as the most sensitive method to measure the glass transition temperature of materials (174). By measuring the elastic and damping behaviour of PAN nanofibres, it has been found that the damping peak, also known as Tan Delta, appears at 125 °C and the node of storage modulus before declination is around 105 °C, as shown in Figure 5.6. The results are in accordance with those in the literature (175, 176). The glass transition is referred to as node of storage modulus before declination, which is 105 °C.
DSC is a commonly used method for measuring the glass transition temperature of polymer materials. Polymers change from the glassy state to rubbery state at the T_g, which presents as a step between different plateaus on the DSC curve. The middle point of the step is referred as T_g (176). Since glass transition between rubbery and glassy state is a reversible change, T_g can be confirmed by DSC with a heating and cooling cycle.

The T_g of PAN powder and PAN nanofibre yarn obtained from DSC is almost the same being at 105 °C (Figure 5.7). Same glass transition points are found on cooling and 2nd heating curves. A board endothermic peak maximized at about 140 °C – 160 °C has been found in the DSC curves of both PAN nanofibre yarn and PAN powder. This broad endotherm peak was not resulted from enthalpy recovery (177), because it is consistently present on both the 1st
heating and the 2nd heating cycles and is associated with melting of the ordered or crystalline region of PAN polymer (89). The broad endothermic peak interfering differentiates the existence of additional glass transition at higher temperature (81). Okajima et al. (93) reported the additional transition peak at 160 °C obtained from DMA on PAN filaments drawn in water at 40 °C - 70 °C and steam annealed at 90 °C - 180 °C. The height of the peaks was in parallel to crystallinity of PAN filaments, where drawing resulted in lower peak and annealing restored the peak. They were explained as some ordered regions of PAN which were destroyed by drawing but could be rebuilt by annealing at high temperature. This is in perfect agreement with that crystallization is low in electrospinning nanofibres (34, 98). The rapid solidification and high elongation rates of electrospinning jets hindered the formation of crystals in semi-crystalline polymer.

In Figure 5.7b, a small exothermal peak of PAN nanofibre yarn appears at about 105 °C, which is related to chain relaxation. Those molecular chains have been drawn and twisted during electrospinning and yarn forming process becomes mobile and relaxed when PAN molecular becomes viscoelastic above glass transition temperature. The same peak is not observed on the 2nd heating and cooling curve.
Figure 5.7, a) DSC curves of PAN polymer powder and b) DSC curve of electrospun PAN nanofibre yarn. The tests have been conducted by heating the samples from 50 °C to 200°C (heating rate 5 °C/min), and cooling immediately to 50 °C (cooling rate 5 °C/min), followed by heating from 50 °C to 200 °C (heating rate 10 °C/min).

5.3.2 Drawing force and up temperature limit

DMA tests have revealed that the maximum drawing ratio increases with increasing the temperature, while the initial modulus and drawing force
decreases accordingly (Figure 5.8). The maximum drawing ratio was about 2 times when the yarn was drawn at 30 °C. When the drawing temperature was close to the glass transition temperature, the maximum drawing ratio increased drastically to about 350 % at 100 °C, and 230% at 80 °C. The maximum drawing ratio continued to increase when drawing was undertaken above the glass transition temperature. The maximum drawing ratio of 540% was obtained when drawing was carried out at 140 °C. The maximum drawing ratio suddenly dropped to below 300%, when the temperature was above 150 °C. The maximum drawing ratio further decreased with the increase in the drawing temperature.

The drawing force changes with the drawing temperature. The drawing force drastically decreased when the drawing temperature increased from 30 °C to 80 °C and then gradually decreased with further increased in the temperature. For the drawing in the temperature range of 140 °C ~ 180°C, the drawing forces had very little change.

![Figure 5.8](image.png)

**Figure 5.8.** Drawing force ~ drawing ratio curves of PAN nanofibre yarn drawn (crosshead speed 400 μm/min) at different drawing temperatures.
Figure 5.9 shows the drawing ratio change of PAN nanofibre yarns under constant drawing force with drawing temperature change at the rate of 1 °C/min using DMA. When the drawing force was above 20 cN, the yarn elongation started at the temperature as low as 40 °C and yarn broke at a small drawing ratio before the temperature reached 80 °C. When the drawing force was lower than 20 cN, the drawing ratio changed apparently when the temperature was higher than 100 °C. Under the drawing force lower than 2 cN, the yarn elongated less than 100%. The elongation started at 120 °C, reached the maximum drawing ratio at about 260 °C, followed by shrinkage. When the drawing force was 2 cN, the yarns started elongation at 120 °C and it can be drawn to a larger extent, but the yarns broke when the temperature reached about 160 °C - 170 °C.

Under the drawing force of 3 cN, the yarn elongation started at about 110 °C. Interestingly, a second elongation was found at near 140 °C. When the force was kept between 5 cN to 7.5 cN, the 2nd elongation occurred also. Higher drawing force shifted the 1st elongation and 2nd elongations slightly to lower temperatures. Under the drawing force of 7.5 cN, the 1st elongation started at about 100 °C and the 2nd elongation at about 135 °C. When the force was kept between 5 cN to 7.5 cN, the yarns can be drawn to above 500%. The 1st elongation allows the yarns to be drawn to about 3 times, while the 2nd allows further stretching to above 6 times. Under the drawing force of 10 cN, the yarn started its 1st elongation at about 95 °C. However the yarn broke when the temperature reached 120 °C, before the 2nd elongation started. The maximum drawing ratio obtained was about 5 times.
Figure 5.9, Drawing ratio ~ temperature curves of drawing PAN nanofibre yarns under different forces

Figure 5.10 shows the elongation speed during drawing PAN nanofibre yarns at constant force when the drawing temperature changes from 40 °C to 160 °C (heating rate 1 °C/min). The yarn drawn under 3 cN had the highest elongation speed of 0.33 mm/min at the 1st elongation stage when the drawing temperature was at about 110 °C. The elongation speed then gradually slowed down to 0.2 mm/min when the temperature increased until 130 °C. When the temperature reached 140 °C, the 2nd elongation started. The 2nd elongation was much faster than the 1st one. The highest elongation speed at the 2nd elongation stage was almost 30 times of that in the 1st elongation. Both the 1st and the 2nd elongation start points shifted to lower temperature when the drawing force increased, while increasing the drawing force did not affect the elongation speed much. The yarn drawn under the 7.5 cN started its 1st elongation at about 95 °C, and the highest elongation speed of 0.32 mm/min took place at 105 °C. Its worth to note that the yarn drawn under 7.5 cN started elongation at a lower temperature and it already reached the maximum drawing ratio before reaching the highest
elongation speed in the 2\textsuperscript{nd} elongation stage. The highest elongation speeds in the 2\textsuperscript{nd} elongation stage under 3 cN and 5 cN were 6.06 mm/min and 7.71 mm/min, respectively.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.10}
\caption{Elongation speed \textasciitilde temperature curves of PAN nanofibre yarns drawn under the drawing force of 3.0 cN, 5.0 cN and 7.5 cN.}
\end{figure}

From the experimental results, the drawing force of 7.5 cN was found to be the most suitable condition to elongate the yarn. It can stretch the yarn to above 6 times of its original length. The most efficient drawing temperature was found in the range between 130 °C to 140 °C, where more than 50 \% of overall elongation took place within 10 minutes (elongation time can be calculated from 1 °C/min heating rate when referring \textbf{Figure 5.9}). The PAN nanofibre yarns became fragile when they were heated above 150 °C. The maximum drawing ratio at a temperature above 150 °C drastically decreased to less than 3.5 times. Therefore, the drawing temperature should be strictly lower than 150 °C. In the further experiments, PAN nanofibre yarns were drawn under 7.5 cN at 140 °C.
5.4 Morphology of hot drawn nanofibre yarns

As shown in Figure 5.11, as-spun PAN nanofibre yarns have a fluffy morphology containing coiled and twisted fibres. These coils and twisted fibres can be eliminated through drawing treatment. The yarns became more compact at a higher drawing ratio, hence improving the uniformity.

Figure 5.11, SEM photos of as-spun, post 2, 4 and 6 drawn yarns.

Figure 5.12 shows the fibre alignment degree directly obtained from SEM images of as-spun, 2, 4 and 6 times drawn yarns. Fibres were randomly oriented in all angles to the yarn axis in as-spun yarn. Fibre counts were slightly higher in the angles within 0 to 60 degree than other angles. The fibre counts in the angles within ± 30 degree to yarn axis were significantly increased in 2 times drawn yarn. Drastic increase of fibre counts in the angles within ± 30 degree to the yarn axis were found in 4 and 6 times drawn yarns,
and fibres in other angles were substantially decreased. The fibre alignment degree was significantly increased to 4 times drawn yarns and plateaued at 6 times drawn yarn.

The diameter and standard deviation of yarns and fibres after hot drawing are shown in Figure 5.13. Before drawing, the as-spun yarns had a diameter of 278.83 ± 30.39 μm. When drawing the yarns to 3 times of their original length, the yarn diameter reduced by 67 %. Further drawing did not significantly decrease the yarn diameter. When drawn to 6 times, the yarn diameter was 84.29 ± 5.4 μm, which was 70 % of the 3 times drawn yarn. The uniformity of yarns improves with increasing the drawing ratio. The influence of drawing on the fibre diameter has a similar trend to that on the yarn. The fibre diameter of as-spun yarn was 812.20 ± 312.72 nm. The fibre diameter decreased to 407.58 ± 141.20 nm when the yarns were drawn to 3 times of the original length. When the yarns were drawn to 6 times, the fibre diameter decreased to 336.44 ± 142.47 nm.
Figure 5.12 Counts in percentage of fibre in angles with the yarn axis of as-spun, 2, 4 and 6 times drawn yarns; and fibre alignment degree of as-spun, and 2, 3 and 4 times drawn yarns represented by counts in percentage of fibres within ± 30 degree to the yarn axis.
Figure 5.13 Effect of drawing ratio on yarn and fibre diameters.

The PAN fibre morphology and diameter distribution are shown in Figure 5.14. The fibres in the yarn before and after drawing treatment were all smooth and have no defects on the surface. Before drawing treatment, the fibres in the yarn stacked loosely in a random way. After drawing treatment, the fibres become orientated along the yarn axis. The higher the drawing ratio, the higher the orientation is.

Before drawing, the fibres in the as-spun yarn had a wide diameter distribution with the diameter in range between 200 nm ~ 1.6 μm. The drawing treatment reduced the fibre diameter and narrowed the diameter distribution. After 4 times drawing of the yarns, the fibres had a diameter in the range of 200 nm ~ 800 nm. Higher drawing ratio, such as 6 times, further narrowed the fibre diameter distribution. However the fibre diameter had a little change.
Figure 5.14, SEM images of fibre morphology and histogram distribution of fibre diameter of un-drawn and post drawn PAN nanofibre yarns.
5.5 Molecular orientations within PAN nanofibres

It has been established that un-oriented PAN molecular chain has a randomly kinked rod like conformation due to the strong repulsive interaction of nitrile groups. The drawing treatment can orientate nitrile groups approximately perpendicular to the extended chain axis (83, 97).

The molecular chain orientation can be characterized by examining the nitrile-drawing vibration at 2244 cm⁻¹ using polarized FTIR. Chain-orientation factor are shown in the following equations (97, 178):

\[
D = \frac{A(\text{parallel})}{A(\text{perpendicular})} \quad (1)
\]

\[
D_0 = 2 \cot^2 \alpha \quad (2)
\]

\[
f = \frac{(D-1)(D_0+2)}{(D_0-1)(D+2)} \quad (3)
\]

Where \(D\) is the dichroic ratio of the FTIR vibration peak intensity \(A\) under parallelly- and perpendicularly- polarized beams. \(D_0\) is the dichroic ratio for the polymer with perfect orientation, wherein the angle \(\alpha\) between the dipole moment vector of the vibration and the chain axis is 68° (179). The orientation factor between 0 and 1 indicates random and perfectly-parallel orientation, respectively.

Dichroic orientation factors of as-spun yarns and those which were drawn 2, 3, 4, 5 and 6 times of their original length are provided in Figure 5.15a. The
orientation of nanofibres along the yarn axis increased with increasing the drawing ratio. The 6 times drawn nanofibre yarn had the highest orientation degree, 0.63. This orientation result was close to that of PAN films or fibres prepared by conventional film/fibre preparation and subsequent drawing treatment (180). It was necessary to indicate that conventional PAN fibres are copolymers. The addition of co-monomers often weakens the repulsion between the C≡N dipoles, allowing the fibres more easily to be drawn.

**Figure 5.15b** shows the dichroic ratio of nitrile groups at the beam angle 0°, 30°, 60° and 90° to the fibre alignment direction. The dichroic ratio for the yarn without drawing was slightly higher at 30° and 60° than that at 0° and 90°. That was probably because the molecular chains of PAN in the nanofibres were slightly stretched along the fibre axis during electrospinning and twisting when the yarn was prepared. After drawing, the yarns increased in the dichroic ratio with increasing the beam angle.

PAN is known as a semi-crystalline polymer with laterally ordered crystalline region separated by amorphous region. The molecular arrangement is illustrated in **Figure 5.16**. Curled, twisted, or contorted molecular chains co-exist in the fibres of the as-spun yarn. Drawing treatment can straighten and extend those molecular chains. It was interesting to note that PAN polymer jet during electrospinning was elongated thousands times. As a result, the PAN molecular chains in the fibres should be extensively drawn. However the experimental tests revealed that the chain orientation in electrospun fibres was not high, even if those fibres were highly orientated. Hot drawing was found to be an effective way to improving the molecular orientation [12, 19](98, 123).
Figure 5.15, a) Orientation factor ~ drawing ratio, b) Dichroic ratio ~ beam angle of the polarized IR at different drawing ratios.
Figure 5.16, A schematic illustration of PAN molecules with laterally ordered crystalline region and amorphous region before and after drawing (160).

WAXD was used to investigate the molecular orientation in crystalline region of PAN nanofibre yarns. As shown in Figure 5.17a, all the yarns have a peak maximum at around $2\theta = 16.8^\circ$, which is the characteristic of (001) reflection of the PAN hexagonal lattice, representing a d-space of 5.25 Å. Compared with the drawn yarns, the un-drawn yarn had a wider full width at half maximum (FWHM) at the (001) reflection, indicating a smaller average crystal size.

Azimuthal peak intensity between $0^\circ$ and $360^\circ$ on the intense reflection peak at $2\theta = 16.8^\circ$ can be used to interpret the orientation information of the chain axis in crystalline PAN nanofibres (181). The orientation of the chain to the yarn axis in crystalline PAN nanofibre yarns is expressed as orientation factor $P_2$ which is same as Herman's orientation factor using following formula (182),
\[ P_2 = \frac{3}{2} \langle \cos^2 \sigma \rangle - \frac{1}{2} \]  

(1)

\[ \langle \cos^2 \sigma \rangle = 1 - 2 \langle \cos^2 \beta_{hk0} \rangle \]  

(2)

\[ \langle \cos^2 \beta_{hk0} \rangle = \frac{\int_0^{\pi/2} I(\beta_{hk0}) \cos^2 \beta_{hk0} \sin \beta_{hk0} \sin \beta_{hk0} \cos 2 \theta_{hk0} \cos \theta_{hk0} \theta_{hk0}}{\int_0^{\pi/2} I(\beta_{hk0}) \sin \beta_{hk0} \sin \beta_{hk0} \cos \theta_{hk0} \theta_{hk0}} \]  

(3)

Where \( \sigma \) is the angle between the chain axis and the yarn drawing direction. Since PAN was laterally ordered and did not have strong and sharp 001 reflection, “\( \sigma \)” was unable to be obtain directly. However, it can be derived indirectly from \( hk0 \) reflections of azimuthal scan (182). \( \beta_{hk0} \) is the angle between the yarn axis, and the normal to the \( (hk0) \) planes responsible for the diffracted peak. \( I_{(hk0)} \) is the intensity of azimuthal scan between 0° and 360° of intense reflection of \( hk0 \) plan.

The orientation factors of the nanofibre yarns before and after drawing are given in **Figure 5.17b**. The orientation increased substantially at 1 times drawing, and then gradually increased with the increase in the drawing ratio, which was consistent with literature reports (98, 181). The chain orientation was low in the as-spun fibres, but it can be substantially improved by a small extent of drawing. This also proved that the rapid elongation and solidification during electrospinning hindered the formation of crystalline region of PAN fibre, which resulted in poor crystallinity and chain orientation, while hot drawing could rebuild the crystalline region, and improve the crystallinity and the chain orientation.
**Figure 5.17**, a) XRD profile of as-spun, and 2, 3, 4 and 5 times drawn yarns. The profiles have been offset for clarity. b) Orientation factor of as-spun, and 2, 3, 4 and 5 times drawn yarn derived from Azimuthal scan on the reflection peak at $2\theta = 16.8^\circ$

### 5.6 Mechanical properties

Mechanical properties of PAN nanofibre yarns have been tested using Sifan-3 single fibre tester. As showed in **Figure 5.18a**, the tensile strength and Young’s modulus increased with increasing the drawing ratio until 5 times of drawing. The decrease in the mechanical property after 6 times drawing could be due to the breakage of some fully extended fibres. This result also suggests
that 5 times could be the largest drawing ratio for electrospun PAN nanofibre yarns. The tensile strength and Young’s modulus of 5 times drawn yarns were 362 ± 37 MPa and 9.2 ± 1.4 GPa, respectively, which were much larger than those of as-spun yarns, respectively being 44 ± 5 MPa and 0.5 ± 0.1 GPa.

**Figure 5.18b** shows the typical stress ~ strain curves of nanofibre yarns before and after drawing treatment. The strain at break of as-spun yarn without drawing is 96.8 %, which is almost 6 times larger than that of drawn yarns.

**Figure 5.18**, a) Ultimate tensile strength and Young’s modulus of nanofibre yarns under different drawing ratios, b) typical stress ~ strain curves of nanofibre yarns under different drawing ratios.
5.7 Conclusions

Drawing at a temperature above the glass transition temperature is essential to obtain PAN nanofibre yarns with desired drawing ratio. Tg of PAN nanofibre yarn in hot water and hot air is found to be about 90 °C and 105 °C, respectively. Yarns can be drawn up to 4 times in hot water and 6 times in hot air. In hot air, the elongation speed at ~140 °C shows obvious difference to it at ~105 °C, indicating a possible physical property change in PAN fibres. Higher drawing ratio and more efficient drawing can be achieved at ~140 °C. A crosshead speed of ~7 mm/min is possible when PAN nanofibre yarns are drawn under constant displacement or constant force with a drawing force of 7.5 cN. The yarns became fragile when they were drawn at a temperature above 150 °C.

The yarns after drawing show compact morphology, with a significant decrease in both yarn and fibre diameters, however, uniformity is improved. Both yarn and fibre diameters show a drastic decrease at 2 to 3 times drawing, and a steady decrease at further higher drawing ratios. The uniformity of yarn and fibre improves with increasing the yarn drawing ratio. Although nanofibre has been elongated many times during electrospinning, the PAN molecular chains do not orientated to a high level in the as-spun nanofibres. Post-electrospinning drawing treatment has been found to be an effective way to increase the molecular orientation. The overall molecular orientation increases monotonously with increasing the drawing ratio, while the orientation in the ordered region has reached a high plateau from 2 time drawing. The fibre alignment and molecular orientation of the yarns increase with the increase in
the drawing ratio. The mechanical properties of the post drawn yarn increase in accordance with the improvement of fibre alignment and molecular orientation. Post 5 times hot-air drawn yarn was found to have the highest tensile strength and modulus.
Conclusions and Future Works

6.1 Main conclusions of the thesis

PAN nanofibre yarns have been successfully produced from a setup composing positively and negatively charged electrospinning spinnerets, a rotating funnel and a yarn winder.

During yarn electrospinning, positively and negatively charged fibres are simultaneously deposited onto the large end of a funnel and formed a nanofibre web. By initially stretching the centre of the nanofibre web to form a cone shape and by the funnel rotation, a twisted yarn can be drawn from the apex of the cone. Fibre with suitable wetness and a proper fibre deposition area are most critical to a stable regular shape nanofibre cone. The wetness of the deposition fibre can be controlled by the spinning distance, the longer the spinning distance the drier the fibre would be. However the fibre deposition area increases substantially with the increase in spinning distance. For the PAN solution used in this research, suitable wetness of deposited fibre and a proper deposition area couldn’t be met at same time by using conventional electrospinning. The disc-aided electrospinning enables much more constrained deposition area and condensed fibre deposition than it from conventional electrospinning. Dry fibre and desired deposition area are made possible at same time by using disc-aided electrospinning.
The nanofibre cone is made of fibres electrospun from positively and negatively charged nozzles. In conventional electrospinning, the negatively charged electrospinning jets have a random initial bending before the jet whipping started. The initial random bending of the jet results in bigger diameter but lower density of fibre deposition than it was from the positively charged jet. It is difficult to make stable nanofibre cone from depositions of different diameters and fibre density from positively and negatively charged electrospinning jet. The disc-aided electrospinning under positive and negative voltage polarity had the same jet flying pattern and the resultant deposition area has little difference. Positively and negatively charged electrospun fibres can be evenly distributed on the nanofibre cone. The nanofibre cone is stable during yarn producing process.

The obtained PAN nanofibre yarn has been drawn above its glass transition temperature in wet and dry conditions. Several methods have been utilized to confirm the glass transition temperature of PAN yarns. Yarns are drawn to several times of their original length in hot water or hot dry air by constant force.

Using the same polymer solution, disc-aided electrospinning and conventional electrospinning produce fibres have similar diameters regardless of voltage polarity, although disc-aided electrospinning required higher voltage for electrospinning.

The yarn and fibre diameter, morphology and mechanical properties of the PAN nanofibre yarn are highly affected by the winding rate and the twist level.
The yarn diameter decreases with increasing the yarn winding rate up to 0.66 m/min. The yarn diameter doesn’t change much by further increasing the winding rate. The increase in the twist level improves yarn diameter distribution. The fibres show improved orientation and more compact with increasing the twist level.

Drawing of PAN nanofibre yarn has been carried out above its glass transition temperature for a desired drawing ratio. Tg of PAN nanofibre yarn has been found to be about 90 °C and 105 °C in hot water and hot air, respectively. In hot air, the elongation speed of drawing at ~140 °C is obviously larger than it at ~105 °C. Higher drawing ratio and more efficient drawing can be achieved at ~140 °C. Above 150 °C, the PAN nanofibre yarn became fragile. The PAN nanofibre yarns can be drawn maximum 4 times in 96 °C hot water and 6 times in hot air at 140 °C.

Post drawn yarns show compact morphology and improved uniformity and have a significant decrease in both yarn and fibre diameters. Yarn and fibre diameters decrease drastically at initial 2 to 3 times drawing followed by a steady decrease at higher drawing ratios. The uniformity of yarn and fibre is improved with increasing the yarn drawing ratio. The molecular orientation and crystallinity are not high in as-spun yarn although the fibres have been elongated many times during electrospinning process. The hot drawing could improve the molecular orientation and crystallinity. The molecular orientation in ordered region of PAN fibre reached a high plateau from 2 times drawing while the molecular orientation in amorphous region continuously increases.
with increasing the drawing ratio. With the increase in fibre alignment and molecular orientation, the yarn mechanical property improves. The yarn drawn 5 times of its original length in hot-air has been found to have the highest tensile strength and modulus.

6.2 Future works

Further works related to this project are suggested to be conducted as below:

(1) To better control of yarn morphology and quality, the influences of funnel diameter, shape and disc electrode diameter on the nanofibre cone and the yarn formation, yarn morphology and mechanical properties need to be further examined and optimized.

(2) Compared with yarn production in commercial textile industry, the nanofibre yarn production from current setup is low. Multiple electrospinning spinnerets or needleless electrospinning could be used for increasing yarn production rate.

(3) Continuous drawing of PAN nanofibre yarns under a constant displacement method could be achieved using two rolling systems, which need to be verified experimentally.
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