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NOMENCLATURE

Tg	Glass transition temperature (°C)
T _m	Melting temperature (°C)
[η]	Intrinsic viscosity
η	Shear viscosity (mPa s)
M_{w}	Weight average molar mass (g mol ⁻¹)
D	Diameter
σ	Tensile stress(MPa)
Е	Young's modulus (MPa)
Т	Temperature (°C)
S	Standard deviation
R_{θ}	Rayleigh ratio
dn/dc	Specific refractive index increment
I_{θ}	Scattered intensity,
λ	Wavelength
V	Volume
с	Concentration
d	Distance
d y	Distance Response value
d y n	Distance Response value Number of observations
d y n ρ	Distance Response value Number of observations Density
d y n ρ R ²	Distance Response value Number of observations Density Multiple correlation coefficient

GLOSSARY OF TERMS & ABBREVIATIONS

Names of Polymers and Chemicals

PLA	Poly(lactic acid)
PLLA	Poly(L-lactic acid)
PDLLA	Poly(D-, L-, lactide)
PLGA	Poly(lactic acid-co-glycolic acid)
PGA	Poly(glycolic acids)
PANi	Polyaniline
PE	Polyethylene
PET	Poly(ethylene terephthalate)
РР	Polypropylene
PAN	Polyacrylonitrile
PEO	Polyethylene oxide
PVA	Polyvinyl alcohol
PVP	Polyvinylpyrrolidone
PS	Polystyrene
PCL	Polycaprolactone
PC	Polycarbonate
PMMA	Poly(methyl methacrylate)
PDO	Polydioxanone
DCM	Dichloromethane

DMF	Dimethyl formamide
DBSA	Dodecylbenzene sulphonic acid
TBAB	Tetra butyl ammonium bromide
HFIP	Hexafluoroisopropanol
THF	Tetrahydrofuran
TFAA	Trifluoroacetic acid

Other abbreviations

ANOVA	Analysis of variance
ASTM	American Society for Testing and Materials
AFM	Atomic force microscopy
AHA	Alpha hydroxy acid
CVD	Chemical vapour deposition
DSC	Differential scanning calorimetry
EDS	Energy dispersive X-ray spectroscopy
FTIR	Fourier transform infra-red spectroscopy
FESEM	Field emission scanning electron microscopy
GPC	Gel permeation chromatography
MRA	Multiple regression analysis
MFC	Microfibril reinforced composite
NFC	Nanofibril reinforced composite

NTE	Neural tissue engineering
OA	Orthogonal array
RH	Relative humidity
SEM	Scanning electron microscopy
SEC	Size exclusion chromatography
S/N ratio	Signal to noise ratio
TEM	Transmission electron microscopy
WAXS	Wide angle X-ray spectroscopy

CHAPTER 1

Introduction

Production of synthetic filaments using electrostatic forces (electrospinning) has been known for over a century. This technique has been used to convert a large variety of polymers into nanofibres and regarded as the only process capable for mass production of nanofibrous mat or nanotextile. A high electric field is applied to the droplet of a fluid coming out from the tip of a needle, which is connected with a positive electrode. This leads to droplet deformation and when the voltage applied overcomes the surface tension of polymer solutions, jets of polymers are ejected from the tip of the nozzle and fly towards the collectors. If there is a break-up, electrospray occurs. At first glance, electrospinning gives the impression of being a very simple and, therefore, easily controlled technique for the production of fibres with dimensions down to the nanometer range. Upon closer inspection, it becomes clear that the electrospinning process is intricate and depends on a number of factors relating to the polymer solution to be elctrospun and process related parameters. These include, inter alia, the types of polymers, viscosity of solutions, polarity and surface tension of the solvents, electric field strength, the distance between spinnerets and collectors and the ambient conditions of the spinning area.

Many polymers have been successfully electrospun into nanofibres including poly(lactic acid) (PLA), nanofibres with diameters less than even 10 nm. Nanofibres are of industrial and scientific interests due to their large aspect (length-to-diameter) ratios and high surface areas per unit volume. The major applications of these nanotextiles include the areas of tissue engineering (scaffolds), drug delivery media, filtration media and clothes protection. To enable the nanofibrous mat in a variety of applications including those in the biomedical field, fibres need to be obtained in a continuous form with considerably fine diameters having minimal variation and with minimum area occupied by beads. Beads are non-porous polymeric material and the main demerit of electro spun fibres.

The relationship between processing parameters and microstructures of nanofibrils are still not well understood. If the field strength is too high, increased instability of the jet may lead to bead formation. On the other hand, if the distance between the needle tip and the collector is such that the field gradient is enough, there are fewer beads formed as the electric field provides sufficient stretching force to the jet. However, at larger distances the fibre diameter increases due to the decrease in the electric field gradient, resulting in less stretching of the fibres. Another factor that may influence the diameter of the fibre is the flight time of the electrospinning jet - a longer flight time allows more time for the fibre to elongate before it is deposited on the collector plate. Similarly shorter flight time makes less elongation, generating coarse fibres. It must be acknowledged that the integration of nanofibres into useful devices requires fibres of wellcontrolled size and uniformity as well as reproducibility of locating them in specific positions. The ability to do so remains a major challenge, and effective parametric analyses are needed to achieve products with the required characteristics. Taguchi method of experimental design offers a scope for selecting the optimal levels of process parameters with minimum number of experiments carried out, thus significantly reducing the time required for experimental investigation.

The present research has included poly(L-lactic acid) (PLLA) as the electrospinnable polymer. It is a biodegradable, thermoplastic and aliphatic polyester derived from renewable resources. A common product, PLA (polylactide) polymer 3051D of NatureWorks[®]LLC, suitable for different fabrication purposes (including injection moulding, sheet extrusion, blow moulding,



thermoforming, film forming or fibre spinning), has been dissolved in the mixture of dichloromethane (DCM) and dimethyl formamide (DMF) and successfully electrospun resulting in fibre diameters ranging from 50 nm to about 400 nm, depending on the proportion of the solvents and polymer concentration.

The main goals of this study are manufacturing and characterisation of the electro spun PLLA nanotextile with uniform and bead-free fibres, so that the product will be acceptable for various purposes. These are achieved via a series of more detailed objectives:

- Demonstration of the possibilities of making bead-free nanofibres with a good range of diameters through electrospinning. It has been shown how the morphology of electrospun nanofibre can be tailored by manipulating the processing parameters.
- 2. Establishment of a desirable set of four control parameters, namely the concentration and feed rate of polymer solution, applied voltage, and the distance between the collector and the needle in the early stage of reserach. The target outcomes are chosen as the nanofibre diameter with minimal variation and minimum mat area occupied by the beads. An additional important parameter in the form of relative humidity has been added later in the study to get an overall idea of the effects of process variables.
- 3. Achievement of a better understanding of the relationship between electrospinning parameters and the morphology of the electrospun product; a systematic study with important parameters with broader levels is essential and the predictive models are developed using multiple regression analysis (MRA).
- 4. Investigation of how operating parameters and solution properties affect the electrospinning process and the resulting fibre morphology. An understanding of the process–structure–property relationship is derived for engineering polymer nanofibres to meet the demands of applications.
- 5. Investigation of the accuracy of the derived model with the necessary experimental results. Suitability of the model is explained for reliable predictions prior to mass productions.

Significant numbers of experiments and tests have been performed using different solvent systems and a wide range of polymer concentrations, processing techniques and manufacturing parameter settings. The data obtained have been examined using conventional techniques, as well as more complex experimental design methodologies (Taguchi analysis).

In Chapter 2, an overview of nanotechnology and nanocomposites is presented before a detailed review of the literature relating to nanofibres is given including different ways of making nanofibres and its applications. This is followed by an analysis of the techniques employed during electrospinning and its history and present scenario. Finally, quality of the nanofibres is described with an in-depth discussion of the phenomena associated with making uniform nanofibres and various processing parameters are described. A brief introduction of PLA as an effective polymer for electrospinning is added as well.

Chapter 3 outlines the materials and methodologies used during electrospinning of PLLA throughout this thesis. It provides details of the solution making, electrospinning process along with the various microscopy and analysis techniques. The technique of development of a novel PLLA based conducting nanofibrous mat through controlled electrospinning has been described.

Before working explicitly on parametric analysis, the Taguchi methodology is described in Chapter 4. Experiments on formation of nanofibres and the effects of many manufacturing parameters are examined, such that the importance of each to the final properties of the material is estimated by a thorough analysis. Finally, a set of suitable spinning parameters have been described for achieving best performances according to their requirements.

Chapter 5 examines the properties of the nanofibrous mat followed by different test results of thermal behaviour, crystallinity and mechanical strength testings. It includes the characterisation of polymer solution with the determination of viscosity, surface tension and conductivity as well. Chapter 6 utilises multiple regression analysis to model the effects/contributions of different factors. A combination of standard statistical tests and scanning micrographs are used to evaluate the proposed models.

Following these chapters, the advantages of electrospinning using single needle for research and its limitations for mass scale have been discussed in Chapter 7. The production techniques of mass scale have been described with an introduction to a syringe pump with multiple syringes.

At the end, all of this research is tied together in a 'Conclusions' chapter. Chapter 8 summarises the published work of the results from this study and additional thoughts for further research are also expressed.

CHAPTER 2

Literature Review

2.1 Nanomaterials and Composites

2.1.1 Definition of nanomaterials

It is essential at the beginning of this review to define what the nanomaterials are. These can be metals, ceramics, polymeric materials, or composite materials. Nanomaterials are those with structural features (particle size or grain size, for example) of at least one dimension in the range of 1-100 nanometer (nm); 1 nm is 10^{-9} m [1, 2]. Popularly, nano is also used as an adjective to describe objects, systems, or phenomena with characteristics arising from a nanometer-scale structure. While "micro" has come to mean anything small, nano emphasises the atomic granularity that produces the unique phenomena observed in nanoscience [3].

Chemistry deals with molecules which have dimensions of the order of 0.1 to 10's of nanometres. Polymers have dimensions which are typically 10's to 100's of nanometres. Combining materials which have one or more dimensions in the nano range creates a nanomaterial [3]. One nanometer spans 3-5 atoms lined up in a row. Nanomaterials are not simply another step in miniaturisation, but a different arena entirely; the nano-world lies midway

between the scale of atomic and quantum phenomena, and the scale of bulk materials [2, 4]. Although widespread interest in nanomaterial is recent, the concept was raised over 50 years ago. Physicist Richard Feynman delivered a talk in 1959 entitled "There's Plenty of Room at the Bottom", in which he commented that there were no fundamental physical reasons that materials could not be fabricated by manoeuvring individual atoms [5]. Dream statement has been realised in less than half a century by consistent efforts and significant contributions from the scientific community across the globe [2, 5, 6]. Progress made in the last few decades has proven the abysmal nature of matter as a whole and the ability to achieve exciting technological advancements for the benefit of mankind.

2.1.2 What is nanotechnology?

At the point of writing, nanotechnology refers to the science and engineering concerning materials, structures and devices where one of the dimensions is 100 nm or less [1, 2]. The world of materials is rapidly progressing with new and trendy technologies, and obviously novel applications. Nanotechnology is among these modern and sophisticated technologies, which is creating waves in modern times. As an advanced technology, it deals with the synthesis of nano-particles, processing of nanomaterials including nanofibres and their applications [7]. The excitement surrounding nanoscale science and technology gives us unique opportunities to develop revolutionary materials. Nanoscale science and technology is a young field that encompasses nearly every discipline of science and engineering. It is a new branch of materials research that is attracting a great deal of attention because of its potential applications in areas such as electronics, optics, ceramics, magnetic data storage and polymer nanocomposites. The unique properties and improved performance of nanomaterials are determined by their sizes, surface structures and inter-particle interactions [8].

2.1.3 Why nanotechnology is required

Wave like (quantum mechanical) properties of electrons inside matter and atomic interactions are influenced by material variations on a nanometer scale. By creating nanometer-scale structures, it is possible to control the fundamental properties of a material, such as its melting temperature, magnetic properties, charge capacity, and even its colour, without changing the material's chemical compositions. Making use of this potential will lead to new, high performance products and technologies that were not possible before [7].

Nano-Tex, the largest manufacturer of nanotextiles, claims: "We engineer molecules to improve the properties of your favorite fabrics" [9]. Their technological breakthroughs are revolutionising the textile industry. They use nanotechnology to transform the molecular structures of fibres and create fabrics that offer unsurpassed performance and comfort. Their treatments are small enough to attach to individual fibres, delivering superior performance characteristics without compromising the look, feel or comfort of the fabric. Instead of overwhelming the fabric with a heavy coating, Nano-Tex products are enhanced through the use of nanotechnology: tiny molecules that permanently attach to fibres without hampering the fabric weave to add superior performance characteristics maintaining the look, feel or comfort of the fabric or comfort of the fabric fabric weave to add superior

Surfaces and interfaces are very important in explaining the behaviour of a nanomaterial. In bulk materials, only a relatively small percentage of atoms will be at or near a surface or interface (like a crystal grain boundary). In nanomaterials, the small feature size ensures that many atoms, perhaps half or more in some cases, will be near interfaces. Surface properties such as energy levels, electronic structure, and reactivity can be quite different from interior states, and give rise to quite different material properties. The birth of the concept is usually linked to a speech by Feynman at the meeting of the American Physical Society held in December 1959 [5, 10], where he asked, "What would happen if we could arrange the atoms one by one the way we want them?"

2.2 Nanocomposites

Composites are widely used in such diverse areas as transportation, construction, electronics, consumer and biomedical products. They offer unusual combination of stiffness, strength and weight that are difficult to attain separately from the individual components [11].

Nanomaterials can be classified into nanostructured materials and nanophase/nanoparticle materials. The former usually refer to condensed bulk materials that are made of grains (agglomerates) with grain sizes in the nanometer size range whereas the latter usually constitute dispersive nanoparticles [8]. Nanostructured materials and nanocomposites are extremely important materials for a wide range of applications. These materials have experienced enormous growth in size and sophistication over the past two decades in terms of both the scientific base and technological and commercial developments. With the study of nano-sized materials, devices and composites, researchers can find ways to make stronger materials, detect diseases in the blood stream, build extremely tiny machines, generate light and energy, and purify water [12]. The development of composite materials with nanostructured reinforcements is well documented; such composites may have metallic, ceramic or polymeric matrics and be developed in bulk or thin film form. In polymer nanocomposites, the reinforcements are typically selected to increase the strength of the material and many workers have demonstrated the benefits of adding exfoliated clays, nanoparticles and even carbon nanotubes [13].

The most advanced nanotechnological fabrication process is microelectronic fabrication, where thin film coatings and lithography are used to create micro - and nano-sized features on computer chips [3]. There is heightened concern today that the development of nanotechnology will negatively impact public health, and it is indisputable that engineered nanomaterials are a source of nanoparticle pollution when not safely manufactured, handled, and disposed of or recycled. Nanoparticles are comparable in size to viruses, where the smallest have dimensions of tens of nanometers [for example, a human immunodeficiency virus (HIV particle) is 100 nm in diameter], and which in the emerging science of nanotechnology might be called "nanoorganisms" [3]. Like viruses, some nanoparticles can penetrate lung or dermal (skin) barriers and enter the circulatory and lymphatic systems of humans and animals, reaching most

bodily tissues and organs, and potentially disrupting cellular processes and causing disease. Research on humans and animals indicates that this ability results primarily from their small size, which allows them to penetrate physiological barriers and travel within the circulatory systems of a host [3].

2.3 Nanomechanics and Nanosciences

Nanotechnology links to both deterministic classical mechanics and chaotic quantum mechanics [4, 14]. Classical mechanics is the mechanics governing the motions of all the objects that can be seen with naked eyes. This mechanics obeys deterministic laws (Newton's law) and it can be controlled to a great extent. On the contrary, quantum mechanics concern controlling motions of electrons, protons and neutrons, which is completely probabilistic. It does not know about the motion of electrons except there is a probability that the electron may be here or there [4, 14]. Nanotechnology is the grey area between classical mechanics and quantum mechanics.

Atoms are roughly angstroms (Å) in size: a hydrogen atom is about 1 Å, a carbon atom is about 2 Å and the diameter of an oxygen atom is about is about 1.75 Å [4]. One Å is one ten billionth of a meter or one-tenth of a nanometer. On the nanoscale quantum-like phenomena can be observed. Making and manipulating matter on the sub-100 nm length scale is a grand challenge for both scientists and engineers. From an engineering standpoint, the sub-100 nm scale is extraordinarily small, and many of the tools that are used routinely to do microfabrication cannot be used for nanofabrication. However, from the chemist's point of view, this length scale, especially above 10 nm, is extraordinarily large. Chemists are really "Angstrom-technologists", not nanotechnologists [15]. In our experiments we find uncertainty: under almost the same conditions we cannot obtain exactly the same nanofibres or beads or microspheres. This is followed by Heisenberg's uncertainty principle in quantum mechanics [4].

Nanotechnology is the study and development of materials at nano levels. Nanoscience is one of the few growing scientific fields of this decade that is enjoying broad based support from governments and industries. The ability to manipulate individual molecules and understand their characteristics at atomic levels has made this field very promising. Electronics and semiconductor industries have been harnessing the potential of nanotechnology to a major extent [16]. Other fields, such as biomedical, polymer, and fibre science, are yet to realise the full potential of nanotechnology. To enable the fullest exploitation of nanotechnology in fibre and polymer science disciplines, a timely and in-depth review of research on nanofibres is essential. Government agencies and nongovernmental agencies have given high priority to both fundamental and applied nanoscience research activities. As elaborated in this review, nanofibres, due to their high surface area and porous structure, have applications in many different fields, such as protective textiles, filtration, drug delivery and tissue engineering among others. The production of nanofibres is still at the laboratory level [16], and it is extremely important to make efforts towards scaled-up commercialisation. A thorough investigation on the scaling up of nanofibre technology is necessary for the growth and development of this field.

2.4 Nanofibres

2.4.1 Introduction

Nanofibre is a nanomaterial in view of its diameter and can be considered a nanostructured material [1]. The term 'fibre' is more common and has been considered from various professional viewpoints. Botanists identify this term with elongated thick-walled cells, biochemists use the term 'fibre' as indigestible plant matter, however textile industry views fibre as natural and synthetic filament such as cotton or nylon, capable of being spun into a yarn or thread [1]. The textile viewpoint is more common and relevant with the present research of polymeric nanofibres. From a geometrical standpoint, an elongated threadlike object or structure produced from different polymers in nanometric range is today's hot topic as nanofibre.

Nanofibres are the ultra-fine solid fibres notable for their very small diameters (lower than 100 nm), their large surface area per unit mass and small pore size [1, 17]. When the diameters of polymer fibre materials are shrunk from micrometers (e.g. $10-100 \ \mu$ m) to submicrons or nanometers (e.g. $10 \times 10^{-3} - 100 \times 10^{-3} \ \mu$ m), there appear several remarkable characteristics, such as very large surface area to volume ratio (this ratio for a nanofibre can be as large as 10^3 times of that of a microfibre). It permits flexibility in surface functionalities and provides superior mechanical performances compared to any other known form of the material [18]. These outstanding properties make the polymer nanofibres to be optimal candidates for many important applications.

Nanofibres are of industrial and scientific interest due to their large aspect (length-to-diameter) ratios, high surface areas per unit volume and the unique nanometre scale architecture built by them. Their potential applications are tissue engineering scaffolds, drug delivery media, filtration media, protecting clothes, composite reinforcements and many more [1, 18, 19]. It is well known that the properties and internal molecular structure of polymer solids are greatly affected by the processing conditions. Therefore, an understanding of the process–structure–property relationship is essential for engineering polymer nanofibres to meet the demands of applications [19, 20].

2.4.2 Different ways of making Nanofibres

A number of processing techniques such as drawing [21], template synthesis [22, 23], phase separation [24], self-assembly [25, 26], techniques of micro- and nanofibrillar composites (MFC/NFC) [27, 28, 29], and electrospinning [1, 18-20, 30, 31], have been used to prepare polymer nanofibres in recent years.

The drawing is a process similar to dry spinning in the fibre industry, which can produce long single nanofibres one-by-one [21]. A millimetric droplet of a material in solution was deposited on a silicon dioxide (SiO₂) surface and allowed to evaporate. The solution became more

concentrated at the edge of the droplet after a few minutes of evaporation due to capillary flow. A micropipette with a diameter of a few micrometers was dipped into the droplet near the contact line with a micromanipulator. The micropipette was then withdrawn from the liquid and moved at a speed of approximately 100 um/s, resulting in a nanofibre being pulled. The pulled fibre was deposited on the surface by touching it with the end of the micropipette. The process is simple [18], however, only a visco-elastic material that can undergo strong deformations while being cohesive enough to support the stresses developed during pulling, can be made into nanofibres through drawing. Added to that, it is a laboratory-scale process, in which the nanofibres have to be produced one by one [18, 21, 3].

The template synthesis [22, 23], as the name suggests, uses a nanoporous membrane as a template to make nanofibres of solid (a fibril) or hollow (a tubule) shape. The membranes contain cylindrical pores with uniform diameters that run through the complete thickness of the membranes, which is typically of the order of 5-50 mm. Each of these pores can be considered as a beaker in which a nanostructure of the desired material is electrochemically or chemically synthesized by oxidative polymerisation. As these pores are cylindrical, a nanocylinder of the desired material is obtained in each pore. Depending on the material and the chemistry of the pore wall, the nanocylinders may be fibrils or tubules. Nanofibres of different diameters can be produced with different templates. The template synthesis method has been used to prepare nanotubules and nanofibrils of polymers, metals, semiconductors, and carbons. However, it is a laboratory scale process limited to the conversion of specific polymers directly into nanofibre structures [18, 22, 23].

The phase separation technique consists of dissolution, gelation and extraction using a different solvent, freezing, and drying, resulting in a nanoscale porous foam [31]. The main mechanism in this process, as the name suggests is the separation of phases due to physical instability. The polymer is dissolved in a solvent to make a homogeneous solution of the required concentration. The solution is transferred to a refrigerator set at the gelation temperature, which is chosen based on the polymer concentration. Once the gel is formed, it is immersed in distilled water for solvent exchange. Then the gel is removed from the distilled water, blotted with filter paper, and then transferred to a freeze-drying vessel and freeze-dried, resulting in a nanofibre matrix.

Various porous structures including porous nanofibre matrices can be easily obtained with this technique by adjusting the thermodynamic and kinetic parameters [18, 32]. The process takes a relatively long period of time to transfer the solid polymer into a nano-porous foam.

The self-assembly is a process [25, 26] in which individual, pre-existing components organise themselves into desired patterns and functions. In general, the self-assembly of nanofibres refers to build-up of nanoscale fibres using smaller molecules as basic building blocks. Liu et al. prepared the nanofibres from dendrimer by casting the dilute solution on a substrate [33]. Two possibilities for the development of dendrimer nanofibres are proposed. Dendrimer aggregates could preform in solution, deposit, and grow into nanofibres on the surface of substrate, or dendrimer molecules could nucleate and grow into nanofibres directly on the substrate surface. Dendrimer nanofibres have both long-term stability and high thermal stability. However, similarly to the phase separation, the self-assembly is time consuming in processing continuous polymer nanofibres.

One recent technique of producing micro- and nanofibrililar composites (MFCs and NFCs) that was described by Shields et al. at the Centre for Advanced Composite Materials (CACM), The University of Auckland (UoA) [27]. MFCs or NFCs are created by blending two homopolymers (virgin or recycled) with different melting temperatures e.g. polyethylene (PE) and poly(ethylene terephthalate) (PET), and processing the blend under certain thermo-mechanical conditions to create in situ fibrils of the polymer that has the higher-melting temperature. These resulting fibrillar composites have been reported to possess excellent mechanical properties and can have wide ranging applications with suitable processing under controlled conditions [27, 28, 29].

Electrospinning has been used to convert a large variety of polymers into nanofibres and may be the only process that has the potential for mass production [18, 31]. Production of synthetic filaments using electrostatic forces (electrospinning) has been known for more than one hundred years. The electrospinning process, in its simplest form, Fig. 2-1, consists of a pipette or a syringe to hold the polymer solution, a collector and a DC voltage supply in the kilovolt range. There is a positive electrode attached to the polymer solution, and a negative electrode attached to the grounded collector. The polymer droplet from the tip of the pipette is drawn into a jet because of the applied high voltage. The charged jet is ejected from the tip at a critical voltage when the repulsive electrostatic force overcomes the surface tension of the polymer fluid. The charge causes the jet to bend in such a way that every time the polymer jet loops, its diameter is reduced due to the evaporation of the solvent in the polymer jet. The jet diameter is eventually reduced to nano-dimensions before it reaches the collector. Once the polymer jet solidifies, the produced nanofibres are collected as a web or mat on the surface of a collector. Although electrospinning appears to be straightforward, it is a rather intricate process that depends on a



Fig. 2-1: Basic schematic diagram of electrospinning process [17]

Laboratory or industrial process	Repeatability	Ease of processing	Advantages	Limitations
Laboratory	Yes	Easy	Simple process	Discontinuous
Laboratory	Yes	Moderately easy	Simple process. Fibres of different diameters can be produced by using different templates.	Limited to a few polymers.
Laboratory	Yes	Easy	Simple process. Batch-to-batch consistency is easily achieved. Mechanical properties of the mat can be tailored by adjusting polymer concentration.	Limited to a few polymers. Nanofibre matrix is directly fabricated.
Laboratory	Yes	Difficult	Good for obtaining smaller fibres	Complex process. Limited to a few polymers. Nanofibre structure is directly fabricated.
Laboratory; Potential for industrial processing	Yes	Relatively long process	Composites have excellent mechanical properties and can have wide ranging applications	Indirect method. It needs a number of machines.
Laboratory; Potential for industrial processing	Yes	Moderately easy	Simple process and straight forward method. Cost effective. A large variety of polymers can be electrospun in nanofibres with fine and uniform diameter.	Jet instability may occur.
	Laboratory or industrial process Laboratory Laboratory Laboratory Laboratory Laboratory; Potential for industrial processing	Laboratory or industrial processRepeatabilityLaboratoryYesLaboratoryYesLaboratoryYesLaboratoryYesLaboratoryYesLaboratoryYesLaboratory; Potential for industrial processingYesLaboratory; Potential for industrial processingYes	Laboratory or industrial processRepeatability processingEase of processingLaboratoryYesEasyLaboratoryYesModerately easyLaboratoryYesEasyLaboratoryYesDifficultLaboratoryYesDifficultLaboratory: Potential for industrial processingYesRelatively long processLaboratory: potential for industrial processingYesModerately easy	Laboratory or industrial processRepeatabilityEase of processingAdvantagesLaboratoryYesEasySimple processLaboratoryYesModerately easySimple process. Fibres of different diameters can be produced by using different templates.LaboratoryYesEasySimple process. Batch-to-batch consistency is easily achieved. Mechanical properties of the mat can be tailored by adjusting polymer concentration.LaboratoryYesDifficultGood for obtaining smaller fibresLaboratory;YesRelatively long processComposites have excellent mechanical properties and can have wide ranging applicationsLaboratory;YesModerately easySimple process and straight forward method. Cost effective. A large variety of polymers can be electrospun in nanofibres with fine and uniform diameter.

 Table 2-1: Comparison of the various processing methods for polymer nanofibres [1]

multitude of molecular, process related, and technical parameters [20, 34]. It is vital to produce nanofibres in a controlled manner so that the process gives high quality fibres with precise fibre

morphology. Various processing methods have been described in Table 2-1, with advantages and limitations as well [1].

2.4.3 Application of nanofibres

Polymer fibres with diameters in the submicrometer range ($<1 \mu$ m) are of considerable interest in a variety of applications. The reduction of the fibre diameter from the micrometer to the nanometer range results in a fibre that has a larger surface area per unit mass on the order of 10³ m² g⁻¹ and permits easier addition of surface functionalities [18]. As a result, nanofibres have been attracting the attention of global materials research these days primarily due to their enhanced properties, which are required for applications in specific areas like filter media and textiles, protective clothing, medical industries that include scaffolds for tissue engineering, wound healing and drug delivery among others. Nanofibres have significant usages in sensors and as reinforcements in composite materials.

Filter and textiles

Both filter and textile applications of nonwoven materials have the common feature that the porous structure of the material controls its properties and functions. Polymeric nanofibres have been used in air filtration applications for more than a decade [35]. Filtration efficiency or capture efficiency of filter media has been shown to be inversely proportional to the diameters of the fibres in the filters. Because of the very high surface area-to-volume ratio and the resulting high surface cohesion of nanofibres, tiny particles on the order of less than 0.5 mm are easily trapped in the nanofibre mats [18]. Polymer nanofibre mats can also be electrostatically charged to provide them with the ability to capture particles by electrostatic attraction without an increase in pressure drop, leading to an improvement in filtration efficiency. For environmental engineering, the function of nanofibrous membranes is to filter moisture and dusts. Unclean air which contains bacteria can also be purified using nano-sized fibrous membranes. If the surface of nanofibres is chemically modified to kill bacteria, this filter media is useful to protect people in residences and offices. Gibson et al. have applied polyurethane and nylon 6 nanowebs over

open cell foams and carbon beads and tested there for air flow resistance. It has been concluded that the airflow resistance, filtration efficiency, and pore sizes of nonwoven filter media can be easily altered by coating the lightweight electrospun nanofibres [36]. Doshi et al. have evaluated composites of nanofibres with spunbond and meltblown fabrics for filtration characteristics [37].

Nonwovens composed of nanofibres can be used in combination with conventional textiles (for example, as interlinings) to modify the properties of the textiles. The objective can be to increase the wind resistance, to regulate the water-vapor permeability, to optimise the thermal insulation behaviour, or to give the textile a specific functionality (such as the lotus effect, aerosol filtering, or protection against chemical or biological hazards) [34]. The thermal insulation of nonwovens is mainly a result of the limited diffusion of air molecules in the materials. The thermal insulation increases significantly with decreasing pore size if the pore diameter of the nonwoven is 10–100 times smaller than the mean free path of the gas molecules (about 70 nm for air at normal pressure) [34]. General Motors Company has been working on nanofibres for different composite applications because of its scratch/wear resistance, low temperature ductility, low flammability, and recyclability [38].

Medical Applications

Nanostructured polymers in the form of nanofibres, hollow nanofibres, core-shell nanofibres, nanotubes, or nanorods have many possible applications in medical industries. The main reason for this wide applicability is that the nanoscale is particularly relevant for biological systems, because proteins, viruses, and bacteria have dimensions on this order [34]. Many viruses, for example, the tobacco mosaic virus or the Marburg virus, have the shape of a nanotube [34]. The potential applications of these nanofibres include areas e.g. tissue engineering (scaffolds), drug delivery media and wound healing.

Tissue engineering

Tissue engineering is an interesting field of application of polymer nanofibres. Tissue scaffolds are utilised to repair damaged human tissue. Seeded cells are adhered and grow on tissue scaffolds immersed in the nutrient culture media and the scaffolds with cells are implanted at the defective area. Researchers around the globe have used various biocompatible and biodegradable

synthetic polymers including poly(lactic) and poly(glycolic) acids (PLA and PGA, respectively) and their copolymers (PLAGA), polycaprolactone (PCL), polydioxanone (PDO), and so on for scaffold fabrication [31, 34, 39]. Electrospun nanofibrous structures meet the essential design criteria of ideal engineered tissue scaffolds based upon their abilities to support and guide cell growth. For tissue-engineering applications, Li et al. have developed an electrospun structure, composed of poly (D, L-lactide-co-glycolide) fibres ranging from 500 to 800 nm in diameter [40]. The structure features a morphologic similarity to the extracellular matrix of natural tissue, which is characterised by a wide range of pore diameter distribution, high porosity, and effective mechanical properties [17, 19]. Matthews et al. studied how electrospinning can be adapted to produce tissue-engineering scaffolds composed of collagen nanofibres (a matrix composed of 100 nm fibre) [41]. The use of polymer nanofibres for biomedical applications is another active research area. In a recent publication, an electrospinning method was used by Zong and coworkers to fabricate bioabsorbable amorphous poly (D, L-lactic acid) (PDLA) and semicrystalline poly(L- lactic acid) (PLLA) nanofibre non-woven membranes for biomedical applications [42]. Textiles made of nanofibres from biodegradable polymers may be helpful in adjusting the degradation rate of a specified biomaterial under in vivo environment [18]. Lannutti et al. has pointed out that an ideal scaffold must satisfy a number of often conflicting demands: (1) appropriate levels and sizes of porosity allowing for cell migration; (2) sufficient surface area and a variety of surface chemistries that encourage cell adhesion, growth, migration, and differentiation and (3) a degradation rate that closely matches regeneration rate of the desired natural tissue [43].

Wound Healing

Another interesting application of electrospun nanofibres is the treatment of large wounds such as burns and abrasions [44, 45]. It is found that these types of wounds heal particularly rapidly and without complications if they are covered by a thin web of nanofibres, in particular, of biodegradable polymers. Such nanowebs have enough pores to assure the exchange of liquids and gases with the environment, but have dimensions that prevent bacteria from entering. Mats of electrospun nanofibres generally show very good adhesion to moist wounds [34]. Furthermore, the large specific surface area of up to 100 m² g⁻¹ is very favorable for the adsorption of liquids and the local release of drugs on the skin, making these materials suitable
for application in hemostatic wound closure [31, 34]. Compared to conventional wound treatment, the advantage is that scarring is prevented by the use of nanofibres [34, 42]. Substances, e.g. soluble drugs, antibacterial agents, were also added for wound healing or functionalising the fibres. A skin mask was produced by directly electrospinning fibres onto the skin surface in order to protect and heal wounds eventually [46]. Textiles made of nanofibres from biodegradable polymers may be helpful in adjusting the degradation rate of a specified biomaterial under *in vivo* environment [18].

Drug delivery

Nanofibre mats due to their high functional characteristics find application as drug carriers for the drug delivery system. Controlled delivery of drugs at a defined rate over a definite period of treatment is possible with biocompatible delivery matrices of either biodegradable or nonbiodegradable polymers. Kenawy et al. investigated the drug delivery potential of electrospun polymers by spinning poly(ethylene*co*- vinyl acetate) (PEVA) and PLA with ethanol and tetracycline hydrochloride as the model drug; the release of tetracycline from electrospun mats was found to be much greater than from cast films. They observed that the electrospun PEVA and 50/50 PLA/PEVA mats gave very smooth release of tetracycline over a period of five days [47]. Researchers have recently focused on the usage of nanofibre membranes that encapsulate medical drugs instead of conventional polymeric materials.

Protective clothing

These days, the worldwide threat of chemical and biological agents by hostile military and terrorist groups has been growing. Protective clothing for military personnel is expected to help maximise the survivability, sustainability, and combat effectiveness of soldiers against extreme weather conditions, ballistics, and nuclear, biological, and chemical warfare [18]. Current protective clothing containing charcoal absorbents has limitations related to weight and water permeability. So a lightweight, breathable fabric, permeable to both air and water vapour, insoluble in all solvents, and highly reactive to deadly chemical agents, is desirable. Such functional and smart clothing for military personnel has been discussed by a few researchers [48]. Gibson et al. have analysed the possibility of using thin nanofibrous layers over the conventionally used nonwoven filtration media for protective clothing [36].

Sensors

The role of sensor is to transform physical and chemical responses into an electrical signal based on the targeted applications. Electrospun polymer nanofibres have been investigated as gas sensors, chemical sensors, optical sensors and biosensors so far, possessing high sensitivity due to the high surface area of nanofibres. Electrospun poly(lactic acid-co-glycolic acid) (PLGA) nanofibre films have been used as a new sensing interface for the development of chemical and biochemical sensors [49, 50]. Highly sensitive optical sensors based on electrospun fluorescent poly(acrylic acid)-poly (pyrene methanol) nanofibre films have also been reported [51, 52].

Other uses

Electrospinning can also be used to create biocompatible thin films with useful coating design and surface structure. These films can be deposited on implantable devices in order to facilitate the integration of these devices with the recipient body. Silk-like polymers with fibronectine functionality (extracellular matrix proteins) have been electrospun to make biocompatible films used on prosthetic devices, aimed for implantation in the central nervous system [53]. Recently biodegradable PLLA based conducting nanofibrous mat has been manufactured, which may be of special interest in tissue engineering [54]. There has also been a report on encapsulation of particles into electrospun polymeric nanofibres [55]. This was achieved by adding insoluble particles, such as gold, pollen spore, algimate to the polymer solution.

Fibre reinforced polymer composite materials have been utilised in aerospace, automobile, sports items and electrical products because of the superior structural properties such as high modulus and strength to weight ratios which cannot be obtained by using single material. Bergshoef and Vancso [56] have fabricated a nanocomposite from electrospun nylon-4,6 nanofibrous mats and epoxy. The nanofibre mats were impregnated with an epoxy resin by dipping them into the diluted resin and then cured at room temperature to produce composites. Tensile tests were performed for the composite and the matrix films, and it was reported that both stiffness and strength of the composite were significantly higher than those of the matrix films, although the fibre content was low (3.9 - 4.6%). Glass fibres, carbon fibres, and poly(p-phenylene terephthalamide) fibres are used for the reinforcement of synthetic materials in many technical products [34]. Another trial for composite reinforcements is carbon nanotube/polymer composite

nanofibres. The idea is that polymer nanofibre itself cannot achieve high mechanical strength and hence carbon nanotube with excellent stiffness and strength has been combined with polymer nanofibres [1], which are currently undergoing a surge in development. The field of polymer nanofibres is relatively new and it is extremely important to make efforts towards scaled-up commercialisation.

2.5 Electrospinning

2.5.1 Introduction

Production of synthetic filaments using electrostatic forces (electrospinning) has been known for several decades. It is currently the only technique that allows the fabrication of continuous fibres with diameters down to a few nanometers. This technique is applicable to virtually every soluble or fusible polymer including polymer alloys, and polymers loaded with chromophores, nanoparticles, or active agents, as well as to metals and ceramics [34]. The electrospinning process, in its simplest form, Fig. 2-1, consists of a pipette or a syringe to hold the polymer solution, a collector and a DC voltage supply in the kilovolt (kV) range. The tensile force is generated by the interaction of the applied electrical field with the electrical charge carried by the polymer solution jet rather than by the spindles and reels used in conventional spinning [57]. As the solution jet travels, the solvent evaporates to form a charged polymer fibre, which is elongated by an electrical force and attracted to the collecting plate, Fig. 2-1, with opposite polarity. While the electrospinning technique has been known for about 70 years, there has been a recent renewed interest in the technique since electrospun fibres have started finding applications in both nanotechnology and biotechnology [30].



2.5.2 History of electrospinning

The application of electric charge to break up liquids into small particles has been well known for over a century. The electrospinning process utilises a high voltage source to inject a charge of a certain polarity into a polymer solution or melt, which is then accelerated towards a collector of opposite polarity. In 1745, Bose described aerosols generated by the application of high electric potentials to drops of fluids [58]. In 1882, Lord Rayleigh investigated the question of how much charge would be needed to overcome the surface tension of a drop [60]. Later, the first devices to spray liquids through the application of an electrical charge were patented by Cooley and Morton, in 1902 and 1903 [60-62].

The origin of electrospinning as a viable fibre spinning technique can be looked back to the early 1930s. In 1934, Formhals patented his first invention relating to the process and the apparatus for producing artificial filaments using electric charges [30]. Using this apparatus, Formhals was able to successfully spin cellulose acetate fibres using an acetone/alcohol solution as the solvent. While the invention of Formhals did show significant improvement over earlier electrospinning methods, there still existed some disadvantages. Due to the close proximity of the collector to the charged polymer solution, the solvent could not completely evaporate before the fibre jet reached the collector, resulting in the formation of a loose web structure. Another consequence of incomplete solvent evaporation was, that the fibres tended to stick to the collector as well as to each other, making removal problematic. Thus, in a second patent Formhals detailed a new process in which, distance between the spinning and collecting sites had been increased thus eliminating many of the problems seen with his earlier apparatus [63]. In his second patent, Formhals also described the use of multiple nozzles for the simultaneous spinning of a number of fibres from the same polymer solution as well as a means to direct the fibre jets towards the collector. In 1940, Formhals patented a new process, in which a polymer solution was directly electrospun onto a moving base thread to generate composite fibres [64].

Following the work of Formhals, the focus turned to developing a better understanding of the electrospinning process. After 30 years, Taylor published his work examining how the polymer droplet at the end of a capillary behaves when an electric field is applied [65]. In his studies he

found that the pendant droplet develops into a cone (now called the Taylor cone) when the surface tension is balanced by electrostatic forces. He also found that the fibre jet is emitted from the apex of the cone, which is one reason why electrospinning can be used to generate fibres with diameters significantly smaller than the diameter of the capillary from which they are ejected. This conical shape of the jet was later referred to by other researchers as the "Taylor Cone" in subsequent literature. By a detailed examination of different viscous fluids, Taylor determined that an angle of 49.3 degrees is required to balance the surface tension of the polymer with the electrostatic forces. The conical shape of the jet is important because it defines the onset of the extensional velocity gradients in the fibre forming process [53].

Shortly after Taylor's work on jet forming, interest shifted away from a fundamental understanding of the electrospinning process to a deeper understanding of the relationships between individual processing parameters and the structural properties of electrospun fibres. In 1971, Baumgarten began to investigate the effect of varying certain solution and processing parameters (solution viscosity, flow rate, applied voltage etc.) on the structural properties of electrospun fibres [66]. He determined the spinnability limits of a polyacrylonitrile/ dimethylformamide (PAN/DMF) solution and observed a specific dependence of fibre diameter on the viscosity of the solution. He showed that the diameter of the jet reached a minimum value after an initial increase in the applied field and then became larger with increasing electric fields. Larrondo and Mandley produced polyethylene and polypropylene fibres from the melt, which were found to be relatively larger in diameter than solvent spun fibres [67, 68]. They studied the relationship between the fibre diameter and melt temperature and showed that the diameter decreased with increasing melt temperature. According to them, fibre diameter reduced by 50% when the applied voltage doubled, showing the significance of applied voltage on fibre characteristics. In 1987, Hayati et al. studied the effects of electric field, experimental conditions, and the factors affecting fibre stability and atomisation [69]. After a hiatus of a decade or so, a major upsurge in research on electrospinning took place due to increased knowledge on the application potential of nanofibres in different areas, e.g. high efficiency filter media, protective clothing, catalyst substrates, and adsorbent materials. Research on nanofibres gained momentum due to the work of Doshi and Reneker [70]; they studied the characteristics of polyethylene oxide (PEO) nanofibres by varying the solution concentration and applied electric potential.

Electrospinning gained substantial academic attention after 1990, which had been partially initiated by the Reneker group [57, 70] and followed by Deitzel [71], Zong [42] and Ramkrishna [1]. One reason for the fascination with the subject is the combination of both fundamental and application-oriented research from different science and engineering disciplines. This rapid development is reflected by the skyrocketing numbers of scientific publications and patents, which has been shown in Fig. 2-2. Up to date, it is generally believed that nearly one hundred



Fig. 2-2: Number of scientific publications and patents per year (1996-2008) (source: SciFinder Scholar)

different polymers, mostly dissolved in solvents (some in melt form) have been successfully spun into ultrafine fibres using this technique (though only half of them have been found by us from the available literature) [34]. Strangely enough, although the electrospinning process has shown to be potential promising and has existed in the literature for quite a few decades, its understanding is still very limited [20, 31, 34]. A systematic review is made in this doctoral

thesis on the researches and developments related to electrospun polymer nanofibres including processing, structure and application.

2.5.3 Theory and process of electrospinning

In electrospinning, a high voltage is applied to a polymer fluid, where charges are induced within the fluid. In conventional spinning, the fibre is subject to tensile, rheological, gravitational, inertial, and aerodynamic forces. The action of these forces has been described by Ziabicki et al. [72]. In electrospinning the tensile force is generated by the interaction of an applied electric field with the electrical charge carried by the jet rather than by the spindles and reels used in conventional spinning [57]. When the free charges in the liquid polymer, which are generally ions, move in response to the electric field, they quickly transfer a force to the polymer liquid. At the tip of the capillary, the pendant hemispherical polymer drop takes a cone like projection in the presence of an electric field. When the applied potential reaches a critical value required to overcome the surface tension of the liquid, a jet of liquid is ejected from the cone tip [65].

Most charge carriers in organic solvents and polymers have lower mobilities, and hence the charge is expected to move through the liquid for larger distances, only if enough time is allowed. After the initiation from the cone, the jet undergoes a chaotic motion or bending instability and is directed towards the oppositely charged collector, which collects the charged fibres [73]. As the jet travels through the atmosphere, the solvent evaporates, leaving behind a dry fibre on the collecting device. For low viscosity solutions, the jet breaks up into droplets, while for high viscosity solutions it travels to the collector as fibre jets [71]. The advantages of the electrospinning process are its technical simplicity and easy adaptability. The apparatus used for electrospinning is simple in construction; however, the behaviour of electrically driven jets, the shape of the jet originating surface, and jet instability are some of the critical areas in the electrospinning process that require further research. Rayleigh [81] and Zeleny [74] gave initial insight into the study of the behavior of liquid jets, later followed by Taylor [65]. As mentioned

earlier, a conical shaped "Taylor cone" with an angle of 49.3° is formed when a critical potential is reached to disturb the equilibrium of the droplet at the tip of the capillary. When a high potential is applied to the solution, electrical forces and surface tension help in creating a protrusion wherein the charges accumulate. The high charge per unit area at the protrusion pulls the solution further to form a conical shape, which on further increase in the potential initiates the electrospinning process by jetting [57]. The jet ejected from the apex of the cone continues to thin down along the path of its travel towards the collector, and the jetting mode has been termed as electrohydrodynamic cone-jet [75]. The charges in the jet accelerate the polymer solution in the direction of the electric field towards the collector, thereby closing the electrical circuit. The jet while moving towards the collector undergoes a chaotic motion or bending instability as suggested by Yarin et al., due to the repulsive forces originating from the charged ions within the electrospinning jet [73]. The bending instability was originally thought to be occurring by a single jet splitting into multiple thin fibre filaments due to radial charge repulsion, which was termed as splaying [70]. Doshi and Reneker argued that as the fibre diameter decreases due to the simultaneous stretching of the jet and the evaporation of the solvent, the increased charge density splits the jet into smaller jets [70]. This splitting is expected to occur repeatedly, resulting in smaller diameter fibres.

Renekar's team has described the stable electrospinning jet in four regions that has been shown in Fig. 2-3 [57]. The jet emerges from the charged surface at the base region, travels through the jet region, divides into many fibres in the splaying region, and stops in the collection region. The base is the region where the jet emerges from the liquid polymer. The geometry of the jet, near the base, is a tapered cone in which the axial velocity of the liquid increases as the polymer is accelerated along the axis of the jet. An electric field at the surface of a liquid produces a force that, if the electric field is strong enough, ejects a jet of liquid from a surface that was essentially flat before the field was applied. The jet is the region beyond the base where the electrical forces continue to accelerate the polymer liquid and to stretch the jet. In this region, the diameter of the jet decreases and the length increases in a way that keeps constant the amount of mass per unit time passing any point on the axis. A stable electrospinning jet travels from a polymer solution or melt to a collector, for example, a metal screen. The jet is driven by a high electrical potential applied between the solution or melt and the collector. Electrical charges, usually in the form of

ions, tend to move in response to the electrical field that is associated with the potential. Splaying occurs in a region in which the radial forces from the electrical charges carried by the jet become larger than the cohesive forces within the jet, and the single jet divides into many charged jets with approximately equal diameters and charge per unit length. As the jet progresses from the base towards the collector, the forces from the external electric field accele rate and stretch the



Fig. 2-3: Electrospinning jet with four regions [57]

jet. Stretching and evaporation of the solvent molecules cause the jet diameter to become smaller. The charge on the fibre tends to expand the jet in the radial directions and to stretch it in the axial direction. As the radius of the jet becomes smaller, the radial forces from the charge can become large enough to overcome the cohesive forces of the fibre and cause it to split into two or more fibres, that is to splay. This jet division process occurs several more times in rapid succession and produces a large number of small electrically charged fibres moving towards the collector. The divided jets repel each other, thereby acquiring lateral velocities and chaotic

trajectories, which gives a bush-like appearance in the region beyond the point at which the jet first splays [57]. Splaying converts a single jet into many thinner jets. Thin fibres can also be created by elongating a single jet if splaying does not occur. Splaying and elongation appear to occur simultaneously in many cases. The collection region is where the jet is stopped. The polymer fibre that remains after the solvent evaporates may be collected on a metal screen. For polymers dissolved in non-volatile solvents, water or other appropriate liquids can be used to collect the jet, remove the solvent, and coagulate the polymer fibre. Mechanical reels or aerodynamic currents can also be used for collection [57].

2.5.4 Electrospinning equipment

The electrospinning setup essentially consists of a capillary tube, a needle attached to a syringe filled with polymer solution, a grounded collector screen, and a high voltage power supply connected between the capillary and the collector in Fig. 2-4. The feeding rate of the polymer solution is usually controlled by using a metering syringe pump. In this process, a charged polymer solution flowing out of the capillary is accelerated towards the grounded collector in a strong electrostatic field [34, 57]. The latter causes the droplet emerging from the capillary end to undergo deformation into a conical shape, previously described, as the "Taylor cone"[65].

As the strength of the applied potential is increased to the point at which the electrostatic force has overcome the surface tension of the solution, a fine jet of the solution emerges. The jet, after an initial straight path, undergoes "bending instability" and a characteristic "whipping motion", (Fig. 2-4), due to the charge-charge repulsion that occurs between the excess charges present in the jet [34, 57]. During this phase, the jet is drawn by at least two orders of magnitude, the solvent evaporates, and the dry fibres deposit onto the collector. Polymer melt, instead of a polymer-solvent solution, can also be used. In the latter case, a heating system that surrounds the reservoir is employed to maintain the temperature [76].



Fig. 2-4: A laboratory setup for an electrospinning experiment [34]

2.5.5 Current scenario

A significant amount of research has been carried out on the fundamental aspects of electrospinning. The major issues that are yet to be resolved, are the finding of process-structure-property relationship for engineering polymer nanofibres and the scaling-up of the process for commercialisation [16, 34]. Electrospinning is regarded as an easy and convenient method of making nanofibres, but the relationship between processing parameters and microstructures of

nanofibrils are still not well understood. A significant amount of the information regarding the electrospinning process comes from empirical observations, but the complexity of the process makes the empirical determination of parametric effects very difficult, if not impractical [20]. It has been well established that both operating parameters and material properties affect the electrospinning process and the resulting fibre morphology [34, 77]. Therefore, an understanding of the process- structure- property relationship is essential for engineering polymer nanofibres to meet the demands of applications [19, 20]. The present research has described a systematic study of electrospinning parameters and the development of predictive models for estimating the effects of various parameters.

Electrospinning apparatus is simple in construction, and there have been no significant developments in the equipment design in the last decade. Research groups have improvised the basic electrospinning setup to suit their experimental needs and conditions. Warner et al. have designed a new parallel plate set-up for effectively controlling the operating variables to quantify the electrohydrodynamics of the process [78]. The parallel plate design is expected to overcome the problem of a non-uniform electric field experienced in the point plate configuration. Jaeger et al. have used a two electrode set-up by placing an additional ring electrode in front of the capillary to reduce the effect of the electrostatic field at the tip and to avoid corona discharges [79]. It has been stipulated that by using the two electrode set-up, a more stable field can be established between the ring electrode and the collector, thereby avoiding the effect of changing shape at the capillary tip over the electric field. Productivity enhancement for commercialising the electrospinning process is under active research, with emphasis on multiple spinneret designs and alternative experimental setup for feed charging. However, there is still a debate on the potential of scaling up this technology for commercialisation [16]. This is an important issue, which government agencies, academia, and industry should pay attention to for further growth and development of the field. Espin Technologies, a nanofibre technology company, is involved in developing a proprietary high speed device that could effectively overcome the traditional drawbacks of low output and high production cost [80]. Donaldson filtration has its own paten ted process set-up for making tens of thousands of square meters of electrospun nanofibre filter media [81]. From the available published literature and the current state of understanding of the



Figs. 2-5: (a) Apparatus for electrospinning side-by-side bicomponent nanofibres [34] (b) side-by-side bicomponent nanofibres [83] (c) self-crimped nanofibres from a side-by-side nanofibre (one side is elastomeric polymer and the other is thermoplastic) [83]

electrospinning process, it is likely that commercial scaling up of the electrospinning process can only be achieved by more fundamental understanding of the process and better control of the instability behaviour of jets that determine the diameter of the fibres [82]. Preparation of nanofibre using two dissimilar materials, via a novel technique of co-axial electrospinning has presented unusual potential for use in many novel applications. Tong Lin et al. have produced side-by-side bicomponent nanofibres by the electrospinning technique, Fig. 2-5 (a), when a special spinneret has been used to direct two polymer solutions into the same jet [83]. The two polymer solutions are delivered to the tip of the nozzle via the small tube and the interlayer between this small tube and the larger co-axial tube separately, and then co-electrospun into core-sheath fibres [83, 84].

The use of several syringes in parallel alignment as electrodes in multijet electrospinning, Fig. 2-6, allows the fabrication of electrospun tissues consisting of different fibre materials [85, 86].



Fig. 2-6: Multiple syringe pump with the capacity of ten needles [picture taken from Electrospinning set-up at Centre for Advanced Composite Materials (CACM), The University of Auckland (UoA)]

Multijet electrospinning is even more intricate than the single-jet process, because of the repulsion between similarly charged jet. A detailed examination of this matter is particularly

important for high efficiencies and complex tissue architecture. In order for electrospinning to be commercially viable, it is necessary to increase the production rate of the nanofibres. To do so, multiple spinning set up is necessary [1, 34], but single jet processing is more conducive to understanding the mechanism.

2.6 Electrospun Nanostructured Network

2.6.1 Structure and morphology

Electrospun nanofibres have been attractive materials for a wide range of applications because of their large surface area to volume ratio and unique nanometer scale architecture. Nanofibres usually have thread-like structures and some fibres can form a ribbon-like fibrous morphology [84]. The fibre diameter varies in the range of 5 nm to 10 μ m. Defects, such as colloid beads or beads on string fibres, occur among the resultant fibres, or even as the major product sometimes depending on the operating conditions and the material properties. By varying the experimental parameters of electrospinning, it is possible to get much variation in the morphology of the nanofibres [17, 77, 84]. At low viscosity of the polymer solution, it is common to find beads when the electrospinning jet breaks up into small droplets. When the viscosity increases, it produces a gradual change in the shape of beads from spherical to spindle-like until a smooth fibre is obtained [77, 84]. Other than beaded and nonbeaded fibres, electrospinning technology can be used to produce other types of fibres with interesting morphology as well as different types of nanofibres.

2.6.1.1 Hollow nanofibres

Hollow nanofibres (also called nanotubes), Figs. 2-7 (a) and (b), are processed from various materials such as carbon, ceramics, metals, and polymers. These are essential in industrial applications, such as separation, gas storage and energy conversion. By employing the

electrospinning process, chemical vapour deposition (CVD) and direct co-axial spinning method, hollow nanofibres can be made [1]. First, the template polymer nanofibres are electrospun before they are coated by sheath material using CVD. Hollow nanofibres are finally formed when the template is removed via annealing. To attain this, the template nanofibre should be stable during the coating but degradable or extractable without destroying the coating layer.

2.6.1.2 **Porous nanofibres**

For a variety of applications, for example, tissue engineering, filtration, catalysis, drug delivery, and nanofibre reinforcement, it can be advantageous if the fibre surfaces are porous, Fig. 2-7 (c), instead of being smooth. It is now possible to generate different fibre topologies during the electrospinning process by choosing particular solvents or solvent mixtures, by varying the humidity, or by using polymer mixtures. When a polymer solution is cast on a support, convective evaporation takes place. During solvent evaporation, the solution becomes thermodynamically unstable leading to separation into two phases: a polymer-rich phase and a polymer-deficient phase. Using a salt leaching/gas forming method, micro-sized pores have been developed by Lee and others in polylactic acid/montmorillonite nanocomposite fibre [87].

2.6.1.3 Flattened or ribbon-like fibres

A thin polymer skin is formed on the liquid jet as a result of solvent evaporation at the jet surface, thereby resulting in a thin layer of solid skin with a liquid core [1]. As a result of atmospheric pressure, the tube collapses in tandem with solvent evaporation from the core. During the course of tube collapse, the circular cross section initially becomes elliptical and thereafter ribbon-like.



Figs. 2-7: SEM images of electrospun (a & b) hollow isotropic carbon fibre [88] (c) porous PLA fibres [34] d) branched fibre formed by the ejection of a secondary jet [34]

2.6.1.4 Branched fibres

Branched fibres, Fig. 2-7 (d), can be made by ejecting smaller jets from the surface of the primary jets. Split fibres are also obtained by the separation of a primary jet into two smaller jets. The elongation of the jet and evaporation of the solvent alter the shape and the charge per unit area carried by the jet. The balance between the electrical forces and surface tension can shift, thereby causing the shape of a jet to be unstable. Such instability can decrease its local charge

per unit surface area by ejecting a smaller jet from the surface of the primary jet or by splitting apart into two smaller jets [1].

Three dimensional fibre structures have also been observed in fibre mats collected on metal surfaces. A honeycomb structure has been electrospun at high voltage on to a piece of cloth backed by an aluminium screen [71].

2.6.1.5 Bi-component nanofibres

A bi-component nanofibre typically consists of two or more polymer components within the same filament. According to the cross-sectional morphology, the bicomponent fibres can be classified into four main types: 'core-sheath', 'side-by-side', 'pie wedge' and 'islands-in-a-sea' [83]. Bicomponent nanofibres, Fig. 2-5 (b), can be produced by the electrospinning technique when a special spinneret, Fig. 2-5 (a), is used to direct two polymer solutions into the same jet. The cross-sectional configuration of the bicomponent nanofibres is dependent on how the two polymer solutions arrange within the jet. In theory, all four types of the bi-component fibres mentioned above should be possible with the electrospinning technique [83, 84]. In practice, however, only two bi-component configurations have been achieved to date: 'core-sheath' and 'side-by-side' nanofibres. With a fibre having a bi-component structure, it is easy to impart single nanofibres with multiple functionalities, which is very useful in making nano-structured devices and sensors for instance. When side-by-side bicomponent nanofibres are prepared using an elastomeric polymer and a thermoplastic polymer, a self-crimped fibre structure is produced as has been shown in Fig. 2-5 (c). The core-sheath nanofibres are prepared by using a co-axial spinneret as the nozzle. During the process, the two polymer solutions are delivered to the tip of the nozzle via the small tube and the interlayer between this small tube and the larger co-axial tube separately, and then co-elctrospun into core-sheath fibres. The dimensions of core and sheath can be adjusted using the right polymer concentration and amount of feed rate [83, 84]. Hollow nanofibres can be manufactured from the core-sheath nanofibres by selectively removing the core from the bi-component fibres.

2.6.1.6 Defective beaded nanofibres

Beads are considered the main demerit of electrospun fibres. These are nonporous polymeric material with different shapes. Beads may be elliptical, spherical, regular or irregular shaped, which have been shown in Figs. 2-8 (a) - (c). Very fine electrospun fibres usually contain some bead-like defects. The existence of fibre beads not only reduces the fibre uniformity, but also leads to reduced fibre surface area and poor mechanical strength [83]. The bead formation mechanism has been studied and attributed to insufficient chain entanglement of polymer macromolecules and low fibre drawing forces. There are many factors influencing the occurrence of beads, such as the applied voltage, viscoelasticity and charge density of the solution.



Figs. 2-8: Different shaped beads (a) irregular (b) elliptical (c) spherical [54]

2.7 Different Factors of Electrospinning

2.7.1 Introduction to process parameters

Although electrospinning is a relatively simple process, requiring simple laboratory equipment to yield fibres down to the nanoscale, the science behind it is not simple at all [20, 34]. The electrospinning process involves electrostatics, fluid rheology and polymer solution properties, which are constantly interacting and influencing each other during the electrospinning process. Important features of electrospinning are [1]:

- (a) Suitable solvent should be available to dissolve the polymer.
- (b) The vapour pressure of the solvent should be suitable so that it evaporates quickly enough for the fibre to maintain its integrity when it reaches the target, but not so quickly as to allow the fibre to harden before it reaches the nanometer range.
- (c) The viscosity and surface tension of the solvent must neither be too large to prevent the jet from forming nor be too small to allow the polymer solution to drain freely from the pipette.
- (d) The power supply should be adequate to overcome the viscosity and surface tension of the polymer solution to form and sustain the jet from the pipette.

There are number of variables that influence the morphology of the resultant electrospun fibres. Doshi and Reneker classified the parameters that control the process in terms of solution properties, controlled variables, and ambient parameters [70]. Solution properties include the viscosity, conductivity, surface tension, polymer molecular weight, dipole moment, and dielectric constant. The effects of the solution properties can be difficult to isolate since varying one parameter can affect the other solution properties (e.g., changing the conductivity can also change the viscosity). Controlled variables include the flow rate, electric field strength, distance between tip and collector, needle tip design, collector composition and geometry and motion of the target screen. Some ambient parameters include temperature, humidity and air velocity in the chamber. All the parameters are shown in a categorised manner in Table 2-2 [1].

Table 2-2: Frocessing par	rameters in electrospinning [1].
Solution properties	Viscosity
	Polymer concentration
	Molecular weight of the polymer
	Electrical conductivity
	Elasticity
	Surface tension
Processing conditions	Applied voltage
	Distance between needle tip and collector
	Volumer feed rate
	Needle diameter
Ambient conditions	Temperature
	Humidity
	Atmospheric pressure

2.7.2 **Discussion of different factors**

Electrospinning is a unique method of producing continuous polymer nanofibres. Despite its relative ease of use, there are a number of variables that can greatly affect fibre formation. The control of fibre morphology can only be achieved through a thorough understanding of the electrospinning process and its influencing factors. The production of nanofibres by the electrospinning process is affected both by the electrostatic forces and the viscoelastic behaviour of the polymer [16, 77]. Material factors, such as solution concentration, viscosity, surface tension, conductivity, solvent volatility and process factors, such as solution feed rate, applied voltage and nozzle-to-collector distance influence the structure and properties of electrospun nanofibres. The spinning environment that includes temperature, humidity and air velocity in the chamber, have significant effects on the forming of fibres.

Viscosity/concentration

Solution viscosity has been found to be one of the biggest determinants of fibre size and morphology when spinning polymeric fibres. The viscosity of the polymer solution depends on both the molecular weight of the polymer and the concentration of the polymer solution [1, 77]. If the molecular weight of the polymer is not varied, solution viscosity is controlled only by changing the polymer concentration. Solution concentration determines the limiting boundaries for the formation of electrospun fibres due to variations in the viscosity and surface tension [71]. At low polymer concentrations, defects in the form of beading and droplets are observed; the process under these conditions is the characteristic of electrospraying rather than spinning. Formation of these droplets is due to the influence of surface tension. By increasing the solution viscosity by increased polymer concentration, uniform fibres are yielded with fewer beads and junctions. An increase in the viscosity results in greater polymer chain entanglements within the solution, which is necessary to maintain the continuity of the jet during electrospinning [1]. This polymer chain entanglement has been found to have a significant impact on whether the electrospinning jet breaks up into small droplets resulting in beads [1, 42]. For solutions that are highly concentrated (and therefore too viscous), the droplet dries out at the tip before jets can be initiated, preventing electrospinning [42, 89]. Researchers have aimed to find a relationship between solution concentration and the fibre diameter. For example, it has been found that increased concentration of gelatin yields fibres with larger diameters, following a power law relationship [90]. Attempts have been made to quantify the minimum polymer concentrations and viscosities required to electrospin fibres. Koski et al. have found that it is possible to spin polyvinyl alcohol (PVA) as long as $[\eta]c > 5$, where $[\eta]$ is the intrinsic viscosity and c is the concentration [91]. For polyethylene oxide (PEO), it has been found that solutions with $[\eta]c > 10$ allow spinning [92]. Despite several approaches, no concrete idea has been found so far for general usage. The diameters of the fibres produced by electrospinning have been found to increase with increasing solution concentration [71, 77]. For example, PLLA fibres with diameters of 100 - 300 nm were produced from 1% (w/v) (g/100 ml) solutions while 5% (w/v) solutions yielded 800 - 2400 nm fibres [93]. However, molecular weight plays a very important role. Patra et al. have found that 4% (w/v) polymer concentration of PLLA (with a molar mass of 1.044×10^5 g mol⁻¹) can produce very fine fibres of 40 - 80 nm with formation of some beads and 10% has made bead-free uniform fibres but with diameters ranging from 200 to 400 nm [77, 94].

In many experiments, including the research of Patra et al. [42, 77, 84, 94] it has been proved that within the suitable range of polymer concentration (depends on the individual polymer) fibre diameter increases with increasing polymer concentration. Megelski et al. found that by increasing the concentration of polystyrene in tetrahydrofuran (THF), fibre diameter became larger and the distribution of pore sizes became narrower [95]. Deitzel et al. found that the diameters of fibres electrospun from PEO/water solution were related to PEO concentration by a power law relationship [71]. A thorough discussion of the relationship between fibre diameter and polymer concentration, using PLLA, are explained in the following Sub-chapters.

Solution conductivity

It has been found that increased solution conductivity or charge density can be used to produce more uniform fibres with fewer beads [42, 96]. Solutions with high conductivity will have a greater charge carrying capacity and thus the fibre jet of a highly conductive solution will be subjected to a greater tensile force in the presence of an electric field. One approach to increasing the solution conductivity has been through the addition of salt; for fibres spun from PDLA [42], PEO [96], and collagen type I-PEO [97] uniformity increased and beading decreased upon the addition of salt. Zong et al. demonstrated the effect of ions by adding ionic salt, on the morphology and diameter of electrospun fibres [42]. They found that PDLA fibres with the addition of ionic salts like sodium/potassium dihydrogen phosphate (KH₂PO₄/ NaH₂PO₄), and sodium chloride (NaCl) produced beadless fibres with relatively small diameters ranging from 200 1000 surfactants dodecyltrimethylammonium to nm. Cationic bromide and tetrabutylammonium chloride were added to polystyrene solutions, and it was found that a small amount prevented bead formation [98]. It has also been found that the addition of ionic compounds, especially ionic surfactant, to the polymer solution for electrospinning can effectively prevent the formation of fibre beads, which is in agreement with the findings of Patra et al. as well [54, 83]. Beads proliferated when electrospinning of PLLA and polyaniline (PANi) solution in common solvent was performed (refer to Section 3.6.3). Efforts to eliminate beaded fibres by adjusting the operating conditions and changing the polymer concentration were unsuccessful in this case [54]. However, the addition of only 1% (g/100 ml)of the quaternary ammonium salt, tetrabutyl ammonium bromide (TBAB), dramatically increased the conductivity of the electrospinning solution of dodecylbenzene sulphonic acid (DBSA) doped PANi and



PLLA, and facilitated the formation of bead-free nanofibres. The dielectric constant of a solvent has a major contribution in making a spinnable polymer solution. Generally, a solution with greater dielectric constant reduces bead formation and the diameter of the resultant electrospun fibre as it makes the polymer solution more effective by making it highly conductive [1].

Volatility of solvent

Electrospinning involves rapid solvent evaporation and phase separations due to jet thinning. Solvent vapor pressure critically determines the evaporation rate and the drying time. Solvent volatility plays a major role in the formation of nanostructures by influencing the phase separation process. Megelski et al. examined the structural properties of polystyrene fibres electrospun from solutions containing various ratios of dimethyl formamide (DMF) and THF [95]. Solutions electrospun from 100% THF (more volatile) demonstrated a high density of pores, which increased the surface area of the fibre by as much as 20 - 40%, depending on the fibre diameter. Solutions electrospun from 100% DMF (less volatile) demonstrated an almost complete loss of microtexture with the formation of smooth fibres. Between these two extremes it was observed that pore size increased with decreased pore depth (thus decreasing pore density) as the solvent volatility decreased.

Solution feed rate

The flow rate of the polymer from the syringe is an important process parameter as it influences the jet velocity and the material transfer rate. The relationship between solution feed or flow rate and fibre morphology has been investigated by a few researchers including Zong and Patra et al. [42, 77, 99]. In general, it is found that lower flow rates yield fibres with smaller diameters. Flow rates that are too high, result in beading since fibres do not have a chance to dry prior to reaching the collector [42, 99]. Taylor realised after his initial work that the cone shape at the tip of the capillary could not be maintained if the flow of solution through the capillary was insufficient to replace the solution ejected as the fibre jet [65]. Megelski et al. examined the effects of flow rate on the structure of electrospun fibres from a polystyrene/THF solution [95]. They demonstrated that both fibre diameter and pore size increased with increasing flow rate. Additionally, at high flow rates significant amounts of bead defects were noticeable, due to the inability of fibres to dry completely before reaching the collector. Incomplete fibre drying also

leads to the formation of ribbon-like (or flattened) fibres as compared to fibres with a circular cross section. Nozzle diameter plays another important role as it controls the volume of the polymer solution to be electrospun. A needle with a very small diameter creates clogging at the needle tip while a large diameter brings excess amount of solution that may build big blobs or beaded nanofibres.

Applied voltage

One of the most important factors among the controlled variables is the effect of field strength or applied voltage. At low voltages or field strengths, a drop is typically suspended at the needle tip, and a jet originates from the Taylor cone producing bead-free spinning (assuming that the force of the electric field is sufficient to overcome the surface tension) [71]. As the voltage is increased, the volume of the drop at the tip decreases, causing the Taylor cone to recede. The jet originates from the liquid surface within the tip, and more beading is seen. As the voltage is further increased, the jet eventually moves around the edge of the tip, with no visible Taylor cone; at these conditions, the presence of many beads can be observed [42, 71]. Deitzel et al. examined a PEO/water system and found that increased applied voltage altered the shape of the surface at which the Taylor cone and fibre jet were formed [71]. It was also observed that for the PEO/water system, the fibre morphology changed from a defect-free fibre at an initiating voltage of 5.5 kV to a highly beaded structure at a voltage of 9.0 kV [71]. The occurrence of beaded morphology has been correlated to a steep increase in the spinning current, which controls bead formation in the electrospinning process. Beaded structure reduces the surface area, which ultimately deteriorates the filtration abilities and tensile strength of nanofibrous mats [83].

Distance between the needle tip and the collector

Varying the distance between the tip and the collector has been examined as another approach to controlling the fibre diameter and morphology. A minimum distance is required to allow the fibres to get sufficient time to dry before reaching the collector. The distance between the capillary tip and collector can also influence fibre size by 1 - 2 orders of magnitude. Additionally, this distance can dictate whether the end result is electrospinning or electrospraying. Doshi and Reneker found that fibre diameter decreased with increasing distance from the Taylor cone [70]. Flight time of the electrospinning jet is another factor that may

influence the diameter of the fibre. A longer flight time allows more time for the fibre to elongate before it is deposited on the collector plate [1, 77]. Similarly a shorter flight time makes less elongation, generating coarse fibres.

Ambient parameters

A few studies have been conducted to examine the effects of ambient parameters (i.e., temperature and humidity) on the electrospinning process. Since electrospinning is influenced by external electric field, any changes in the electrospinning environment will also affect the electrospinning process. A change in temperature causes the variation of the solvent evaporation rate and the solution viscosity, which are two opposing factors affecting the mean fibre diameter [100]. Mit-Uppatham et al. spun polyamide-6 fibres at temperatures ranging from 25 to 60°C [101]. They found that increasing the temperature yielded fibres with decreased fibre diameters, and they attributed this decline in diameter to the decrease in the viscosity of the polymer solutions at increased temperatures. The humidity was varied by Casper et al. while spinning polystyrene solutions [102]. Their work showed that increasing the humidity resulted in the appearance of small circular pores on the surfaces of the fibres. The humidity of the environment also determines the rate of evaporation of the solvent in the solution. At a very low humidity, a volatile solvent may dry rapidly. The evaporation rate of the solvent may be faster than the removal of solvent from the tip of the needle. As a result the electrospinning process may only be carried out for a few minutes before the needle tip is clogged [1]. The composition of the air and its velocity in the electrospinning environment do affect the electrospinning process. Different gases have different behaviour under a high electrostatic field [1].

In summary, researchers have highlighted studies that examined the effects of manipulating each parameter in the electrospinning process and the resulting fibre morphology. It is difficult to isolate the effects of many of the parameters since they are interrelated. For example, changing the solution concentration/viscosity affects other solution properties, such as the conductivity and surface tension. Nevertheless, a large number of distinct polymers have been electrospun but very little systematic investigation (of the suitable conditions required) for successful spinning has been conducted. Typically, a trial-and-error approach has been employed in which the solution properties and spinning parameters are varied until uniform, defect-free fibres are

obtained. A parametric analysis has been performed in this study to develop a systematic knowledge and get a suitable combination of parameters and their levels. Based on the knowledge gathered a regression analysis has been performed with a broader range of parameters and their extended levels, to get a clearer direction for successful electrospinning.

2.7.3 Factors influencing manufacture of bead-free uniform fibres

Chain entanglement among the polymer molecules is mainly determined by the chain length, polymer concentration in the solution, and polymer structure. In a very dilute solution, with a given molecular weight, the polymer molecules are isolated by the solvent itself. With increased polymer concentration, the polymer intermolecular distance decreases. Effective chain entanglement will occur when the polymer concentration is greater than a critical value, which is called 'overlap concentration' [83]. In relation to the chain entanglement, nanofibres electrospun from different polymer concentrations vary in fibre morphology in Figs. 9 (a) - (c) and Figs. 10 (a) - (c). The total concentration of polymer appears to be the most significant factor in controlling bead formation [77, 83, 94]. An increase in the polymer concentration results in greater polymer chain entanglements within the solution, which is necessary to maintain the continuity of the jet during electrospinning [77, 94]. In addition, increased polymer concentration increases the surface tension of the solution, which is beneficial because lower surface tension tends to favour bead formation [4]. Since uniform fibres are normally electrospun from polymer solution having a relatively high polymer concentration, increasing the polymer concentration has been a conventional way to improve fibre uniformity. However, with the increase in polymer concentration in electrospinning, the average diameter of resultant electrospun fibres also increases, Fig. 2-10 (c), even though the fibres may have good uniformity.

Concentration of the polymer solution plays a major role in determining the fineness of the nanofibril, but when beads are concerned, it influences in opposite manner [94]. It still remains a

great challenge to electrospin a wide range of polymer materials into uniform and bead-free fibres with a diameter below 100 nm [20, 83, 94].



Figs. 2-9: SEM micrographs of PLLA nanofibres with using different polymer concentrations (w/v) (a) 4% (b) 7% and (c) 10% (solvent mixture DCM/DMF : 60/40, applied voltage 10 kV, spinning distance 100 mm, feed rate 1 ml hr⁻¹) [20]

Low molecular weight is another cause of insufficient chain entanglement in solution, because lower molecular weight gives shorter molecular chain length, hence reducing the chance of chain entanglement. The example in Figs. 2-11 (a) and (b), shows that when a low molecular weight polyvinylpyrrolidone (PVP) is electrospun, individual beads are produced even when the PVP concentration is as high as 30% w/v (g/100ml) [83]. However, under the same operating conditions, a high molecular weight of PVP can be electrospun into uniform fibres even when the solution contained only 6% (w/v) of PVP [83]. For some polymers, such as polystyrene (PS), polycarbonate (PC) and polycaprolactone (PCL), increasing the polymer concentration is not always effective to stop the formation of fibre beads, even at a high polymer concentration [83].



Figs. 2-10: SEM micrographs of PLLA nanofibres with high magnification using different polymer concentrations (w/v) (a) 4% (b) 7% and (c) 10% (solvent mixture DCM/DMF : 60/40, applied voltage 10 kV, spinning distance 100 mm, feed rate 1 ml hr⁻¹) [20]



Figs. 2-11: (a) PVP particles electrospun from 30% (w/v) of PVP (Mw of 10,000), (b) PVP nanofibres electrospun from 6% (w/v) of PVP (Mw of 1,300,000) (ethanol as solvent, applied voltage of 20 kV, spinning distance of 15 cm, flow rate of 1ml hr⁻¹) [83]

It has been found that the addition of ionic compounds, especially ionic surfactant, to the polymer solution for electrospinning can effectively prevent the formation of beaded fibre [58, 91]. As shown in Fig. 2-12 (a), beads proliferated when electrospinning of poly(L-lactic acid) (PLLA) and polyaniline (PANi) solution in common solvent has been performed. Efforts to eli-



Figs. 2-12: (a) Beaded nanofibres from CHCl3:DMF solution of DBSA doped PANi and PLLA (b) bead-free nanofibres from the same solution with 1% (w/v) TBAB [54]

minate the beaded fibres by adjusting the operating conditions and changing the polymer concentration were unsuccessful in this case. However, the addition of only 1% (w/v) of the quaternary ammonium salt, tetrabutyl ammonium bromide (TBAB), dramatically increased the conductivity of the electrospinning solution of dodecylbenzene sulphonic acid (DBSA) doped PANi and PLLA and facilitated the formation of bead-free nanofibres in Fig. 2-12 (b). Fong and co-workers [96] have also suggested that the net charge density carried by the electrospinning jet is an important factor that greatly influences the morphology of the electrospun products, together with the viscosity and surface tension of the solution. Their results have shown that beads become smaller and the shape becomes more elliptical as the net charge density is increased. The increased charge density would strengthen the interaction between the jet and electric field and the charge repulsion within the jet. Filament stretching is, therefore, enhanced considerably, leading to uniform and fine fibres.

2.8 Poly(lactic acid)(PLA) as Electrospinnable Polymer

2.8.1 Biodegradable and renewable polymer

Researchers around the globe have used various biocompatible and biodegradable synthetic polymers including poly(lactic) and poly(glycolic) acids (PLA and PGA, respectively) and their copolymers (PLAGA), polycaprolactone (PCL), polydioxanone (PDO), and a few others for scaffold fabrication [31, 39, 83]. Polylactic acid or polylactide (PLA) has been selected as the electrospinnable polymer for the entire project. It is a biodegradable, thermoplastic and aliphatic polyester derived from renewable resources. PLA has additional drivers that make it unique in the market place [103]. The starting material for the final polymer from which it is ultimately produced can be derived from the fermentation of agricultural by-products which are 100% renewable resources. Biodegradable materials are substances that will decompose in a natural environment. They have the ability to break down safely and relatively quickly by biological means into the raw materials of nature and disappear into the environment as biomass. PLA

rapidly degrades in the environment, giving by-products of very low toxicity and eventually carbon dioxide and water.

2.8.3 Properties of PLA

Lactic acid is the basic building block for PLA, Fig. 2-13, which is poly (2-hydroxy propionic acid) [103]. Lactic acid is highly water soluble and it plays a role in several biochemical processes. It has a hydroxyl group on the carbon atom adjacent to the carboxyl group, making it an alpha hydroxy acid (AHA). In solution, it can lose a proton from the acidic group, producing the lactate ion $CH_3CH(OH)COO^-$. It is miscible with water or ethanol and is hygroscopic [103].

PLA is a rigid thermoplastic polymer that can be semi crystalline or totally amorphous, depending on the stereopurity of the polymer backbone. Lactic acid is the basic building block for PLA. The most common form of lactic acid is L (-)-Lactic acid (2-hydroxy propionic acid), but D (+)-lactic acid can also be produced by microorganisms or through racemisation and this "impurity" acts much like other comonomers (as in other polymers such as PET or PE). Similar to PET where isophthalic acid is copolymerised in the backbone at low levels (1-10%) to control the rate of crystallisation, D-lactic acid is incorporated into L-PLA to optimise the crystallisation kinetics for specific fabrication process [103]. L- lactide is highly crystalline, but the presence of a few percent of d- lactide makes the polymer amorphous. Control of the ratio of L to D monomer content is an important molecular feature of PLA and has a large effect on material properties. This study uses poly (L-lactic acid) (PLLA) that is PLA synthesised from the more common L optical isomer (denoted PLLA) instead of the D or dl isomers, since L-lactic acid, the product of PLA hydrolysis, occurs naturally in the metabolic pathway in humans [104]. The methyl group in the monomer makes PLLA more hydrophobic than any other; it also presents a steric hindrance that gives PLLA a higher solubility in organic solvents and significantly slows hydrolysis such that PLA typically degrades within 30 to 50 weeks [104, 105].



Fig. 2-13: Structure of lactic acid [103]

Polylactic acid is stiff but brittle, so it is necessary to use plasticisers to improve elongation and impact properties. Plasticisers can increase elongation up to 300% with a tensile strength of 40 MPa. PLA resins can be tailor-made for different fabrication purposes including injection moulding, sheet extrusion, blow moulding, thermoforming, film forming or fibre spinning [103]. Typical properties of PLA made by NatureWorks[®] LLC (the 3051D grade used in this project) are given in Table 2-3 [106].

Nanoscale fibres of PLLA have attracted the interest of numerous researchers. Yang et al. and some other groups have utilised electrospun PLA scaffolds to investigate morphology and biodegradation rates which could be used for applications e.g. tissue scaffold, drug delivery and a few others [87, 107].

Tensile strength and Young's modulus of PLA are also comparable to those properties of PET. PLA can be formulated to be either rigid or flexible and can be copolymerised with other materials. Some of the beneficial characteristics of fibre products made from PLA, Table 2-4, include its natural soft feel, ease of processing, and unique stain and soil resistance. PLA shows

Physical properties	PLA resin (general purpose)	ASTM Method
Specific gravity	1.25	D 792
Melt index, g/10 min (210 °C /2.16 Kg)	10-25	D1238
Relative viscosity	3.0-3.5	
Crystalline Melt Temperature (⁰ C)	150-165 ⁰ C	D 3418
Glass transition Temp (⁰ C)	55-65	D 3417
Clarity	Transparent	
Mechanical Properties		
Tensile Yield Strength, psi (MPa)	7000 (48)	D 638
Tensile Elongation, %	2.5	D 638
Notched Izod Impact, ft-lb/in (J/m)	0.3 (0.16)	D 638
Flexural Strength (MPa)	12.000 (83)	D 790
Flexural Modulus (MPa)	555,000 (3828)	D 790

Table 2-3:	Typical physical a	and chemical	properties o	f PLA	(This	table l	has be	een t	aken	from	the	web-sit	e of
NatureWork	as PLA) [106].												

Table 2-4:	Comparison of	various properties	of PLA with other	r natural and synthetic	polymers [103]
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Fibre properties	N6	РЕТ	Acrylics	PLA	Rayon	Cotton	Silk	Wool
Specific gravity	1.14	1.39	1.18	1.25	1.52	1.52	1.34	1.31
Tenacity (g/d)	5.5	6.0	4.0	6.0	2.5	4.0	4.0	1.6
Moisture regain (%)	4.1	0.2-0.4	1.0-2.0	0.4-0.6	11	7.5	10	14-18
Elastic recovery (5% strain)	89	65	50	93	32	52	52	69
Flammability	Medi- um	High smoke	Medi- um	Low smoke	Burns	Burns	Burns	Burns slowly
UV resistance	Poor	Fair	Good	Good	Poor	Fair	Fair	Fair

excellency at resistance to stain with coffee, cola, tea, lipstick and such items. It is a nonvolatile and odourless polymer. PLA also burns with low smoke generation. It has good ultraviolet resistance and is easily dyeable. It brings good wickability of moisture to applications [103].

CHAPTER 3

Manufacturing, Testing and Analysis Techniques

This chapter explains the details of the manufacturing procedures used in this thesis, from materials selection and solution preparation through to formation of the nanofibres. It addresses the practical considerations of polymer processing via nanofibre spinning, collection of fibres and finally visualisation through scanning electron micrographs. Following this, the perfomance of electrospinning operations has been analysed through the measurements of fibre diameter and bead area using image processing software.

3.1 Background

The combined use of two techniques, namely electrospray and spinning, is made in a highly versatile technique called electrospinning. This technique is applicable to virtually every soluble or fusible polymer [34]. A high electric field is applied to the droplet of a fluid coming out from the tip of a die, which acts as one of the electrodes. This leads to the droplet deformation and finally to the ejection of a charged jet from the tip of the cone accelerating towards the counter
electrode leading to the formation of continuous fibres. There is an ever increasing interest in this field of electrospinning, shown by both researchers in the academic institutions and industries as evident from the increased number of publications and review articles every year (refer to Section 2.5.2). The primary requirement of the process is to obtain nanofibres in continuous form with fine diameters and minimum variations. Secondly, the fibre network has to have minimum area occupied by beads to enhance the network's porosity. Beads are considered the main demerit of electrospun fibres. These are nonporous polymeric material with different shapes. The existence of fibre beads not only reduces the fibre uniformity, but also leads to decreased fibre surface area and poor mechanical strength [83]. These two important characteristics, when achieved, render the nanofibre mats acceptable for many membrane type applications. Electrospinning is obviously a convenient method of manufacturing polymer-based multifunctional and high performance nanofibres, but to control the electrospinnability and finally to achieve the desired morphology of electrospun fibres, suitable for various uses, are challenging. It has been well established that both operating parameters and material properties affect the electrospinning process and the resulting fibre morphology [34, 77, 84]. Therefore, an understanding of the process-structure-property relationship is essential for engineering polymer nanofibres to meet the demands of applications [5]. In the present work, an attempt has been made to fabricate a nanofibrous mat by electrospinning and the results of a systematic investigation of the effects of varying manufacturing parameters on the electrospinning are reported. Poly(lactic acid) or polylactide (PLA) has been selected as the electrospinnable polymer. A particular product, PLA 3051D has been used in the entire project as the variety of products made with this grade continues to grow rapidly (refer to Section 2.8). Polylactic acid is a renewable and biodegradable polymer that motivated this work. It is a unique polymer that in many ways behaves like polyethylene terephthalate (PET), but also performs a lot like polypropylene (PP), a polyolefin [103]. PLA is a promising polymer and electrospinning is the platform technology for generating nanofibrous mat for various purposes.

3.2 Manufacturing of Nanofibres

One attractive feature of electrospinning is the simplicity and inexpensive nature of the setup; the typical electrospinning setup consists of a syringe pump, a high voltage source, and a collector. During the electrospinning process, a polymer solution is held at a needle tip by surface tension. The application of an electric field using the high-voltage source causes a charge to be induced within the polymer, resulting in charge repulsion within the solution. This electrostatic force opposes the surface tension; eventually, the charge repulsion overcomes the surface tension, causing the initiation of a jet. As this jet travels, the solvent evaporates and an appropriate collector can be used to capture the polymer fibres. One take up roller may be fitted to collect and wind the nanofibres web. However, in the present research a stationary collector has been used to collect the nanofibres. Finally, these have been visualised under a scanning electron microscope (SEM). Initially, feed rate was controlled by gravity. After successfully achieving nanofibres in the early stage of research, a closed cabinet for electrospinning purpose has been built and a programmable syringe pump for controlled feed rate and an advanced power supply device have been applied for further research.

3.2.1 Electrospinning set-up

Polymer solution was delivered to the top of a needle through a glass syringe as a capillary tube. Initially, feed rate has been adjusted by giving a slope to the glass syringe, Fig. 3-1, nanofibres have been spun successfully through electrospinning of PLLA with different solvent combinations. For further research, a new set-up was built at the Centre for Advanced Composite Materials (CACM), The University of Auckland (UoA). The closed cabinet, Fig. 3-2, is made of transparent poly(methyl methacrylate) (PMMA) thick sheet, for dust protection, reduced air turbulence and extra security for the operator. The details of equipment will be discussed in the following Sub-chapters.



Fig. 3-1: Electrospinning apparatus (early set-up)

3.2.2 Polymer selection

The present study uses PLA synthesized from L optical isomer [denoted poly(L-lactic acid) (PLLA)] as the electrospinnable polymer. It is a biodegradable, thermoplastic and aliphatic polyester derived from renewable resources. PLA properties are also comparable to those properties of PET. PLA can be formulated to be either rigid or flexible and can be copolymerised with other materials. Typical properties of PLA made by NatureWorks[®]LLC (the 3051D grade used in this project) are discussed in Table 2-3 (Section 2.8.3). The variety of products made with PLA 3051D continues to grow rapidly [106]. This common product of PLLA has been dissolved in the mixture of dichloromethane (DCM) dimethyl formamide (DMF) and successfully electrospun resulting in fibre diameters ranging from 50 nm to about 400 nm depending on the proportion of the solvents and polymer concentration.



Fig. 3-2: Electrospinning set-up for this study

3.2.3 Materials

Electrospinning of PLLA was accomplished using solutions of PLLA (using NatureWorks[®]LLC 3051D) with a weight average molar mass about 1.044×10⁵ g mol⁻¹ and polydispersity 1.352 [as measured using gel permeation chromatography (GPC)]. Some solvents, such as dichloromethane (DCM), methanol, tetrahydrofuran (THF) hexafluoroisopropanol (HFIP), Trifluoroacetic acid (TFAA) and dimethyl formamide (DMF), were used to find out the suitable combination of solvents for successful electrospinning of PLLA. Finally, the combination of DCM and DMF was used for the entire study as it produced fine and uniform nanofibres consistently. For manufacturing PLLA-based conducting nanofibres, dodecylbenzene sulphonic acid (DBSA) doped polyaniline (PANi) mixed with PLLA has been dissolved in a common solvent (mixtures of chloroform and DMF), and the mixture was successfully electrospun to engineer bead-free superfine PANi/PLLA nanofibres. A tetra butyl ammonium bromide (TBAB) was used as an additive to increase the conductivity of the solution. Aniline (99%), procured



Fig. 3-3: (a) Programmable syringe pump (b) high voltage power supply

from Acros Organics, ammonium persulphate (98%), purchased from Ajax Chemicals and DBSA obtained from Acros Organics were used to synthesise DBSA doped PANi (PANi-DBSA). Chloroform (98%), DCM (98%) and DMF (98%) and TBAB were purchased from Sigma-Aldrich and used without further purification. Three saturated salt solutions have been made from lithium chloride (Sigma-Aldrich), sodium chloride (Ajax Finechem Pty Ltd) and potassium sulphate (Merck) to maintain the required relative humidity (RH) inside the electrospinning cabinet.

All experiments were performed in the set-up, Fig. 3-2, which was contained in a cabinet made of transparent PMMA sheets. The set-up included a power supply capable of generating high voltage, a syringe as a capillary tube and a stationary collector as a target. Polymer solution was delivered to the top of a needle through a hypodermic glass syringe (Popper & Sons, Inc) with capacity of 5 ml as a capillary tube and the flow of the liquid spinnable polymer was controlled using a programmable syringe pump, shown in Fig. 3-3 (a) (Cole-Parmer Hz 50/60, cat# 789100C). The same type of hypodermic needle (20G1TW, 0.9 × 25 mm from BD PrecisionGlideTM Needle) was used throughout the experimental work. The power supply, Fig. 3-3 (b), was a Spellman DEL HVPS INST 230-30R unit that could generate up to 30 kV. A metal screen and a heavy metal stand (pictures are shown in following Sub-chapter 3.2.5) have been made for collecting nanofibres.

3.2.4 Solution preparation

Supplied PLLA pellets were granulated in a grinder for easy and quick dissolution in different solvents. The weight average molar mass of PLLA has been found at about 1.044×10^5 g mol⁻¹ by GPC and polymer was found to be amorphous from XRD, as discussed in Chapter 5. Concentrations of 4% and 7% were made by dissolving 1.0 and 1.75 g pellets respectively in the mixture of 25 ml of DCM/DMF at a proportion of 90/10, 80/20, 70/30 and 60/40 (by volume). At a later stage, polymer concentrations of 4, 7 and 10% (w/v) [x% w/v means x g of solute in 100 ml of solvent] were made by adding 1, 1.75 and 2.5 g PLLA powders, respectively in a

mixture solution of 25 ml, prepared by mixing DCM and DMF (60:40 by volume) with 15 ml and 10 ml, respectively. Solutions were prepared with the aid of ultrasonication for 2 hours at room temperature. Ultrasonication offers great potential in the processing of liquids by improving the mixing and chemical reactions through alternating low-pressure and high-pressure waves in the liquid. A single solvent or different combinations of solvents (methanol, DCM, DMF, THF, HFIP, TFAA, chloroform and acetone) mixed in different proportions, were made to investigate the ability of solvent to make fine and uniform fibres. For producing PLLA-based conducting nanofibres, PLLA was dissolved in CHCl₃/DMF mixtures with proportions (v/v, CHCl₃:DMF) 50:50, and 70:30, to make a PLLA concentration of 10 % (w/v). The PLLA solution (2 parts by volume) was then mixed with a DBSA-doped PANi solution (1 part by volume) to give solutions with 6.7 % (w/v) PLLA and 1.7% (w/v) DBSA-doped PANi in 67:33 and 80:20 CHCl₃:DMF. 1% (w/v) TBAB was added to half of the solution for the testing. The details will be discussed in the respective Sub-chapters. All solutions were prepared and stored at the same room temperature (20⁰C) before the electrospinning process started.

3.2.5 Electrospinning operation

Polymer solution was delivered to the top of a needle through a programmable syringe pump at a rate of 0.5 - 2 ml hr⁻¹. The power supply used had a capacity of 30 kilovolts (kV). However, 6-15 kV was sufficient for this study. The positive electrode from the high voltage supply was connected to the needle. A heavy metal stand, Fig. 3-4 (b), as collector was attached to the other end of the electrode, which serves as the negative terminal. In the process, polymer solution is charged to a very high electrical potential. Because of the electric field, a charge is induced on the liquid surface. The mutual charge repulsion causes a force opposite to the surface tension of the polymer solution. As the electric field increases, the hemispherical surface of the solution at the tip of the capillary tube extends to form a cone-like structure, a "Taylor cone", [65] as discussed earlier in the theory of electrospinning. A metal screen, Fig. 3-4 (a), to collect nanomat/nanotextiles for other testing purposes (tensile strength, thermal behaviour, etc.) has been used. A heavy metal stand, Fig. 3-4 (b), was used for holding the aluminium (Al) stubs to

collect the nanofibres for visualisation in SEM. The distance between the collector and the needle tip was varied in the range of 60 - 120 mm. During electrospinning of the PLLA the spin-

Table 3-1: Some electrospinning conditions

Electrospinnable polymer	Poly (L-lactic acid) (3051D)
Concentration of polymer (PLLA) (w/v)	4-10%
Feed rate of programmable syringe pump	0.5–2 ml hour ⁻¹
Volume of the syringe	5 ml
Diameter of the hypodermic needle	0.48 mm (internal)
Applied voltage	8-12 kV
Distance between needle tip and collector	70-120 mm
Stationary collector	Aluminium screen

*Note: x% w/v means x g of solute in 100 ml of solvent



Fig. 3-4: Stationary collectors (a) metal screen (b) heavy metal stand

ning started at a voltage of 7 kV as the cone started forming. After increasing to 8 kV, a clear jet of fibres was established. Electrospun fibres were projected directly on to the SEM stubs which were polished and cleaned beforehand. Some electrospinning conditions used in this study are given in Table 3-1.

After projecting the nanofibres for 15 - 20 seconds on the SEM stub, the process was stopped. The stubs were dried for 8 hours in the atmosphere and then collected in a closed plastic container for visualisation in the SEM. The resultant nanofibres were found to be in the range of 50 - 400 nm depending on the parametric conditions, which was satisfactory indeed.

3.2.6 Nanotextiles

The textile industry, considered as a traditional industry, is an important and necessary part of the global manufacturing industry and provides employment to several million (or even more) people. With increasing international competition, it has been generally recognised that manufacturing traditional textile products may no longer be sufficient to sustain a viable business, and the textile industry may have to move towards more innovative and higher-quality products. Conventional mechanical fibre-spinning technologies cannot produce robust fibres with a diameter smaller than about 2 μ m [108]. Nanotextile, a more generalised term, is a flexible material consisting of a network of natural or artificial fibres (average diameter of 50-1000 nm) that are woven or non-woven. The use of textiles is pervasive in both product design and architectural applications. In the present study, PLLA nanofibres have been collected on the metal screen, as nonwoven mesh that consists of thousands of individual fibrils with diameters in the nanorange. From a textile viewpoint, these nanofibrous mats, Figs. 3-5 (a) and (b), have been termed as nanotextile/nanomat in the manuscript; however, the emphasis here is focused on electrospinning.



Fig. 3-5: Collected nanomat (a) on metal screen (b) nanomat

3.2.7 Safety measures

During this project, primary safety measures were taken against two risks: from the chemicals and from the high electrical voltage. Safety glasses, protective gloves and clothes, and good ventilation were compulsory. The flammability of solvents properties has been considered with the use of high voltages and as a result only small quantities of solution have been used. The electric risk added obvious problems of insulation. The power supply has been protected by a very sensitive fuse, as the risk of electrocution and electric arc were very important if the air contained a high level of moisture. A person standing within a distance of 50 cm can receive projections of both fibres and the chemicals. All the chemicals were handled with gloves and within a fume cupboard. DCM and DMF are harmful if swallowed or inhaled and may be harmful by skin contact [109]. During electrospinning of the PLLA-PANi mat, special care was taken in regard to chloroform. A mask was worn at all times and solution preparation was done strictly within the fume cupboard. The electrospinning operation was performed in the closed cabinet, Fig. 3-3, for dust protection, reduced air turbulence and for the extra security of the operator. However, some polymers might emit unpleasant or even harmful smells, so the processes should be conducted within chambers having a ventilation system. Furthermore, as a DC voltage in the range of 10 - 30 kV was necessary to generate the electrospinning, the researchers must be careful to avoid touching any part of the charged jet during manipulation.

3.3 Sample Preparation

Nanofibres were collected on a stationary collector in the electrospinning process. Aluminium (Al) stubs were kept on the stationary collector through the holes made on it, and nanofibres were projected directly on to the metal stub. The stubs were designed for the purpose of visualisation under a scanning electron microscope (SEM). After projecting the nanofibres for 15 - 20 seconds on the Al stub, the electrospinning process was stopped for a while. The stubs were taken out, dried for 8 hours in the atmosphere and then collected in an air-tight plastic container. Silica gel was kept inside the container to keep the nanofibre samples completely dry. A definite process of cleaning and polishing the Al stubs was established, Figs. 3-6 (a) - (d), by the trial and error method. Old and previously used stubs were put in acetone and ultrasonicated for 30 minutes. Then these were dried and carefully rubbed on emery paper to make a clear surface. During rubbing, Al stubs, Fig. 3-6 (c), were finger-rotated and polishing was continued until a smooth white surface was created. This process was followed by another acetone wash. Finally, the stub was dried and polished with a metal-polish paste. During polishing, changing the position of the stubs was very important to ensure a uniformly clean and glossy surface throughout the stub face. The surface started shining as soon as the stubs were polished with a soft fleecy cloth. Finally, the stubs were immersed in acetone and ultrasonicated for 30 minutes and were dried in soft tissue paper. The used stubs could be cleaned with less effort after reusing for the same purpose. A previous coating can be removed in an ultrasonic bath with acetone. A

clear and bright surface could be achieved by simply using a metal polish, avoiding the use of emery paper. Cleaning time and effort depended on how dirty the stubs were and for what purpose these have previously been used. By trial and error, cleaning and polishing process could be established and degree of cleaning required could be estimated visually. The surfaces of the stubs could be checked under a microscope in the middle of the cleaning and polishing process.



Fig. 3-6: (a) Al stubs in sample holder (b) flat surface for cleaning (c) cleaning by emery paper and metal polish (d) two of four stubs with white nanofibres

3.4 Techniques of Analysis

The electrospun nanofibres were studied under a Philips XL30S scanning electron microscope (SEM) after the nanomat had been coated with platinum in the Department of Chemical and Materials Engineering. Clear pictures of beaded or nonbeaded nanofibres were taken, and afterwards, by using image processing software (UTHSCSATM ImageTool), measurements of nanofibre diameter and bead area were taken and analysed.

3.4.1 Scanning electron microscopy (SEM)

The SEM is a high resolution microscopic tool to produce largely magnified images which are formed by using electrons rather than light. It utilises an electron beam to excite the electrons near the surface of a specimen, most commonly using an Everhart-Thornley detector to detect the low energy 'secondary' electrons that are emitted as a result of this excitation. There are two main types of electron microscope, the transmission electron microscope (TEM) and the scanning electron microscope (SEM). Light which is used as a source of illumination for the sample in light microscope has a wavelength of approximately 500 nm and therefore the resolution of the light microscope is limited. In practice, this means that the maximum magnification obtainable with a light microscope is X1000. Electrons used to view the sample in an electron microscope have an effective wavelength of about 0.1 nm and so allow much greater resolution and therefore greater magnification of the sample [110]. In the SEM, Fig. 3-7, the image is formed and presented by a very fine electron beam, which is focused on the surface of the specimen. The beam is scanned over the specimen in a series of lines and frames called a raster, just like the (much weaker) electron beam in an ordinary television.



Fig. 3-7: SEM instrument (at top) with chamber

The sputter coater, Polaron SC 7640, was used for coating standard SEM samples. It is designed to give a very thin, minimal metal coating suitable for SEM viewing. The normal target used is platinum (Pt) or gold (Au). In the case of visualisation of PLA nanofibres, the samples were coated with Pt for 300 seconds.

3.4.2 Morphological study of nanofibres using Imagetool

SEM images were used in conjunction with image analysis software, UTHSCSATM ImageTool [111] to determine the average diameter of the PLLA nanofibre and the area of beads. In order to ensure the accuracy of the results, experiments were replicated five times. From each experimental SEM-micrograph, eight individual fibre strands were considered and therefore, from five repetitions, a total of 40 fibres were considered from the same set of experimental conditions to estimate the range of diameters and their variations. For an individual nanofibril, measurements of diameter were taken in five different places and finally average diameter has been calculated. Similarly for an individual bead, area was calculated using the software, and the total area occupied by beads was calculated by adding all of them. On the basis of measurements of five repetitions, derived from imagetool software, the average diameter, standard deviation and finally S/N ratios [112] were calculated for analysing the parametric effect. S/N ratios take into account both the degree of variability in the response data and the closeness of the average response to the desired value that is explained in Sub- chapter 4.2.2.1.

3.5 Manufacturing of Nanotextile from Poly(L-lactic acid) (PLLA)

Electrospinning of PLLA was accomplished using solutions of PLLA in different concentrations of various solvents. In the early stage of research, the solvents - namely DCM, methanol, DMF, HFIP, THF and TFAA- were used to make a nanofibrous mat for finding the performances of the solvents in individual or in combinations - those are shown in scanning micrographs in the next Sub-chapter. Finally, the combination of DCM and DMF performed well and different proportions have been checked to find out the ability to make uniform nanofibres consistently.

PLLA was dissolved in a mixture of DCM and DMF (60:40 by volume) to prepare different concentrations. As recommended in reported studies [1, 42, 71], a concentration of 4 - 10% (w/v) (x% w/v means x g of solute in 100 ml of solvent) and a feed rate of 0.5 - 2 ml hour ⁻¹ were chosen for this study. It is to be noted that although a feed rate of 0.5 ml hour ⁻¹ performed well

at times, it had a tendency to clog the needle tip. So precautions had been taken by cleaning the tip frequently. As the electric field increased beyond 7 kV, the hemispherical surface of the solution at the tip of the capillary tube extended to form a cone-like structure. A constant volume flow rate was maintained using a syringe pump, set to keep the solution at the tip of the tube without dripping. The electric potential, the flow rate, and the distance between the capillary tip and the collection screen were adjusted so that a stable jet was obtained. Once a stable jet was produced, electrospinning was continued for a considerable time.

Commercial aluminium foil used for collecting the nanofibres, was kept at a distance so that the solvent could evaporate and nanofibres could get enough flight time to dry. Aluminium stubs that had been well cleaned to create a smooth and glossy surface, were used to collect the sample for visualisation under SEM. The distance between the collector and the needle tip was maintained at 80 - 120 mm; white nanofibres adhered smoothly on the aluminium foil with a voltage in the range of 7 - 12 kV. The power supplied should be adequate to overcome the viscosity and surface tension of the polymer solution to form and sustain the jet from the pipette. An increase in electric potential tends to stretch the polymer more, resulting in decreased fibre diameter up to a certain level. A maximum voltage of 12 kV has been found suitable for effective stretching; further increase in voltage generates too much acceleration on the polymer solution resulting in nanofibres with irregular sizes due to insufficient flying time for solvent evaporation. Three saturated salt solutions were made from lithium chloride, sodium chloride and potassium sulphate to maintain the required relative humidity (RH) inside the cabinet. Temperature was controlled inside the electrospinning cabinet using ice and / or hot air. At the beginning of the research, the ambient temperature $(20^{\circ}C)$ and humidity (40%) were kept unchanged, where the effects of other parameters were examined.

3.5.1 Selection of solvents

The choice of solvent is critical as the properties of the polymer solution have the most significant influence on the electrospinning process [1]. The dielectric constant of a solvent has a

major contribution in making a spinnable polymer solution. Generally, a solution with greater dielectric constant reduces the bead formation and the diameter of the resultant electrospun fibre [1]. Solutions with high conductivity will have a greater charge-carrying capacity than solutions with low conductivity. Thus the fibre jet of highly conductive solutions will be subjected to a greater tensile force in the presence of an electric field than will a fibre jet from a solution with a low conductivity. In addition, the volatility of solvent plays a major role in the formation of nanostructures by influencing the phase separation process [16, 113]. As the fibre jet travels through the atmosphere towards the collector, a phase separation occurs before the solid polymer fibres are deposited. This process is greatly influenced by the volatility of the solvent. To find a suitable combination of solvents, various solvents [DCM, methanol, DMF, HFIP, THF, TFAA] were examined in individual or in combination of two. Zong et al. used a mixed solvent of DCM and DMF with a ratio of 60:40 to dissolve the semi-crystalline PLLA [42]. Lee et al. had investigated chloroform as a good solvent [108]. However, there are concerns about safety with chloroform whereas HFIP and THF have been reported safe, easy and convenient solvents by many researchers. These solvents have been used as well, but spinnability (Figs. are shown in Sub-chapter 3.5.3), was not acceptable.

DMF with a high dielectric constant is an effective solvent component. Together with a dielectric constant, DMF has low vapour pressure and high boiling point that can make the solution more effectively spinnable. More electric charges carried by the electrospinning jet impose higher elongation forces, resulting in finer fibres [42, 54]. DCM is a unique solvent to dissolve aliphatic polyesters like PLLA. However, due to its low boiling point (39.8°C) and high volatility, the tip of the spinneret/needle is easily clogged while the polymer solutions are electrospun in this solution. Thus, DMF (boiling point 153°C) can be added in a significant proportion to increase the boiling point of the resultant solution and finally to achieve dry and fine fibres. Different proportions of DCM and DMF have been made for making polymer solutions to extract suitable performances, (Figs. are shown in Sub-chapter 3.5.3) of electrospinning. However, a mixture of DCM and DMF (60:40 by volume) consistently produced fine, uniform and beaded/non-beaded nanofibres. It was supported by Zong et al., they used a mixed solvent of DCM and DMF with the same proportion to dissolve the semi-crystalline PLLA [42]. The details of the performances are discussed in Chapter 4, parametric analysis.



3.5.2 Measurement of nanofibre diameter and bead area

From the scanning micrographs, measurements of fibre diameter and bead area of nanofibrous mat were taken using the imagetool software (UthanscaTM). In order to ensure the accuracy of the results as mentioned earlier, experiments were replicated five times, as outlined in Sub-chapter 3.4.2. From each experimental SEM-micrograph, eight individual fibre strands were considered and therefore, from five repetitions, a total of 40 fibres were considered from the same set of experimental conditions to estimate the range of diameters and their variations. For an individual nanofibril, measurements of diameter were taken at five different places of the same strand, and finally the average diameter was calculated. Similarly, for a particular experiment, the bead area was calculated from corresponding scanning micrograph, using the software, and the total area occupied by beads was calculated by adding them up. From a particular experiment (using 4% of polymer concentration, with a feed rate of 1 ml hr⁻¹, applied voltage of 8 kV and the distance of 80 mm between the needle tip and collector), a nanofibre sample has been visualised and fibre diameter and beads are shown in two micrographs, Figs. 3-8 and 3-10 (from the same experi -



Fig. 3.8: Scanning micrograph of PLLA nanofibres for a particular experiment using 4 % (w/v) polymer concentration in mixture solvent of DCM/DMF

Diameter range (nm)	Number of individual nanofibres				
	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5
0-50	2	2	2	2	
50-100	2	3	3	4	6
100-150	2	3	2	1	2
150-200	2		1	1	
200-250					

Table 3-2: Diameter ranges of 40 individual nanofibrils



Fig. 3-9: Frequency distribution bar graph of diameter ranges of same nanofibres of Table 1.

ment) with high and low magnifications respectively. For five repetitions from the same experiment, five micrographs were considered and from each micrograph eight strands of nanofibres were measured by using imagetool software. For 40 nanofibres, a frequency distribution bar graph, Fig. 3-9, has been made to show the variation of nanofibre diameters. From the Table 3-2, the diameters varied from 50 nm to 200 nm with no single strand being more than 200 nm. The average diameter was calculated to be 88.31 nm. Similarly, for the same experiment, bead area was calculated from a scanning micrograph, Fig. 3-10, with low magnification and the total area occupied by the beads was calculated to be 192.72 (μ m)².



Fig. 3-10: Scanning micrograph of same PLLA nanofibres in low magnification

3.5.3 Morphology of nanofibres depending on solvents

PLA granules were dissolved in DCM to make a solution concentration of 4% (w/v) (x% means x g of solute in 100 ml of solvent) with the aid of ultrasonication, but spinnability was not achieved. A polymeric thin layer, Fig. 3-11 (a), was observed only with specific conditions of feed rate 1 ml hr⁻¹, voltage 8 kV and the distance 80 mm. PLA granules dissolved slowly and only partially in the mixed solvent (60/40) of DCM and methanol and the electrospinning jet was not formed well, mostly polymeric blobs, Fig. 3-11 (b), were found. PLA pellets were found undissolved in methanol to make a 4% (w/v) solution. A solution was made in TFAA, but due to the solvent's high volatility, electrospinning was almost unsuccessful and only a few microfibres were visible.



Fig. 3-11: Scanning micrographs using 4% PLLA (a) polymeric thin layer using DCM (b) big polymeric blobs using mixed solvent (60/40) of DCM and methanol



Fig. 3-12: (a) Different shaped small and large beads with THF (b) spherical beads with HFIP

THF and HFIP resulted in clear solutions after dissolving the polymer, but mostly beaded fibres were found in electrospinning (specific conditions of feed rate 1 ml hr ⁻¹, voltage 8 kV and workable distance 80 mm). Scanning micrographs, Figs. 3-12 (a) and (b), using THF and HFIP, show the electrospun mat with only a few micro/nanofibres. The selection of solvents is crucial as the resultant solution has the most significant impact in electrospinning performances, as discussed in the previous Sub-chapter 3.5.1. Finally, the combination of DCM and DMF was used as it built fine and uniform nanofibres consistently, keeping the other factors favourable [20, 77].

Starting with the proportion of DMF at 10% and maintaining other spinning parameters within the suitable range (feed rate of 1 ml hr⁻¹, voltage of 8 kV and distance of 100 mm), large sized elliptical beads, Fig. 3-13 (a), were found. By increasing the proportion of DMF, bead area became less, Figs. 3-13 (a) - (d), and the diameter reduced significantly. At a proportion of 40%, very few beads were visible with an average diameter of 151 nm. This was, indeed satisfactory.



Fig. 3-13: Scanning micrographs of nanofibres using DCM/DMF with a proportion of DMF (a) 10% (b) 20% (c) 30% (d) 40% [specific conditions with feed rate of 1 ml hr⁻¹, voltage of 8 kV and workable distance of 100 mm]

Keeping the polymer concentration at 10% and maintaining other spinning parameters at a high level (within the experimental range as has been discussed at length in the Section 6 on regression analysis) and a feed rate of 1 ml hr⁻¹, bead-free nanofibres were produced. Though fibre diameter, Fig. 3-14 (b), was found to be slightly coarse in the range of 250 - 400 nm, the nanofibres were bead-free and uniform, Figs. 3-14 (a), and were consistently made. It proved the

effectiveness of the mixed solvent (DCM/ DMF) with a proportion of 60/40, and throughout the study, the same proportion was used. Viscosity and conductivity of this effective polymer solution were also checked (refer to Section 5) as these two factors are the most important in building nanofibres from a polymer solution.



Figs. 3-14: (a) Scanning micrographs of nanomat with polymer concentration of 10% (w/v) with (a) beadfree nanofibres in low magnification (b) nanofibres with high magnification [specific conditions: feed rate of 1 ml hr⁻¹, voltage of 10 kV and workable distance of 100 mm]

3.6 Manufacturing of PLLA-based Conducting Nanofibrous Mat

3.6.1 Introduction and requirements

Electrically conductive polymers, also known as synthetic metals, [114, 115] are finding an increasing number of applications in many areas of applied chemistry and physics. Multi-functionalised micro/nanostructures of conducting polymers in neat or blended forms have received much attention because of their unique properties and technological applications in

electrical, magnetic and biomedical devices. They are of special interest for tissue engineering because new technologies will require biomaterials that not only physically support tissue growth but also are electrically conductive, and thus able to stimulate specific cell functions or trigger cell responses. They are effective for carrying current in biological environments and can thus be considered for delivering local electrical stimuli at the site of damaged tissue to promote wound healing. Common classes of organic conductive polymers include polyacetylene, polypyrrole, polythiophene, polyaniline and poly(para-phenylene vinylene). The present research has focused on polyaniline (PANi) as the conducting polymer and PLLA as the biopolymer. Mattioli-Belmonte et al. [116] have demonstrated that PANi is biocompatible in vitro and in long-term animal studies in *in vivo*. A few researchers have electrospun conducting polymers with other polymers including gelatine and poly(ethylene oxide); however, the quality of the nanofibres produced was not given primary attention [114, 117]. In this study, dodecylbenzene sulphonic acid (DBSA) doped PANi and PLLA have been dissolved in a common solvent [mixtures of chloroform and dimethyl formamide (CHCl₃: DMF)], and the solutions successfully electrospun. DMF enhanced the dielectric constant of the solvent, and tetra butyl ammonium bromide (TBAB) was used as an additive to increase the conductivity of the solution. DBSA-doped PANi/PLLA mat exhibits an almost bead-free network of nanofibres that has extraordinarily smooth surface and diameters in the range of 75 - 100 nm. A previous study has demonstrated the possibilities of making bead-free PLLA nanofibres with a good range of diameters through electrospinning [77, 94]. It has also been shown that the morphology of the electrospun nanofibres can be tailored by manipulating the processing parameters. The application of that concept in the present electrospinning of PLLA-PANi has successfully produced bead-free uniform and fine nanofibres from PANi/PLLA solution. This novel system can open up new and interesting opportunities for applications in biomedical devices, biodegradable materials, and sensors, among other things. Significant conductivity has been found for PANi/PLLA nanofibrous mats. It is intended that the product will be incorporated into electromagnetic devices and medical aids.

3.6.2 Experimental

DBSA-doped PANi has been supplied by the Department of Chemistry, UoA. PLLA was dissolved in CHCl₃/DMF mixtures with proportions (v/v, CHCl₃: DMF) 50:50, and 70:30, to give PLLA concentration 10% (w/v). PLLA solution (2 parts by volume) was then mixed with DBSA-doped PANi solution (1 part by volume) to give solutions with 6.7% (w/v) PLLA and 1.7% (w/v) DBSA-doped PANi in 67:33 and 80:20 CHCl₃:DMF. 1% (w/v) TBAB was added to some of the solutions. Polymer solution was delivered to a stainless steel syringe needle by a glass hypodermic syringe as described in the manufacturing part of PLLA. As recommended in recent studies [42, 71] including Patra et al. [77, 94], a solution feed rate (1-2 ml hr⁻¹) with constant polymer concentration and molar mass were chosen for this study. The distance between the collector and the needle tip was maintained at 80 - 100 mm and the voltage was kept in the range 8 - 10 kV. For finding the performance, initially a smaller amount of DMF (20%) was used with chloroform and the resultant electrospun nanofibres, Fig. 3-15 (a), showed a number of large beads. By manipulating the parameters, the area occupied by beads could be reduced, but still bead-free network was not achievable in Fig. 3-15 (b). After increasing the proportion of DMF, nanofibres, Fig. 3-15 (c), were found with less bead area. The ambient temperature (20°C) and relative humidity (40%) were kept unchanged throughout the electrospinning experiments.

3.6.3 Bead-free nanofibres using electrolyte

DMF enhanced the dielectric constant of the solvent, and TBAB was used to increase the conductivity of the solution. The addition of only 1% (w/v) of this quaternary ammonium salt TBAB dramatically increased the conductivity of the electrospinning solution of DBSA-doped PANi and PLLA, and facilitated the formation of bead-free nanofibres, Figs. 3-15 (d) and (e), with low and high magnifications, respectively. Together with dielectric constant, DMF has low vapour pressure and high boiling point, which made the solution more effectively spinnable.



Figs. 3-15: Scanning micrographs of (a) beaded nanofibres from a 80:20 CHCl₃: DMF solution (b) nanofibres from the same solution with increased voltage and workable distance (c) nanofibres with fewer beads from a 67:33 CHCl₃: DMF solution (d) bead-free nanofibres from a 67:33 CHCl₃: DMF solution with TBAB (e) fine nanofibres at higher magnification from the same solution



Larger electrical charges carried by the electrospinning jet imposed higher elongation forces, resulting in finer fibres. In addition, a larger distance could provide a longer flight time to elongate and dry the fibre before it is deposited on the collector plate [42]. DBSA-doped PANi/PLLA mat exhibited an almost bead-free network of nanofibres that had extraordinarily smooth surfaces and diameters in the range of 75 to 100 nm.

3.6.4 Conductivity of the nanomat

Bulk AC conductivity across the fibremat using a potentiostat with impedance spectroscopy software (PAR Versa STAT3) was determined. Significant conductivity was found for the PANibased PLLA mat. Bulk AC conductivity was 0.02 mS cm⁻¹ at 10 kHz and 0.002 mS cm⁻¹ at 125 Hz. A film cast from the PANi/PLLA/TBAB solution had conductivities of 0.161 and 0.07 mS cm⁻¹ at 10 kHz and 1 Hz, respectively. The high interaction between the components and the rapid evaporation of the solvent during electrospinning resulted in nanofibres with a lower degree of crystallinity in comparison with cast films. Probably because of the low crystallinity and the high porosity of the nonwoven mat, the electrical conductivity of the electrospun fibre mats was lower than that of the blend films produced by casting.

3.7 Concluding Remarks

This chapter provides a broad overview of the electrospinning manufacturing process, the materials and equipment used, and the analysis techniques utilised during this research. Some of the conclusions are:

- Poly(L-lactic acid) nanofibrils can be successfully electrospun from commonly used, PLA (3051D) pellets into fine and uniform nanofibres.
- A solvent mixture of DCM and DMF at a proportion of 60/40 has performed consistently well in the entire study. Fine, smooth and uniform nanofibres have been manufactured by manipulating the process parameters efficiently. Bead-free nanofibres with diameters in the range of 200 and 400 nm are easily achievable. Nevertheless, producing below 100 nm is quite challenging.
- A novel electrospun poly(L-lactic acid) based conducting nanofibrous mat has been developed. A conducting polymer, polyaniline (PANi) has been added to the PLLA by dissolving in common solvents and a blended nanotextile with fine and bead-free nanofibres, has been manufactured through controlled electrospinning.

Parametric (Factorial) Study of Electrospinning

Parametric (Factorial) study of electrospinning is split into two parts: (i) a selection of factors and their study through Taguchi methodology, and (ii) finally, the impact of different factors in the formation of smooth nanofibres with uniformity and fineness. This chapter outlines the producing of a quality nanotextile by manipulating the process parameters and investigates the impact of various factors in shaping the nanofibres. It provides details of the methodology, results and conclusions for suitable parametric combinations to produce poly(L-lactic acid) (PLLA) nanofibres.

4.1 Quality of Nanofibres

Nanofibres are attractive for their nanoscale diameters, high surface area to volume ratio, their porous structure and obviously, their light weight. When the diameters of polymer fibre materials are shrunk from micrometers (e.g.10-100 μ m) to submicrons or nanometers (e.g.10 ×10⁻³-100 ×10⁻³-100 ×10⁻³ μ m), there appear several remarkable characteristics, such as a very large surface area to volume ratio (this ratio for a nanofibre can be as large as 10³ times that of a microfibre). It permits flexibility in surface functionalities and provides superior mechanical performances compared to any other known form of the material [18]. Non-woven textiles composed of electrospun fibres have small pore sizes compared to commercial textiles, making them excellent candidates for use in filtration and membrane applications. These outstanding properties make

the polymer nanofibres optimal candidates for many important applications.

The making of nanofibres through electrospinning is an easy task, but to control the fibre diameter and its morphology in the nanometric range is challenging. One of the issues in electrospinning is that very fine electrospun fibres usually contain some bead-like defects. Beads are the nonporous polymeric material; they are created if the polymer solution is not stretched enough, due to many reasons.

4.1.1 Nanofibrous network

Nanofibres and nanofibre mats are relatively recent additions to the world of materials. Although a random deposition of electrospun fibres gives a nonwoven fibre structure, the web morphology varies depending on the polymer properties and the operating conditions. Usually, the nanofibres are accumulated by a simple physical interaction and the fibres do not bond with each other. However, when the electrospinning distance is very short, the solvent has insufficient time to evaporate from the filaments because of the short flying time [84]. Wet or semi-dry nanofibres are stuck and bonded together, Fig. 4-1 (a), forming an interconnected fibre web [53]. As the fibres are continuous with long strands and very short periphery, thousands of nanofibrils are being interlaced or joined through crossover points making an unbreakable mesh. For nonwoven materials, the number of fibres and the number of crossover points determine the relative tensile strength of the fibre assembly.

4.1.2 Beaded nanofibres

Beads, Figs. 4-1 (a) and (b) are considered the main demerits of electrospun fibres. These are nonporous polymeric material and created due to many reasons [refer to Section 2.7.3]. There are different shapes of beads. They may be of elliptical, spherical, regular or irregular shape. These defectives even become the main products when the polymer concentration is very low. Although low polymer concentration is favoured to produce finer nanofibres, it leads to the

emergence of colloid beads or beads-on-string fibres in Fig. 4-1 (b). The existence of beads, not only reduces the fibre uniformity, it also leads to reduced fibre surface area, porosity and poor mechanical strength.



Figs. 4-1 (a) nanofibrous network with a few beads (b) beads-on-string nanofibres

4.2 A Parametric Analysis of Electrospinning

4.2.1 Background

Nanofibres are of industrial and scientific interest due to their large aspect (length-to-diameter) ratios and high surface areas per unit volume. The major applications of these nanotextiles include the areas of tissue engineering (scaffolds), drug delivery media, filtration media and clothes protection. The porosity and pore size of the resulting nanofibrous mat or fabric are crucial for filter media to determine the efficiency as well as pressure drop and permeability. This filtering efficiency increases with a reduction in fibre diameter [118]. Researchers around the globe have used various biocompatible and biodegradable synthetic polymers including poly(lactic) and poly(glycolic) acids (PLA and PGA, respectively) and their copolymers (PLAGA), polycaprolactone (PCL), polydioxanone (PDO), and a few others for scaffold fabrication [31, 34, 39]. Electrospun nanotextiles meet the essential design criterion of ideal engineered tissue scaffolds based upon their ability to support and guide cell growth. Most publications indicate that an electrospun nanofibrous structure is capable of supporting cell attachment and proliferation. Cells seeded on this structure tend to maintain phenotypic shape and have their growth guided according to nanofibre diameter and orientation. Electrospinning can also be used to create biocompatible thin films with useful coating design and surface structure. Nanotextiles, made of fibres from biodegradable polymers may be helpful in adjusting the degradation rate of a specified biomaterial under in vivo environment [18]. Although no systematic research on the influence of nanofibre diameter on the degradation behaviour of polymers has been reported, there is evidence that diameters do affect the degradation features and related mechanical properties of the materials used. Furthermore, it has been theorised that the cells attach and organise well around fibres with diameters smaller than the diameters of the cells [18, 119]. Although electrospinning appears to be straightforward, it is a rather intricate process that depends on a multitude of molecular, process related, and technical parameters [34]. It is vital to produce nanotextiles in a controlled manner so that the process gives high quality fibres with precise fibre morphology. The primary requirement of the process is to obtain nanofibres in continuous form with fine diameters and minimum variations. Secondly, the fibre network has to have minimum area occupied by beads to enhance the network's porosity and

strength. These two important characteristics, when achieved, render the nanofibre mats acceptable for many membrane-type applications. The relationships between processing parameters and microstructures of nanofibrils are still not well understood. If the field strength is too high, increased instability of the jet may lead to bead formation [42, 71]. On the other hand, if the distance between the needle tip and the collector is such that the field gradient is enough, there are fewer beads formed as the electric field provides sufficient stretching force to the jet. However, at larger distances the fibre diameter increases due to the decrease in the electric field gradient, resulting in less stretching of the fibres [87]. Another factor that may influence the diameter of the fibre is the flight time of the electrospinning jet - a longer flight time allows more time for the fibre to elongate before it is deposited on the collector plate [89]. Similarly, a shorter flight time results in less elongation, generating coarse fibres. It must be acknowledged that the integration of nanofibres into useful devices requires fibres of well-controlled size and uniformity as well as reproducibility of locating them in specific positions. The ability to do so remains a major challenge [17], and effective parametric analyses are needed to achieve products with the required characteristics. The Taguchi method of experimental design offers scope for selecting the optimal levels of process parameters with the minimum number of experiments carried out, thus significantly reducing the time required for experimental investigation. The primary objective of the present work is to use this method to establish a desirable set of four control parameters, Table 4-1, namely, the concentration and feed rate of polymer solution, appl-

Factors	Description	Level 1	Level 2	
А	Concentration of polymer solution (%w/v)	4	7	
В	Feed rate of polymer solution (ml hour ⁻¹)	1	2	
С	Distance (mm)	80	100	
D	Voltage (kV)	8	10	

 Table 4-1:
 Factors and levels used in the experiments

*Note: x% w/v means x g of solute in 100 ml of solvent

ied voltage, and the distance between the collector and the needle. The target outcomes have been chosen as the diameter of the nanofibres with minimal variation and minimum mat area occupied by the beads.

4.2.2 Taguchi method

Taguchi stresses that quality variation is the main enemy of quality engineering, and every effort should be made to reduce the variation in quality characteristics. The Taguchi method [112, 120] is a well-known approach in the modern robust design process, primarily based upon the statistical design of experiments (DoE). The design offers a scope for finding the optimum settings of the control factors with the minimum number of experiments carried out to achieve a particular goal or output. It is also effective in elucidating the effects of multiple factors individually and interactively, on product quality. The method provides optimised process conditions with minimal sensitivity to the different causes of variation, and is aimed at producing high quality products with relatively low development and manufacturing costs [120].

4.2.2.1 Introduction to Taguchi methodology

When an understanding, improvement or optimisation of a product or process is required, the design of the experimental procedure often determines the amount and quality of the information gathered and the conclusions that can be drawn from it. Experimental design uses predetermined inputs to produce a set of data pertaining to an output characteristic that is of interest. The main input parameters in any experiment are the experimental elements (factors) and their possible settings (levels). The Taguchi method is aimed at finding a robust setting of control factors to make the product or process insensitive to the noise factors (121, 122], and to optimise them against the target outcomes. In order to execute a robust design, Taguchi employs two key tools,

namely signal to noise (S/N) ratio to assess the quality, and an orthogonal array (OA) to arrange the experiments that can accommodate many design factors simultaneously. Taguchi suggests an S/N ratio as the objective function for matrix experiments as S/N ratios take into account both the degree of variability in the response data and the closeness of the average response to the desired value. The calculation of the S/N ratio is of considerable interest when completing an experimental design.

The OA of experiments is to determine the optimum level for each factor and to establish the relative significance of an individual factor in terms of its main effects on the outcome. To achieve the 'lower is better' characteristics (i.e. small diameter and bead area) the S/N ratio is given by:

$$S/N = -10\log \frac{1}{n} \sum_{i=1}^{n} y^2$$
 (4-1)

where y represents the results of measurement, n is the number of observations and subscript i indicates the number of simulation design parameters in the OA table. A greater S/N ratio always corresponds to more robust quality characteristics regardless of their category [112].

An analysis of variance (ANOVA) is performed as well to see which process parameters are statistically significant. Another tool, F-test [123] has been used to see which process parameters have significant effects on the performance characteristics. This is accomplished by separating the total variability of the S/N ratios, which is measured by the sum of the squared deviations from the total mean of the S/N ratio, into contributions by each of the process parameters and the error. First, the total sum of the squared deviations SS_T from the total mean of the S/N ratio, η can be calculated as:

$$SS_T = \sum_{i=1}^m (\eta_i - \bar{\eta})^2$$
 (4-2)

where *m* is the total number of experiments in OA, and η_i indicates the S/N ratio for the *i*-th experiment [120, 124].
4.2.2.2 Why Taguchi methodology has been used

The purpose of performing an experimental design analysis is to gather the maximum amount of robust system information from a limited number of carefully designed trials. This is achieved by selecting the factors and levels considered to have the most influence on the output value, and utilising a method of statistical analysis popularised in the fields of optimisation and quality control through the teachings of Taguchi [112, 120, 121, 125]. Taguchi's OA can provide a simple and systematic methodology for finding a set of suitable spinning parameters. The parameters used in this work as described earlier in Table 4-1, are the concentration and feed rate of polymer solution, applied voltage, and the distance between the collector and the needle. The selection of parameters is explained in the next Section. The target outcomes have been the nanofibre diameter with minimal variation and minimum mat area occupied by the beads. From the S/N ratio approach, the parametric combination can be found suitable when it provides maximum value for fibre diameter and bead area separately. ANOVA approaches can provide parameter's contribution straightaway mathematically. One can be reassured whether these two different approaches converge on the same type of parametric selection or not. An easy and shortcut way of deciding the best parameter combinations and an individual parameter's direct contribution in making the final product makes Taguchi methodology of well accepting and cost effective to industry.

4.2.2.3 Parameter selections with their levels

The viscosity and conductivity of the solution determine the extent of elongation of the solution [1, 126]. The viscosity of the polymer solution depends on both the molecular weight of the polymer and the concentration of the polymer solution [1, 77]. In the current study, the molecular weight of the polymer was not varied. Furthermore, the conductivity of the polymer solution was also not considered as a variable because the relative proportion of the two solvents, DCM and DMF, was kept constant (60:40 by volume). Starting with the proportion of DMF at 10% (refer to Section 3.5.1) and maintaining other spinning parameters within the suitable range (feed rate

of 1 ml hr⁻¹, voltage of 8 kV and distance of 100 mm), large-sized elliptical beads, Fig. 3-14 (a), were found. With the increasing proportion of DMF, bead area became much less, Figs. 3-14 (a) - (d) (shown in Section 3.5.1) and the diameter also reduced significantly. At a proportion of 40-

Solvent	Dielectric constant	Boiling point (⁰ C)
Acetone	20.7	56
Chloroform	4.8	61
Dichloromethane	8.93	39.8
Tetrahydrofuran	7.47	66
Dimethylformamide	36.71	153
Toluene	2.38	111
Acetic acid	6.2	118
Methanol	33	65
Water	80	100

Table 4-2: Dielectric constant and boiling points of solvents

%, very few beads were visible with a diameter of 150 - 200 nm, which was indeed satisfactory. DMF with a high dielectric constant is an effective solvent component. DMF has low vapour pressure and a high boiling point (153^{0} C), Table 4-2, which can make the solution more effectively spinnable when it is combined with DCM with a low boiling point (39.8^{0} C) and high volatility. The feed rate of the polymer solution is an important parameter because it determines

the amount of solution available for stretching to form nanofibres and plays a vital role in determining the fibre diameter and bead formation [42]. As recommended in reported studies [17, 42, 71], a concentration of 4 - 7 % w/v (g/100 ml) and a feed rate of 1 - 2 ml hour $^{-1}$ were chosen for this study. Using a polymer concentration of 3% and other spinning parameters within the suitable range (feed rate of 1 ml hour ⁻¹, voltage of 8 kV and tip-to-collector distance of 100 mm), electrospinning of PLLA was performed and heavily beaded fibre networks were created. It is to be noted that although a feed rate of 0.5 ml hour ⁻¹ performed well at times, it had a tendency to clog the needle tip. Higher electrical forces (i.e. larger applied voltage) provide extra stretch to elongate the fibres and thus make nanofibres with reduced diameters. The starting voltage in this study was 6 kV but as the spinning rate increased with increasing voltage, at voltages higher than 12 kV the spinning rate became too fast to control and jet flow diverged. Consequently, 8 - 10 kV was selected as an appropriate voltage range. As the distance between the collector and the needle tip was increased, electrospinning produced a nanofibre network with fewer beads. An 80 - 100 mm range of distance was found to be appropriate for this study. Other experimental variables were kept constant to isolate the effects of the four parameters that were varied. Experiments were performed (refer to Sub-chapter 3.5) in a closed chamber, Fig. 4-2, and attention was paid to maintaining the same relative humidity (40%) and ambient temperature $(20^{\circ}C)$ for the duration of the experiments.

4.2.2.4 Design of experiment

As outlined in previous Section 4.2.2.2, the purpose of performing an experimental design analysis is to gather the maximum amount of robust system information from a limited number of carefully designed trials. The analysis is performed by entering the test results into the correct columns of the design matrix and calculating the average effects for all the factors at each level. The estimated effects are plotted for each factor and the larger the line connecting the high and low effect levels for any factor, the more significance it is likely to have on the output. In the present study, the principal characteristics of robustness for the electrospinning of PLLA include the making of fine nanofibres with the least number of beads and a reduced sensitivity to external noise. Therefore, two performance indices have been considered: fibre diameter and bead area. In the presented set of experiments, Table 4-1, four factors (the concentration and feed rate of polymer solution, applied voltage, and the distance between the collector and the needle) and two levels of each have been considered. Instead of normal factorial design (2⁴), eight run OA is chosen due to its capability to check the interactions among various factors [112]. Each process parameter is assigned to a column and each row of the matrix represents one trial. The sequence in which these trials are carried out has been randomised and the two levels of each factor are represented by '1' or '2' in the matrix.



Fig. 4-2: Electrospinning set-up for this study

The experimental layout plan for the electrospinning process parameters using L_8 OA is shown in Table 4-3, whereas Table 4-4 (presented in the next Sub-chapter) shows the actual data for fibre diameter and bead area along with their computed S/N ratios. Tables 4-5 and 4-6 show the ANOVA results of two characteristics separately. Completed design matrices consisting of two

response tables for S/N ratios of fibre diameter (Table B-1) and bead area (Table B-2) are located in Appendix B. In order to get a clear idea of the various factors and their interactions, a set of 16 (2⁴) confirmatory experiments were performed to get a clear idea of the effects of various contributing factors. The results of the 16 experiments for fibre diameter and bead area and their corresponding S/N ratios are described in Table 4-7 in Section 4.4. Experimental results and S/N ratios for fibre diameters with replications, Table B-3, are provided in Appendix B.

Experiment number	Electrospinning parameter level						
	Α	В	С	D			
	Polymer conc (%w/v)	Feed rate (ml hour ⁻¹)	Distance (mm)	Voltage (kV)			
1	4	1	80	8			
2	4	1	100	10			
3	4	2	80	10			
4	4	2	100	8			
5	7	1	80	10			
6	7	1	100	8			
7	7	2	80	8			
8	7	2	100	10			

 Table 4-3: Experimental layout plan using eight runs

4.2.3 Results and Discussion

4.2.3.1 Signal to noise (S/N) ratio approach

The diameter ranges of nanofibres for two successive experiments (#1 and #2) are shown in Figs. 4-3 (a) and (b) through frequency distribution bar graphs. The results are then substituted into Equation (4-1) to obtain the corresponding S/N ratios in Table 4-4. Since the experimental design is orthogonal, it has been possible to separate out the effects of each spinning parameter at different levels with their interactions. In addition, the total mean S/N ratio for the eight experiments is also calculated for two output characteristics, Figs. 4-4 (a) and (b). Vertical distances of A1A2 and D1D2, Fig. 4-4 (a), suggest that polymer concentration (factor A) and voltage (factor D) are more significant for achieving small fibre diameters. Feed rate (factor B) and distance between the needle and collector (factor C) are of relatively low significance. It appears that the interactions between the factors do affect the response a little. The low polymer concentration (A_1) and comparatively high voltage (D_2) appear to be the best choice to get fine fibre diameters. Although the other two factors are relatively insignificant on the average S/N responses, a low feed rate and a long distance have shown some positive impacts in making finer fibre diameters which will be discussed later. Therefore, experiment #2 in Table 4-4 is the best for achieving small diameters, Fig. 4-5 (a), and an optimal parameter combination of $A_1B_1C_2D_2$ (among eight runs) has the maximum S/N value of -34.18 with the average nanofibril diameter of about 51nm. Individual factor contribution can be calculated with the help of response tables for S/N ratios of fibre diameter and bead area through ANOVA. The fully-described response tables are appended (Appendix B).



Figs. 4-3: Frequency distribution bar graphs of diameter range of nanofibres for three experiments (a) Exp #1 (b) Exp #2 (c) Exp #8

(a)





Figs. 4-4: Estimated factor effects for (a) fibre diameter (b) bead area

Exp- number	Factors			Designation	R	lesult	Calculated	S/N ratio	
	Α	В	С	D		Fibre diameter	Bead	S/N ratio	S/N ratio
	Poly- conc	Feed rate	Dis- tance	Volt- age		(nm)	$(\mu m)^2$	diameter (-dB)	area (-dB)
1	1	1	1	1	$A_1 B_1 C_1 D_1$	88.31	192.72	38.95	45.73
2	1	1	2	2	$A_1 B_1 C_2 D_2$	51.02	201.16	34.18	46.07
3	1	2	1	2	$A_1 B_2 C_1 D_2$	75.08	184.10	37.68	45.31
4	1	2	2	1	$A_1 B_2 C_2 D_1$	98.14	165.92	40.06	44.44
5	2	1	1	2	$A_2B_1C_1D_2$	146.03	94.27	43.3	39.56
6	2	1	2	1	$A_2 B_1 C_2 D_1$	162.67	102.73	44.35	40.26
7	2	2	1	1	$A_2 B_2 C_1 D_1$	144.16	104.14	43.22	40.37
8	2	2	2	2	$A_2 B_2 C_2 D_2$	135.06	76.86	42.67	37.86

Table 4-4: Experimental results for fibre diameter and bead area and their corresponding S/N ratios

On the other hand, Fig. 4-4 (b) suggests that polymer concentration (factor A) is the most significant factor in controlling beads. In comparison, feed rate has a smaller but noticeable influence. It can also be suggested that factors C and D do not impact much in making beads if these are kept within the experimental range. However, the interaction between feed rate and needle-collector distance has a considerable influence on the average S/N response. The desirable combination for making minimum area occupied by beads, Fig. 4-5 (d), turns out to be $A_2B_2C_2D_2$ which is experiment #8 in Table 4-4 with an S/N value of -37.86. The diameter range of the nanofibres is shown in Fig. 4-3 (c). The bead area calculated by using image-tool has been found to be 76.86 (μ m)².



Figs. 4-5: Scanning micrographs of nanofibres from Exp #2 (a) nanofibres in higher magnification (b) nanofibres with beads in lower magnification and from Exp #8 (c) nanofibres in higher magnification (d) nanofibres with beads in lower magnification

4.2.3.2 Analysis of variance (ANOVA)

Analysis of variance (ANOVA) results for fibre diameter, using Equation (4-2) has been shown in Table 4-5. It can be confirmed that the polymer concentration and applied voltage are the two significant electrospinning parameters that affect the fibre diameter, with contributions of 76.5% and 10.5%, respectively. The change of feed rate in the given range, Table 4-2, has no

considerable effect on fibre diameter and has not shown any contribution from ANOVA analysis either. In Table 4-6, F-ratio and contribution (%) show that polymer concentration is the most dominating factor whose contribution goes up to 93% in making beads. In comparison to this, feed rate, applied voltage and distance between the needle tip and the collector have negligible contributions.

Source of variation	Sum of squaresDegree of freedom		Mean square	F ratio	Contribution (%)		
A	4.02	1	4.02	143.57	76.5		
В	0.06	1	0.06	2.14	1.1		
D	0.55	1	0.55	19.64	10.5		
AB	0.32	1	0.32	11.42	6.1		
AC	0.06	1	0.06	2.14	1.1		
BC	0.24	1	0.24	8.57	4.6		
Error	0.028	1	0.028				
Total	5.278	7					

Table 4-5: Results of ANOVA technique for fibre diameter

Table 4-6: Results of ANOVA technique for bead area

Source of variation	Sum of squares	Degree of freedom	Mean square	F ratio	Contribution (%)
Δ	4 31	1	4 31	574 67	93.09
B	0.10	1	0.10	13 33	2.16
Č	0.04	1	0.04	5.33	0.86
D	0.03	1	0.03	4.0	0.65
BC	0.15	1	0.15	20	3.24
Error	0.015	2	0.0075	-	
Total	4.645	7			



4.2.3.3 Discussion

Both the S/N ratio approach and the ANOVA method draw similar conclusions in the study. Polymer concentration contributes much in making small fibre diameters. From Table 4-4, it is evident that in the first four experiments, S/N ratios for fibre diameter are higher as they have unchanged low polymer concentration. From experiments #2 and #3, it is clear that the S/N ratios are higher in comparison to those from experiments #1 and #4. This is due to level 2 of factor D, i.e applied voltage of 10 kV. Always, a higher electrical force makes a positive impact in providing extra stretch to elongate the fibre, thus producing reduced diameters. From both techniques of data analysis, it is clear that polymer concentration has an enormous influence on making bead-free nanofibre mats. An increase in the polymer concentration results in greater polymer chain entanglements within the solution, which is necessary to maintain the continuity of the jet during electrospinning. This polymer chain entanglement has been found to have a significant impact on whether the electrospinning jet breaks up into small droplets resulting in beads [1]. Other researchers [17, 42, 71] have suggested that for a given voltage, when feed rate is increased, there is a greater volume of solution that is drawn away from the needle tip. As a result, the solvent may not get sufficient time to dry and requires a longer distance to evaporate the large quantity of solvent necessary for producing a considerable quantity of nanofibres. This is evident from the interaction effect of factors B and C, Fig. 4-4 (b), which is interestingly more than the individual effects of these two factors. According to Tan et al. [126], the morphology of the electrospun nanofibres is primarily affected by polymer concentration, its molecular weight and electrical conductivity of the solvent, followed by voltage and feed rate. The interaction effects between factors A and B and between A and C are also not that significant for bead area. Scanning micrographs of results from experiment #8, Figs. 4-5 (c) and (d), confirm nanofibres with the least number of beads, although the diameters are found to be in the range of 100 - 200 nm (average ~135 nm) in Fig. 4-3 (c). This is obviously not very fine but shows visibly less variation in diameters, which is still a very good result.

4.3 What does Taguchi Analysis tell us about Parameter Combinations?

Taguchi's OA provides a simple, systematic and efficient methodology for finding a set of suitable spinning parameters. S/N ratio and ANOVA approaches have converged on the same type of parametric selection. Taguchi analysis gives the best result for experiment #8 with the parametric combination of $A_2B_2C_2D_2$ keeping all the factors at high levels as it makes the minimum area occupied by beads, Fig. 4-5(d), with a maximum S/N value of -37.86. Experiment #2 in Table 4-3 is the best for achieving small diameters, Fig. 4-5 (a), and an optimal parameter combination of $A_1B_1C_2D_2$ (among eight runs) has the maximum S/N value of -34.18 with the average nanofibril diameter of about 51 nm. But it has produced a number of beads, Fig. 4-5 (b) as well. The concentration of the polymer solution plays a major role in making the fineness of the nanofibril, but where beads are concerned, it influences in a reverse way. The ANOVA results indicate that the polymer concentration contributes 93% in making beads. A lower polymer concentration with a low feed rate and relatively high voltage and distance between the needle tip and the collector appear to produce bead-like textures with fine fibres.

Although a full statistical analysis has produced a slightly different set of parameters with marginally improved results (discussed in next Sub-chapter 4.4), Taguchi provides the advantage of saving time and overly-avoiding tedium, particularly in regard to a greater number of parameters and levels.

4.4 Full Statistical Analysis and Bead-free Network

Full statistical analysis of normal factorial design (2^4) involving 16 runs was performed to get a clear idea of the effects of various contributing factors. To ensure the accuracy of the results, experiments were replicated five times as well. Experimental results of 16 experiments for fibre diameter and bead area and their corresponding S/N ratios have been described in Table 4-7. Figs. 4-7 (a) - (d) suggest that a low polymer concentration (factor A) and low feed rate (factor

B) produce fine fibres but with a number of beads. However, experiment #4 makes the network with a reasonably small area occupied by small-sized beads, Fig. 4-7 (d), when distance between needle and collector (factor C) and applied voltage (factor D) are on the higher side. Therefore,

Exp No	Factors			Designation	Result		Calculated S/N ratio		
	A Poly conc.	B Feed rate	C Distance	D Voltage		Fibre diameter (nm)	Bead area (µm) ²	S/N ratio for fibre diameter (-dB)	S/N ratio for bead area (-dB)
1	1	1	1	1	$A_1 B_1 C_1 D_1$	88.31	192.72	38.95	45.73
2	1	1	1	2	$A_1 B_1 C_1 D_2$	56.07	208.65	35.00	46.17
3	1	1	2	1	$A_1 B_1 C_2 D_1$	72.59	213.78	37.23	45.98
4	1	1	2	2	$A_1 B_1 C_2 D_2$	51.02	201.16	34.18	46.07
5	1	2	1	1	$A_1 B_2 C_1 D_1$	67.72	199.23	36.72	45.02
6	1	2	1	2	$A_1 B_2 C_1 D_2$	75.08	184.10	37.68	45.31
7	1	2	2	1	$A_1 B_2 C_2 D_1$	98.14	165.92	40.06	44.44
8	1	2	2	2	$A_1 B_2 C_2 D_2$	61.64	209.76	35.85	45.32
9	2	1	1	1	$A_2 B_1 C_1 D_1$	153.69	76.34	43.80	38.02
10	2	1	1	2	$A_2B_1C_1D_2$	146.03	94.27	43.30	39.56
11	2	1	2	1	$A_2B_1C_2D_1$	162.67	102.73	44.35	40.26
12	2	1	2	2	$A_2 B_1 C_2 D_2$	386.02	26.11	51.79	34.56
13	2	2	1	1	$A_2 B_2 C_1 D_1$	144.16	104.14	43.22	40.37
14	2	2	1	2	$A_2 B_2 C_1 D_2$	250.74	132.89	48.01	41.32
15	2	2	2	1	$A_2 B_2 C_2 D_1$	150.58	98.67	43.64	38.91
16	2	2	2	2	$A_2B_2C_2D_2$	135.06	76.86	42.67	37.86

 Table 4-7: Experimental results of 16 experiments for fibre diameter and bead area and their corresponding S/N ratios

experiment #4 is the best for achieving small diameters, Fig. 4-5 (a), and an optimal parameter combination of $A_1B_1C_2D_2$ has the maximum S/N value of -34.18 with the average nanofibril diameter of about 51 nm. Figs. 4-8 (a) - (d), on the other hand, suggest that a low polymer concentration with high feed rate does not help in controlling bead formation; in addition, it makes coarse nanofibres. Polymer concentration (factor A) appears to be the most significant factor in controlling beads. Figs. 4-9 (a) - (d) indicate that high polymer concentration and low feed rate, with unchanged applied voltage and workable distance, make the minimum number of





Figs. 4-6: Scanning micrographs of nanofibres from Exp #12 (a) nanofibres in higher magnification (b) nanofibres with beads in lower magnification (c) bar graphs of diameter ranges of nanofibres.

beads with relatively coarse fibres. Parameter combination of $A_2B_1C_2D_2$ in experiment #12 produces an almost bead-free network, Fig. 4-6 (b), but with fibre diameters in the range of 325 - 425 nm in Figs. 4-6 (a) and (c). High polymer concentration with high feed rate yields a network with fine fibres with reasonably little area occupied by beads. Experiments #13 - 16, with high polymer concentration, Table 4-7, respectively, make significantly better networks with moderately fine fibres and small bead areas in Figs. 4-10 (a) - (d) compared to other experimental results.



Figs. 4-7: Scanning micrographs of nanofibres from four experiments (a) Exp # 1 $A_1B_1C_1D_1$ b) Exp # 2 $A_1B_1C_1D_2$ (c) Exp # 3 $A_1B_1C_2D_1$ d) Exp # 4 $A_1B_1C_2D_2$

The scanning micrograph from experiment #16, Fig. 4-10 (d), confirms the existence of nanofibres with the least number of beads, although the fibres are not very fine. It also shows less variation in diameters, Table B-3 in Appendix B, which makes the parametric combination quite good. However, in the full statistical analysis, experiment #12, Table 4-7, with a parameter



Figs 4-8: Scanning micrographs of nanofibres from four experiments (a) Exp # 5 $A_1B_2C_1D_1$ b) Exp # 6 $A_1B_2C_1D_2$ c) Exp # 7 $A_1B_2C_2D_1$ (d) Exp # 8 $A_1B_2C_2D_2$

combination of $A_2B_1C_2D_2$ gives very good results. It makes the fibres almost bead-free, Fig. 4-9 (d), with fibres looking almost uniform having diameters, Fig. 4-6 (b), specifically in the range

of 328 - 437 nm in Table B-3. The bead area becomes $26.11 \ (\mu m)^2$, with the maximum S/N value of -34.56. This can be treated as the most desirable because although this parametric combination produces relatively coarse fibres, the bead-free mat of uniform fibres could be very useful for biomedical or biotechnological purposes. These results are in agreement with those of Zong et al. [42], who have shown that a low solution feed rate, higher concentration and charge density of the solution create better conditions for minimum bead formation. In comparison, feed rate has a



Figs. 4-9: Scanning micrographs of nanofibres from four experiments (a) Exp # 9 $A_2B_1C_1D_1$ (b) Exp # 10 $A_2B_1C_1D_2$ (c) Exp # 11 $A_2B_1C_2D_1$ (d) Exp # 12 $A_2B_1C_2D_2$

smaller but noticeable influence. So a low polymer concentration is favourable for reducing the diameter of nanofibres, but it makes beads. On the other hand, a high polymer concentration is favourable to make the network with less, or a practically zero number of beads, although a tendency to produce coarse fibres does exist [77, 94]. The ANOVA results from Taguchi method have also indicated that the polymer concentration makes a large contribution towards the creation of beads.



Figs. 4-10: Scanning micrographs of nanofibres from four experiments (a) Exp # 13 $A_2B_2C_1D_1$ (b) Exp # 14 $A_2B_2C_1D_2$ (c) Exp # 15 $A_2B_2C_2D_1$ (d) Exp # 16 $A_2B_2C_2D_2$

4.5 Concluding Remarks

Chapter 4 presents the results of several detailed investigations of morphological changes with the changing of independent variables of electrospinning. From these investigations through Taguchi methodology, several important and interesting conclusions can be established about the effect of various factors.

- Taguchi's orthogonal array is very suitable for analysing the performance of electrospinning and its parameters. It provides a simple, systematic and efficient methodology for finding a set of suitable spinning parameters. Although a full statistical analysis might produce a slightly different set of parameters with marginally improved results, Taguchi provides the advantage of saving time and reducing tedium to a mimimum.
- S/N ratio and ANOVA approaches bring the same conclusions that the concentration of the polymer solution plays a major role in determining the fineness of the nanofibril. However, the results have opposite trends where beads are concerned. Applied voltage plays an important role in determining the nanofibre diameters. A lower polymer concentration with a lower feed rate and relatively high voltage and distance appear to produce bead-like textures with finer fibres.
- Furthermore, to make bead-free nanofibres, it is necessary to keep the polymer concentration on the high side at the cost of slight coarse diameter. The ANOVA results indicate that polymer concentration contributes 93% in the making of beads.
- On the basis of this parametric analysis, a systematic study with a broader range of parameters with extended levels is made using regression analysis, to get a clearer idea of the effects of different invariables of electrospinning. To achieve a better understanding of the relationship between electrospinning parameters and the morphology of the

electrospun product, this study has made predictive models using multiple regression analysis (MRA), which will be discussed in Chapter 6.

However, it is worth mentioning here that this parameter combination A₂B₁C₂D₂ was not included in Taguchi's eight-run scheme, although the result from the combination A₂B₂C₂D₂ was very close. Therefore, the decision on whether to use full statistical analysis or Taguchi's design of experiments should depend on the number of parameters, their levels and the availability of time and resources.



CHAPTER 5

Characterisation of Nanofibrous Mat

This chapter examines the properties of the nanofibrous mat followed by different test results of thermal behaviour, crystallinity and mechanical strength testings. It also includes the characterisation of polymer solution with the determination of viscosity, surface tension and conductivity.

5.1 Introduction to Various Properties of Nanofibrous Mats

Nanofibres and nanofibre mats are relatively recent additions to the world of materials. Electrospun polymer nanofibres in the form of membrane have many potential applications in the field of bioengineering, environmental engineering and biotechnology, energy and electronics, defence and security as introduced in Chapter 2. Research activities on the electrospinning of nanofibres have been successful in spinning submicron range fibres from

variety of polymeric solutions and melts. Although some reports are available on the structure and morphological properties of polymeric nanofibres, there is very little information in the public domain on the electrohydrodynamics of the electrospinning process. Polymers with attractive chemical, mechanical, and electrical properties e.g. high conductivity, high chemical resistance, and high tensile strength have been spun into ultrafine fibres by the electrospinning process, and their application potential in areas e.g. filtration, optical fibres, drug delivery system, tissue scaffolds, and protective textiles have been examined [71, 127]. When the diameters of polymer fibre materials are shrunk from micrometers (e.g. 10-100 µm) to submicrons or nanometers (e.g. 10×10^{-3} - 100×10^{-3} µm), there appear several remarkable characteristics, such as a very large surface area to volume ratio (this ratio for a nanofibre can be as large as 10^3 times of that of a microfibre). This larger surface area permits flexibility in surface functionalities and provides superior mechanical performances compared to any other known form of the material [18]. Deitzel et al. have measured the atomic percentage of fluorine in electrospun nanofibres made of polymethylmethacrylate-tetrahydroperfluorooctylacrylate blends [128]. It was shown that the atomic percentage of fluorine in the near-surface region of the electrospun fibres is about double the atomic percentage in the bulk polymer. Nanofibres are attracted for their nanoscale diameters, their porous structure and light weight. These outstanding properties make the polymer nanofibres to be optimal candidates for countless advanced applications. Nanofibres have been reported to have marked differences in their physical/morphological, thermal and mechanical properties (biological properties as well, in case of biodegradable nanofibres) compared to regular fibres and bulk polymers.

Physical properties

Physical properties include the geometric properties of nanofibres and the morphological aspects of nanofibrous mats. Geometric properties such as fibre diameter, diameter distribution, fibre orientation and fibre morphology (e.g. cross-section shape and surface roughness) can be characterised using scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) [40, 89, 95]. AFM can also be used to characterise the roughness of fibres. The roughness

value is the arithmetic average of the deviations of height from the central horizontal plane given in terms of millivolts of measured current [89].

Electrospinning generally affords smooth fibres with a circular cross-section; only in exceptional cases does the cross-section differ from this form [34]. The surface area and the surface area-to-volume ratio of the nanofibre can easily be calculated from the diameter, if the nanofibre has a smooth surface. But in most cases the nanofibre surface is not smooth, since its morphology is based on the processing methods and parameters. Indent pores are generally observed on the wall of electrospun nanofibres and a special instrument may be needed to measure the surface area of these nanofibres [18, 129]. In the present study, the electrospun PLLA nanofibres were studied using a Philips XL30S scanning electron microscope (SEM) after the nanomat was coated with platinum, in the Department of Chemical and Materials Engineering. Clear images of beaded or non-beaded nanofibres were taken, and using image processing software (UTHSCSA ImageToolTM), measurements of nanofibre diameter and bead area were made and analysed.

Since the nanofibre membranes have a porous structure, morphological properties include pore geometry and density. The porosity and pore size of nanofibre membranes are important for applications in filtration, tissue templating, protective clothing and so on [40, 130]. Pore size measurement can be conducted with, for example, a capillary flow porometer [40]. For a variety of applications, for example tissue engineering, filtration, catalysis, drug delivery, and nanofibre reinforcement, it could be advantageous if the fibre surfaces are not smooth or are porous. For example, pores function as anchoring points for cells in tissue engineering, increase the surface area in filtration or catalysis, modify the wetting properties and hence the matrix - fibre coupling in fibre strengthening, and alter the kinetics of drug release. Pores can also influence the kinetics of biodegradation of bioerodible nanofibres. In fact, it is now possible to generate different fibre topologies during the electrospinning process by choosing particular solvents or solvent mixtures, by varying the humidity, or by using polymer mixtures [34].

Hydrophobicity is also related to the morphology of the nanofibre and nanofibrous membrane. The hydrophobic nature of a nanomat has a direct impact on the avenue of its usage [1]. For example, in membrane distillation, where water must not enter the membrane, a hydrophobic membrane must be used. Surface chemical properties of nanofibres also can be evaluated by their hydrophilicity, which can be estimated measuring the water contact angle of the nanofibre membrane surface [18].

Thermal properties

During electrospinning from a polymer solution, structure formation within the nanofibres is controlled by the simultaneous processes of evaporation of the solvent and extreme elongation of the solidifying fibres. A volume element of the jet travels from the electrospinning nozzle to the counter electrode, where the solid fibre is deposited, in a time frame of $0.1 \le [34]$. After this time period, both of the processes mentioned above are completed, and the fibre is solid. Consequently, the time limit for structure formation is typically less than 0.01 s. [34]. Thermal analysis has been carried out on a number of electrospun polymeric materials to understand the relationship between nanostructure and thermal properties. Differential scanning calorimetry (DSC) studies have indicated that electrospun PLLA fibres have lower crystallinity, glass transition temperature (T_{o}) , and melting temperature (T_{m}) than semicrystalline PLLA resins [42]. The crystallinity of the PLLA fibres was observed to be completely retarded by electrospinning, and wide angle R-ray diffraction (WAXD) patterns of the electrospun PLLA fibres confirmed highly oriented fibres. This decrease in crystallinity has been shown to be a general phenomenon and has been observed in polyglycolide (PGA), and polyacrylonitrile (PAN) [42]. Deitzel et al. inferred that polyethylene oxide (PEO) nanofibres retained the same crystal structure as PEO powders, while there is a clear indication of reduced crystalline order in nanofibres [71]. Bognitzki et al. concluded with the help of a DSC thermogram that the degree of crystallinity of electrospun PLLA fibres was in the order of 40% [129].

Mechanical properties

Electrospun polymer nanofibres have several possible applications such as filtration, tissue scaffolds, protective clothing, and a few others, as discussed earlier (Section 2.4.3). To achieve

durability in those applications, the mechanical properties of nanomats as well as single nanofibres are very important. There arise some questions as to what happens to the mechanical properties of a single fibre when the fibre diameter shrinks from micron to nano-size level. When fibre diameter shrinks, the crystalline structure of a single fibre is affected by the spinning conditions. For materials reinforcement, the strength and stiffness of single nanofibres is particularly important [34]. However, very few experimental investigations on the stress–strain behaviour of single electrospun nanofibres have been reported: atomic force microscopy (AFM) was used in most of these cases [131]. The testing of single nanofibres requires much expertise since it is not an easy task to prepare the sample and to apply the loading to a nanofibre.

Nanofibre reinforced polymer composites have shown more highly enhanced mechanical properties than the corresponding unfilled or carbon/glass fibre filled composites. Young's modulus of a nanofibre composite based on styrene-butadiene rubber has been found to be 10-fold greater than the pure rubber [132]. There is little information available on the mechanical properties of nanofibres and nanofibre composites and research on a variety of polymers is essential for a greater understanding of the contributions of nanofibres to the mechanical and performance-related characteristics of nanofibre in the present study have shown a modulus of 120 - 220 MPa during tensile testing of nanomat produced using a high polymer concentration of 10 % and above. This is due to slippage between the nanofibrils during load bearing. Strain becomes larger due to the opening up of the whole network resulting in less modulus. However, these values represent high performance compared to Young's modulus values reported by other researchers that are discussed next in Sub-chapter 5.3.

The biological properties of biodegradable nanofibres are very interesting. Cell proliferation on nanofibre mats has been tested by seeding cells on these mats [40, 133]. Scaffolds of PLLA nanofibres coated with collagen II variants were placed in separate wells of a microtiter plate. Chondrocytes were seeded onto the scaffolds at about 10,000 cells per well and cultured for up to 50 days. It was shown that collagen II supports the motility of chondrocytes. Publications related to the biodegradability of nanofibre mats *in vitro* or *in vivo* are not currently available. The nanofibre mats can be placed in phosphate-buffered saline at 37°C in an incubator or

implanted into animals, and biodegradability can be measured from the mass loss, the strength loss, and morphology change over a period of time [18].

5.2 Molecular Structure

5.2.1 Crystalline structure

The frozen-in chain orientation is of great significance for the properties of nanofibres. Experimental analysis of the electrospinning process shows that the magnitude of the elongation of the fibres is very high (up to a factor of 10^5), while the rate of elongation is up to $10^5 \text{ s}^{-1}[134]$. According to one estimate, a high degree of chain orientation is probable if the product of the elongation rate and the chain relaxation time exceeds 0.5 [135]. For polymer solutions that are suitable for electrospinning (with respect to molecular weight and concentration), relaxation times of 0.1 - 0.01 s have been reported [80, 136], hence chain orientation should always occur during electrospinning. Chain relaxation will be promoted if the deposited fibres contain traces of solvent; however, it depends on the vapour pressure of the solvent.

The crystalline structure of electrospun polymer nanofibres has been investigated using X-ray diffraction (XRD), and DSC. With respect to the size effect, when polymer fibres shrink from micrometer to nanometer scale, interesting phenomena show how the crystalline structure is created in nanofibres and how different they are in comparison with the crystalline structure of bulk polymers. How processing parameters influence the crystalline structure of the nanofibre is discussed in the next Sub-chapters.

5.2.2 Crystallinity determination by X-ray diffraction (XRD)

X-ray diffraction (XRD) is a powerful non-destructive technique for characterising crystalline materials. It provides information on structures, phases, preferred crystal orientations (texture) and other structural parameters such as average grain size, crystallinity, strain and crystal defects. XRD peaks are produced by constructive interference of the monochromatic beam scattered from each set of lattice planes at specific angles. The XRD pattern is a fingerprint of periodic atomic arrangements in a given material. According to Bragg's Law [137]

$$n\lambda = 2d \sin\theta \qquad (1)$$

where (θ) is the angle of incidence, d is the distance between atomic layers in a crystal, λ is the wavelength of the incident X-ray beam, and n is an integer.

Two samples of thin film, one from bulk PLLA powder and other one from an electrospun mat, were made for investigation by XRD, using a Philips D 5000 X-ray powder diffractometer. The electrospun mat was prepared using a mixed solvent (DCM/DMF) in the proportion of 60/40 with a suitable combination of electrospinning parameters (polymer concentration 10% w/v, feed rate 1 ml hr⁻¹, voltage 10 kV and distance 100 mm). This combination of parameters consistently produced uniform and bead-free nanofibres (refer to Section 3.5.3). XRD analysis, with scan range (20) 5 to 50⁰, gave approximately the same results for both bulk sample and electrospun mat. The absence of sharp reflections, Fig. 5-1, for both samples, suggests that extensive crystallisation of PLA did not occur. The broad diffuse band is typical of amorphous polymers.

5.2.3 Thermal behaviour of nanomat using differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is used to study the response of materials to temperature change. It is a thermoanalytical technique in which the difference in the amount of heat required to maintain equality of the temperatures of a sample and reference, during heating and cooling at a known rate, is determined as a function of temperature. The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transition

more (or less) heat will need to flow to it than the reference to maintain both at the same temperature. Whether more or less heat must flow to the sample, depends on whether the process is exothermic or endothermic. For example, as a solid sample melts to a liquid it will require more heat flowing to the sample to increase its temperature at the same rate as the reference. This



Fig. 5-1: XRD pattern of films made from bulk PLLA and electrospun mat

is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid. Likewise, as the sample undergoes an exothermic process (such as crystallisation) less heat is required to raise the sample temperature. By evaluating the difference in temperature between the sample and reference, differential scanning calorimeters are able to quantitatively determine the amount of energy absorbed or released during such transitions.



Fig. 5-2: DSC scans of bulk PLLA powder and electrospun mat

Two samples with approximately the same weight (6 mg), one from bulk PLLA powder and the other from electrospun PLLA mat, were subjected to heating at 10°C min⁻¹ and cooling at 5°C

min⁻¹, in an atmosphere of flowing oxygen-free nitrogen, in the temperature range of 0 - 200°C. The DSC scans, Fig. 5-2, show that cold crystallisation occurred for the electrospun mat. The glass transition temperature (T_g) of bulk polymer appeared in the range of 54 - 55°C; but for the electrospun mat a smaller T_g was observed. The melting temperature (T_m) was found almost the same (149°C) for both samples. The details are discussed in Section 5.2.4.

5.2.4 Molecular weight

5.2.4.1 Effect of molecular weight in electrospinning

The molecular weight of the polymer is proportional to the average length of the polymer chains, which in turn has an effect on the viscosity of the polymer solution. The chain length determines the amount of entanglement of the polymer chains in the solvent. Another way to increase the viscosity of the solution is to increase the polymer concentration. Similar to increasing the molecular weight, an increase in the concentration will result in greater polymer chain entanglements within the solution, which is necessary to maintain the continuity of the jet during electrospinning. Generally, it is observed when a polymer of higher molecular weight is dissolved in a solvent, its viscosity will be higher than for a solution of the same polymer with a lower molecular weight. With a deeper understanding, when the two solutions contain the same number of polymer molecules per unit volume, the solution of the higher molecular weight polymer will undoubtedly be the more viscous. One of the conditions necessary for successful electrospinning where fibres are formed, is that the solution must have sufficient viscosity [1]. As the jet leaves the needle tip during electrospinning, the polymer solution is stretched as it travels towards the collection plate. During stretching of the polymer solution, the entanglement of the molecule chains prevents the electrically driven jet from breaking up, thus maintaining a continuous solution jet.

5.2.4.2 Determination of molecular weight using gel permeation chromatography (GPC)

The electrospinnability of a polymer is very sensitive to molecular weight. A too low value limits the interactions between the macromolecules and too high a value may cause fibrillation or clogging of the needle tip. Thus determination of molecular weight is very important before the estimation of electrospinning performance. Several methods have been explored to determine the molecular weight, but gel permeation chromatography (GPC), Fig. 5-3, with light scattering photometers is generally used.



Fig. 5-3: GPC Apparatus

In this arrangement, GPC columns are utilised to effect a separation of the molecules by size and hence molecular weight of the eluting molecules, determined by a light scattering photometer or other detector. To obtain molecular weight, light scattering detectors utilise the Rayleigh Equation, which states that the intensity of the light scattered by molecules in solution is proportional to the concentration and molecular weight of the molecules, multiplied by an optical constant. By measuring the intensity of the scattered light and the concentration, and determining the optical constant, we can determine the molecular weight.

The columns consist of a stationary phase of packed particles with a fixed pore size. The packing particles are made from a porous polymer, with diameter 5 μ m. As the solution containing the dissolved sample passes through the column, the small molecules infiltrate into the pores of the packing particles, while larger molecules are unable to penetrate because of their size. This causes the small molecules to pass through an effectively larger volume in the column. In addition, the flow rate around the packing particles is faster than the flow rate through the pore spaces. It results in the separation of molecules according to size, with the larger molecules eluting from the column first, and the smaller molecules eluting last [138].

Application of the basic theory of laser light scattering to determine the average molecular weights makes use of the angle-dependent Rayleigh ratio (R_{θ}).

$$\mathbf{R}_{\theta} = \mathbf{I}_{\theta} \quad \mathbf{r}^2 \ / \left(\mathbf{I}_0 \ \mathbf{V}\right)$$

 $[I_{\theta} = \text{scattered intensity}, I_{0} = \text{intensity of the incident beam, V} = \text{volume of the scattering medium, r} = \text{distance between the scattering volume and the detector, } I_{\theta (solvent)} = \text{scattered intensity of the solvent.}]$

To describe scattering of a solution of solvent and solute, the scattering from pure solvent must be subtracted.

$$R_{\theta} = [I_{\theta} - I_{\theta \text{ (solvent)}}] r^2 / I_0 V$$

Knowing the Rayleigh ratio at a number of different angles leads directly to the weight average molecular weight of the solute molecules.

5.2.4.3 Test results

Determination of the absolute molecular mass of PLLA (3051D) using light scattering is based on the principle that the amount of light scattered is directly proportional to the product of the polymer molar mass (M), concentration of the polymer in solution (c), and the square of the specific refractive index increment (dn/dc).

I_{scattered}
$$\alpha$$
 Mc(dn/dc)²

The specific refractive index increment expresses the rate of change of refractive index with respect to the concentration of the solute. Complete characterisation of a polymer begins with determining (dn/dc) for the polymer in an appropriate solvent [139]. For these experiments, tetrahydrofuran (THF) was the solvent of choice because PLLA is soluble in THF. For each solution, dn/dc was measured using a Brookhaven BI-DNDC differential refractometer at 535 nm operated in static mode at 50°C, with five solutions of each polymer in THF at concentrations between 0.5 and 5.0 mg ml⁻¹. The results in summary are as follows:

For PLLA (3051d) : dn/dc = 0.041; polydispersity = 1.352 ± 0.004; weight average molar mass, M_w = 1.044×10⁵ g mol⁻¹

Results in detail, with all data and plots including dn/dc results are given in Appendix C; Fig. C-1 for the plots of dn/dc, Fig. C-2 for strip chart chromatogram and Fig. C-3 for peak ID. All the data were provided by Michel Nieuwoudt, The Department of Chemistry, UoA.

5.2.5 Discussion and concluding remarks

In electrospinning, polymer nanofibres are formed by the creation and elongation of an electrified fluid jet. Control of the process produces fibres with nanometer scale diameter, together with various cross-sectional shapes, beads, branches and buckling coils. For polymers

that can be crystallised, solidification is connected with the formation of crystals. The short crystallisation times, typical of electrospinning, lead to crystallites that tend to be small and to contain defects; so a lower degree of crystallisation is found [34, 42]. From the XRD analysis, it was observed that the degree of crystallinity of the electrospun PLLA fibres was very similar to that of bulk samples [140]. The molecular weight of the polymer is proportional to the length of the polymer chain, and the chain length determines the amount of entanglement of the polymer chains in the solvent. The PLLA used in this research had a high average molar mass (M_w =1.044 × 10⁵ g mol⁻¹), so the average chain length (if they exist) may be getting the time of solidification, very few chain molecules of short length (if they exist) may be getting the time to be aligned and others may run out of time for orientation.

It is considered that fibre crystallinity is affected by the electrostatic field and time of crystallisation during the flight of the jet. As the voltage is gradually increased from zero, the polymer molecules become progressively more ordered. When a very high voltage is applied, the polymer molecules are accelerated and the time of the jet flight from needle tip to the collector is shortened, resulting in decreased time for crystallisation. Consequently, higher voltage and longer distance are key factors for obtaining more ordered polymer chains, in the case of a stationary collector [1, 141]. In the present study, the applied voltage and distance between the needle tip and collector were adjusted so that required electrical forces are just available to build uniformly elongated and bead-free fibres and neither extra electrical force nor time are available to make improved crystallinity. Zhao et al. reported that the crystallinity of electrospun ethyl-cyanoethyl cellulose (E-CE)C fibres increased with increasing voltage [141]. However, at voltages greater than 50 kV the crystallinity decreased with increased voltage.

If the nanofibres are collected by a rotating drum or disk, higher rotation speed may lead to higher elongation of the polymer jet and alignment of polymer chains along the longitudinal direction of the fibres. Lee et al. compared the crystallinity of polycaprolactone (PCL) nanofibres and PCL film; in the XRD profile there was a significant decrease in crystallinity of nanofibres [142]. As the retardation of crystallisation occurred in nanofibres, crystallinity of nanofibres was lower than that of PCL film.

From the DSC scans, Fig. 5-2, a smaller T_g of the electrospun fibres than bulk, was found and cold crystallisation occurred during heating of the specimen. We attribute these effects to suppressed crystallisation during stretching and solidification of wet or semi-dry nanofibres. Suppression of crystallisation is analogous to quenching: the stretched chains do not have enough time to organise themselves in a suitable crystal-form before they solidify. This result is in agreement with the observations of Zong et al., who reported that as-received PLLA exhibited a crystallinity of 35.5% whereas the electrospun PLLA membrane exhibited significantly lower crystallinity, glass transition temperature and melting temperature [42]. Tg is decreased due to the large surface area to volume ratio of nanofibre. The high evaporation rate followed by rapid solidification in the final stages of electrospinning is thought to be the reason for the low crystallinity. By contrast, the melting temperature (T_m) of both materials remained almost the same, Fig. 5-2, which may be attributed to spun PLLA mats having the same crystal structure as PLLA powder. Deitzel et al. inferred that PEO nanofibres retained the same crystal structure as PEO powders, while there is a clear indication of reduced crystalline order in nanofibres [71]. From cooling curves, Tg is found to be the same for both specimens as melting eliminates the previous thermal history of electrospun polymers.

5.3 Mechanical Properties of Nanofibres

5.3.1 Sample preparation and determination of tensile strength

Electrospun fibres have nanostructured surface morphologies with tiny pores that influence mechanical properties like tensile strength, elongation and Young's modulus. Nanofibres and nanofibre mats have been characterised using a variety of methods. The structure, morphology, and geometry of nanofibres and the porosity and tensile properties of nanofibre mats can be investigated through conventional techniques and instruments. However, the measurement of mechanical properties of nanofibres is challenging because of the small size of the fibres and many precautions have to be taken in sample preparation.
Tensile tests were performed with an Instron 5567 machine, Fig. 5-4 (a), at CACM, UoA. Electrospun fibrous mats were cut into rectangular pieces, with width of 7 mm, gauge length of 25 mm and thickness that ranged from 0.06 to 0.1 mm. A sharp-edged specimen was prepared, so that no single fibre came out of the surface. Much care was taken in preparing and then gripping specimens in order to avoid severe damage. The specimen strips were put into self-tightening grips, Fig. 5-4 (b), designed primarily for precision testing of elastomeric and other flexible material. These film grips provide excellent testing accuracy for thin films as they provide a non-slip gripping action due to their rubber-coated wire capstans. A 5 N load cell was used and tests were performed at crosshead speed 5 mm min⁻¹ at room temperature. The films were monitored with a video camera while being tested, and the test was stopped immediately after fracture. Different polymer concentrations were used while electrospinning the nanomat, keeping other spinning parameters in suitable ranges (feed rate of 1 ml hr⁻¹, voltage of 10 kV and distance of 100 mm) [77, 94]. The concentration of the polymer solution has direct control of the mass of the product/nanofibrous mat as the molecular weight of the PLLA (3051 D) was not changed.

As a single nanofibre is very weak, the resulting non-woven mat is so delicate that any direct touch on the mat surface during manipulation can damage the fibres. Uniaxial tensile testing of PLLA electrospun mats gave Young's modulus values in the order of 25 - 221 MPa and tensile strength of 1 - 6 MPa with increasing polymer concentrations from 4 to 12% (w/v), (g/100 ml) whereas neat PLLA has tensile modulus and strength of 3828 MPa and 83 MPa respectively [106]. This is obviously due to slippage between the nanofibrils during load bearing, and most of the fibres cannot contribute in sharing the load. Strain is not due to simply stretching of the nanofibres which are gripped; it becomes eventually larger due to opening up of whole network. A stretched sample (Fig. 5-5) was examined with a microscope during tensile testing. However, PLLA mat produced from a high concentration (12%) (w/v) of polymer solution, has shown high modulus of 221 MPa compared to the results of other researchers; values up to 180 MPa have been reported for the tensile modulus of PLLA mat [104]. Nanoscale fibres of PLLA have attracted the interest of numerous researchers. Yang et al. and other groups have investigated morphology and biodegradation rates for electrospun PLA scaffolds which could be used for





Figs. 5-4: (a) Instron 5567 (b) Specimen during elongation



Fig. 5-5: Microstructure of a stretched specimen during measurement of tensile strength

such applications as tissue scaffolds and drug delivery [87, 104, 107]. Several studies have shown that electrospun nanofibres feature very good mechanical properties. For example, Young's moduli values up to 50 GPa were reported for PAN nanofibres with a high degree of orientation (as determined by XRD) [38]. For comparison, bulk samples of PAN with no preferred orientation showed moduli of only 1.2 GPa. The Young's moduli measured for PEO nanofibres were distinctly higher than those measured for bulk samples. The orientation induced by electrospinning is reason for the increased stiffness [131].

5.3.2 Improvement of tensile strength with increasing polymer concentration

Recent advances in processing are leading toward the control of the cross-sectional shape and alignment of nanofibres. A variety of cross-sectional shapes, e.g. branched fibres, flat ribbons, and ribbons with other shapes, have been successfully electrospun [40]. The processing

parameters recently investigated by Patra et al. and Zong et al. include solution properties (viscosity, elasticity, conductivity, and surface tension), processing conditions (processing voltage, needle tip diameter, and distance from needle tip to collector), and ambient conditions [20, 42, 77]. They, and Demir et al., found that the fibre diameter increased with increasing polymer concentration [89].

Under the conditions for nanofibrous matrix formation, the average fibre diameter does not change statistically with polymer concentration or gelation temperature. Generally, the filament is very thin and surrounded primarily by air [53]. Higher concentration produces coarse fibres and thereby the air space is reduced between the fibres, resulting in decreased porosity. The mechanical properties (Young's modulus and tensile strength) increased with decreased porosity. The surface area-to-volume ratio of the nanofibrous matrices was two to three orders of magnitude higher than those of nonwoven fabrics fabricated with textile technology [24].

Five different polymer concentrations in the range of 4 - 12% (w/v) (x% w/v means x g of solute in 100 ml of solvent) were used to produce nanotextiles of randomly oriented fibres, and tensile strength was determined. Nanostructures using polymer concentration of 4, 7 and 10% (w/v) are shown in Figs. 5-6 (a) - (c). The averaged tensile modulus and ultimate tensile strength of the nanostructured materials made from the solutions with different concentrations are summarised in Table 5-1. The results are plotted in Fig. 5-7 for an obvious comparison. From Table 5-1 and Fig. 5-7, it is apparent that the highest mechanical performance of the fibre membrane has been achieved from the polymer solution with the highest concentration.

Nanomat with a polymer concentration of 4% (w/v) showed poor strength with Young's modulus of 25.2 MPa. This may be attributed to the fact that the 4% (w/v) concentration provided the finest fibre mat compared with the other (higher) concentrations and resulted in the tightest cohesion, but at the same time gave rise to far more beads, Fig. 5-6 (a), than did the solution with a concentration of 7% (w/v). As the area occupied by beads is significant, Fig. 5-6 (a), the numbers of nanofibres and crossover points are smaller, resulting in less cohesion in between nanofibres, hence poorer mechanical performance was obtained for the nanofibre mat made from the solution with 4% (w/v) concentration than mats made from the solutions of higher

concentration. As concentration increased, beads were likely to be elongated; a few beads were found at 7% (w/v), Fig. 5-6 (b), and the number of beads decreased to zero, Fig. 5-6 (c), as less solvent was present to be evaporated and the maximum amount of polymeric material was formed into nanofibres. The solution with a polymer concentration of 10% produced bead-free and uniform nanofibres, Fig. 5-6 (c), and showed a significantly high Young's modulus (slope of





Figs. 5-6: Scanning micrographs of nanofibrous mat using polymer concentration (a) 4% (b) 7% (c) 10% (w/v)



the stress - strain curve) of 119 MPa. The solution with a polymer concentration of 12% utilised the maximum amount of solid material with maximum crossover points in building uniform fibres that can efficiently participate in contributing load, resulting in a high tensile modulus of 221 MPa.

Prediction of the mechanical behaviour of nonwovens or foams depends on the interactions among the fundamental units of these structures [53]. For nonwoven materials, the number of fibres and the number of crossover points determines the relative tensile strength of the fibre assembly. Similarly, the stiffness of a nonwoven mat varies directly with its density. Young's modulus, E, is related to density, ρ , by the following equation:

$$E_{E_0} = (\rho_{\rho_0})^2$$

where E_0 and ρ_0 are the modulus and density of the bulk material [53, 143].

PLLA nanotextile has shown considerable mechanical strength due to a continuous fibrous network with fibres anchoring each other and the number of crossover points. The Young's modulus and tensile strength increase with polymer concentration and a quadratic dependence of Young's modulus on polymer concentration is observed in Fig. 5-7. This is probably due to the linear increase in fibre network density. Therefore, the mechanical properties of the nanofibre matrix can be tailored to specific property needs by adjusting polymer concentration without affecting the fibre diameter.

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Polymer concentration (% w/v)	Young's modulus (MPa)	Ultimate tensile strength (MPa)
4	25.2	0.9
7	46.1	1.8
8	60.7	1.9
10	119.1	3.3
12	221.0	6.0

 Table 5-1: Tensile properties for different polymer concentrations

*Note: x% w/v means x g of solute in 100 ml of solvent



Fig. 5-7: Young's modulus of PLLA mat as a function of polymer concentration

5.3.3 Tensile modulus considering area fraction

A specimen with a geometric area $50 \times 20 \text{ mm}^2$ was cut from a nanofibrous mat using a polymer concentration of 10%. The thickness of the specimen was measured as 0.028 mm. The calculated mass of the mat was 0.035 g [assuming the density of 1.25 g cm⁻³ for PLLA (3051 D) specified in the datasheet] [106]. The actual mass was determined as 0.0079 g by weighing with an electronic balance. By measuring the mass of five different specimens with the same geometrical area, the average mass of the specimen was determined. An area fraction was calculated as a ratio of the actual mass to the calculated mass. For the specimen made from the solution with a polymer concentration of 10%, the area fraction was estimated as 0.22. Area fraction can also be measured from a SEM micrograph by considering the area of nanofibres situated in the same plane. However, it is not a reliable because it is difficult to determine which fibres are on the same plane. When considering in-plane nanofibres from the corresponding micrograph of the specimen, the total area of solid strands was found to be in the range of 20 - 30% of the area of the whole micrograph; both techniques show similar types of results. A generalised trend of calculating stress assuming geometrical area is not very accurate for a porous nanotextile. An effective tensile modulus of 541.4 MPa was calculated considering the physical area (i.e. corrected geometrical area) occupied by PLLA nanofibrils. Similarly, for the nanotextile with a polymer concentration of 12%, (area fraction is 0.31) effective modulus was found to be 712.9 MPa.

5.3.4 Concluding remarks on improved strength of aligned fibres

Nanofibres and nanofibre mats have been characterised through a variety of methods. The structure, morphology, and geometry of nanofibres, and the porosity and tensile properties of nanofibre mats can be investigated with conventional techniques and instruments. However, the measurement of mechanical properties of nanofibres such as tensile modulus, strength, and elongation is challenging because of the small size of the fibres. Such measurements are crucial for the proper use of nanofibres. The established test techniques and standards for determining

the tensile behaviour of microfibres are inadequate in the case of manipulation or testing of nanofibres because of the nanometer scale dimensions of these fibres [8]. As a result, publications on the tensile properties of nanofibres are rare in the literature.

It is conceivable that a high degree of fibre orientation along a preferred direction increases the stiffness and strength of the nonwoven mat. According to Matthews et al. Young's modulus (slope of the stress-strain curve) increases from 100 MPa for nonwovens with no preferred fibre orientation to 900 MPa for nonwovens with fibres oriented along the elongation direction [41]. Theron and co-workers have successfully obtained aligned nanofibre filaments with the use of a rotating disc collector with a sharp edge, and achieved higher tensile strength [144]. However, Sriramkrishna et al. pointed out that drastic property difference is hardly seen between two fibre directions. Even if nanofibres are collected with a rotating drum, there is no certainty that nanofibres can be unidirectionally oriented [1].

The tensile strength and Young's modulus of PLA are comparable to those properties of PET. Mechanical characterisation of randomly oriented nanofibres indicates that both the fibre diameter and the beads on the fibre surface can influence the mechanical performance of electrospun nanofibre membranes. Huang et al. pointed out that the finest fibre mat generally exhibits higher tensile modulus and ultimate tensile strength. However, in agreement with the present results, if there are beads on the fibre surface the situation may be different [31]. The nanofibre mats with the smallest fibre diameter but with beads on the fibre surface exhibit poorer mechanical performance than those with the largest fibre diameter without any beads. Quite a few researchers have manufactured fine, smooth and uniform nanofibres by manipulating the process parameters efficiently [77, 83, 94, 126]. Bead-free nanofibres with diameters below 100 nm is quite challenging [77, 83, 84, 94]. Consequently, producing PLLA mat with finest fibres and no bead is practically unachievable; in this case, the best nanotextile will be those with highest mechanical performances.

5.4 Characterisation of Polymer Solution

The properties of the polymer solution have a significant influence on the electrospinning process and the resultant fibre morphology. The viscosity and conductivity determine the extent of elongation of the solution [1, 127]. The viscosity of the polymer solution depends on both the molecular weight of the polymer and the concentration of the polymer solution. In the current study, the molecular weight of the polymer was not varied. Consequently, the fibre morphology was dependent on solution viscosity. For solutions that are too concentrated (and therefore too viscous), the droplet dries at the tip before a jet can be initiated, preventing electrospinning [1, 77]. High viscosity can create difficulties in pumping the solution through the syringe needle, and the needle tip may get clogged. When the polymer concentration is too low, the product is many beads or microspheres.

The initiation of electrospinning requires the charged solution to overcome its surface tension. Solution concentration decides the limiting boundaries for the formation of electrospun fibres due to variations in the viscosity and surface tension [71]. At low polymer concentrations, defects in the form of beading and droplets are observed; the process under these conditions shows the characteristics of electrospraying (refer to Sections 2.5.2 and 4.1) rather than spinning. Formations of these droplets are due to the influence of surface tension. Attempts have been made to quantify the minimum viscosity and surface tension required to electrospin fibres with preferably no bead.

Another approach, namely increasing the solution conductivity or charge density can be used for producing more uniform fibres with fewer beads [42, 96]. Solutions with high conductivity have a greater charge carrying capacity than solutions with low conductivity. Thus the fibre jet of highly conductive solutions is subjected to a greater tensile force in the presence of an electric field than is a fibre jet from a solution with low conductivity. At concentrations below 4% (w/v), the electrospinning process generated a mixture of fibres and droplets. Electrospinning from solutions with concentrations higher than 10% (w/v) was found to cause clogging at the needle tip. One nanotextile sample was made using a polymer concentration of 12% (w/v) by taking

extreme precautions, with the intention of testing mechanical performance; nevertheless, it was challenging to produce such a nanomat. For that reason polymer solutions of 4 to 10% (w/v) were used for determination of viscosity, surface tension and solution conductivity and beyond this range of polymer concentration electrospinning performance was not satisfactory (refer to Section 3.5.3).

5.4.1 Determination of viscosity of polymer solution

A glass viscometer, Canon 100/C55, was used, Fig. 5-8 (a), for measuring the viscosity of polymer solutions of PLLA of weight average molar mass 1.044×10^5 g mol⁻¹. Viscosity is the measure of the resistance of a fluid to deformation by either shear or extensional stress. Relative viscosity can be measured by finding the ratio of the efflux times of solution and solvent. Shear viscosities were measured for three different concentrations of PLLA via the relationship:

Shear viscosity = efflux time \times viscometer constant \times density(5-1)

Polymer concentration of 4, 7 and 10% (w/v) [x% w/v means x g of solute in 100 ml of solvent] were made by adding 1, 1.75 and 2.5 g PLLA powder, to 25 ml of a mixture of DCM and DMF (60:40 by volume) (60:40 by volume) with 15 ml and 10 ml, respectively. Solutions were prepared with the aid of ultrasonication for 2 hours at room temperature $(20^{0}C)$ and afterwards passed through the capillary of the viscometer. Efflux times were measured starting with the mixed solvent, for which the efflux time was 37.28 seconds. The efflux times for solutions with concentration 4, 7 and 10% (w/v) were noted as 461, 1964 and 6716 seconds respectively. Using equation (5-1), shear viscosity was calculated as 7.8, 33.6 and 116.5 mPa s; the results are shown in Table 5-2. The viscometer constant was 0.015 (available from manufacturer's website) [145]. Density was measured by weighing the unit volume of each solution and taking the average of five measurements. Experiments were performed at a temperature of 20^oC and relative humidity of 40% throughout the study.

Concentration of polymer solution (% w/v)	Density (g cm ⁻³)	Shear viscosity (mPa s)
4	1.13	7.8
7	1.14	33.6
10	1.16	116.5

Table 5-2: Shear viscosity of three PLLA solutions

5.4.2 Determination of surface tension of polymer solution

The surface tension for each solution of PLLA was determined by the Wilhelmy Plate method, using an Analite Surface Tension Meter, 2141 [shown in Fig. 5-8 (b)]. In this method the force exerted at the break point of a meniscus formed between a thin plate and the fluid whose surface tension is to be determined, is measured. The thin plate and petri dish (for the liquid sample) were cleaned by rinsing with acetone, as cleanliness is a major contributor in obtaining accurate and repetitive results. The results are shown in Table 5-3. Experiments were performed at ambient temperature of 20° C and relative humidity of 40%.

Surface tension (mN m ⁻¹)		
34.1		
35.2		
36.8		

Table 5 3.	Surface	toncion	of three	DITA	colutions
1 able 5-5:	Surface	tension	of three	PLLA	solutions



Figs. 5-8: (a) Viscometer (b) Surface tension meter (c) Solution conductivity meter

5.4.3 Determination of solution conductivity of polymer solution

Solution conductivity was measured using a conductivity meter, CDM 230 MeterLab[®] as shown in Fig. 5-8 (c). The instrument was calibrated with a known solution of potassium chloride (KCl) and the conductivity of each solution of PLLA was measured in five replicate determinations. The average conductivity of the solutions including that of a solution with concentration 7% (w/v) with addition of 1% (w/v) of the cationic salt tetrabutyl ammonium bromide (TBAB) are shown in Table 5-4.

4% 7% 10%	nductivity (µ5 cm)	Polymer solution (DCM/DMF : 60/40)	
7% 10%	10.2	4%	
10%	11.0	7%	
	11.9	10%	
7% with 1% TBAB	634.0	7% with 1% TBAB	

Table 5-4: Solution conductivity of PLLA solutions

5.4.4 Discussion and concluding remarks

As shown by the results in Table 5-2, polymer concentration has a great impact on viscosity; an increase of 75% (w/v) in polymer concentration results in increased viscosity of more than 300%. Solution surface tension and viscosity play important roles in determining the range of concentrations from which continuous fibres can be obtained in electrospinning. At low viscosity (7.8 mPa s), surface tension has a dominant influences on fibre morphology and below a surface tension of 34.1 mN m⁻¹, drops are formed instead of fibres. At high concentration (above 10%) processing is prohibited by inability to control and maintain the flow of a polymer solution to the tip of the needle, and by the cohesive nature of the high viscosity solutions. These solutions had viscosities in the range of 7.8 - 116.5 mPa s and surface tensions in the range of 34.1 - 36.8 mN m⁻¹. However, PLLA with a significantly high weight average molar mass (1.044×10^5 g mol⁻¹) was used in the research. The molecular weight is proportional to the length of the polymer chain, which in turn has an effect on viscosity as the polymer chain length determines the amount of entanglement of the polymer chains in solution.

The total concentration of polymer appears to be the most significant factor in controlling bead formation. An increase in the polymer concentration and thus viscosity results in greater polymer chain entanglements within the solution, which is necessary to maintain the continuity of the jet during electrospinning. This polymer chain entanglement has been found to have a significant impact on whether the electrospinning jet breaks up into small droplets resulting in beads [1]. A minimum amount of polymer chain entanglements and thus viscosity is necessary for electrospinning. In addition, increased polymer concentration increases the surface tension of the solution, which is beneficial because lower surface tension tends to favour bead formation [4]. The beads are mainly caused by reduced surface tension that minimises the surface area. In the case of very low concentration, surface tension becomes minimal and polymer solutions cannot withstand the electrical forces and break down into drops. Fong et al. added ethanol to polymer solution due to its low surface tension and found the formation of smooth fibres [96]. The addition of surfactants was found to yield more uniform fibres. When viscosity and surface tension of the solution are appropriately tuned with the applied electrical forces, break-up (if

there is break-up, electrospray occurs) of the polymer drop at the needle tip is avoided and a stable jet is formed [4].

Fong and co-workers [4, 96] have suggested that the net charge density carried by the electrospinning jet is an important factor that greatly influences the morphology of the electrospun products, together with the viscosity and surface tension of the solution. Their results have also shown that beads become smaller and the shape becomes more elliptical as the net charge density is increased, which is in agreement with the observations of Patra et al.[94] and Zong et al. [42]. In the present study conductivity of 11.0 μ S cm⁻¹ (for a polymer concentration of 7%) was sufficient to control the beads and uniformity of the fibres as viscosity and surface tension also participated in controlling the beads and uniformity of the nanofibres. Addition of ionic compounds, especially ionic surfactants, to the polymer solution for electrospinning can effectively prevent the formation of beads. Beads proliferated when electrospinning of PLLA and PANi solution in a common solvent was performed [54]. Efforts to eliminate the beaded fibres by adjusting the operating conditions and changing the polymer concentration were unsuccessful in this case. However, the addition of only 1% (w/v) of TBAB dramatically increased the conductivity of the electrospinning solution of DBSA doped PANi and PLLA, and facilitated the formation of bead-free nanofibres. Addition of TBAB increased the conductivity more than 60 times (Table 5-4). It is worth noting that it is not necessary to add a salt to the solution if the viscosity of the solution can contribute significantly to forming bead-free uniform nanofibres.



CHAPTER 6

Regression Analysis of Electrospinning Process

This chapter utilises multiple regression analysis to model the effects of different factors. A combination of standard statistical tests and scanning micrographs are used to evaluate the proposed models. Finally, suitability of the models has been examined for reliable predictions prior to mass production.

6.1 Introduction and Requirement of a Model

Interest in electrospinning has recently escalated due to the ability to produce nanoscale materials in a straight forward manner. One attractive feature of electrospinning is the simplicity and inexpensive nature of the set-up. However, the process is complex with the resulting jet (fibre) diameter being influenced by numerous material, design, and operating parameters. The effects of varying manufacturing parameters on the electrospinning of nanotextiles

have been reported by Deitzel [71], Zong [42], Patra [77] and a few others [1, 127] as well. It has been well established that both operating parameters and material properties affect the electrospinning process and the resulting fibre morphology [34, 77, 83]. Nevertheless, the physical and mathematical descriptions of the electrospinning process remain challenging, despite several reported parametric studies performed under various experimental configurations. A significant amount of information regarding the electrospinning process comes from empirical observations, but the complexity of the process makes the empirical determination of parametric effects very difficult, if not impractical [20]. Researchers have highlighted studies that examine the effects of manipulating individual parameter in the electrospinning process and the resulting fibre morphology [146]. It is difficult to isolate the effects of many of the parameters since they are interrelated. For example, changing the solution concentration/viscosity affects other solution properties, such as the conductivity and surface tension. Nevertheless, a large number of distinct polymers have been electrospun but very little systematic investigation for successful spinning has been conducted. Predictions of as-spun nanofibre diameter and/or diameter distribution have not been found to be reliable. Typically, a trial-and-error approach has been employed in which the solution properties and spinning parameters are varied until uniform, defect-free fibres are obtained. To achieve a deeper understanding of the relationship between electrospinning parameters and the morphology of the electrospun product, a detailed study has to be done and a suitable theoretical model of the electrospinning process needs to be derived. The model should indicate which parameters have the major influences in shaping the fibre size. Hence, these parameters are the ones to focus on in empirical studies. Theoretical prediction and understanding of the parametric effects on jet radius and morphology could significantly reduce experimental time by identifying the conditions most likely, to yield specific qualities prior to production. In this Chapter, a regression model has been developed to get a clearer idea of the effects of different invariables of electrospinning.

6.2 Inclusion of Parameters in the Model

Each of the important factors has been taken into consideration during inclusion of parameters for the detailed study. It has to be emphasised that PLA (3051D) used in this study is a very common product of NatureWorks[®]LLC, and the variety of products, made with this polymer continue to grow rapidly (refer to Section 3.2.2) [9]. To find a suitable combination of solvents, electro spinning of PLLA was performed using various solvents individually or in combinations of two. The choice of solvent is very crucial in electro spinning (refer to Section 3.5.1). Finally, the combination of DCM and DMF performed well, and different proportions have been checked to determine the possibility of making uniform nanofibres consistently (refer to Section 3.5.3). However, a mixture of DCM and DMF (60:40 by volume) consistently produced fine, uniform and beaded/non-beaded nanofibres. The research of Zong et al. supports this - they used a mixed solvent of DCM and DMF with same proportion to dissolve the semi-crystalline PLLA [42]. This solution was capable of making almost bead-free nanofibres, hence there was no need to enhance the solution conductivity by adding any salt or electrolyte. Therefore, vapour pressure and dielectric constant have not been considered as parameters in the detailed study, as the same solvent system has been used throughout the research. Addition of electrolyte can enhance the performances of making bead-free nanofibres; however, increased polymer concentration can also be employed to produce this. The mass and size of the nanotextile product are important and they are generated from the amount of polymer in the solution. Hence, high polymer concentration is eventually preferable to the addition of electrolyte or increasing solution conductivity.

The feed rate of the polymer solution is also an important parameter because it determines the amount of solution available for stretching to form nanofibres and plays a vital role in determining the fibre diameter and bead formation [42].

Two other governing parameters are applied voltage and humidity. Higher electrical forces (i.e. larger applied voltage) provide extra stretch to elongate the fibres and thus produce nanofibres with reduced diameters. With increased voltage, the acceleration of the fibre also increases [1].

This reduces the flight time of the electrospinning jet, resulting in increased diameter as the jet does not have enough time to stretch and elongate before depositing on the collector. Therefore, to achieve the same performances, increased voltage needs longer distances to solidify the nanofibres during the same flight time. It has been recommended that independent of the polymer, solvent and the solution concentration, a voltage of 1 kV per centimetre between the nozzle and collector can be used [118]. Workable distance has not been considered as a separate parameter in the present study; it must be mentioned that in the parametric study its contribution was not significant [refer to Section 4.2.3.2]. However, as effects of applied voltage and workable distance are inter-related, effective voltage as 1 kV per centimetre has been considered in the study. Relative humidity is a major parameter to be undertaken in the study; its inclusion and importance are discussed in Sub-chapter 6.2.2.

6.2.1 Selection of parameter levels

The four factors, namely i) concentration of polymer solution, ii) feed rate, iii) applied voltage and iv) relative humidity of the closed area, have been considered at three different levels, as shown in Table 6-1, to produce nanofibres under various conditions. As recommended in the studies reported [1, 42, 71], and previous parametric analysis as well [77], a concentration of 4 - 10% (w/v)(g/100 ml) and a feed rate of 0.5 - 2 ml hour ⁻¹ were chosen for this study. Spinnability has been checked with different polymer concentrations, Figs. 6-1 (a) - (d), starting with a concentration of 3% (w/v). Polymer concentration of 7% (w/v) makes uniform nanofibres with a few beads; at higher concentrations, fibres are bead-free and uniformity is of the highest order, Fig. 6-1 (d), when other parameters are suitably maintained. A polymer concentration of 3% are not acceptable, Fig. 6-1 (a), as major beads are produced. At very high concentrations (above 10%) processing is hindered by an inability to control and maintain the flow of polymer solution to the tip of the needle and by the cohesive nature of the high viscosity solutions. However, a nanomat was produced with difficulty using a polymer concentration of 12% (w/v) for the purpose of testing the mechanical strength (refer to Section 5.3.2). It is to be noted that although a feed rate

Factors	Description	Level 1	Level 2	Level 3
А	Concentration of polymer solution (%w/v)	4	7	10
В	Feed rate of polymer solution (ml hour ⁻¹)	0.5	1	2
С	Voltage (kV)	8	10	12
D	Relative humidity (%)	20	40	75

Table 6-1: Factors and levels used in the study

*Note: x% w/v means x g of solute in 100 ml of solvent



Figs. 6-1: Scanning micrographs of nanofibres with suitable parametric conditions using different polymer concentrations (a) 3% (b) 4% (c) 7% and (d) 10% (w/v)

of 0.5 ml hour ⁻¹ performed well at times, it had a tendency to clog the needle tip. So precautions were taken by cleaning the needle tip frequently. The starting voltage in this study was 6 kV and the spinning rate increased with increasing voltage. At voltages higher than 15 kV, the spinning rate became too fast to control and the jet flow diverged. Consequently, 8 - 12 kV was selected as the appropriate voltage range. Considering, effective applied voltage of 1 kV per centimetre between the nozzle and collector, 8, 10 and 12 kV have been used with a workable distance of 80, 100 and 120 mm respectively.

6.2.2 Ambient parameters

Ambient parameters such as relative humidity (RH), temperature and gas composition also influence the electrospinning process and the outcome. Temperature and relative humidity have considerable influences in shaping the fibre diameter as both play an important role in drying the fibres. Since electrospinning is influenced by the external electric field, any changes in the electrospinning environment will also affect the electrospinning process. The composition of the air and its velocity in the electrospinning environment do affect the electrospinning process. Different gases have different behaviour under a high electrostatic field [39]. These are not discussed; eventually air is the only electrospinning medium used in this study.

6.2.2.1 Effect of temperature on the fibre morphology

A change in temperature causes the variation of the solvent evaporation rate and the solution viscosity, which are two opposing factors affecting the mean fibre diameter [100]. Keeping relative humidity at 40% and the other parameters at suitable levels (polymer concentration of 7%, feed rate of 1 ml hr⁻¹, voltage of 10 kV and workable distance of 100 mm) (refer to Section 4.4) the effects of temperature have been examined for PLLA nanofibres at a temp of 10 - 40^oC; the diameter variation was very less in two types of electrospun fibres produced at 20^oC and 40^oC, Figs. 6-2 (a) and (b). However, it is important to mention that at higher temperatures, the

diameter was found to be slightly less, but not significantly. It is attributed, the viscosity of the polymer solution is decreasing with increased temperatures and that plays in producing reduced diameters. With a high humidity (75%) and varied temperature (10-40°C), Fig. 6-3, electrospun nanofibres were examined and no considerable impact was found due to the change of temperature. As temperature was not found to be critically important, it was not considered for further analysis.



Figs. 6-2: Scanning micrographs of nanofibres with suitable parametric conditions and RH at 40%, using different temperature (a) 20^{0} C (b) 40^{0} C

6.2.2.2 Effect of humidity on the fibre morphology

It was realised that the RH of the environment would determine the rate of solvent evaporation in the solution. It may make the nanofibres thicker or thinner, depending on the chemical nature of the polymer and high RH may even cause the formation of pores on the fibre surface. Generally, finer diameters have been found in lower RH environment during electrospinning of PLLA, and a higher RH caused rather coarse diameters (average 500 nm) with the possibility of bead formation while keeping other parameters at suitable values, as mentioned earlier [1, 20].

In order to understand the overall effect of changing RH on the resulting fibre diameter, three different RH values, 20, 40 and 75%, have been investigated in this study by using different saturated salt solutions (refer to Section 3.5). To observe the impact of RH on diameter, suitable parametric conditions (mentioned in Section 6.2.2.1) of electropinning were maintained and the



Fig. 6-3: Electrospinning action in specific RH and temperature

temperature (20^{0}C) was kept unchanged inside the electrospinning cabinet using ice and/or hot air. The effect of humidity on fibres is attributed to the development of porous and sticky fibres. At higher humidities, polymer solutions solidify slowly and thus the fibre formation process cannot be completed within the flight time of the jet, resulting in coarse, irregular and sticky fibres as shown in Fig. 6-4 (c). A low RH (20%) ensures quick and efficient drying and provides extra stretch to make superfine fibres, Fig. 6-4 (a), as compared to nanofibres, Fig. 6-4 (b), produced at a RH of 40%.



Figs. 6-4: Scanning micrographs of nanofibres with suitable parametric conditions and a temperature of 20° C using different RH (a) 20 % (b) 40 % (c) 75%

This is in agreement with Casper et al. [102]; their work showed that while spinning polystyrene solutions, increasing the humidity resulted in the appearance of small circular pores on the surface of the fibres. At a low RH, a volatile solvent like DCM may dry rapidly causing effective stretching of fibres as slightly more time is available due to quick drying of the polymer jet. However, in case of very low RH, the needle tip can be clogged; as a result the electrospinning process may only be carried out for a few minutes [39]. In the present study, at low RH, fine fibres have been produced with a diameter of 50 - 60 nm in Fig. 6-4 (a). Inclusion of RH has completed this parametric analysis compared to previous research (refer to Section 4) carried out to find the suitable parametric conditions with RH assumed to remain constant [77].

6.2.3 Systematic study considering major parameters

The quality of the nanofibres produced using electrospinning is defined by their fineness and variations of diameter. The porosity and pore size of the resulting nanofibrous mat or fabric are crucial for filter media to determine the efficiency as well as pressure drop and permeability. This filtering efficiency increases with a reduction in fibre diameter [118]. Researchers around the globe have used various biocompatible and biodegradable synthetic polymers including poly(lactic) and poly(glycolic) acids (PLA and PGA, respectively) and their copolymers (PLAGA), polycaprolactone (PCL), polydioxanone (PDO) and many others for scaffold fabrication [31, 39, 83], as discussed in the earlier Sections. Electrospun nanotextiles meet the essential design criteria of ideal engineered tissue scaffolds based upon their ability to support and guide cell growth. Although no systematic research on the influence of nanofibre diameter on the degradation behaviour of polymers has been reported, there is evidence that the diameter does affect the degradation features and related mechanical properties of the materials used. Furthermore, it has been theorised that the cells attach and organise well around fibres with diameters smaller than the diameters of the cells [18, 119]. Therefore, fibre diameter is considered as an outcome or dependant variable in multiple regression analysis (MRA) to facilitate quality control of the nanofibres produced. Variation in fibre diameter has not been considered as an outcome; it is to be mentioned electrospun samples with uniform diameters have been taken in consideration for this study. A few complex processes (refer to Section 5.2.5) are responsible for final shaping of nanofibres, hence slight variation in fibre diameter is always found. To control the uniformity of fibre diameter in nanorange is quite challenging. Researchers including Zong, Deitzel, Lin, Patra [42, 71, 77, 83, 94] produced nanofibres with a reasonable variation of 15 - 20% in diameter during electrospinning.

The governing parameters investigated are the concentration and feed rate of polymer solution, applied voltage and the relative humidity of the enclosed area. Primary input parameters have been accounted for this study. For example, viscosity and surface tension play important roles in shaping the nanofibres, but the primary input factors are the polymer concentration and the molecular weight of the polymer, as they determine the number of chain molecules and its entanglements. In the present study, the same PLLA (3051D) has been used, so molecular weight

is unchanged. Hence, only polymer concentration is responsible for the determination of viscosity and surface tension of the material. Solution conductivity is generated by the number of ions present in the solution and it is dependent on the dielectric constant of the solvent. As viscosity, surface tension and solution conductivity are the resultant factors responsible in spinning action, they have been shown in Table 6-2 for three different concentrations of PLLA. Significant solution conductivity has been found as DMF has a high dielectric constant (36.71). Similarly, feed rate is a key parameter as it determines the amount of solution available for stretching to form nanofibres. As found the results in Table 6-2, polymer concentration has a great impact on viscosity; increase of 75% (w/v) polymer concentration results in increased viscosity of more than 300%. Solution surface tension and viscosity play important roles in determining the range of concentrations from which continuous fibres can be obtained in electrospinning. At a low viscosity of 7.8 mPa s (4% of polymer concentration) surface tension plays a major role in spinning action and below a certain level (34.1 mN m⁻¹) of surface tension, droplets are likely to reach the target (as electrospray occurs) instead of solid fibres. So for active spinnability, solutions must have viscosities in the range of 7.8 - 116.5 mPa s and surface tensions in the range of 34.1 - 36.6 mN m⁻¹, as shown in Table 6-2. Nevertheless, PLLA with a significantly high molar mass $(1.044 \times 10^5 \text{ g mol}^{-1})$ was used in the research.

Concentration of polymer solution (% w/v)	Density (g cm ⁻³)	Shear viscosity (mPa s)	Surface tension (mN m ⁻¹)	Conductivity (µS cm ⁻¹)
4	1.13	7.8	34.1	10.2
7	1.14	33.6	35.2	11.0
10	1.16	116.5	36.6	11.9

 Table 6-2: Viscosity, surface tension and solution conductivity of polymer solutions of three different concentrations

Primary parameters have been taken together and their combined actions have been studied with multiple regression analysis. The parametric study has demonstrated (refer to Chapter 4) the possibility of making bead-free nanofibres with a good range of diameters through electrospinning and has established a suitable parametric combination using Taguchi methodology [77]. On the basis of this parametric analysis, a systematic study with a broader range of parameters with extended levels is performed, to get a clearer idea of the effects of different invariables of electrospinning.

6.3 Multiple Regression Analysis (MRA)

Regression analysis has become a very popular statistical tool for analysing multifactor data. It may be broadly defined as the analysis of relationships among variables [147]. It includes any techniques for modelling and analysing several variables, when the focus is on the relationship between a dependent variable and one or more independent variables. More specifically, regression analysis helps us understand how the typical value of the dependent variable changes when any one of the independent variables is varied, while the other independent variables are held constant. It models the relationship which is expressed in the form an equation connecting the response or dependent variable, y, and one or more regressors or independent variables, x_1 , x_2 , x_p

 $y = b_0 + b_1 x_1 + b_2 x_2 + \dots (6-1)$

where b_0 , b_1 , b_2 b_p , are regression coefficients.

6.3.1 Application of MRA in the model

For this study, four factors namely, concentration of polymer solution, feed rate, applied voltage and relative humidity of the closed area, have been considered. These are shown as independent variables in Table 6-1, while the fibre diameter is the outcome or dependent variable. The MRA was carried out using Microsoft Excel Data Analysis tool pack. A confidence level of 95% was set for all regression analyses. After the model is fitted, the correlation of the model to the actual data is assessed. When the multiple correlation coefficient, or more frequently R² value comes closer to 1, one can conclude there is a good fit with the data [147]. Analysis of the present model is evaluated as,

 $\log D = \log A + n_1 \log (PC) + n_2 \log (FR) + n_3 \log (VOLT) + n_4 \log (RH) - (6-2)$

Therefore, $D = A \times (PC)^{n1} \times (FR)^{n2} \times (VOLT)^{n3} \times (RH)^{n4}$ ------ (6-3) where D is fibre diameter (nm), PC is polymer concentration (% w/v), FR is feed rate of polymer solution (ml hour ⁻¹), VOLT is applied electrical voltage (kV) and RH is relative humidity (%) inside the cabinet.

6.3.2 Design of experiment

Four factors with three different levels of each have been considered, as shown in Table 6-1. However, in order to facilitate the analytical process, instead of normal factorial design (3^4) , a 9-run orthogonal array (OA), Table 6-3, based on Taguchi's Design of Experiment technique, was chosen due to its capability of checking the interactions among various factors [112, 120]. The sequence in which these trials were carried out has been randomised and the three levels of each factor have been represented by '0', '1' and '2' in the matrix. Each of the nine conditions was repeated once and the other eighteen combinations of conditions, yielding uniform nanofibres were used to produce the electrospun samples. Therefore, a total of 36 experiments were carried out in an effort to ensure the accuracy of the MRA. For the linear regression, varying one

parameter at a time, 8 samples have been considered from the same experimental run and therefore for three levels, 24 data (Table D-1 to D-4, in Appendix D) were considered for the analysis. From each experimental SEM-micrograph, the average diameter was taken from 40 measurements (8×5) as discussed in Section 3.5.2.

Experiment number	Electrospinning parameter level			
	Α	В	D	
	Polymer concentration	Feed rate	Voltage	Humidity
1	A_0	B_0	C ₀	D_0
2	A_0	B_1	C_1	D_1
3	\mathbf{A}_0	B_2	C ₂	D_2
4	A_1	B_{0}	C ₁	D_2
5	A_1	B_1	C ₂	D_0
6	A_1	B_2	C_0	D_1
7	A ₂	B_0	C ₂	D_1
8	A ₂	B_1	C_0	D_2
9	A_2	B_2	C_1	\mathbf{D}_0

Table 6-3: Experimental layout plan using nine runs (L₉)

* Note: Level 1, 2 & 3 has been depicted as 0, 1 & 2 respectively in the experimental layout plan.

6.4 Results and Discussion

6.4.1 Model development

In order to establish the relationship between the fibre diameter and each of the two primary factors of electrospinning, polymer concentration and feed rate, a linear regression analysis was carried out by considering individually the effects of varying polymer concentration and feed rate on the resulting fibre diameter. The results are shown in Figs. 6-5 (a) and (b), with two forms of data fit, a simple linear form and a power law. From these individual linear regression results, it appears that despite scattering of the fibre diameter formed from each polymer concentration or feed rate, the polymer concentration-fibre diameter correlations show better agreement in predicting the experimental behaviour, compared to those from feed rate-fibre diameter equations. Both the power law and the linear relationships describe the experimental trend with very similar accuracy, judging from the close R^2 values [147]. Therefore, either form of the relationship can be used to predict the diameter of the nanofibres when considering only one particular operational parameter. The polymer concentration is shown to have a stronger effect on the final diameter with its resulting trend lines displaying generally higher slopes, Figs. 6-5 (a) and (b). All the data of linear regression for two individual factors have been shown in Tables D-1 through D-4, located in Appendix D.

To determine the effects of multiple parameters on the resulting fibre diameters, an MRA has been carried out. The general equations considering polymer concentration and feed rate together for determination of diameter is shown in Equation (6-4).

$$D = 10^{0.920} \times PC^{1.463} \times FR^{0.266} \qquad R^2 = 0.9556 \qquad (6-4)$$

If all of the essential parameters of electrospinning, including applied voltage and RH, are taken into account, a more general equation can be derived, as given in Equation (6-5),

$$D = 10^{-0.676} \times PC^{1.410} \times FR^{0.208} \times VOLT^{0.515} \times RH^{0.719} \qquad R^2 = 0.8567 \dots (6-5)$$



Figs. 6-5: Typical regression results of fibre diameter against (a) polymer concentration and (b) feed rate [Error bars indicating \pm one standard deviation]

where D is fibre diameter (nm), PC is polymer concentration (%w/v), FR is feed rate of polymer solution (ml hour ⁻¹), VOLT is applied electrical voltage (kV) and RH is relative humidity (%) inside the cabinet. Compared to the experimental data obtained for specific electrospinning conditions, the values calculated by the general equation can predict the trend with sufficient accuracy. However, even with a reasonably high modelling accuracy, predictions made from the derived equations may sometimes not be able to match the experimental data for a particular set of electrospinning conditions. All data of dependent and independent variables, Tables D-5 and D-6, are located in Appendix D. The effect of each variable on the outcome may be linear (but in most cases, it is not). When multiple variables are considered for a single output, the relationship will hardly be linear anymore, so a power law relationship involving more than one variable is a reasonably good choice.

Using Equation (6-4), the effects of PC and FR on the fibre diameter have been displayed in a similar manner as in Figs. 6-6 (a) and (b). These show clearly that most of the experimental data lies within a $\pm 15\%$ zone of the predicted values. Hence, it can be stated confidently that the derived general equations can be used as reasonably reliable guides for estimating the fibre diameter of nanofibres produced from electrospinning poly (lactic acid).

Comparing the values of R² from two equations, it is also evident that the general equation derived using two parameters, polymer concentration and feed rate, gives a better estimate of the resulting fibre sizes and further inclusion of voltage and humidity provides worse results. Nevertheless the R² value of 0.857 for Equation (6-5) has shown that it can be used to model the multi-factor experimental behaviour with sufficient accuracy. Reflecting on the results mentioned earlier from the linear regression, it is also clear from both equations that the effect of polymer concentration on the final fibre size is much stronger than that of feed rate. On the other hand, although the exponents for VOLT and RH show higher values than that of FR, as found in a previous research [77], both VOLT and RH are not deemed as critical as the PC and FR (the solution properties) for deciding the final fibre diameters in a controlled environment, due to the facts that follow. Firstly, FR plays an important role in controlling the amount of polymer to be electrospun and secondly, RH is not an easily controllable operational factor. In addition, the stretching of nanofibres through electrical forces depends not only on the magnitude of the vol-



concentration and (b) feed rate

tage applied, but also on the distance between the needle tip and the collector (referring to the voltage factor of 1 kV cm⁻¹). All the important parameters (within the same solvent system) with a suitably working range of levels have been included in the MRA; therefore, the model developed has performed efficiently to determine the contributions of production parameters and has become more reliable.

6.4.2 Microscopic study

The effects of PC and FR modelled using Equation (6-4), can be firmly supported by the findings from a previous research that suggested, the polymer concentration is the most significant factor of electrospinning; analysis of variance has shown that polymer concentration contributes 76% in determining fibre diameter [77]. Polymer concentration has played the only role to maintain the solution viscosity as the molar mass remains unchanged. When considered a PLLA mat with varying polymer concentration (PC) using a suitable parametric range of $B_1C_1D_1$ (FR of 1 ml hour-1, VOLT of 10 kV & RH of 40%), fibre diameter has become larger, Figs. 6-7 (a) - (c), with the increase of PC. With 10% PC, coarse fibres, Fig. 6-7 (c), of great uniformity and beadfree structures are found. This is due to the increase of polymer concentration, resulting in greater polymer chain entanglements within the solution, which is necessary to maintain the continuity of the jet during electrospinning. When viscosity is high (116.5 mPa s), Table 6-2, it may discourage secondary jets from breaking off from the main jet, which may contribute to the increased fibre diameter [1]. Above that (>10% PC) processing is prohibited by an inability to control and maintain the flow of liquid polymer to the tip of the needle due to the cohesive nature of high viscosity solutions. At low viscosity (<7.8 mPa s), it minimises the surface area of the polymer fluid. Below a certain 34.1 mN m⁻¹ of surface tension, it breaks up into droplets, Fig. 6-1 (a), when PC of 3% (w/v) is used.

For the effect of FR, it has also been suggested [1, 42, 71] that for a given voltage, when feed rate is increased, there is a greater volume of solution that can be drawn away from the needle tip. As a result, the solvent may not get sufficient time to dry and may require longer distance to



Figs. 6-7: Scanning micrographs of nanofibres with suitable parametric conditions $B_1C_1D_1$ using different polymer concentrations (w/v) (a) 4% (b) 7% and (c) 10%

evaporate the larger quantity of solvent necessary for producing a considerable quantity of nanofibres, thus producing those nanofibres with increased diameter as shown in Figs. 6-8 (a) - (c). The accuracy of predicting the fibre size using the regression result, Equation (6-4), has been well supported by the microscopic structures of Figs. 6-7 (a) - (c) and Figs. 6-8 (a) - (c). As shown from the experimental data, the scattering of the diameter values (Fig. D-1 in Appendix D) is more severe with increased polymer concentration, Fig. 6-5 (a), and there is a similar pattern for feed rate with a lesser extent of variation, Fig. 6-5 (b). This is attributed to the fact that both parameters estimate the amount of spinnable material. In addition to its more significant effect on deciding the final fibre size, PC also displays a considerable capability of controlling the size variation in the electrospun fibres, compared to FR. Higher PC produces

v=v List of research project topics and materials



Figs. 6-8: Scanning micrographs of nanofibres with suitable parametric conditions $A_1C_1D_1$ using different feed rate (a) 0.5 (b) 1 and (c) 2 ml hour ⁻¹
when considering a particular sample of electrospun mat, using high polymer concentration of 10% (w/v) with a suitable parametric range of $B_1C_1D_1$ (FR of 1 ml hour ⁻¹, VOLT of 10 kV & RH of 40%), nanofibrous networks consist of highly uniformed fibres with an average diameter of 275 nm as shown in Fig. 6-9 (d). However, as shown in Fig. 6-5 (a) the error bar shows significant variations in the diameter of 238 - 312 nm. This is due to the inclusion of fibre diameters from 8 different samples, Tables D-1 and D-3 in Appendix D, for the same experiment (A₂B₁C₁D₁). As mentioned in Section 6.2.3, during electrospinning 15 - 20 % variation in fibre diameter can be possible in nanorange, but a suitable parametric combination may create nanofibres with high uniformity (Excel Tables of data are shown in Appendix D).



Figs. 6-9: Scanning micrographs of nanofibres with suitable parametric conditions $B_1C_1D_1$ of using polymer concentration (w/v) of 4% (a) fine fibres with beads; (b) same magnified fibres with variations in diameter and polymer concentration (w/v) of 10% (c) bead-free and coarse fibres (d) same magnified fibres with high uniformity

The effect of humidity on fibres is dealt with the development of porous and sticky fibres in Fig. 6-4 (c). As explained earlier, polymer solutions solidify slower at high RH (75%) and thus the fibre formation process cannot be completed within the flight time of the jet, while at low RH (20%) it ensures quick and efficient drying and provides more elongation to make finer fibres in Fig. 6-4 (a). The power supplied should be adequate to overcome surface tension of 34.1 mN m⁻¹ (corresponding viscosity of 7.8 mPa s) of the polymer droplets to form and sustain a jet from the pipette. An increase in electric potential tends to stretch the polymer more resulting in decreased fibre diameter up to a certain level. A maximum voltage of 12 kV has been found suitable for effective stretching, further increase in voltage generates too much acceleration on the polymer solution, resulting in nanofibres with irregular sizes due to insufficient flying time for solvent evaporation. Despite the apparent simplicity of the electrospinning process, structure formation within the nanofibres is quite complicated. It is controlled by the simultaneous processes of evaporation of the solvent and the extreme elongation of the solidifying fibres [42]. The stretched chains do not have enough time to organise themselves into a suitable position before they become solidified and it depends on the number of chain molecules as well. The high evaporation rate, followed by rapid solidification at the final stage of electrospinning, is expected to be the reason for less crystallinity and disordered size of solid fibres [1, 42]. Therefore, the effects of these two parameters, voltage and humidity, are not easily controllable for producing the final diameter during phase transition efficiently; however these do have strong impact on shaping the nanofibres.

As found in the results shown in Table 6-2, polymer concentration has a great impact on viscosity; increase of 75 % polymer concentration results in increased viscosity of more than 300%. Solution surface tension and viscosity play important roles in determining the range of concentrations from which continuous fibres can be obtained in electrospinning. At low viscosity (7.8 milli.pascal.sec), surface tension has the dominant influences on fibre morphology and as mentioned earlier, below 34 mN m⁻¹ of surface tension, drops are formed instead of fibres. At a very high concentration (> 10%) processing is hindered by the cohesive nature of the high viscosity polymer solutions. Therefore, viscosities in the range of 7.8 - 116.5 mPa s and surface tensions in the range of 34 - 37 mN m⁻¹ (Table 6-2) are the limiting boundaries of spinning nanofibres efficiently. However, PLLA with a significantly high molar mass $(1.044 \times 10^5 \text{ g mol}^-)$

¹) was used in the research. The molecular weight represents the length of the polymer chain, which in turn has an effect on viscosity as the polymer length determines the amount of entanglement of the polymer chains in the solution.

6.5 Validations of MRA and Suitability of the Model

When comparing particular experimental data with calculated results using Equation 6-5, an average of 10 - 15% variation can be expected (Table D-7 in Appendix D) depending on the experimental conditions. A less than 5% variation in fibre diameter is found with operational conditions of A₂B₁C₁D₁ (PC of 10%, FR of 1 ml hour-1,VOLT of 10 kV & RH of 40%) and A₂B₁C₂D₁ (PC of 10%, FR of 1 ml hour-1, VOLT of 12 kV & RH of 40%) in Figs. 6-10 (a) and (b). However, with experiments $A_0B_2C_2D_2$ (PC of 4%, FR of 2 ml hour⁻¹, VOLT of 12 kV & RH of 75%) and A₂B₂C₂D₂ (PC of 10%, FR of 2 ml hour ⁻¹, VOLT of 12 kV & RH of 75%), Figs. 6-10 (c) and (d), more than 20% variation is found to have occured. It is expected that the MRA modelling works well with all the operational parameters kept within the experimental range of this study, such as the results from experiments $A_2B_1C_1D_1$ and $A_2B_1C_2D_1$ where the differences between the estimated and experimental values are small (only 0.7% for condition $A_2B_1C_1D_1$). The experimental rows are high lighted in Table D-7. Even when comparing two experimental results for the same operational (repeat) condition of $A_2B_1C_1D_1$ (experiment # 16 & 34, Table D-7 in Appendix D), the variation in average fibe diameter is not significant. They are found to be 257 and 271 nm respectively. A similar type of the result is found with operational condition of A₂B₁C₂D₁, (experiment # 17 & 35, Table D-7 in Appendix D) where the resultant diameters are 278 and 285 nm respectively. When using the derived model to predict the resulting fibre diameter under the extreme conditions of this study, particularly for VOLT and RH, the predictive capability of the MRA model is compromised, e.g. experiments $A_0B_2C_2D_2$ and $A_2B_2C_2D_2$, where all the conditions are mostly at the high end of the experimental spectrum. At higher voltage, amount of charges become too high to control the stretching of polymer solution resulting in unpredictable diameter as explained in Section 6.2.2.2. With the addition of high humidity (75%) and high voltage (12 kV), this control becomes worse than any one. With

the hard-to-control parametric effect of VOLT and RH, at their highest levels, the experimental results have become inconsistent causing the large discrepancy in the estimated outcome.



Figs. 6-10: Scanning micrographs of nanofibres with parametric conditions (a) $A_2B_1C_1D_1$ (b) $A_2B_1C_2D_1$ (c) $A_0B_2C_2D_2$ (d) $A_2B_2C_2D_2$ (e) confirmatory test

In order to assure the validity of MRA, an electrospinning experiment under randomly selected conditions was performed using PC of 8% (w/v), FR of 1.5 ml hour $^{-1}$, VOLT of 9 kV and RH of 35%. The average fibre diameter from this experiment has been found to be 161.4 nm, Fig. 6-10 (e), whereas Equation (6-5) gives an estimated fibre diameter of 173.2 nm, which shows close agreement.

Finally, it is worth mentioning that due to the interpolative nature of the MRA technique, using the derived results for modelling electrospinning with extreme conditions or beyond the covered range (particularly for VOLT and RH) makes the prediction inaccurate and chaotic, and therefore may not be reliable. However, this problem could be overcome by selecting the experimental conditions carefully. The MRA model developed in this study has been proved to reliably predict the resultant fibre diameter within the commonly used operational parameter range for electrospinning. The technique can be easily expanded to build the capability for estimating the electrospun fibre diameters by selecting the necessary manufacturing parameters and their range.

6.6 Concluding Remarks

A general equation involving major production parameters to predict the resultant fibre diameter for electrospinning of PLLA nanofibres has been derived using multiple regression analysis. Polymer concentration has been confirmed from the linear regression analysis as the most important parameter in electrospinning of PLLA nanofibres with controllable effect. The polymer concentration-fibre diameter equation can describe the experimental behaviour more accurately than the feed rate-fibre diameter relationship, despite feed rate also having a significant effect on deciding the fibre diameter, by controlling the amount of polymer to be electrospun. A general equation using two parameters, polymer concentration and feed rate, gives a better indication when other parameters are suitably maintained. While combining humidity and applied voltage, the prediction of fibre diameters produced becomes less satisfactory but is still acceptable. This study has shown that prior to the mass production of nanotextiles, experimental time could be significantly reduced by identifying the most suitable production conditions that would yield nanofibres of specifically required qualities.

CHAPTER 7

Nanofibrous Mat using Multiple Syringes

7.1 Introduction

The major disadvantage of carrying out the process by the standard capillary method is the low rates at which they can usually generate nanofibres. Productivity is measured by the polymer volume delivered per unit time by a syringe pump. Hence the concentration of the solution is primarily responsible as it controls the amount of fibre-forming polymer. Measurement of the throughput of polymer solution is currently the only way to determine the productivity of a particular electrospinning process line. The production speed could be indicated by weight/unit area (assuming constant thickness) of a nanofibrous mat, but because of the extremely low weight of the nanofibrous mats, it is challenging to weigh in-line [118].

Typically, output of polymer fluid from a single capillary is in the range of 0.5 - 4 ml hour ⁻¹. One way to increase the production is to multiply the number of nozzles. When multiple jets are

employed, it is possible to spin different types of polymer simultaneously. The ratio of the polymer fibres is determined by the ratio of the number of syringes containing different polymer solutions. In this study, one programmable multi-syringe pump has been used to produce PLLA nanofibrous mats and their structure has been studied in comparison to nanofibre mats, made by using a conventional single syringe pump.

7.2 Manufacturing of Nanotextiles using Multiple Syringes

The experiments were performed in the same cabinet made for the single syringe pump (refer to Section 3.2.3). The set-up included a programmable multi-syringe pump (Cole-Parmer Hz 50/60, cat# 789232C), power supply capable of generating high voltage, syringes as capillary tubes and a stationary collector with transverse movement option. Polymer solution was delivered to the top of multiple needles through hypodermic glass syringes with capacity of 5 ml as a capillary tube and the flow of the liquid spinnable polymer was controlled using programmable multi-syringe pump, shown in Fig. 7-1. Three syringes were used for manufacturing a nanotextile mat from PLLA; however, the set-up had a capacity for running ten syringes, Fig. 7-1, at a time. Additional arrangement of using Uhing®-Rolling ring drives (Joachim Uhing KG GmbH & Co) provided a transverse movement to the stationary collector (Al screen) for collection of nanofibres. This arrangement was necessary to collect the nanofibres uniformly in a controlled way throughout the width of the collector. These devices, Fig. 7-1, are friction drives which convert the constant rotary movement of a plain shaft into a traversing movement.

A polymer solution of 10% concentration was taken in each of three identical syringes and all were subjected to the same applied voltage of 10 kV. The electrospun fibres were collected on a metal screen collector, Fig. 7-1, which was attached with the negative electrode. The workable distances between the individual tips of the nozzles and the collector were kept nominally at 100 mm. Inter-nozzle distance was 270 mm as designed and in the centre, there was a gap of 350 mm. It provided a significant distance between the 5th and 6th syringes considering it from either side. Electrospinning experiments were carried out at room temperature of 20^{0} C, RH of 40%

and in normal atmospheric pressure. The surrounding gas was air. Solutions were prepared and stored at the same room temperature before the electrospinning process started.



Fig. 7-1: Collection of nanofibres on a stationary collector with a traverse movement



7.3 Sample Preparation and Study of Nanofibrous Structure

Aluminium (Al) stubs were kept on the metal screen through the holes made on it, and nanofibres were projected directly from three simultaneous needles on to the metal stubs. As the collector screen was shifting its position due to traverse movement, nanofibres were collected simultaneously from all nozzles. After projecting the nanofibres for 15 - 20 seconds on the Al stubs, the electrospinning process was stopped for a while. Stubs were taken out, dried for 8 hours in the atmosphere and then collected in an air-tight plastic container. The nanofibres collected on metal stubs were coated with Pt and then visualised through SEM as described in Section 3.3 and 3.4.

7.4 Comparative Studies of Morphologies using Two Techniques

In order to investigate the effect of simultaneous electrospinning of polymer nanofibres from multiple nozzles, both types of experiments (single-jet and multiple-jet) were performed using suitable parametric conditions (with a feed rate of 1 ml hr ⁻¹, applied voltage of 10 kV and a workable distance of 100 mm between the needle tip and collector), with a polymer concentration of 10%. With a single jet spinning, these combinations of parameters with same polymer-solvent system (refer to Section 3.5.1) produced consistently bead-free nanofibres that were produced by the multiple syringes. In comparison with single jet, these show the broader distribution of fibre diameters whereas single jet consistently produced nanofibrous mats of uniform diameters in Figs. 7-2 (c) and (d). With closer inspection of Figs. 7-2 (a) - (d), it can been realised that the average diameters of nanofibres from both types of electrospinning do not differ significantly; however, multiple jets produced slightly coarser fibres in comparison with those produced from single jet spinning.

In a multiple-nozzle arrangement, the process becomes intricate because of the repulsion between similarly charged jets [1, 34]. In this case, not only the externally applied electric field and self-induced electrical charges influence the jet path, but also mutual-charge interactions



Figs. 7-2: SEM images at two different magnifications (a) and (b) nanofibres with uneven diameters from multiple nozzle system; and (c) and (d) nanofibres with uniform diameters from single nozzle system

between different jets contribute in pulling the liquid polymer towards the collector [144]. The envelope cones of the inner jets are squeezed along the line on which the jets are located. This phenomenon was slightly visible through the naked eye as well, which revealed that the diameters of the inner envelope cones were larger in the direction perpendicular to the line on

which the jets were located compared to those of the outer jets. Fig. 7-3 shows a smaller area of nonwoven mat where fibres were deposited heavily due to closeness of the jets. It was realised [144] that in the case of a double-jet electrospinning process, the repulsion of the jets results in the collection of a mat of non-uniform thickness. The effect, however, can be reduced by the introduction of more jets. In a large number of jets, the inner jets develop in the same way as jets in single-jet electrospinning processes, which leads to the uniformity of the non-woven mat produced. However, it is unavoidable to make same fibre shapes delivered by the side needles. Another criterion is the solvent evaporation that plays a major role in multi-nozzle spinning. Solvent evaporation in the side jets is significantly higher than of that in the centre. In the case of a large number of jets, these effects are more pronounced, eventually producing coarse fibres in the central area, compared to those produced from the side nozzles.



Fig. 7-3: Uneven deposition of the nanofibres

7.6 Discussion with Merits and Demerits

Chapter seven presents the results of investigations of morphological changes of two types of electrospinning (single-jet and multiple-jet). Several important conclusions can be drawn from the results of the research:

- Electrospinning is a relatively simple process with a huge potential for application in different areas, but its main drawback is the low productivity. Assuming the feed rate for electrospinning of 2 ml hr⁻¹, and a solution concentration of 10% (w/v) (0.1 gm solute in a solution of 1 ml), the mass of nanofibres collected from a single needle after an hour is only 0.2 gm. In order to make electrospinning commercially viable, it is necessary to increase the production rate of the nanofibres. To do so, a multiple spinning setup is necessary to increase the yield while maintaining the uniformity of the nanofibre mesh. In addition to that, multiple nozzles can be used in electrospinning to make multi-component blend nanofibrous mats.
- Although multiple nozzles have been introduced in electrospinning as a means of increasing the production rate, there is a complication of interjet interaction. In spite of various uses of multiple jets, a detailed physical understanding of the outcome of interjet interaction is not available in the literature. A decrease in the nozzle spacing leads to a greater repulsion between the jets [34, 148]. On the other hand, in the case of a large number of jets, closeness of the jets sometimes results in overlapping. This results in an increased deposition rate over a smaller area. Homogeneous fibre distribution and uniformity in mass per unit area are the necessary requirements for an ideal nanotextile; however, it needs rigorous control of manufacturing parameters.
- Evaporation of the solvent can substantially impede the electrospinning process and there may be a possibility of remaining solvent residues in the final product. An alternative method might be electrospinning from the melt [1, 34]. Although the efficiency of melt electrospinning is generally much higher than that of solution electrospinning, the melt

electrospinning of technologically relevant polymers leads to fibre diameters that are not competitive (more than 1 μ m) with those obtained by solution electrospinning. This happens due to the high melt viscosities of the polymers [149]. Eventually, polymer solutions of high viscosities produce coarse fibres.

- Because of the high viscosities, the electrospinning of polymer melts requires large electrode separations, which, in turn, require higher electric fields. Under normal atmosphere, such large electric fields lead to the danger of electric shock [1, 34]. In addition to that, there must be a constant heat supply to the reservoir containing the polymer solution for electrospinning, so that the polymer remains in a molten state.
- Although the use of multiple syringes can increase the production rate of electrospinning, there is a complication of clogging of the needles during the spinning. Another way to avoid this problem is to make use of needleless electrospinning method [150]. The process is based on a rotating roll dipping in a bath of polymer solution.

CHAPTER 8

Conclusions

8.1 Conclusions

Electrospinning is a relatively simple process for yielding fibres down to nanoscale. The versatility of electrospinning includes the fact that fibres of different morphology and made of different materials can be made through electrospinning. For achieving uniform and bead-free nanofibres, thorough understanding of process parameters and polymer solution properties are essential. Following are the important conclusions that can be drawn from the results of the research:

• In general, it is observed that fibres become more uniform and with less area occupied by beads with increasing polymer concentration in solution; fibre diameters also increase significantly with increasing polymer concentration (thus viscosity increases as well). At lower concentrations, increasingly thinner fibres are formed, with additional beads along the fibre axis. At a very high dilution, fibre formation no longer takes place. Reducing the polymer concentration is the quicker way to produce fine nanofibres, but it produces

- beads. Producing a nanotextile with bead-free and uniform nanofibres, particularly for fibre diameters less than 100 nm is almost unachievable. In the present study, at a low viscosity (7.8 mPa s) of the poly(L-lactic acid) (PLLA) solution, surface tension has a dominant influence on fibre morphology and below a surface tension of 34.1 mN m⁻¹, drops are formed instead of fibres.
- The formation of beads can be prevented by increasing the polymer concentration (and thus viscosity) and the electrical conductivity of the solution. Appropriate solvent viscosities typically range from tens to hundreds of millipascals.second, and electrical conductivities in organic solvents typically range from nano- to microsiemens per centimeter. The fibre morphology can also be directed significantly by the appropriate choice of solvent mixture (high-boiling/low-boiling solvents). Spinning ability of PLLA using dichloromethane (DCM) and dimethyl formamide (DMF) (at a proportion of 60/40) as solvent-mixture, is found only when viscosities are in the range of 7.8 116.5 mPa s and surface tensions in the range of $34.1 36.8 \text{ mN m}^{-1}$. However, PLLA with a significantly high weight average molar mass $(1.044 \times 10^5 \text{ g mol}^{-1})$ was used in the research.
- PLLA nanotextile has shown considerable mechanical strength due to continuous fibrous network with fibres anchoring each other and the number of crossover points. Stiffness has varied directly with its density; density is regulated by the solid material that is generated from the polymer concentration. The solution with polymer concentration of 10% has produced bead-free nanofibres with diameters of high uniformity; however, it produces coarser diameters. This product has shown a high Young's modulus of 119 MPa and tensile strength of 3.3 MPa. Nanomat with polymer concentration of 12% had high modulus and strength of 221 MPa and 6 MPa, respectively. Nevertheless, it is challenging to make nanofibres using a very high concentration/viscosity as it dries up quickly from the needle tip and gets clogged. Mechanical properties of the nanofibre matrix can be estimated/regulated by adjusting the polymer concentration without affecting the fibre diameter.

- S/N ratio and ANOVA approaches of Taguchi analysis provide the same conclusion that the concentration of polymer solution plays a major role in determining the fineness of the nanofibril, but when the beads are considered, the influence is just the opposite. Applied voltage also plays an important role in determining the nanofibre diameters. A lower polymer concentration with a lower feed rate and relatively high voltage and distance appear to produce bead-like textures but with fine fibres. Furthermore, to make bead-free nanofibres, it is necessary to keep polymer concentration on the high side at the cost of slightly coarser diameter.
- Taguchi's orthogonal array (OA) has functioned well for analysing the performance of electrospinning and has provided a set of suitable spinning parameters. It is worth mentioning that a full statistical analysis might provide slightly better results keeping the parametric combination outside the Taguchi OA; however, the latter provides a quicker way of getting reasonably good results that are quite acceptable to manufacturers. Therefore, the decision on whether to use full statistical analysis or Taguchi's design of experiments should depend on the number of parameters, their levels and the availability of time and resources.
- Depending on the application, fibres with different morphology and structures can be produced by using specific parameters and set-ups.
- It might not always be wise to make a general recommendation for a definite polymer concentration and the resulting viscosity, electrical conductivity and surface tension for the best performances of electrospinning operation, because the ideal values of these factors vary considerably with the polymer solvent systems.
- Multiple regression analysis (MRA) has established a general equation of predicting resultant fibre diameters that has worked well. When major parameters i.e. polymer concentration, feed rate of the polymer solution, applied effective voltage and relative humidity are kept within the commonly used operational parameter range for electrospinning, it has provided a remarkably fine prediction. However, when using the

derived model to predict the fibre diameter under the extreme conditions of this study, particularly for applied voltage and relative humidity, the predictive capability of the MRA model is compromised.

- A general equation involving two parameters, polymer concentration and feed rate, gives best indication of predicting resultant fibre diameters when other parameters are suitably maintained. While combining humidity and applied voltage (hard-to-control the effects), the prediction of fibre diameters produced becomes less satisfactory but is still obviously acceptable.
- This study has proved that prior to the mass production of nanofibrous mat, experimental time could be significantly reduced by identifying the most suitable production conditions that would yield nanofibres of specific required qualities.
- Lastly, it can be mentioned that the multiple nozzle system is necessary, but single jet is more conducive to understanding the mechanism.

8.2 Achievements and Recommendations for Further Work

8.2.1 List of publications

A major portion of the research presented in this thesis has been published in peer-reviewed journals and presented at conferences around the world. A list of publications and conference presentations (presenting author shown in italics) is given in Appendix A.

8.2.2 Recommendations for further work

This work contributes to manufacture and characterisation of elctrospun nanotextiles with high mechanical performances, made of bead-free fibres with diameters of high uniformity. It is recommended that further research work should be carried out as mentioned below.

- Single nozzle system of electrospinning can easily make fine and uniform nanofibres at the cost of poor productivity. Production speed can be increased by increasing the nozzle numbers up to ten; however, the interactions between neighbouring jets have to be clearly understood. Non-uniform thickness of the mat can be reduced by the introduction of more jets.
- With the addition of a suitable surfactant to the polymer solution, a nanotextile can be produced using very high polymer concentration (>12%). Surfactant may work as a lubricant to prevent clogging of the needle. Polymer solution with high concentration provides improved tensile strength due to having more solutes in it, thus increasing density of the nanomat. The increased tensile strength of nanomat can open up new and interesting opportunities for applications in filters, textiles and many others.
- By employing a circular rotating disc as a collector, the nanofibres can be aligned in parallel to a great extent. It is conceivable that a higher degree of fibre orientation along a preferred direction can enhance the mechanical properties of nonwoven mat.
- The MRA model developed in this study has been proved to reliably predict the resultant fibre diameter within the commonly used operational parameter range for electrospinning. It is recommended that this technique can be easily expanded to make it more capable for estimating the electrospun fibre diameters by selecting (or increasing) the necessary manufacturing parameters and their broader range.



CHAPTER 9

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Appendix A

List of publications

- S. N. Patra, R. J. T. Lin and D. Bhattacharyya, "Regression analysis of manufacturing electrospun nonwoven nanotextiles", <u>Journal of Materials Science</u> (2010) 45: 3938-3946.
- 2. **S. N. Patra** and D. Bhattacharyya, "Characterisation of Electrospun Poly(lactic acid) Nanofibre Networks", <u>Composite Interfaces</u>, (2010) 17: 273-282.
- S. N. Patra, D. Bhattacharyya, S. Ray and A. J. Easteal, "Electrospun Poly(lactic acid) based Conducting Nanofibrous Networks" <u>Institute of Physics</u>, IOP Conf. Series: Materials Science and Engineering (2009) 4 (1): 2020 doi:10.1088/1757-899X/4/1/012020.
- 4. **S. N. Patra**, A. J. Easteal and D. Bhattacharyya, "Parametric study of manufacturing poly(lactic) acid nanofibrous mat by electrospinning" <u>Journal of Materials Science</u> (2009) 44: 647–654.
- 5. **S. N. Patra** and D. Bhattacharyya, "Poly(lactice acid) based Conducting Nanofibrous Quality Mat through Electrospinning" <u>The World Journal of Engineering</u>, (accepted)
- S. N. Patra and D. Bhattacharyya, "Poly(lactice acid) based Conducting Nanofibrous Quality Mat through Electrospinning" Seventeenth International Conference on Composites/Nano Engineering (ICCE – 17) Hawaii, USA, Issue Supplement (July 2009) pp.795.
- D. Bhattacharyya and S. N. Patra, "Manufacturing of Conducting Polymer Based Nanotextile through Electrospinning"; <u>Invited Paper (#O-029-IT)</u> at the Fourth China-Europe Symposium on Processing and Properties of Reinforced Polymers, (June 2009) Guilin, China, CD-ROM.
- S. N. Patra, D. Bhattacharyya, S. Ray and A. J. Easteal, "Nanostructured Electrospun Network Using Conducting Polymer" Workshop on Processing, Microstructure and Performance of Materials (PMPM), (April 2009), The Chemical & Materials Engineering, The University of Auckland, New Zealand, pp.111-116.

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- S. N. Patra, D. Bhattacharyya and A. J. Easteal, 'Characterisation of Electrospun Poly(lactic acid)) Nanofibril Networks', Second International Conference on Polymer Blends, Composites, IPNS, Membranes, Polyelectrolytes and Gels: Macro to Nano Scales (ICBC 2008), (Sept 2008), Kottayam, India, Paper # CL8.
- S. N. Patra, D. Bhattacharyya, "Electrospun Nanostructured PLLA based Conducting Fibrous Networks", <u>Poster</u>, International symposium on Recent Developments and Applications in Polymer Nanostructured Materials, (June 2009), Melbourne, Australia.

Appendix B

Tables of Parametric Study, Chapter 4

Table B-1: Response table for S/N ratios of fibre diameter

		A (-dB)		B (-dB)		C (-dB)		AB (-dB)		AC (-dB)		BC (-dB)		D (-dB)	
Exp	s/n (-dB)	1	2	1	2	1	2	1	2	1	2	1	2	1	2
1	38.95	38.95		38.95		38.95			38.95		38.95		38.95	38.95	
2	34.18	34.18		34.18			34.18		34.18	34.18		34.18			34.18
3	37.68	37.68			37.68	37.68		37.68			37.68	37.68			37.68
4	40.06	40.06			40.06		40.06	40.06		40.06			40.06	40.06	
5	43.3		43.3	43.3		43.3		43.3		43.3			43.3		43.3
6	44.35		44.35	44.35			44.35	44.35			44.35	44.35		44.35	
7	43.22		43.22		43.22	43.22			43.22	43.22		43.22		43.22	
8	42.67		42.67		42.67		42.67		42.67		42.67		42.67		42.67
	324.41	150.87	173.54	160.78	163.63	163.15	161.26	165.39	159.02	160.76	163.65	159.43	164.98	166.58	157.83
Total															
No	8	4	4	4	4	4	4	4	4	4	4	4	4	4	4
Ave	40.55	37.72	43.39	40.19	40.91	40.79	40.32	41.35	39.76	40.19	40.91	39.86	41.25	41.65	39.46
Effect	L1-L2	5.67		0.72		-0.47		-1.59		0.72		1.39		-2.19	

		A (-dB)		B (-dB)		C (-dB)		AB (-dB)		AC (-dB)		BC (-dB)		D (-dB)	
Exp	s/n (-dB)	1	2	1	2	1	2	1	2	1	2	1	2	1	2
1	45.73	45.73		45.73		45.73			45.73		45.73		45.73	45.73	
2	46.07	46.07		46.07			46.07		46.07	46.07		46.07			46.07
3	45.31	45.31			45.31	45.31		45.31			45.31	45.31			45.31
4	44.44	44.44			44.44		44.44	44.44		44.44			44.44	44.44	
5	39.56		39.56	39.56		39.56		39.56		39.56			39.56		39.56
6	40.26		40.26	40.26			40.26	40.26			40.26	40.26		40.26	
7	40.37		40.37		40.37	40.37			40.37	40.37		40.37		40.37	
8	37.86		37.86		37.86		37.86		37.86		37.86		37.86		37.86
Total	339.6	181.5 5	158.05	171.62	167.98	170.97	168.63	169.57	170.03	170.44	169.16	172.01	167.59	170.8	168.8
No	8	4	4	4	4	4	4	4	4	4	4	4	4	4	4
Ave	42.45	45.39	39.51	42.91	42	42.74	42.16	42.39	42.51	42.61	42.29	43	41.9	42.7	42.2
Effect	L1-L2	-5.88		-0.91		-0.58		0.12		-0.32		-1.1		-0.5	

Table B-2: Response table for S/N ratios of bead area

Experiment No		Fact	ors			Results	/ replicatio	Average diameter (nm)	S/N ratios (-dB)		
	A	В	С	D	Y1	Y2	¥3	¥4	Y5		
1	1	1	1	1	98.10	90.01	85.92	76.97	90.55	88.31	38.9466
2	1	1	1	2	56.52	51.07	54.31	46.17	47.04	56.07	35.0003
3	1	1	2	1	68.46	71.35	67.32	79	76.8	72.59	37.2344
4	1	1	2	2	48.66	58.12	60.40	59.40	53.76	51.02	34.1819
5	1	2	1	1	55.29	87.82	65.17	63.66	66.67	67.72	36.7236
6	1	2	1	2	98.83	75.13	80.73	67.76	52.93	75.08	37.6823
7	1	2	2	1	120.29	119.14	104.19	86.28	60.81	98.14	40.0571
8	1	2	2	2	73.43	58.15	65.52	54.74	56.36	61.64	35.8522
9	2	1	1	1	166.7	142.24	132.44	185.49	141.57	153.69	43.8025
10	2	1	1	2	135.76	159.31	144.33	152.62	138.11	146.03	43.3045
11	2	1	2	1	133.18	143.54	208.06	179.87	148.68	162.67	44.3485
12	2	1	2	2	366.95	362	328.81	437.64	434.68	386.02	51.7857
13	2	2	1	1	143.38	151.12	153.23	155.46	117.6	144.16	43.2169
14	2	2	1	2	277.44	252.32	260.47	231.37	232.08	250.74	48.0055
15	2	2	2	1	175.02	151.27	131.32	173.74	121.56	150.58	43.6445
16	2	2	2	2	135.29	108.67	147.67	153.67	129.95	135.06	42.668

 Table B-3:
 Experimental results and S/N ratios for fibre diameters with replications
Appendix C

Technical Data and Plots of GPC for the Determination of Molecular weight, Chapter 5

ASTRA 4.70.07 summary Report for PLLA (3051 D)

File : G:\SOUMENDR\PLLA (3051 D).ADF

Sample ID : PLA in THF at 3mg/ml , fr 1.0 ml/min, 200ul inj loop

COLLECTION INFORMATION Collection time : Mon Dec 18, 2006 12:50 PM

Instrument type : DAWN DSP

Cell type : K5

Laser wavelength: 632.8 nm

Solvent name : THF

Solvent RI : 1.403

Calibration constants

DAWN : 2.1180e-05

» AUX1 : 1.0243e-04

Flow rate : 1.000 mL/min

-

PROCESSING INFORMATION	
Processing time	: Wed Dec 20, 2006 10:52 PM
DAWN/AUX1 delay	: 0.217 mL
Fit method / model	: Debye
Calculation method	: dn/dc + AUX Constant
USING FITTED DATA	: MM fit = 3 rd order Radius fit = 3 rd order
Detectors used	: 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18

RESULTS	PEAK #1
Volume (mL)	: 18.750 - 25.142
Slices	: 768
A2 (mol mL/g ²)	: 0.000e+00
Fit degree	: 1
Injected Mass (g): 6.0000e-04	
Calc. Mass (g)	: 7.3598e-04
dn/dc (mL/g)	: 0.041
Polydispersity(Mw/Mn)	: 1.352±0.004
Polydispersity(Mz/Mn)	: 1.792±0.007

Molar Mass Moments (g/mol)

Mn	: 7.720e+04 (0.3%)
Mw	: 1.044e+05 (0.13%)
Mz	: 1.384e+05 (0.27%)

R.M.S. Radius Moments (nm)

Rn	: 22.5 (3%)
Rw	: 20.3 (2.1%)
Rz	: 20.0 (1.3%)



Fig. C-1: dn/dc plot of PLLA (3051 D)

-v-List of research project topics and materials





All data and plots of dn/dc and molecular weight determination using GPC have been supplied by Michel Nieuwoudt, The Department of Chemistry, The University of Auckalnd.

Appendix D

Excel Charts of Regression Analysis and Figures, Chapter 6

poly conc	diameter		D-cal	+15%D-cal	-15%D-cal
4	63.74				
4	68.75				
4	70.31				
4	79.18				
4	77				
4	69.93				
4	88.04				
4	49.69	70.83	65.94508	75.83684	56.05332
7	110.44				
7	148.47				
7	121.3				
7	114.36				
7	116.39				
7	123.17				
7	124.81				
7	171.44	120.0078	148.4774	170.7491	126.2058
10	271.83				
10	238.29				
10	261.72				
10	232.39				
10	285.18				
10	290.86				
10	304.95				
10	312.73	274.7438	249.0662	286.4261	211.7063

Table D-1: Results of fibre diameter with changing polymer concentration

feedrate	diameter		D-cal	+15%D-cal	-15%D-cal
0.5	111.18				
0.5	114.04				
0.5	122.98				
0.5	117.34				
0.5	80.16				
0.5	121.97				
0.5	123.93				
0.5	108.75	112.5438	108.0056	124.2064	91.80476
1	110.44				
1	148.47				
1	121.3				
1	114.36				
1	123.17				
1	114.16				
1	123.17				
1	116.39	121.4325	129.2	148.58	109.82
2	156.28				
2	176.93				
2	141.94				
2	188.73				
2	149.08				
2	163.25				
2	143.99	-			
2	163.25	160.4313	154.5535	177.7365	131.3705

 Table D-2: Results of fibre diameter with changing feed rate

poly conc	diameter		D-cal	+15%D-ca	-15%D-cal	Variation
4	63.74					-3.34%
4	68.75					4.25%
4	70.31					6.62%
4	79.18					20.07%
4	77					16.76%
4	69.93					6.04%
4	88.04					33.51%
4	49.69	70.83	65.94508	75.83684	56.05332	-24.65%
7	110.44					-25.62%
7	148.47					-0.01%
7	121.3					-18.30%
7	114.36					-22.98%
7	116.39					-21.61%
7	123.17					-17.04%
7	124.81					-15.94%
7	171.44	120.0078	148.4774	170.7491	126.2058	15.47%
10	271.83					9.14%
10	238.29					-4.33%
10	261.72					5.08%
10	232.39					-6.70%
10	285.18					14.50%
10	290.86					16.78%
10	304.95					22.44%
10	312.73	274.7438	249.0662	286.4261	211.7063	25.56%

Table D-3: Results of fibre diameter with changing polymerconcentration with variation (%)

feedrate	diameter		D-cal	+15%D-ca	-15%D-cal	Variation
0.5	111.18					2.94%
0.5	114.04					5.59%
0.5	122.98					13.86%
0.5	117.34					8.64%
0.5	80.16					-25.78%
0.5	121.97					12.93%
0.5	123.93					14.74%
0.5	108.75	112.5438	108.0056	124.2064	91.80476	0.69%
1	110.44					-14.52%
1	148.47					14.91%
1	121.3					-6.11%
1	114.36					-11.49%
1	123.17					-4.67%
1	114.16					-11.64%
1	123.17					-4.67%
1	116.39	121.4325	129.2	148.58	109.82	-9.91%
2	156.28					1.12%
2	176.93					14.48%
2	141.94					-8.16%
2	188.73					22.11%
2	149.08					-3.54%
2	163.25					5.63%
2	143.99					-6.83%
2	163.25	160.4313	154.5535	177.7365	131.3705	5.63%

Table D-4: Results of fibre diameter with changing feed rate with variation (%)

Fibre dia	PC(g/100r	FR (ml/hr)	volta(kv)	humid%	Log(D)	Log(PC)	Log(FR)
44.78	4	0.5	10	40	1.651084	0.60206	-0.30103
50.06	4	0.5	10	40	1.699491	0.60206	-0.30103
56.49	4	0.5	10	40	1.751972	0.60206	-0.30103
50.43	4	0.5	10	40	1.702689	0.60206	-0.30103
63.74	4	1	10	40	1.804412	0.60206	0
68.75	4	1	10	40	1.837273	0.60206	0
70.31	4	1	10	40	1.847017	0.60206	0
79.18	4	1	10	40	1.898615	0.60206	0
· 74.8	4	2	10	40	1.873902	0.60206	0.30103
70.02	4	2	10	40	1.845222	0.60206	0.30103
85.72	4	2	10	40	1.933082	0.60206	0.30103
81.63	4	2	10	40	1.91185	0.60206	0.30103
111.18	7	0.5	10	40	2.046027	0.845098	-0.30103
114.04	7	0.5	10	40	2.057057	0.845098	-0.30103
122.98	7	0.5	10	40	2.089834	0.845098	-0.30103
117.34	7	0.5	10	40	2.069446	0.845098	-0.30103
110.44	7	1	10	40	2.043126	0.845098	0
148.47	7	1	10	40	2.171639	0.845098	0
121.3	7	1	10	40	2.083861	0.845098	0
114.36	7	1	10	40	2.058274	0.845098	0
156.28	7	2	10	40	2.193903	0.845098	0.30103
176.93	7	2	10	40	2.247801	0.845098	0.30103
141.94	7	2	10	40	2.152105	0.845098	0.30103
188.73	7	2	10	40	2.275841	0.845098	0.30103
268.4	10	0.5	10	40	2.428783	1	-0.30103
182.18	10	0.5	10	40	2.260501	1	-0.30103
256.66	10	0.5	10	40	2.409358	1	-0.30103
174.45	10	0.5	10	40	2.241671	1	-0.30103
271.83	10	1	10	40	2.434297	1	0
238.29	10	1	10	40	2.377106	1	0
261.72	10	1	10	40	2.417837	1	0
232.39	10	1	10	40	2.366217	1	0
278.45	10	2	10	40	2.444747	1	0.30103
296.56	10	2	10	40	2.472113	1	0.30103
305.42	10	2	10	40	2.484897	1	0.30103
309.56	10	2	10	40	2.490745	1	0.30103

Table D-5: Multiple regression with 2 factors

	JUNINAR	001201							
	Rearession	Statistics							
	Multiple F	0.977529							
	R Square	0.955563							
	Adjusted	0.95287							
	Standard I	0.055936							
	Observati	36							
	Observati								
	ANOVA	df		1/10	E	anificanco	E		
	Pogrossio	uj 2	2 220245	1 110172	F 25/ 012/	1 97E 22	r		
	Regidual	22	0 103253	0.003120	554.0154	4.07L-23			
	Total	25	2 222509	0.003123					
	TULAI		2.323336						
		a officient	andard Fra	t Ctat	Dualua	Lauran 050/	Inner OFI	ouver 05.00	
	Interest	0.010720		10 42025	1 255 10	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	1 016000	0 933376	1 016002
	Intercept	1 162042	0.04/359	25 70250	1.20E-19	1 2/7724	1.010082	1 247224	1.010082
		0.265510	0.050922	25.70259	5 2EE 00	0 10025	1.3/8821	0 19925	0.242697
	LUB(FK)	0.205518	0.03793	7.000271	5.23E-U8	0.18832	0.34208/	0.18832	0.542087
	DESIDUAL								
	RESIDUAL	JUIPUI							
	hcor.eti-	dicted la	Docid.al-	dard Dasi-	uals				
(Juservatioi	1 7200200	nesiauais	1 20050	uuis				
	1	1.720639	-0.00950	-1.28059					
	2	1.720639	-0.02115	-0.38937					
	3	1.720639	0.031332	0.576864					
	4	1.720039	-0.01795	-0.33049					
	5	1.800508	0.003844	0.070768					
	0	1.800568	0.036704	0.075/71					
	/	1.800568	0.046449	1.8051//					
	8	1 200/07	_0.098047	-0.12144					
	10	1 200497	-0.0000	-0.12144					
	10	1.000497	-0.05326	-0.04940					
	11	1.000497	0.032363	0.508145					
	12	2 076214	-0.031332	-0 55579					
	1/	2.076214	-0.01916	-0 3527					
	14	2.076214	0.01362	0.250765					
	16	2.076214	-0.00677	-0.12461					
	17	2.156143	-0,11302	-2.08078		r			
	18	2.156143	0.015495	0.28529					
	19	2.156143	-0.07228	-1.33081					
	20	2.156143	-0.09787	-1.80189					
	21	2,236072	-0,04217	-0.77638					
	21	2,236072	0.011729	0.215949					
	22	2,236072	-0,08397	-1.54594					
	25	2,236072	0.039769	0.732189					
	25	2.302842	0.12594	2.318708					
	25	2.302842	-0,04234	-0.77956					
	20	2.302842	0.106516	1.961083					
	28	2.302842	-0.06117	-1.12624					
	29	2.382771	0.051526	0.948655					
	30	2.382771	-0,00567	-0.10431					
	31	2.382771	0.035066	0.645598					
	32	2.382771	-0,01655	-0.30478					
	33	2.4627	-0.01795	-0.33054					
	34	2.4627	0.009412	0.173289					
	34	2.4627	0.022197	0.408675					
	36	2 4627	0.028044	0.516332					
			····						

Dia(D)	PC(g/100	FR(ml/hr)	volta(kv)	humid%	Log(D)	Log(PC)	Log(FR)	Log(Volt)	Log(Hum)
44.47	4	0.5	8	20	1.64807	0.60206	-0.301	0.90309	1.30103
75.38	4	1	10	40	1.87726	0.60206	0	1	1.60206
98.14	4	2	12	75	1.99185	0.60206	0.30103	1.07918	1.87506
254.23	7	0.5	10	75	2.40523	0.8451	-0.301	1	1.87506
80.412	7	1	12	20	1.90532	0.8451	0	1.07918	1.30103
105.23	7	2	8	40	2.02214	0.8451	0.30103	0.90309	1.60206
273.99	10	0.5	12	40	2.43773	1	-0.301	1.07918	1.60206
308.66	10	1	8	75	2.48948	1	0	0.90309	1.87506
162.67	10	2	10	20	2.21131	1	0.30103	1	1.30103
62.68	7	0.5	10	20	1.79713	0.8451	-0.301	1	1.30103
104.18	7	0.5	10	40	2.01778	0.8451	-0.301	1	1.60206
126.75	7	1	12	40	2.10295	0.8451	0	1.07918	1.60206
297.51	7	2	10	75	2.4735	0.8451	0.30103	1	1.87506
301.7	7	2	10	40	2.47958	0.8451	0.30103	1	1.60206
172.07	7	2	12	40	2.23571	0.8451	0.30103	1.07918	1.60206
257.53	10	1	10	40	2.41083	1	0	1	1.60206
278.96	10	1	12	40	2.44554	1	0	1.07918	1.60206
738.77	10	2	12	75	2.86851	1	0.30103	1.07918	1.87506
52.59	4	0.5	8	20	1.7209	0.60206	-0.301	0.90309	1.30103
79.18	4	1	10	40	1.89862	0.60206	0	1	1.60206
120.29	4	2	12	75	2.08023	0.60206	0.30103	1.07918	1.87506
247.2	7	0.5	10	75	2.39305	0.8451	-0.301	1	1.87506
89.89	7	1	12	20	1.95371	0.8451	0	1.07918	1.30103
107.2	7	2	8	40	2.03019	0.8451	0.30103	0.90309	1.60206
268.4	10	0.5	12	40	2.42878	1	-0.301	1.07918	1.60206
293.49	10	1	8	75	2.46759	1	0	0.90309	1.87506
208.06	10	2	10	20	2.31819	1	0.30103	1	1.30103
71.01	7	0.5	10	20	1.85132	0.8451	-0.301	1	1.30103
87.58	7	0.5	10	40	1.9424	0.8451	-0.301	1	1.60206
139.86	7	1	12	40	2.14569	0.8451	0	1.07918	1.60206
229.48	7	2	10	75	2.36074	0.8451	0.30103	1	1.87506
296.26	7	2	10	40	2.47167	0.8451	0.30103	1	1.60206
206.16	7	2	12	40	2.3142	0.8451	0.30103	1.07918	1.60206
271.83	10	1	10	40	2.4343	1	0	1	1.60206
285.37	10	1	12	40	2.45541	1	0	1.07918	1.60206
689.36	10	2	12	75	2.83845	1	0.30103	1.07918	1.87506

Table D-6: Multiple regression with 4 factors

Rearession	Statistics								
Multinla C	0 975579								
R Square	0.925578								
	0.838203								
Standard I	0.030205								
Obconvati	0.119525								
Observati									
ANOVA	-16		140			r			
<u> </u>	af .	55	MS	F	gnificance	F			
Regressio	4	2.638661	0.659665	46.33021	1.19E-12				
Residual	31	0.441388	0.014238						
Total	35	3.080049							
0	Coefficients	andard Err	t Stat	P-value	Lower 95%	Upper 95%	ower 95.09	pper 95.0%	i
Intercept	-0.6755	0.369765	-1.82684	0.077367	-1.42964	0.078641	-1.42964	0.078641	
Log(PC)	1.409706	0.151777	9.288012	1.81E-10	1.100155	1.719258	1.100155	1.719258	
Log(FR)	0.207801	0.085829	2.421101	0.02152	0.032751	0.382852	0.032751	0.382852	
Log(Volt)	0.515445	0.330437	1.559888	0.128938	-0.15849	1.189376	-0.15849	1.189376	
Log(Hum)	0.719232	0.103029	6.980897	7.8E-08	0.509104	0.92936	0.509104	0.92936	
RESIDUAL	OUTPUT								
Observatio	dicted Log	Residuals	dard Resid	uals					
1	1.511908	0.136159	1.212471						
2	1.840924	0.036332	0.323528						
3	2.140643	-0.1488	-1.32501						
4	2,317333	0.087894	0.782674						
5	2.00784	-0.10252	-0.91291						
6	2 196139	-0 174	-1 54943						
7	2 380162	0.174	0 512674						
, 8	2 548302	-0.05882	-0 5238						
9	2 247947	-0.03664	-0 32627						
10	1 904472	-0 10734	-0.95586						
11	2 120982	-0 1032	-0 91895						
12	2.120302	-0 121/	-1 08106						
12	2.22433	0.1214	0 276578						
1/	2.442442	0.031035	2 070120						
14	2.240091	0.233404	0.45502						
15	2.200905	0.00012	0.43392						
10	2.401903	0.000923	0.075470						
10	2.442/10	0.002020	1 496000						
10	2.701022	0.10000/	1.400090						
19	1 040034	0.200990	0 512720						
20	1.840924	0.05/691	0.513/29						
21	2.140643	-0.06041	-0.53/9/						
22	2.31/333	0.075/15	0.674229						
23	2.00784	-0.05413	-0.482						
24	2.196139	-0.16594	-1.4777						
25	2.380162	0.048621	0.432957						
26	2.548302	-0.08071	-0.71869						
27	2.247947	0.070242	0.625487						
28	1.904472	-0.05315	-0.47331						
29	2.120982	-0.17858	-1.59019						
30	2.22435	-0.07866	-0.70042						
31	2.442442	-0.0817	-0.7275						
32	2.246091	0.225582	2.00876						
33	2.286905	0.0273	0.2431						
34	2.401903	0.032395	0.288467						
35	2.4427 16	0.012692	0.113019						
							and the second second		

Table D-6: Multiple regression with 4 factors (continued)

List of research project topics and materials

Exp no	Des Mat	Dia(D)	PC(g/100ml	FR(ml/hr)	volta(kv)	humid%	Calculated	% var	variation
1	A0B0C0D0	44.47	4	0.5	8	20	32.8123	35.53%	0.3552844
2	$A_0B_1C_1D_1$	75.38	4	1	10	40	70.208191	7.37%	0.0736639
3	$A_0B_2C_2D_2$	98.14	4	2	12	75	140.39099	-30.10%	-0.3009523
4	$A_1B_0C_1D_2$	254.23	7	0.5	10	75	210.09516	21.01%	0.2100707
5	$A_1B_1C_2D_0$	80.412	7	1	12	20	103.15828	-22.05%	-0.2204988
6	$A_1B_2C_0D_1$	105.23	7	2	8	40	159.18221	-33.89%	-0.3389337
7	$A_2B_0C_2D_1$	273.99	10	0.5	12	40	242.90762	12.80%	0.1279597
8	$A_2B_1C_0D_2$	308.66	10	1	8	75	357.80871	-13.74%	-0.1373603
9	$A_2B_2C_1D_0$	162.67	10	2	10	20	179.45596	-9.35%	-0.0935381
10	$A_0B_0C_1D_0$	62.68	7	0.5	10	20	81.117309	-22.73%	-0.2272919
11	$A_1B_0C_2D_1$	104.18	7	0.5	10	40	133.61497	-22.03%	-0.220297
12	$A_1B_1C_2D_1$	126.75	7	1	12	40	169.92046	-25.41%	-0.2540628
13	$A_1B_2C_1D_2$	297.51	7	2	10	75	281.0921	5.84%	0.0584075
14	$A_1B_2C_1D_1$	301.7	7	2	10	40	178.76716	68.77%	0.6876702
15	$A_1B_2C_2D_1$	172.07	7	2	12	40	196.54499	-12.45%	-0.1245261
16	$A_2B_1C_1D_1$	257.53	10	1	10	40	255.5543	0.77%	0.007731
17	$A_2B_1C_2D_1$	278.96	10	1	12	40	280.96838	-0.71%	-0.0071481
18	$A_2B_2C_2D_2$	738.77	10	2	12	75	511.01619	44.57%	0.4456881
19	$A_0B_0C_0D_0$	52.59	4	0.5	8	20	32.8123	60.28%	0.6027526
20	$A_0B_1C_1D_1$	79.18	4	1	10	40	70.208191	12.78%	0.1277886
21	$A_0B_2C_2D_2$	120.29	4	2	12	75	140.39099	-14.32%	-0.1431786
22	A1B0C1D2	247.2	7	0.5	10	75	210.09516	17.66%	0.1766097
23	$A_1B_1C_2D_0$	89.89	7	1	12	20	103.15828	-12.86%	-0.1286206
24	$A_1B_2C_0D_1$	107.2	7	2	8	40	159.18221	-32.66%	-0.3265579
25	$A_2B_0C_2D_1$	268.4	10	0.5	12	40	242.90762	10.49%	0.1049468
26	$A_2B_1C_0D_2$	293.49	10	1	8	75	357.80871	-17.98%	-0.1797572
27	$A_2B_2C_1D_0$	208.06	10	2	10	20	179.45596	15.94%	0.1593931
28	$A_0B_0C_1D_0$	71.01	7	0.5	10	20	81.117309	-12.46%	-0.1246011
29	$A_1B_0C_2D_1$	87.58	7	0.5	10	40	133.61497	-34.45%	-0.3445345
30	$A_1B_1C_2D_1$	139.86	7	1	12	40	169.92046	-17.69%	-0.176909
31	$A_1B_2C_1D_2$	229.48	7	2	10	75	281.0921	-18.36%	-0.1836128
32	$A_1B_2C_1D_1$	296.26	7	2	10	40	178.76716	65.72%	0.6572396
33	$A_1B_2C_2D_1$	206.16	7	2	12	40	196.54499	4.89%	0.0489201
34	$A_2B_1C_1D_1$	271.83	10	1	10	40	255.5543	6.37%	0.0636878
35	$A_2B_1C_2D_1$	285.37	10	1	12	40	280.96838	1.57%	0.0156659
36	A2B2C2D2	689.36	10	2	12	75	511.01619	34.90%	0.3489984

Table D-7: Comparison between actual results and calculated results of MRA



Figure for Regression Analysis, Chapter 6



Fig. D-1: Experimental data of fibre diameter against (a) polymer concentration and (b) feed rate