SCISSION OF ELECTROSPUN POLYMER FIBRES BY ULTRASONICATION

A thesis submitted in fulfillment of the requirements for the degree of Doctor of Philosophy

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ERRATA

P35, Section 2.4.6 is added at this page to include another method to produce short polymer fibre as suggested by Prof. B Fox.

2.4.6 Shear-enhanced solution precipitation

This is a one-step method to produce short Poly(ethylene-co-acrylic acid) (PEAA) polymer fibres which was prepared by dissolving the PEAA in ammonia ammonia (Sutti, Lin et al. 2011). The solution was injected into the non-solvent i.e ethanol, butanol and isopropanol as the dispersing medium whilst being stirred using a high speed mixer. The processing parameter such as the dispersing medium (nonsolvent) and the polymer solution concentration affect the formation of the nanofibres. Note that, from these results it was observed that the distribution of the fibres' diameter was large (i.e. 0.1 µm to 1 µm) with the average length of 20-40 μ m for a polymer concentration of 12.6 wt/vol%, and 0.1 μ m to 0.3 μ m with average length of 10-20 µm for 3 wt/vol%. It was also shown that at higher shear mixer speeds, shorter fibres were produced (average 5-10 µm). The author discussed that the production of short nanofibres was due to the precipitation of the polymer when it was injected into the non-solvent and shear flow in the systems that resulted in elongation of the precipitates. The morphology of the precipitate produced i.e short fibres/particulates depends on the kinetics of the deformation of the polymer and kinetics of its solidification process. This suggests that the morphology obtained in this study was only applicable for PEAA polymer with further in depth research for other polymers still required. Meanwhile, the ultrasonication method that we proposed here was more general, as we have shown that it can be applied to any polymer fibres, thus reducing the time required for researching the suitable process. In addition, we also can maintain the fibre diameter (with small variation in the fibre diameter and the fibre length as oppose to this study).

P75, the following paragraph was added in Section 3.3 to include the literature suggested by Prof. B Fox.

The inclusion of acetone to aid the dispersion of nanofibers needs to be use with caution. It is noted that the acetone is difficult to vaporize (Liao, Marietta-Tondin et al. 2004) and has been shown to alter the epoxy network formation and reduce the mechanical properties (R.Loos, F.Coelho et al.). Due to this, excess acetone was removed after acetone and carbonised PAN mixture was sonicated.

Continue at the back of thesis

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P216: The following literatures are added in the List of References.

Sutti, A., T. Lin, and X. Wang, *Shear-Enhanced Solution Precipitation: A Simple Process to Produce Short Polymeric Nanofibers*. Nanoscience and Nanotechnology, 2011. 11: p. 8947-8952. R.Loos, M., L.A. F.Coelho, and S. H.Pezzin, *The effect of acetone addition on the properties of epoxy*. Polímeros, 2008. 18: p 76-80

RESPONSE TO COMMENT BY EXAMINER

Comment by Prof. B Fox:

Chapter 3 provides a description of all of the materials and methods utilised for the study, however the TEM section requires further elaboration, particularly in terms of sample preparation which can be complex for this material. Refer to: "High strength and high modulus carbon fibers," Carbon, Volume 93, November 2015, Pages 81-87, ISSN 0008-6223, DOI: 10.1016/j.carbon.2015.05.016 and other recent work published by Satish Kumar for sample preparation information.

Response:

1

TEM was used to examine the morphology of the carbonised PAN, in accordance with previously published literature (Zhou, Lai et al. 2009) where the carbon fibres were dispersed and deposited onto a TEM copper grid. However, apart from surface morphology, TEM characterisation was also used to calculate the crystallite size and spacing, requiring different sample preparation reported by Chae et al (Chae, Newcomb et al. 2015). Briefly, the cross section of the carbon fibres needs to be characterised through curing the sample in epoxy before it was cut and subsequently ion milled in preparation for TEM imaging. In our research, TEM characterisation is a complementary characterisation method to show that the polyacrylonitrile electrospun fibre has been converted into carbon fibre, and we used Raman Spectoscopy and XRD measurement to further support this. The crystallite size was calculated using XRD measurement and TEM micrograph only showed the morphology of the carbonised PAN fibres. Therefore, we believe for morphological assessment and qualitative characterisation, our method of TEM sample preparation was sufficient.

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Marini Sawawi May 2015

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I would like to acknowledge Dr. Tim Williams, Dr Flame Burgmann, Dr Xi-Ya Fang, Ms Ellen Lavoie, Mr. David Vowles, Mr. Renji Pan of Monash Centre for Electron Microscopy (MCEM) for their technical assistance in using scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

Special thanks also to my friends and family, especially my parents who encouraged and support me endlessly. Last but not least, my appreciation goes to my husband and kids (Afrina, Nukman and Alya) who made sacrifices and stood by me through thick and thin. I dedicate this dissertation to them.

Most importantly, I am grateful to Allah the Almighty who made this work possible.

Abstract

The scope of this research is to study the use of ultrasonication, using a probe sonicator to produce short fibre from electrospun webs of four types of polymer poly(styrene) (PS), poly(methyl methacrylate) (PMMA), poly(acrylonitrile)(PAN) and poly(*L*-lactic) acid (PLLA). Scissioning of the usually long, continuous non-woven electrospun web would be useful as a means to produce short discrete fibres in significant amounts. Such materials are useful for numerous applications, including composite reinforcement and biomedical applications such as vessels for the containment and release of drugs.

Optimisation of the electrospinning parameters were carried out to produce electrospun fibres from the four polymers that were beads-free, and whose nanofiber constituents had submicron diameters. It was found by producing and testing non-woven webs that had roughly similar fibre diameters, as well as similar tensile strength and elastic modulus, that the ductility of the electrospun polymer was the key determinant as to whether the web could be ultrasonically scissioned. Thus, ultrasonication is an effective method to scission brittle/submicron electrospun fibre such as PS and PMMA, whilst post-treatments such as UV-Ozone irradiation and heat treatment of the electrospun fibres were required for polymers such as PAN and PLLA. Without such post-treatment, PAN and PLLA were unable to be scissioned, regardless for how long the samples were sonicated. The success of the post-treatments was due to either reductions in ductility reduction or induced flaws on the electrospun fibres, the latter acting as points for the initiation of failure, facilitating the scissioning of these more ductile materials.

The potential mechanisms involved in scissioning were also investigated and discussed, and relate to bubble cavitation and collapse caused by the ultrasonication probe. These mechanism ranged from the effect of the impact of the jet resulting from imploding bubbles leading to erosion and pitting which would create point of weakness for crack initiation, to fibre buckling for long fibres that were oriented parallel to the bubble surface during bubble growth, leading to rotation and buckling of the fibres when the bubble collapsed. The shorter fibres that align normal to the bubble surface experience a difference in velocity for both fibre ends when the bubble implodes. The highest velocity at the end nearest to the bubble wall compared to the farthest end thus leads to tensile failure. The effects of the sonication parameters on the scission process were investigated and it was found that the sonication parameter such as run time, lapsed time, amplitude and solvent types affects the scission efficiency, with the bulk temperature of the solvent and the concentration of dissolved gas in the solvent showing no effect on the short fibre length.

The effects of scissioning electrospun PAN prior to and after carbonisation process were also investigated. It was found that the scissioned-carbonised (asspun web was sonicated prior to carbonisation) showed no significant difference in terms of the surface morphology, carbonaceous quality and electrical conductivity compared with the carbonised-scissioned (the as-spun web was carbonised followed by sonication scissioned). Methods of composite preparation for carbonised PAN short fibre/epoxy were investigated and it was found that the solvent blending method was superior to prepare the composite compared with a high speed mixing technique and no solvent, with some improvement on the flexural strength and modulus observed for the scissioned-carbonised/epoxy compared with the carbonised-scissioned/epoxy composite and the epoxy resin alone.

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Journal Publication

Sawawi, M., T. Y. Wang, D. R. Nisbet and G. P. Simon (2013). "Scission of electrospun polymer fibres by ultrasonication." Journal of Polymer 54(16): 4237-4252

Conference Presentations

Sawawi, M., D. R. Nisbet and G. P. Simon "Scission of Polystyrene Electrospun Fibres using Ultrasonication Method" Poster presentation at World Hybrid Conference, UNIMAS, October 2013

Sawawi, M., D. R. Nisbet and G. P. Simon "Electrospun Polystyrene Short Fibres using Ultrasonication Method " presented at 30th Australasian Polymer Symposium, Tasmania, Australia, February 2012

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Chapter 6

Chapter 1 - Introduction

1.1 Background

Electrospinning has become a common technique for the fabrication of polymeric fibrous webs that have been used for a variety of applications including membrane technologies, sensors and (in particular) for tissue engineering to produce scaffolds that mimic features of the extracellular matrix [1-6]. Electrospinning results in the production of continuous fibres that are deposited on to a collector as a non-woven web. However, there are many applications where short, individual nanofibres would be advantageous compared with a continuous web, but it is intrinsically difficult to retrieve individual electrospun fibres in large quantities. The use of parallel, knifeedge electrode collectors has been one method used to obtain individuallyaligned, separated fibres for the purpose of single fibre testing, however only very limited amounts of fibre can be produced in this way [7, 8].

To date, there has been little work reported on producing individual, short micron-length fibres directly from conventional electrospun webs. The ability to convert an electrospun web into discrete, short fibres of nanometre dimension would be advantageous as it would lead to a methodology to produce significant quantities of short fibres. Such short fibres may be desirable for a number of applications, such as additives for incorporation into polymers and films to enhance properties such as modulus and toughness, whilst maintaining the transparency of the nanocomposite due to the similarity of the refractive index of the polymeric nanofibres and the matrix. Short fibres would also be very useful for biomedical applications, such as vessels for the containment of drugs, or in tissue engineering as injectable fibrous scaffolds such as in anisotropic cavities that result from injuries such as stroke. It would also be beneficial to have short fibres in hydrogel systems, where they can act as tissue scaffolds or as slow drug release vehicles. The anisotropic, high aspect ratio of such fibres means that they could have the effect of structurally reinforcing the hydrogel, in addition to their functional properties. In this case, the mechanical properties of the fibres are important and arise due to the high levels of orientation of polymer molecular chains within the short fibres. Such fibres are also amenable to further chemical functionalisation, which may be useful for dispersion and to provide more "cell-friendly" surface. In this research, the use of ultrasonication as a method to produce short fibres from a non-woven, electrospun web is explored, with the effects of material property and processing parameters on the final short fibres produced being investigated.

There have been a few reports of non-ultrasonic methods to breakdown the non-woven electrospun webs into short fibres (often for composite reinforcement) that have resulted in varying degrees of success. The most common method reported to date for the scission electrospun fibre webs into short fibres involves mechanical methods such as mortar grinding [9, 10], rubber milling [11], cryogenic milling [12], razor blade cutting under liquid nitrogen cooling [13] and cryomicrotoming [14]. Other methods such as UV irradiation in combination with ultrasonication have also been employed [15], but the intention of this method was to produce smaller, controlled fibre bundles, as opposed to the individual fibres sought in this study. A recentlyreported method to produce short fibre uses electrospinning alone where the key to this process is the combination of two poor solvents, which when combined produces a solubility that is near the solubility for the good solvent of the polymer to be electrospun. This polymer-solvent system would allow electrospinning to take place at a low polymer solution concentration and resulted in fibre jet break-up which ultimately leads to short fibres, instead of a continuous web. This method is still in its infancy and so far studies are limited to certain polymer with small quantities of short fibres being produced [16-18].

In this work we demonstrate that we can use ultrasonication directly, under appropriate conditions, to produce short nanofibres from electrospun webs. For this we use an ultrasonic probe apparatus that is already widely-used in most laboratories for applications such as cleaning and mixing with a working frequency of 20 kHz [19]. During sonication, such a probe causes bubbles in the fluid medium to grow and collapse, and in so doing, release energy which can be used to scission the nanofibres. Bubble growth is initiated from cavities with a diameter of 1 μ m and grows to ca. 50 μ m under negative pressure [20]. These bubbles grow in 20 μ s, and can collapse over a time of the order of ns [21].

This method has previously been utilised to facilitate the dispersion of carbon nanotubes in a solvent or mixture [22], where it has also been shown that it can lead to carbon nanotube scission [23]. Most researchers currently use sonication for the mixing of carbon nanotubes (CNTs) in solution, and size reduction is often of secondary interest. The basic mechanism for the scission of carbon nanotubes has not been fully elucidated, although a number of papers have made a series of instructive observations. Recently Hennrich et al. [22] investigated the decrease in length of CNTs and the underlying mechanisms during ultrasonic processing, making clear that the break-up was due to an associated cavitation phenomenon (bubble growth and collapse) within the solvent, which leads to local regions of high strain and shear stress.

To date, there has been little study on the use of sonication as a method to produce small fibres from electrospun polymeric webs. Transverse fragmentation of fibres by firstly chemically-modifying poly(lactide) nanofibres by aminolysis [24, 25], in combination with some sonication has been reported. However in this case, the scission of fibres was due largely to the preceding chemical treatment, and the sonication was used more to disperse the resultant, chemically-cut fibres, rather than being the primary process for fibre scission. One recent study has reported in passing, the direct use of ultrasonication as a means of producing short fibres from electrospun The short fibres produced were subsequently incorporated into a webs. hydrogel for a tissue engineering applications [26] and incorporated to improve interactions between the hydrogel and the cells. However, in this work sonication was used as a means to an end to produce short nanofibres, with any investigation of the control of scission events and a mechanistic understanding being outside the scope of that research.

Here, we have investigated the effect of the ultrasonication on electrospun webs, varying material properties and processing variables, in order to gain a more detailed understanding of how to optimise the resultant short nanofibres and obtain a mechanistic understanding of the process itself. Subsequently, post-treatment of the electrospun fibres produced from polymers that were hard to scission (PLLA and PAN) were investigated to facilitate short fibre production from these materials as well. Finally, the effect of carbonising the short fibre produced from electrospun poly(acrylonitrile) (PAN) webs, as opposed to initial carbonisation prior to sonication, and their subsequent incorporation into epoxy was explored to study the difference between the mechanical properties of final composite.

1.2 Research Hypotheses and Research Aims

The overall aim of this project was to produce short fibres from electrospun fibres using the ultrasonication. Four types of polymers were electrospun and used to investigate the potential of this method for the scission of electrospun fibres. An understanding of the scission process of polymeric nanofibres by sonication was also sought. This was followed by a manipulation of the ultrasonication parameters and processing conditions to allow control over the resultant short nanofibres, such as their length. The effect of carbonising the short electrospun poly(acrylonitrile) (PAN), as opposed to the as-spun web prior to sonication, was also studied, with the short fibres being incorporated as an additive in composite reinforcement. The specific aims of this project thus are:

• To study the effect of ultrasonication on different types of electrospun polymers (i.e poly(styrene), poly(methyl methacrylate), poly(acrylonitrile) and poly(*L*-lactic) acid) and to understand the mechanism by which the scission of electrospun webs occurs via ultrasonication.

• To optimise the ultrasonication method by manipulating the ultrasonication parameters and conducting post-treatment of the as-spun webs to allow strategic manipulation and production of short fibres.

• To produce the short carbonised fibres from PAN and to exploit these for composite reinforcement, in particular to vary the mechanical properties of the resulting composite.

In addition to their application in polymeric nanocomposites, an understanding of the ultrasonication phenomenon could also be useful in other areas, where short nanofibres may be desirable, such as in biomaterials applications, although this will not be explicitly studied as part of this work.

1.3 Layout of thesis

The general layout of the thesis is as follows; a literature review on the electrospinning process, application of electrospun fibres in composite systems, ultrasonication process and the methods used to produce short fibres to date are presented in Chapter 2. The materials, sample preparation and experimental techniques are presented in Chapter 3. Chapters 4 to 6 present the experimental outcomes and discussion of these results.

Chapter 4 investigates optimisation of the electrospinning process for the four types of polymers being researched. This is followed by the initial study of the ability of the ultrasonication process to scission electrospun webs. The results from this chapter are used in Chapter 5 to further explore the ultrasonication process parameters that influence the short fibre final morphology and also to investigate the influence of post-treatment of the electrospun webs and its influence on the subsequent scission process.

Chapter 6 describes the production of carbonised short electrospun PAN and the incorporation of scissioned-carbonised (scissioning of PAN electrospun web followed by carbonisation of the short fibre) and carbonisedscissioned (carbonisation of electrospun PAN web followed by scissioning by ultrasonication). The properties of these fibres alone is presented and discussed. They are also then incorporated into epoxy composite systems, and methods to improve such dispersion such as mixing method and the addition of surface active agents are discussed, with the resultant mechanical properties of the short fibre composites determined.

Chapter 7 presents the general conclusions of thesis, and recommends areas for future research.

Chapter 2 - Literature Review

2.1 Introduction

The electrospinning process has been widely-used as a method to produce nanometre diameter fibres because it is simple and the parameters to control the fibre properties can be readily manipulated. The nanofibres produced are normally formed as fairly dense, random or aligned continuous, non-woven fibre webs. Such nanofibre meshes are suitable for many applications such as in tissue engineering where they can be used to mimic the extracellular matrix (ECM), or in many other disciplines such as filter manufacturing and as the reinforcing phase in composites.

However, according to the literature, research on the method used to produce short fibres from such long, continuous electrospun webs is still in its infancy. Such short fibres, with a nanometre diameter, could be useful in a range of applications. This architecture would have, for example, a great potential application in drug delivery systems where the short electrospun fibres could be loaded with drugs at the point of electrospinning, preferably in enclosed capsules within the fibres such as for inhalation therapy [27]. They could be used as biodegradable scaffolds, able to be injected into the cell to promote survival, growth and/or differentiation [26]. In this chapter, the processes of electrospinning and ultrasonication will be discussed, rather than the wide reaching applicability of short fibre technology. This will be followed by a review of the existing methods that have been used to date to scission the long, continuous fibre web. The last section will cover the application of short fibres in composite reinforcements especially for carbonised PAN, as this represents one of the aims of this thesis.

2.2 Electrospinning

Electrospinning is a method that makes use of electrical charge with polymer solutions to produce fine filaments. The basic concept dates from 1902 [28] and a series of patents were obtained by Formhals commencing in the 1930s [29] to produce polymer threads from various polymers using electrostatic force. This method has subsequently been recognised as a fast and simple process for making continuous, sub-micron to nano-size fibres, when compared with other conventional methods such as drawing, template synthesis, phase separation, and self-assembly. It also has been used to produce various types of fibre materials ranging from natural polymers, synthetic polymers, polymer solutions, polymer melts and biopolymers. One of the attractive aspects of electrospinning is the flexibility of the process. Using this technique the morphology of the fibres can be readily varied by changing the processing conditions, allowing the production of fibres with solid, porous and core-shell morphologies. Solid and porous fibres can be obtained by changing the processing condition such as types of solvents used and humidity, whilst the core-shell morphology is obtained through setting up an inner and outer needle during electrospinning [30-33].

In its most basic form, electrospun webs are produced from a relatively simple process that consists of a pipette to hold a dissolved polymer solution, a high voltage source and a collector. A widely-used schema of various electrospinning set-ups (vertical, horizontal and core-shell) is shown in Figure 2.1.

Briefly, the positive electric field induces charges in the polymer solution, and once this charge build-up exceeds that of the surface tension, a Taylor cone is formed [34]. At this critical voltage, a polymer jet erupts from the cone tip, accelerating through the electric field towards the collector. As the jet travels towards the collector, the solvent evaporates and a solidified polymer fibre is collected. There are a number of parameters that influence the morphology of electrospun nanofibres, some of which include: the concentration of polymer solution, applied voltage, solution feed rate, working distance and ambient parameters [2, 3, 35], and these are summarised in the following section.



Figure 2.1 Schematic drawing showing a) vertical, b) horizontal [3] and c) core-shell electrospinning set up [30].

2.2.1 Parameters influencing the output of the electrospinning

process

The parameters that influence the electrospinning process can be divided into three main categories a) polymer solution properties b) processing parameters and c) environmental effects during spinning. Controlling and varying these parameters will affect the morphology and dimensions of the fibre produced, which can range from circular solid filaments, to flatted ribbons, to porous and beaded structures.

2.2.1.1 **Polymer solution properties**

Polymer solution properties depend on the viscosity, polymer molecular weight, surface tension and conductivity. Solution viscosity is one of the most profound parameter that affects the fibres' diameter. The higher the solution viscosity, the greater the diameter of the fibres produced. However, lowering the viscosity too much will cause beads to form as part of the nanofibres [36]. This is due to insufficient polymer chain entanglements in the solution, leading to jet break-up during electrospinning. Factors that contribute to the solution viscosity are the solution concentration and molecular weight of the polymer. The molecular weight of a polymer represents the average length of the polymer chain and this in turn determines the concentration of entanglements in solution (depending on concentration). The greater the degree of chain entanglement, the higher the solution viscosity will be. Thus, the viscosity of a polymer with higher molecular weight is greater than the same polymer of a lower molecular weight (for the same concentration). The simplest method to increase the solution viscosity is by using a higher concentration of polymer in the solution, this also having a direct effect on the concentration of polymer chain entanglements. For example, beadless electrospun fibres of poly(D,L-lactide) acid can be produced in the range of 20 to 40 wt% polymer concentration [37]. Large beads were generated when the concentration was below 20 wt%, whilst concentrations greater than 40 wt% resulted in clogging of the needle due to the droplet drying out before the fibres formed. The relationship between viscosity and beads production is shown in Figure 2.2, where the numbers of beads are reduced as the viscosity is increased.



Figure 2.2 SEM images showing relationship between viscosity and beads production [2].

A higher solution viscosity (greater polymer concentration in solution) also results in a larger fibre diameter due to a greater resistance of the solution to being stretched arising from the repulsive charges on the droplet surface. During the initial stages of electrospinning, the charged solution needs to overcome its surface tension. Surface tension is the force that leads to a decrease in a surface area per unit mass of the liquid, so as to reduce surface area and thus energy. Therefore, in a low viscosity solution where the concentration of free solvent molecules is greater, the solvent molecules will tend to congregate and adopt spherical shape, whilst a high viscosity solution leads to a better interaction between solvent-polymer molecules so that when the jet erupts, the solvent will spread over the entangled molecules and the tendency of the solvent molecule to come together will be reduced, leading to a beadless fibre. One method to reduce the underlying surface tension is by the addition of surfactant where the hydrophilic and hydrophobic group in the surfactant will interact with the polar and non-polar phase of the solvent. This will reduce the surface tension and improve the fibre morphology (making it more uniform and beadless) [38, 39]. Apart from this, the addition of ions such as salts and cationic surfactants also improve the conductivity of the solution by increasing the amount of charge in the solution, also assisting in fibre stretching during electrospinning, leading to the production of a finer fibre.

2.2.1.2 Electrospinning processing parameters

The processing parameters which are relevant to electrospinning involve the manipulation of the: voltage, working distance, feed rate and types of collector – all of which help determine the morphology, architecture and the properties of the fibrous web. The magnitude of the applied voltage is a key
critical parameter influencing the electrospinning dynamics [2, 3, 40]. Only after the threshold voltage is reached does fibre formation occur, since it is at this point that the electric field causes sufficient accumulation of charge on the droplet to exist and initiate fibre elongation from the Taylor cone. For instance, it has been observed that the increase in applied voltage leads to higher electric fields, that will induce additional stretching of the polymer solution, thereby leading to the formation of thinner fibres [2, 41].

Another important parameter is the distance between the tip and the collector (known as the working distance) that can also be readily manipulated to control fibre diameter and morphology. A minimum distance is required to allow the solvent time to evaporate before reaching the collector. When the working distance is too small, the jet flight time is decreased, thus the solvent has less time to fully evaporate, leading to beaded fibres. Greater distances may also lead to a decrease in the electrostatic field, resulting in less stretching and difficulty maintaining jet continuity, and therefore leading to bead formation [2].

The type of a collector onto which the nanofibres are spun is also able to modify the morphology and physical characteristics of the electrospun web, in particular the resultant fibre orientation. A collector is normally a conductive substrate, electrically grounded to ensure the potential difference between the source and collector is stable. Currently, there are a range of collectors being used, depending on whether random or aligned fibres are required. A flat, static collector would result in an electrospun fibre web where the fibres are randomly distributed, whilst a rotating cylindrical collector would produce a web with the fibre directions broadly aligned in the direction of the tangential surface velocity of the rotating drum. It has been reported that such webs consisting of aligned fibres lead to an improvement in the mechanical properties of the web [42]. The production of aligned fibres has been reported to be able to be produced using a number of experimental techniques such as rotating mandrel, rotating disc collector and parallel electrodes. A rotating mandrel is a simple method in which the fibres become located and aligned on the surface of the rotating cylindrical collector. It was found that the degree of alignment improves with the rotational speed [42], although some nanofibres remain misaligned. Other methods such as a rotating disc collector yield more aligned fibres, but the area of deposition is small and precisely controlling the alignment becomes difficult when the deposited area is thick [43-45]. A summary of these methods and many other useful electrospinning assemblies has been summarised by Teo and Ramakrishna et al [46].

2.2.1.3 Environmental conditions during electrospinning

Another parameter that affects the morphology of the electrospun web involves control of the environmental conditions during spinning such as temperature and humidity [3, 35, 47]. In the presence of humidity, polymers dissolved in volatile solvent produce porous nanofibres [47, 48]. Fast evaporation of the volatile solvent leads to a decrease in temperature at the fibre surface, leading to moisture condensation in a humid environment, that results in pore formation [2, 3].

2.3 Ultrasonication

The term *ultrasound* in general refers to any sound which is of a frequency beyond that to which the human ear can respond i.e. greater than 16 kHz [49]. In the ultrasound methodology, ultrasonic equipment uses a transducer to convert electrical energy into sound (acoustic) energy. This equipment has a frequency of 20 to 100 kHz for low frequency and more than 2 MHz for high frequency ultrasound [49]. Some of the applications of ultrasound in industrial field are shown in Table 2.1 [50].

Field	Application
Biology, Biochemistry	Homogenisation and cell disruption: Power ultrasound is used to rupture cell walls in order to release contents for further studies.
Engineering	Ultrasound has been used to assist drilling, grinding and cutting. It is parti- cularly useful for processing hard brittle materials e. g. glass, ceramics. Other uses of power ultrasound are welding (both plastics and metals) and metal tube drawing.
Dentistry	Cleaning and drilling of teeth, also for curing glass ionomer fillings.
Geography, Geology	Pulse/echo techniques are used in the location of mineral and oil deposits and in depth gauges for seas and oceans. Echo ranging at sea has been used for many years (SONAR).
Industrial	Pigments and solids can be easily dispersed in paint, inks and resins. Engi- neering articles are often cleaned and degreased by immersion in ultrasonic baths. Two less widely used applications are in acoustic filtration and metal casting.
Medicine	Ultrasonic imaging $(2-10 \text{ MHz})$ is used, particularly in obstetrics, for observing the foetus and for guiding subcutaneous surgical implements. In physiotherapy lower frequencies $(20-50 \text{ kHz})$ are used in the treatment of muscle strains, dissolution of blood clots and cancer treatment.

 Table 2.1 Industrial applications of ultrasound [50]

In the case of the application of ultrasonics to liquids i.e ultrasonication, the sound wave is transmitted through the liquid in alternating compression and rarefaction cycles. If the negative pressure during the rarefaction is strong enough to overcome the intermolecular forces binding the liquid, the liquid will be "torn apart", resulting in formation of microbubbles in a process known as cavitation [49, 51-54]. In practice, this occurs at a pressure much less than those required to overcome the tensile strength of the liquid, since there are always dissolved gas and dust particles present which act as nucleating sites [51]. Bubble growths are initiated from cavities with a diameter of 1 µm and grow to ca. 50 µm under negative pressure [20]. Under such sonication conditions, the bubble grows in 20 µs, and can collapse over a time of the order of ns [21]. These bubbles are constantly growing and collapsing during ultrasonication, with the collapsing bubbles producing intense local heating (hot spot) and high pressure regions (in the middle of collapsing bubble) [51, 55]. The magnitude of the pressure and temperature variations in this local region has been reported to reach 5000°C and approximately 1000 atm, respectively [55]. The chemical (as in material synthesis) and mechanical (as in particle size reduction) effect of ultrasonication on the mixture can be divided into 2 main categories homogeneous and heterogeneous liquid-liquid or liquid-solid mixtures. Homogeneous liquid mixtures involve mixing of two or more types of liquid which would result in molecular bond breakage. Figure 2.3 show the subsequent effect of cavitation collapse in the homogeneous liquid phase, where a very high pressure and temperature occurs in the middle of collapsed bubble.



Figure 2.3 Effect of sonication in the homogeneous liquid phase [49].

In contrast, the collapse of a bubble near a solid-liquid interface in heterogeneous systems creates an impact of a jet where the bubble collapsed will be antisymmetrical, driving high-speed jets of liquid into the surface (Figure 2.4), and thus leading to shockwave damage.



Figure 2.4 The effect of a bubble collapsing near a solid surface, leading to an impact of the jet [49].

This jet can reach velocities of hundreds of meters per second, contributing to the impingement, erosion and potentially surface damage and fragmentation of brittle materials [56, 57].

2.3.1 Factors Affecting Cavitation

The use of ultrasonication, such as the reduction in polymer chain length by cleaving or the modification of particles size, is largely caused by the cavitation phenomenon [58]. As such, it is important to understand the factors that affect such cavitation, as these will be used as parameters to assist in designing the appropriate experimental conditions in this research. There are a number of factors which affect cavitation [49, 51]. One of the most important factors is the nature of the solvent, and its physical behaviour. As the intermolecular forces in the liquid must be overcome in order to create bubbles, a liquid with a high density, surface tension and viscosity will have a higher cavitation threshold and higher energy to cause the liquid to cavitate [51]. For example, the theoretical acoustic pressure necessary for water to cavitate is 1500 atm, whilst in practice the cavitation normally occurs below 20 atm [50]. Experimental evidence has shown that gas molecules and particulate in the liquid is the contributing factor to the lower cavitation threshold.

The volatility of the solvent also affects cavitation, with a more volatile solvent leading to less cavitation impact, as vapour from the solvent enters the bubble, and cushions the collapse of the bubble (note: this latter aspect which influences bubble collapse is a key aspect when understanding and controlling the ability of this process to cause the scission of polymer nanofibres).

Ultrasound frequency is another factor that affects the cavitation [59, 60]. Very high frequency ultrasound equipment (MHz range) shows less sonochemical effects due to the reduced time for the bubble to grow and collapse, leading to less shock waves and reduced temperature hot spots and pressure [49, 51]. However, at low frequencies such as at 43 kHz, 153 kHz and 480 kHz, it has been reported that an increase in frequency will increase the cavitation effects [61] due to the number of bubbles formed from cavitation increasing with the reduction in ultrasound wavelength, leading to a lower cavity lifetime.

Ultrasound intensity, which is related to the amount of energy supplied, also has an effect on the cavitation [49, 51] since there is a certain amount of energy needed to surpass the cavitation threshold in order for cavitation to take place. An increase in energy above the threshold will lead to cavitation, and further increases will enhance the cavitation effects. This will lead to an increased bubble size, causing a greater effect during collapse and implosion [61]. Further increases above the optimum level may also lead to a decrease in the sonochemical efficiency of cavitation [51], one of the reasons being that with the increase in energy, the bubble may grow so large during the expansion (rarefaction) cycle, that the time available for collapse is insufficient [49] leading to less impact during bubble collapse and thus a reduced efficiency [62]. This suggests that selection of the energy (power amplitude) is an important variable in these experiments.

Cavitation is also affected by dissolved gases in the solvent. Apart from acting as nucleating sites, dissolved gases also influence the maximum temperature, T_{max} and pressure, P_{max} generated during the collapse of bubbles. This relationship can be seen in the equation below:

$$T_{\max} = T_o [P_m(\gamma - 1)/P]$$
Equation 2.1
$$P_{\max} = P [P_m(\gamma - 1)/P]^{\gamma/(\gamma - 1)}$$
Equation 2.2

where T_o is the temperature of the liquid/solvent, P_m is the pressure in the bubble after collapse, P is the pressure before collapse (usually assumed to the vapour pressure of the liquid and γ is the ratio of specific heats of dissolved gas or vapour. Thus greater sonochemical effects - which implies more cavitation - are observed for a systems saturated with a monatomic gas (such as Argon, Ar), rather than diatomic gases (air, O₂, H₂, N₂) and polyatomic gases (eg CO₂) [49, 51]. However, other factors such as solubility of the gas in the solvent will also influence cavitation. The inclusion of highly soluble gases in a solvent will reduce the cavitation threshold, as the existing bubbles will act as the nucleating sites, and promote cavitation. However, this will also lead to a greater amount of gas entering the bubbles which cushion the collapse, resulting in less sonochemical reactivity [63]. Once again, there are competing effects in this process.

Sonication temperature is another factor affecting the cavitation as it will affect the solvent properties. An increase in temperature will lead to an increase in vapour pressure, hence allowing more vapour to enter the cavitation bubble and reduce the strength of its implosion, as mentioned above [64].

2.3.2 Applications of ultrasonication in liquids

Ultrasonication has been widely used in surface cleaning (sterilisation) [19], individual polymer chain scission (as opposed to electrospun polymer fibres, as in this work) [64-68], dispersal of fillers [69] and modification of powder particle size [70]. Two particular applications of ultrasonication that are most relevant to the research presented here are its use in causing chemical bond scission and carbon nanotube (CNT) scission.

2.3.2.1 Chemical Bond Scission

The application of sonication in chemistry (sonochemistry) has been used extensively to assist chemical reactions but also (and of more relevance to this work) to break primary bonds in polymers. The effect of cavitating bubbles on polymer chains can lead to a reduction in molecular weight, whereby covalent bond breakages occur with no chemical change to the material [55, 65, 68, 71]. For polymers, this reduction in molecular weight has been shown to decrease as the solvent temperature increases (polyacrylamide and poly(ethylene oxide)) [64]. This was attributed to the increase in vapour pressure as the temperature increased, cushioning the implosion of the cavitated bubbles, as has been discussed previously (Vijayalaksmi et al [64]).

2.3.2.2 Scission of Carbon Nanotubes

Since there is limited discussion regarding the use of ultrasonication to producing short polymer nanofibre from electrospun webs, it is important to summarise how the process has been utilised and understood for the scission of carbon nanotubes, and what factors influence its effectiveness in reducing the length of those materials. Carbon nanotubes are materials which have extraordinary electrical and mechanical properties and are widely studied for use in electronic devices [72], as fibre reinforcement [73, 74] and also in biomedical sensors [75]. A major shortcoming of carbon nanotubes for some of these applications is the agglomeration that occurs between them due to their high surface area, and thus extensive van der Waals inter-tube interactions [76], along with their large aspect ratio and high levels of entanglement – all of which can make them difficult to disperse [75]. Therefore much research has been focused on dispersing the nanotubes, whilst trying to avoid damaging their chemical structure [75].

However, sonication of carbon nanotubes in an aqueous solution alone would generally not be effective for the scission of nanotubes because they are highly hydrophobic and the high concentration of van der Waals forces along the tubes surface leads to agglomeration and difficulty in dispersion [77]. For ease of dispersion, debundling and scission of the single-walled carbon nanotubes (SWNTs), sonication is often used in combination with other treatments such as acid treatment [75, 77, 78] or in combination with surfactants [77-79]. An appropriately acidic mixture (such as sulfuric and nitric acid) will lead to the oxidation of the nanotube surface [75, 80]. This oxidation will induce surface flaws and increase the likelihood of shortening the carbon nanotubes at these defects [75] if put under stress such as by sonication. The addition of surfactants in the sonication solvent has been used to improve the wetting, adhesion characteristic and dispersion stability of carbon nanotubes [81]. It has been observed that surfactants such as sodium dodecylbenzene sulfonate (NaDDBS) can be used to encourage the dispersion of the carbon nanotube due to the interactions between the benzene ring and the carbon nanotube surface that stabilises the tubes in solution [79]. This promotes dispersion and reduces tube agglomeration, contributing to effective scissioning during such sonication. Yudasaka et al [82] used a monochlorobenzene (MCB) solution of polymethylmethacrylate (PMMA) with SWNTs to better disperse them before sonication and scission. This allowed the PMMA to "wrap" the SWNT, and it was found after sonication that the SWNT remained 'wrapped' by the polymer. After the subsequent removal of the polymer by combustion in oxygen at 350°C, the neat, shortened carbon nanotubes remained.

It has also been reported that the scission and debundling of carbon nanotubes can be facilitated using a mixture of ultrasonication and ozone gas (O_3) treatment [83, 84]. It was found that this produced a similar effect to that of pre-acid treating the carbon nanotubes, with the ozone gas oxidising the nanotube surface. This study demonstrated that sonication in deionised water alone would be ineffective for both dispersion and shorten the nanotubes, since the shortened nanotubes would reagglomerate after sonication ceased. However, with the combination acid/ozone treatment, the nanotubes were stable after 60 days with the reduction of size down to 150 nm [84]. The mechanism of scission largely depends on the position of the nanotubes relative to the bubble during the event of bubble implosion, and is also dependent on how it approaches (or is drawn towards) the imploding bubble. If the long axis of the nanotube aligns normal to the bubble surface, this would lead to a high frictional force between the fibre and solvent, which causes a high tensile force at the nanotube centre [22, 85]. The schematic of the nanotube position normal to the imploding bubble leads to a high velocity profile near the surface, and the lowest velocity profile at the farthest end is shown in Figure 2.5.



Figure 2.5 Schematic representation of velocity profile near imploding bubble and the resulting relative liquid velocity near a stretched nanotube [22].

However, nanotubes that become aligned tangential to the bubble surface receive an axial compression deformation that results in the buckling and fracture of the nanotube occur due to atom ejection [86, 87].

Recent modelling work by Pagani et al [87] suggests that the mode which dominates (tangential or radial) depends on the size of the nanotube. Whilst the growth of the bubble causes tangential alignment of the nanotubes, shorter nanotubes rotate radially and are drawn towards the nanotube, with subsequent tensile stretching and failure. Longer nanotubes do not rotate in such a fashion, but rather the opposing torques at either end cause bending and buckling (which may also lead to failure and/or scissioning), as shown in Figure 2.6.



Figure 2.6 Schematic of the forces and torques near collapsing bubble, leading to CNT buckling [87].

The mode of deformation and the ultimate molecular failure mechanisms invoked are also often related to the precise chemical structure of the materials, such as defects in carbon nanotubes or the carbon-framework.

Other researchers have proposed alternate mechanisms to explain nanotube scission, such as bubble implosion leading to high temperatures that can cause failure on the nanotube surface [75], although others refute such claims and state that such extreme thermal events are unlikely to occur [86, 88]. It has also been proposed that bubble collapse would lead to microjets that impinge on the surface leading to their ultimate failure [55, 89, 90], which is the mechanism by which ultrasonication is used to clean surfaces contaminated by organics, such as soiled silicon wafers. It is likely, therefore, that any scissioning of polymer nanofibres that occurs is a combination of these factors, depending on the material and the processing conditions.

2.3.2.3 Mathematical modelling of Carbon Nanotube Scission

Mathematical modelling of the tensional and buckling mechanisms that have been reported, in relation to the above discussion about CNT scission, is presented below. Initial models relating to the tensile failure mechanism in CNTs found that the CNTs length has a power law relationship with ultrasonication time, where $L \sim t^{-m}$ with various value of power law exponent, m such as $m\sim0.5$ [22] and $m\sim0.22$ [85]. The disagreement between the experimental result and the mathematical model itself caused Pagani et al to propose the recent model that covers both tensile and buckling mechanism through their simulation works [87].

When the nanotube aligns normal to the bubble surface during implosion, the nanotube end that is nearest to the bubble surface will experience the highest velocity compared to the farthest end, creating high frictional force between the solvent molecule and CNT, with the highest force in the middle of CNTs length (as in Figure 2.5). The failure of the CNT (in the middle) will only occur if the tensile force in the stretched segment is greater than the force required to break the tubes. To calculate the maximum force that is experienced by the mid-section of CNTs, the simplification of the drag force, F equation acting on a circular cylinder of length, L moving as a rigid body parallel to its long axis in a fluid for a large aspect ratio body is given by

$$F = 2\pi\mu LV$$
 Equation 2.3
where V and μ is the relative velocity and fluid viscosity respectively. The
relative velocity, V, as a function of distance, x and strain rate, $\dot{\epsilon}$ is

$$V(x) = \dot{\epsilon x}$$
 Equation 2.4

The force per unit length (f(x)) of CNT given by[22],

$$f(x) = 2\pi\mu\dot{\epsilon}x$$
 Equation 2.5

The net force at the nanotube center, F_M is obtain by integrating the absolute value of f(x) from -L/2 to +L/2,

$$F_M = \frac{1}{2}\pi\mu\dot{\epsilon}L^2$$
 Equation 2.6

The force required for the tube to break-up is

$$F_c = \sigma_{break} A$$
 Equation 2.7

where $\sigma_{break} = \sigma_{UTS}$ (ultimate tensile strength). The CNT break-up occurs when F_M exceeds F_c . Equation 2.7 demonstrates that the tensile strength of the CNT will determine the ability of it to be scissioned. From the calculation by [22, 87], it was estimated that for CNTs, the scissioning process will cease when *L* is less than 120 nm, since at this point $F_M \ge F_c$.

One of the alternative deformation mechanisms occurs when the CNT are oriented parallel to the bubble surface during bubble growth, and the bubble collapse leads to rotation and buckling of nanotube. This then causes failure when the radius or curvature is sufficiently small [87], which has also been observed from experimentation [91]. The critical compressive load for buckling, F_b is derived from the Euler's equation by modelling the nanotube as a stiff, slender and inextensible beam [87].

$$F_b = \frac{\pi^2 E I_M}{L^2}$$
 Equation 2.8

where I_M is the moment of inertia and E is Young modulus. Break-up of the CNT occurs when the minimum radius of curvature, ξ_c is less than the critical value where

$$\xi_c < \xi_{c,crit} = \frac{ED}{2\sigma_{break}}$$
 Equation 2.9

with *D* is the CNT's diameter.

The tensile and buckling mechanism modelling demonstrates that the mechanical properties of the material are the key factor for successful scissioning, as indicated by Equation 2.8 and 2.9.

It is important to note that this modelling is applicable for CNT, which are known to be quite brittle. In this research, we will try to adopt these two modelling mechanisms as a starting point to propose the scissioning mechanism of our electrospun polymer nanofibres.

2.4 Fabricating short electrospun fibres

A few methods have been previously reported to scission the electrospun fibre webs, although even for these methods the amount of detailed work is minimal.

2.4.1 Ultrasonication

Brief research on the scissioning of the electrospun web using ultrasonication was discussed by Hsieh et al [26]. In their work, the electrospun fibres of genipin crosslinked collagen and poly(ε -caprolactone-*co*-D,L-lactide) (P(CL:DLLA) fibres were fragmented into smaller segments (short fibres) using a tip sonicator with the frequency of 20 kHz at 25 % amplitude, for a total time of 60 s. The electrospun fibres were fragmented to allow them to be injected through a 30 gauge needle for an *in vitro* cell study, where the short electrospun fibres were used as substrates for cell adhesion. However, details on the short fibre results such as its final morphology and the effect of the sonication condition on the fibres were not presented.

2.4.2 Direct electrospinning

A recent method reports using electrospinning alone to produce short fibres (instead of non-woven web) without further post processes such as cutting [16-18]. In this method, two poor solvents, with the solubility parameter of this two solvent mixture close to the solubility parameter of a good solvent for the particular polymer were selected to be the solvent in the polymer solution. It was found that varying the polymer concentration in solvent systems would produce the fibre morphology that was transformed from a beaded morphology to short fibres, and subsequently to continuous fibres. The poor solvent mixture has a low surface tension and affects the polymer-solvent interaction by reducing the tensile strength of the polymer solution. It was proposed by Fathona and Yabuki [17] that the mechanism for the fibre break-up was due to the repulsive force, F_R from the surface charges and longitudinal force, F from the applied voltage that exceed the tensile strength, F_t of the polymer solution jet, leading to jet break-up, as shown in the schematic in Figure 2.7.



Figure 2.7 Diagram for the force of the polymer solution jet: a) a straight pass after ejection; b) at the breaking point [17].

This mechanism leads to thinning of the fibres' edges and finally causes break-up of the fibres into short fibres. It is worth noting that in method the resultant short fibre length depended on the location of the fibre on the collector. For instance, it was found that the extremely short fibres were found at the corner of the collector, which also reflected the non-uniform, short fibre length obtained across the collector [18].

This method of producing short fibres is still very new and to date only limited types of polymers such as cellulose acetate [16] and polymethylsilsesquioxane [18] have successfully been electrospun to produce short fibres. Further research is necessary in relation to other polymer systems, with control of the length and quantity of the resulting short fibre produced still needing improvement.

2.4.3 Mechanical cutting

The most common method for the scission of electrospun fibres that has been reported involves the use of a mechanical process such as using mortar grinding [9, 10] which was found most effective for brittle electrospun webs, such as carbonised polyacrylonitrile [9]. Ball milling [92], rubber milling [11] and cryogenic milling [12] have all been shown to be better options for the scission of electrospun webs when compared to manually grinding by mortar, where the cycle and rate of the impactor can be accurately controlled. However, it is difficult to make comparisons between each of the techniques, as the characteristic of the resultant short fibres has not been clearly reported. Another mechanical method reported has been razor blade cutting under liquid nitrogen [13] to produce short magnetic composite fibres from a mixture of a methyl methacrylate-vinyl acetate copolymer combined with superparamagnetic cobalt nanoparticles, yielding fibres of approximately 50 to 100 µm length. Thieme et al [27] reported the use of a motor-driven blade to cut solidified electrospun fibre and ethanol mixtures in liquid nitrogen. The fibres were separated from the cutting medium by centrifugation, allowing fibres of length 5-15 µm to be produced.

Another method to create discrete fibres that has been reported involved 1 μ m step-sliced cryomicrotoming to produce short nylon

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electrospun fibres, although this involved many tedious, repeated steps [14]. This method was developed by the researchers in response to their difficulty in scissioning nylon electrospun fibres using a 3 mm microtip sonicator for 30 min due to a lack of sufficient energy to cause scission. This led the researchers to using cryomicrotoming to scission the fibres, and subsequently sonication to disperse the fibres. These processes were repeated three times until short fibres of about $4.0 \pm 3.0 \,\mu\text{m}$ were obtained.

2.4.4 Ultraviolet(UV) degradation

Another method to cut the electrospun fibre webs involved using UV light. In this method, the UV light was shined through masks with welldefined slit sizes and inter-slit distances which were laid on top of the web to cut poly(butadiene) electrospun fibres [15]. The UV light was used to cause photocrosslinking reactions in the presence of a photoinitiator (PI) which was added during electrospinning (as well as a crosslinking agent). The fibres were covered with UV masks, and the exposed fibres crosslinked under UV radiation which subsequently became insoluble. The non-crosslinked material component was removed by immersion of the fibres into the solvent. The short fibre length was controlled by the width of the slits of the UV mask. Although this was able to scission the fibres, the aim was to produce smaller, controlled fibre bundles, as opposed to the individual fibres we seek to produce in this work.

2.4.5 Aminolysis

Other methods such as aminolysis [24, 25] in combination with sonication have been used to cut polylactic acid (PLA) electrospun fibre, although the microtip sonication employed here was for the dispersal of the chopped fibres and not for the direct scissioning of them. In this process, the smaller pieces of electrospun fibre webs were immersed in distilled 1,6-hexanediamine and ethylene diamine at 37° C. A gentle shear stress was exerted using an orbital shaker to assist the fragmentation. After reaction, the resulting nanocylinders were lyophilized (freezed-dried) by a freeze dryer. This method has successfully produced short PLA fibre with the average length down to ca 5 μ m. However, it was found that due to polymer degradation from UV light, the molecular weight was also reduced significantly by about 60 %, even only after 1 hr of aminolysis treatment.

2.4.6 Shear-enhanced solution precipitation

This is a one step method to produce short Poly(ethylene-co-acrylic acid) (PEAA) polymer fibres which was prepared by dissolving the PEAA in ammonia [93]. The solution was injected into the non-solvent i.e ethanol, butanol and isopropanol as the dispersing medium whilst being stirred using a high speed mixer. The processing parameter such as the dispersing medium (non-solvent) and the polymer solution concentration affect the formation of the nanofibres.

Note that, from these results it was observed that the distribution of the fibres' diameter was large (i.e. 0.1 μ m to 1 μ m) with the average length of 20-40 μ m for a polymer concentration of 12.6 wt/vol%, and 0.1 μ m to 0.3 μ m with average length of 10-20 µm for 3 wt/vol%. It was also shown that at higher shear mixer speeds, shorter fibres were produced (average 5-10 µm). The author discussed that the production of short nanofibres was due to the precipitation of the polymer when it was injected into the non-solvent and shear flow in the systems that resulted in elongation of the precipitates. The morphology of the precipitate produced i.e short fibres/particulates depends on the kinetics of the deformation of the polymer and kinetics of its solidification process. This suggests that the morphology obtained in this study was only applicable for PEAA polymer with further in depth research for other polymers still required. Meanwhile, the ultrasonication method that we proposed here was more general, as we have shown that it can be applied to any polymer fibres, thus reducing the time required for researching the suitable process. In addition, we also can maintain the fibre diameter (with small variation in the fibre diameter and the fibre length as oppose to this study).

2.5 Carbonisation of Polyacrylonitrile (PAN) electrospun fibres

Carbonisation of PAN was undertaken in the research described in this thesis, and thus this process is reviewed here. PAN is one of the most widelyused polymeric precursors for carbon fibre which produced a higher carbon yield compared to other precursor such as cellulosic, vinylidene chloride, pitch and phenolic resins [94]. It also produces carbon fibre with high mechanical strength and modulus with excellent electrical and thermal conductivities [95, 96]. In general there are 3 stages involved in the production of PAN based carbon fibres which are: stabilisation, carbonisation and graphitisation – all shown in Figure 2.8.



Figure 2.8 PAN fibre precursor in carbon fibre production [97].

The stabilisation step is considered to be the main step that determines the quality of the carbon fibre produced, in terms of its final properties [97, 98]. This step involves heating the fibre in oxygen environment at the temperature

of 180° C - 300° C. In this step, the chemical structure of the fibre will be changed due to cyclisation, dehydrogenation and oxidation, as shown in Figure 2.9.



Figure 2.9 Structural changes during stabilisation steps of PAN carbonisation [97].

During cyclisation, the linear nitrile group $C \equiv N$ bonds convert into double bonds C = N forming a ladder structure. Dehydrogenation requires oxygen and involves the elimination of water. Oxygen that reacts with the polymer back bone during oxidation provides a greater stability of the ladder structure, which further enables high temperature heat treatments to be undertaken. The black appearance of stabilized PAN has been attributed to the presence of this polymeric ladder structure as shown in Figure 2.10 [97].



Figure 2.10 Ladder structure of PAN [97].

Further heat treatment of the fibre from 800°C to 3000°C in an inert atmosphere is known as the carbonisation step, where the aromatic growth and polymerization occurs. Low heating rates of 2°C/min to 5°C/min is used to avoid large amount of heat being released, resulting in melting. It was found that low modulus carbon was obtained for a carbonisation temperature of 1000°C, whilst heating to 1500°C produced an intermediate modulus carbon [97]. Nitrogen gas or argon gas is normally used to provide inert environment during these heat treatments. Argon gas was found to improve the strength of carbon due to a higher viscosity and density of the gas, as compared to nitrogen [94]. A higher temperature carbonisation from 1600°C to 3000°C is referred as graphitisation, and is normally used to produce commercial carbon fibre from PAN precursor [94]. This result in a higher modulus carbon, with about 99% of PAN converted into carbon [97].

2.6 Electrospun Fibre Applications in Composites

Whilst electrospun fibres have been used in many functional applications such as tissue engineering, wound healing, filter masks and drug delivery, their mechanical properties can also be exploited when used as composite reinforcement, due to the nano-dimensions of the fibres themselves. Matrix-fibre reinforcement is a well-established method for improving the properties of materials [74]. The introduction of nanofibres within a matrix has the potential to lead to new and potentially improved properties, compared to the conventional (micrometer-sized) fibres due to their large interfacial area, enabling the load to be transferred to the fibre across the filler-matrix interface more efficiently. Although electrospinning has grown rapidly in terms of the amount of research reported, surprisingly few studies to date have reported the application of electrospun fibres in composite reinforcement [11, 42, 99, 100].

In terms of producing short fibres from the electrospun webs to be incorporated in a polymer matrix, early work by Kim and Reneker group involved ball milling of the web to produce short fibres prior to blending with the styrene-butadiene rubber [11], and the results showed that the Young's Modulus, tensile strength and tear strength increased by ca 900 %, 30 % and 90 %, respectively. A recent paper produced short electrospun polyimide (PI) nanofibre with a length of 50 to 500 µm using a motor driven blade in a cooled environment [101]. The electrospun PI web was cooled in the liquid nitrogen prior cutting process. The resultant short fibres were then dispersed in polyamic acid(PAA) which had been diluted with dimethylformamide The mixture was casted into a film and dried to produce PI (DMF). composite. The mechanical testing conducted showed the improvement of 53 % and 87 % of tensile strength and modulus, respectively, compared to the PI neat resin [101]. Similar findings were obtained by the same researchers who prepared short electrospun nylon-6/thermoplastic polyurethane (TPU) composites where a reinforcement concentration of 3.5 wt% short fibre resulted in an enhancement of 185 % modulus and high transparency of more than 85 % in the visible light range [102].

Other studies have attempted to impregnate the as-spun electrospun webs with a crosslinking resin, where the web as a whole acts as the reinforcement [99, 100, 103-106]. It was found that such a type of reinforcement also has improved the mechanical properties of the composite substantially. For example, electrospun nylon 6/epoxy composite had an increased modulus of some 36 times [99] and an impregnation of nontransparent electrospun cellulose nanofibre into poly(vinyl) alcohol produced a composite film with a high visible light transmittance as much as 75 %, and increased the mechanical strength by 50 % and Young's Modulus by more than 600 %.

Research on the application of electrospun fibres into dental composites also showed that the nanofibres may be suitable to replace the traditional reinforcement material such as short glass fibres, silica or glass particles [107]. In this research, the non-woven electrospun web from coreshell electrospinning of polyacrylonitrile (PAN) and polymethylmethacrylate (PMMA) were laminated into a 2,2-bis-[4-(methacryloxypropoxy)-phenyl]-propane (Bis-GMA) dental resin, combined with camphorquinone photo-initiator via a layer-by-layer arrangement before being photo-cured. It was found that the reinforcement could provide an increase of 65 % in toughness of the composite, compared to the neat resin.

Another report of an interesting attempt to reinforce a matrix using electrospun nanofibres involved core-shell electrospinning [108]. In this

study, the PMMA and PA-6 (Nylon 6) was used to produce shell (PMMA) and core (PA-6) electrospun nanofibres. Heat treatment of the core-shell electrospun fibres at specific temperature and pressure resulted in melting of the outer PMMA shell, with PA-6 nanofibres remaining and reinforcing the PMMA matrix. The result showed that at the optimum PA-6 content (2.5 %), the tensile strength and modulus of the transparent composite was increased by 20 % and 32 %, respectively, with less than 10 % reduction in transmittance [108].

Of particular interest has been the use of electrospun polyacrylonitrile (PAN) webs as a precursor for developing nanosized carbon fibres for use as reinforcement in composites [109-113]. The heat treatment which involves both stabilisation and carbonisation, was able to successfully convert PAN precursor nanofibres into carbon nanofibres that possessed not only mechanical strength, but also electrical and thermal conductivity. Studies have shown that increasing the carbonisation temperature (from 1000°C to 2200°C) lead to higher electrical conductivities, tensile strength and Young's Modulus of carbon nanofibre bundle [109, 113]. The reinforcement of carbon fibre fillers resulted in a conductive polymer that can be used in various applications such as sensors [114] and protective coatings [114]. A study by Aussawathein [112] showed that the volume resistivity of the epoxy reinforced non-woven carbon nanofibre (carbonised PAN) was 1.05 Ω .cm, compared to $10^{10.5} \Omega$.cm of the neat resin, a significant improvement in the electrical conductivity level of the composite.

In this thesis, the possibility of using sonication to produce short PAN nanofibres, the scission of which has been conducted either before or after carbonisation, was investigated.

Chapter 3 - Materials and Experimental method

3.1 Introduction

In this chapter, the materials and experimental methods that are presented in this thesis will be discussed. The range of materials used, which include the polymers, solvents and additives (such as surfactants) used in the electrospinning and ultrasonication process, will be detailed. The method to produce the electrospun fibres, as well as the ultrasonication method to scission them into short fibres is presented. Since some of the fibres are carbonised to produce graphitised, conducting materials, this methodology is also outlined. The thermosetting epoxy system into which the scissioned fibres are incorporated is discussed, as well as the different methods to incorporate the nanofibres.

3.2 Materials

Four types of polymer materials were electrospun to produce nonwoven electrospun webs, namely: polystyrene (PS), poly(methyl methacrylate) (PMMA), poly *L*-lactic acid (PLLA) and poly(acrylonitrile) (PAN). The polymers were chosen because of their difference in terms of their structure, mechanical properties and potential applications. For example, PS and PMMA are both relatively brittle, amorphous thermoplastics with glass transitions of approximately 100°C. PLLA is a semi-crystalline, polyesterbased thermoplastic and is becoming widely-used as a renewable material (biodegradable), as well as being important in biomedical applications. PAN is also amorphous, and is a precursor material from which carbon fibres can be produced, and this forms a significant part of our research work. Carbon fibres are often used as a reinforcing component of a composite, leading to an increased in mechanical properties, as well as electrical conductivity, as detailed in Chapter 2.

3.2.1 Polystyrene (PS)

Polystyrene is a vinyl polymer and produced from styrene monomer by free radical polymerisation. It possesses a long hydrocarbon backbone with a benzene ring linked to every other carbon unit, as shown in Figure 3.1. Polystyrene is clear and hard and normally used in packaging, laboratory ware, and electronics. The excellent physical and processing properties make polystyrene suitable for a range of applications.



Figure 3.1 Repeating unit of polystyrene.

The polystyrene used in this work has an average molecular weight (M_w) of 230 000 and was supplied by Sigma Aldrich, Australia.

3.2.2 Poly(methyl methacrylate) PMMA

Poly(methyl methacrylate) is a transparent, thermoplastic vinyl polymer, and is often used as an alternative to glass. Some of the advantages of PMMA are good mechanical strength, weather resistance and good optical properties such as clarity and transparency. It is a rigid and brittle amorphous polymer with T_g of about 100°C. Figure 3.2 shows the repeat unit of PMMA.



Figure 3.2 PMMA repeat structure.

PMMA was obtained in white powder form from Sigma Aldrich, Australia. Different average molecular weight materials were used including: 107 000 (lowest Mw, PMMA1), 186 000 (intermediate Mw, PMMA2) and 486 000 (highest Mw, PMMA3).

3.2.3 Poly(acrylonitrile) (PAN)

Poly(acrylonitrile) is generally a copolymer with acrylonitrile as the main component. It is a thermoplastic, semicrystalline polymer and is widelyused in applications such as filter membrane and fibres for textiles. PAN is one of the chemical precursors to produce carbon fibres which are widely-used in civil and aircraft structures. In this project, PAN with an average molecular weight $M_w = 150,000$ was purchased from Sigma Aldrich, Australia.

Figure 3.3 Poly(acrylonitrile) chemical structure.

3.2.4 Poly (*L*-lactic) Acid (PLLA)

PLLA is a thermoplastic, semi crystalline polymer. It has become widely-used recently due to its biocompatibility and biodegradability [115]. Lactide monomer can be derived from agricultural sources such as corn and potato starch, making it relatively low in cost. It can exist as two enantiomers, L-lactic and D-lactic acid and Figure 3.4 shows the L-lactic acid monomer structure where the L isomer rotates the plane of polarized light clockwise, whilst the D isomer rotates it counterclockwise. For PLLA, the L-Lactic monomer is polymerised to form PLLA.



Figure 3.4 Polylactic acid (PLA) monomer chemical structure with *L*-Lactic acid as a monomer for PLLA.

PLLA has a low degree of crystallinity value, in the range of 0-37 % [115]. In this project, we are using poly(L-lactide) acid with inherent viscosity of 0.9-1.2 dL/g which was obtained from Lactel, USA. It is in the form of pellets which are a brownish, translucent colour.

3.2.5 Epoxy Resin

Epoxy resins are one of the most commonly-used thermosetting polymer systems for composite application due to their good stiffness, strength, dimensional stability, excellent chemical and wear resistance, low shrinkage during cure and good mechanical properties. In this study, we are using a commercially-available Dalchem 521 obtained from Dalchem Pty Ltd, Australia. It is a low viscosity, room temperature-cured two phase epoxy system consisting of Part A (Diglycidylether of Bisphenol-A, DGEBA) and Part B: Hardener (Cycloaliphatic amines).

3.2.6 Surfactants

In the electrospinning process (described below) dodecyl trimethyl ammonium bromide (DTAB) is used as a surfactant for PS, PLLA and PMMA electrospinning, in order to improve the spinnability of the polymer solution by reducing the surface tension and increase its conductivity [116]. The polymer solutions were prepared using DMF or DMT (for PMMA electrospun solvent), a mixture of chloroform and acetone (for PLLA electrospun solvent) and chloroform with DMF (for PS electrospun solvent). The addition of surfactant is able to assist in the improvement of the morphology of electrospun fibres by the eliminating of beads and reducing nanofiber diameter [116-118]. It is a cationic surfactant with chemical formula of CH₃(CH₂)₁₁N(CH₃)₃Br and an average molecular weight of 308.34 g/mol and is supplied by Sigma Aldrich, Australia

In addition, surfactants were also incorporated into composites made with scissioned fibres and epoxy resin. For example, it was found that carbonised PAN fibres required the addition of surfactants to aid their wetting and dispersal into epoxy resin matrices. For this purpose, a commerciallyavailable surfactant, BYK9076 (BYK Inc, US) which is an alkylammonium salt (a cationic surfactant) was used as a dispersant of carbon nanofibres in composite systems [119-122]. Further details on this surfactant such as its chemical structure are not available.

In general, a cationic surfactant has a permanently charged (positive) 'head' group. In carbon fibre composite applications, the cationic surfactant interacts with carbon fibres via its hydrophobic segment (tail), whilst the ionic, hydrophilic segment associates with the epoxy moiety via hydrogen bonding. The surfactant thus acts as a coupling agent that introduces steric, repulsive forces between carbon fibres and overcomes the attractive van der Waals forces between the carbon surfaces of the different particles. The inclusion of this additive is thus intended to improve the interfacial adhesion between fibre-matrix interface, allowing improved loading transfer between matrix and nanoparticle, and thus improved properties such as strength.

3.2.7 Solvent

The types of solvents chosen in this work were based on those which had been previously reported to work well, for dissolving the various polymers, as described in the literature. They were chloroform, dimethylformamide (DMF), dichloromethane (DMT) and acetone, and all were purchased from Merck Pty Ltd, Australia. For ultrasonication processing, the media used were deionised water obtained from a Direct-Q3 water purification system, Millipore and ethanol (96% grade) from Merck Pty Ltd.
3.3 Sample preparation method

3.3.1 Electrospun polymer solution

Although the four polymeric materials electrospun as part of this work, have been previously published by others [2, 109, 123-125], differences in the raw materials used and processing parameters would lead to different nanofibre morphologies to those previously reported, as well as their ultimate properties. Thus, before scissioning electrospun fibre webs, much time was spent to optimise the process, in particular to control the diameter and morphology of the nanofibres produced. The optimisation was required to produce fibres with diameters within the submicron range, bead-free morphologies with uniform dimension (less standard deviation between average fibre diameters). The parameters which could be varied include: changing the solvent (including mixtures of them), polymer concentration and processing parameters.

The PLLA electrospun webs were prepared using chloroform, chloroform with 1 mM DTAB and chloroform with acetone (3:1 ratio) in 1 mM DTAB. For chloroform-DTAB mixtures, 308.5 mg DTAB was added to 10 mL chloroform to obtain a 0.1 M stock solution. The solution was diluted to 1 mM by adding 100 μ L of the stock solution into 9.9 mL of as received chloroform. 0.65 g of PLLA was added into 10 mL of chloroform with 1 mM DTAB solvent mixtures to obtain 6.5 wt/v% polymer solutions. The PLLA-solvent mixture was dissolved overnight using a magnetic stirrer. The solution

was then placed in a 10 mL syringe with a gauged needle, using the parameters given in Table 3.1. The electrospinning process was conducted using an electrospinner built in the laboratory which used a high voltage supply from Gamma High Voltage Research (USA), whilst the syringe pump is from Razel Scientific Instruments, Inc. (USA). The fibres were collected onto a flat metallic collector covered by aluminium (Al) foil. After collection, the non-woven web was stored in a desiccator under vacuum prior to further use. This procedure was repeated for a range of concentrations, until beadless fibres with a submicron range diameter were obtained.

Using a similar protocol, nanofibers of the other polymers such as PMMA, PAN and PS were also prepared, using the conditions shown in Table 3.1. However, there was a slight difference in the preparation of PS, where some of the samples were collected on a rotating mandrel to produce an aligned orientation of the fibres within the electrospun web, so that effect of fibre orientation on the ultrasonication scission process could be investigated.

Table 3.1	Electros	pinning	parameters
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	Solvent system	Concentration (%)(w/v)	Feed rate (ml/hr)	Voltage	Needle size	Working	Mandrel speed
Material				(+kV)	(G)	Distance	(m/s)
						(cm)	
PLLA	chloroform	6.5	2.4	20	18	15	N/A
PLLA	chloroform	8	2.4	20	18	15	N/A
PLLA	chloroform (1mM DTAB)	8	2.4	20	18	15	N/A
PLLA	chloroform (1mM DTAB)	12	2.4	20	18	15	N/A
PLLA	chloroform (1mM DTAB)	13.7	1.6	20	18	15	N/A
PLLA	chloroform (1mM DTAB)	15.3	1.6	20	18	15	N/A
PLLA	chloroform+acetone (3:1)(with 1mM DTAB)	13	1.2	20	18	16	N/A
PLLA	chloroform+acetone (3:1)(with 1mM DTAB)	13.7	1.2	20	18	16	N/A
PLLA	chloroform+acetone (3:1)(with 1mM DTAB)	13.7	1.2	15	18	16	N/A
PLLA	chloroform+acetone (3:1)(with 1mM DTAB)	13.7	1.2	10	18	16	N/A
PLLA	chloroform+acetone (3:1)(with 1mM DTAB)	15	1.2	15	18	16	N/A

PLLA	chloroform+acetone (3:1)(with 1mM DTAB)	16	1.2	25	18	16	N/A
PMMA1	DMT	6	2.4	20	23	10	N/A
(Mw=107000)							
PMMA2	DMT	5	2.4	20	23	10	N/A
(Mw=186000)							
PMMA3	DMT	2	2.4	20	23	10	N/A
(Mw=486000)							
PMMA3	DMT(with 1mM DTAB)	8	2.4	20	18	15	N/A
PMMA3	DMT (with 1mM DTAB)	10	2.4	20	18	15	N/A
PMMA3	DMF (1mM DTAB)	5.7	1.6	20	18	15	N/A
PMMA3	DMF (1mM DTAB)	6.5	1.6	20	18	15	N/A
PMMA3	DMF (1mM DTAB)	7	1.6	25	18	15	N/A
PAN	DMF	10	1.6	20	18	16	N/A

PS	Chloroform + DMF (1 mM DTAB)	12	1.6	15	18	6	N/A
PS	Chloroform + DMF (1 mM DTAB)	8	1.6	15	18	6	6.3
PS	Chloroform + DMF (1 mM DTAB)	12	1.6	20	18	6	6.3
PS	Chloroform + DMF (1 mM DTAB)	16	1.6	20	18	6	6.3

3.3.2 Post-treatment of electrospun fibres prior ultrasonication

3.3.2.1 UV-Ozone treatment of PLLA and PAN electrospun web

As part of the investigation on the effect of surface modification on the nanofibres which were difficult to scission by ultrasonication (PLLA and PAN), the effect of surface treatment of these materials, prior to scissioning, was investigated. This involved their exposure to a combination of an ultraviolet and ozone environment. In order to achieve this, the fibre web was cut to an approximate size of 5 cm², placed in the UV Ozone ProcleanerTM UV PC 220 (USA) and irradiated for 12 min with an intensity of 14.75 mW/cm², at a distance of approximately 1 cm. In this instrument, a high intensity mercury vapour lamp generates 254 nm light which cleaves the bonds of organic molecules on the surface. A strong emission at 185 nm converts atmospheric oxygen into reactive ozone, which attacks and oxidises the organic polymer.

3.3.2.2 Thermal ageing treatment

Physical ageing of polymer involves densification and is a reversible way in which to vary properties without chemical or physical modification of the structure [126]. During isothermal ageing at temperatures below the glass transition temperature (T_g), chain mobility becomes restricted as the chains become more closely packed, often leading to the materials becoming more embrittled [127]. The ageing temperature (T_a) used is usually ranging from 5°C to about 25°C below the T_g [126, 128-130]. Since polymer ageing generally leads to a decrease in ductility, this potentially could alter the efficacy of the scission process by ultrasonication. In this work, we investigated the effect of physically ageing of PS, which is relatively easy to scission, and PLLA representing a relatively difficult to scission material. The aim of this was to determine the effects of ageing on resultant short fibre properties, whilst also encouraging the cleavage of nanofibers of difficult-to-scission materials such as PLLA.

In order to determine an optimal ageing temperature for PS, Differential Scanning Calorimetry (DSC) (Pyris, Perkin-Elmer) analysis was performed on the fibres to determine the T_g and T_a before the annealing process. The calibration of the DSC was performed during heating using indium and zinc as the standard material, with all scans performed at 10°C/min. To erase any previous thermal history, the sample was heated 130°C (slightly above T_g) for 2 minutes. The sample was then cooled to 30°C prior to heating up to 150°C at the rate of 10°C/min. The T_g measurement was obtained from the DSC thermogram, as the mid-point of the step change in heat capacity, as shown in Figure 3.5.



Figure 3.5 Measurement of T_g from DSC thermogram[131].

From the DSC spectrum, the T_g for PS is 103°C (ca. 100°C) and from that, T_a was varied from 75°C to 90°C (5°C to 25°C below T_g). For the ageing measurement through DSC, the as-spun webs were heated to 130°C for 2 min (to remove any thermal history), the sample then being cooled to the ageing temperature, T_a , at a rate of 10°C/min and held for 12 hr. After isothermal ageing, the sample was cooled at 10°C/min to 30°C, prior to a heating cycle also at 10°C/min to above T_g to investigate the effect of ageing on the thermogram. The process of annealing the sample above T_g effectively erased the ageing, and the subsequent heating run was collected after cooling the sample. In this way, the unaged sample was scanned before and after the ageing run. The change in enthalpy during physical ageing can be determined by the difference between the aged and unaged scans, which leads to an endothermic overshoot at the glass transition [132]. Figure 3.6 shows the ageing enthalpy which can be obtained directly from DSC measurement.



Figure 3.6 Excess of enthalpy in aged sample [133].

From DSC data the best ageing temperature for PS was 85°C which was approximately 15°C below T_g (100°C) for 14 hr. Once this was determined the actual annealing of the electorspun fibre web took place in a vacuum oven at 85°C for 14 hr, whilst for PLLA where the T_g was determined by DSC to be 55°C, a temperature of 40°C was taken as ageing temperature for a duration of 14 hr. In the PLLA experiment, the ageing temperature was not varied since the T_g for PLLA is low, resulting in great difficulty in accurate controlling temperatures below 40°C using a normal vacuum oven. The aged samples were then stored in a desiccator prior to ultrasonication.

3.3.2.3 Crystallisation of PLLA

It was found from the literature that the crystallinity of as-spun PLLA was quite low 0 - 30 % [115]. As with most semi-crystalline polyesters, DSC thermograms of this material demonstrated a cold crystallisation peak (above T_g , but below T_m) where crystallisation occurs for some samples that are not fully crystallised, during the DSC scan. Annealing the sample in the temperature region of this cold crystallisation process thus increases crystallinity. The degree of crystallinity of a given sample at room temperature (before scanning) was determined by scanning the sample and measuring the cold crystallisation exotherm and subtracting this from the eventual melting endotherm. This endotherm contains both the crystallinity that was present prior to commencement of scanning, and the additional crystallinity developed by scanning the sample through the cold crystallisation region. Therefore, the difference between the melting endotherm and the cold crystallisation exotherm is a measure of the degree of crystallinity that existed before the sample was scanned/annealed in the cold crystallisation region [134]. The cold crystallisation and melting endotherm of a semicrystalline material can be seen in Figure 3.7.



Figure 3.7 DSC thermogram showing cold crystallisation exotherm and melting endotherm [134].

The degree of crystallinity can be calculated from Equation 3.1 and 3.2 [134],

% crystallinity =
$$\frac{\Delta H_m - \Delta H_c}{\Delta H_{m1.0\%0}}$$
 100% Equation 3.1

where ΔH_m is the enthalpy of melting, ΔH_c is the enthalpy of crystallisation, and $\Delta H_{m100\%}$ is the enthalpy of melting for a fully crystalline polymer. When further crystallisation does not result from heating, the degree of crystallinity may be estimated from the melting peak, as shown in Equation 3.2:

% crystallinity =
$$\frac{\Delta H_m}{\Delta H_{m10\%}}$$
 100% Equation 3.2

Crystallinity is likely to be important in the context of ultrasonication scissioning because the degree of crystallinity would affect the structure and mechanical properties of polymers. A DSC heating scan was performed on the as-spun PLLA to determine the percentage crystallinity. From this thermogram, the cold crystallisation temperature was found to be around 75° C (Figure 5.30).

Isothermal heating of the sample at this temperature for 15 min was used to vary the degree of crystallinity, which could then be determined using DSC, as described above. If the sample was annealed for a sufficiently long time (such as the 15 min described above), the rescan of the sample showed no evidence of an exothermic cold crystallisation process, and only a melting endotherm was observed.

As before, the conditions found appropriate in the DSC were replicated for larger samples, by placing the electrospun web into the vacuum oven for 15 min at 75°C, and subsequently cooled at room temperature, prior to the ultrasonication, scissioning process.

3.3.2.4 Annealing treatment

Heating of the samples to cause thermal ageing and/or crystallisation has been described above. Another annealing process was undertaken which was particularly relevant to a material such as PS. This involved annealing the sample above T_g (as compared to below T_g , as in thermal ageing). By heating the nanofiber web above T_g , it was intended to reduce the built up stresses that would likely exist within the fibres as they are rapidly formed by evaporation of the solvent. To achieve this stress relaxation effect in PS, the web was heated in a vacuum oven at about 110°C which is 10°C above T_g for 10 min, 30 min and 60 min, and then cooled at room temperature, followed by sonication.

3.3.3 Preparation of short electrospun fibres by ultrasonication

This section described how the basic ultrasonication process was conducted. Initially, the four types of polymer as mentioned in Section 3.2 which is PS, PMMA, PAN and PLLA were sonicated until a break-up of the electrospun web was observed. Further investigation of the effect of varying the ultrasonication parameters were conducted using PS and PMMA which can be scissioned using ultrasonication directly.

In the scissioning process, the electrospun webs were peeled off the collection plate, and a 1 cm² area cut with a sharp knife, before being placed randomly in a glass vial (25 mm in diameter) containing 15 mL of MiliQ water. The sonication was carried out using a Vibracell 750W (Sonics & Materials, Inc, USA) sonicator probe with a probe diameter of 13 mm, and a working frequency of 20 kHz. The probe was positioned ca. 1 cm from the bottom of the vial. The processing parameters such as total run time, amplitude % and lapsed ON/OFF time were varied. The water used for this study was at ambient conditions, except for the study on nucleation effect where MiliQ water was degassed in a vacuum oven for 12 hr prior to use.

In general, ultrasonication was conducted in a beaker cooled by water-ice slurry to maintain the processing temperatures below 30°C, since ongoing sonication raises the solvent temperature, even when using ON/OFF pulsed exposure. Other less extreme methods of cooling (such as packing the sonication vessel in ice) were also undertaken in one part of the work, to allow higher

temperatures of the sonication medium to be obtained. Therefore, the effect of temperature as a variable in processing temperatures between 30°C and 90°C could be semi-quantitatively achieved after significant sonication times.

After completion of the ultrasonic treatment, short fibres in the solvent suspension were placed on a scanning electron microscope (SEM) stub, which was covered with double-sided carbon tape to allow adhesion to the stub. Prior to imaging using SEM, the sample was dried overnight in the fumehood followed by 2 hr in vacuum oven at 60°C and platinum coated at 1 nm thickness with a sputter coater, Cressington 208HR, (UK).

A summary of the sonication conditions used to understand the influence of parameters on resultant materials properties is shown in Table 3.2.

	Electrospun	Alignment	Solvent	Total sonication run	Lapsed	Sonication
Parameter varied	material			time (all is min except	sonication	amplitude
				as stated in seconds,s)	ON/OFF time	(%)
					(s)	
Electrospun materials	PS, PMMA,	random	water	1,40s,	2/2	80
	PLLA and PAN			1, 35 , 35		
				40 1 2 2 4	2.12	
Run time	PS and PMMA	random	Water	40s, 1,2,3,4	2/2	80
	DC	معدما		12249	2/2	80
	PS	angned	water	1,2,3,4,8	212	80
Solvent types (athenol	DC	aligned	wator	12248	2/2	80
Solvent types (ethallol	r S	angneu	water,	1,2,3,4,0		80
and water)			ethanol			
			ethunor			
Initial fibre orientation	PS	Aligned	water	1,2,3,4,8	2/2	80
		_				
		and				
		random				

Table 3. 2 Summary of sonication conditions for samples investigated by varying different conditions

Initial fibre diameter	PS at 3 different	aligned	water	1,2,3,4,8	2/2	80
	fibre diameter					
	range					
Lapsed ON/OFF	PS	aligned	water	3	0, 2/2, 2/6, 5/5	80
sonication time						
Sonication amplitude	PS	aligned	water	3	2/2	50,60,70,80
Sonication temperature	PS	aligned	water	1,2,3,4,8	2/2	80
Dissolved gas	PS	aligned	water	1,2,3,4,8	2/2	80
(Air and ,He)						
UV-Ozone post-	UV-Ozone	random	water	29,18	2/2	80
treatment	irradiated_					
	PLLA and PAN					

Ageing post-treatment	Aged PS Aged	Aligned	water	20s, 1, 2, 3,4	2/2	80
	PLLA	random		35		
Annealing post-	Annealed PS	Aligned	water	20s, 1, 2, 3,4	2/2	80
treatment	Annealed PLLA	random		35		
Recrystallisation	Recrystallised	random	water	35	2/2	80
	PLLA					
Composite production	carbonised	random	water	30	2/2	80
(carbonised PAN)	scissioned					

3.3.4 Carbonisation of electrospun PAN fibres

This work aimed to carbonise PAN into a rigid and potentially electrically conductive material. The interest was to attempt to either scission the sample before or after carbonisation of the web, determining the most appropriate method for the production of short carbon fibres using ultrasonication. The route for preparation of carbonised PAN fibres can be summarised in Figure 3.8.



Figure 3.8 Preparation route of carbonised short electrospun PAN fibres.

Initially, the short electrospun PAN was intended to be prepared by direct ultrasonication, followed by carbonisation of the short fibres as in Method 1. However, our findings showed that the method was unsuccessful and thus, a UV-Ozone treatment on the electrospun web prior to sonication was performed as in Method 2. In this method, the web was irradiated for 12 min followed by ultrasonication for 18 min (to achieve full break-up of the web) prior to carbonisation. The ultrasonication processing was performed in 15 mL water for 18 min at 80 %, 2/2 lapsed ON/OFF time using a 25 mm diameter vial. After completion of sonication, the supernatant was mixed with 20 % ethanol (about 3 mL) and placed in a centrifuge (Hettich Universal 1200, Germany) for 10 min at about 80 % power intensity (ca 1000 rpm). The addition of ethanol assisted the centrifugation process due to the low density of electrospun polymers, resulting in most of the short fibres floating on the water surface.

After the centrifugation process, the short fibres were retrieved using a pipette and placed in a beaker for drying purpose. The drying process was undertaken in the fumehood for approximately 3 days to remove excess water. This was followed by a subsequent dry in a vacuum oven until constant weight was achieved. Following this, the short fibres were further dried at 60°C in a vacuum oven at -100 kPa overnight to ensure complete drying. This process was repeated until a sufficient amount of short electrospun fibres were obtained. The dried, short electrospun PAN fibres were placed in alumina crucible for carbonisation using a tube furnace (KMT-GSL-1600X) and the initial weight of

the short fibres were determined. The crucible was then placed in the centre of the tube furnace to ensure optimal, even heating. Converting the PAN electrospun fibre into carbon fibre involved 2 stages, stabilisation and carbonisation [135-137]. Stabilisation involved a heat treatment of short electrospun PAN in the range of 280°C in air (oxygen) to allow oxidation to take place, whilst carbonisation was performed at 1200°C in high purity argon.

For the stabilisation step, the heat treatment was conducted up to 280°C at the rate of 2°C/min with a holding time at the final temperature of 1 hr. During this stabilisation stage, air flow was maintained throughout the experiment. After the stabilisation step, the furnace was evacuated until -0.1 MPa, followed by purging with argon gas up to '0' gauge pressure. This evacuation-purging process was repeated three times to ensure oxygen was removed in the furnace. At the final step of argon purging, the 2-way relief valve was open and continuous flow of argon was maintained throughout the experiment.

At carbonisation step, the furnace temperature was raised to 1200°C at the same rate of 2°C/min with the holding time of 1 hr at that maximum temperature. The carbonisation is considered complete when the conversion of PAN fibres to carbon was evident from Raman spectroscopy and Transmission Electron Microscope (TEM) images (discussed further in Section 6.2.2). After carbonisation was completed, the carbonised PAN was removed and weighed to determine the weight that had been lost during carbonisation. The short fibres

produced using Method 2 will be referred to as scissioned-carbonised electrospun PAN fibres.

Meanwhile, in Method 3, the as-spun web was used directly for the same stabilisation and carbonisation procedure followed by ultrasonication to scission the fibres. In this method, the electrospun PAN web was cut using scissors (ca 2 cm x 5 cm) and arranged layer-by-layer to fit in the crucible. After the carbonisation process was complete, the carbonised electrospun PAN was sonicated in water for 30 min at 80 % amplitude and 2/2 lapsed ON/OFF time to produce the carbonised short electrospun PAN fibres which will be referred to as carbonised-scissioned samples.

3.3.5 Preparation of carbonised PAN short fibre/epoxy composites

Carbonised short electrospun PAN fibre/epoxy composite were prepared using the carbonised-scissioned and scissioned-carbonised short fibre, with and without the addition of surfactant alkylammonium salt, BYK9076 (BYK Inc, US) which has previously been used as a dispersant of carbon nanofibres/nanotubes in the composite systems [119-122]. These components were combined using high speed mixing alone using SpeedMixer DAC 150 FVZ, FlackTek,Inc (South Carolina), or by incorporating solvent (acetone) in combination with high speed mixing and exposure to an ultrasonication bath FXP12D, Unisonics,(Australia) for 30 min. High speed mixing or shear mixing is a mixing mode that largely (but not entirely) avoids bubbles, even with a viscous media, due to a combined rotation around the mixing chamber axis, and an orbital motion of the mixing head.

The investigation of the preparation method (either using high speed mixing alone or a combination of the solvent method with high speed mixing and ultrasonication bath) for the PAN/epoxy was performed using carbonised-scissioned short fibre. It is important to note that obtaining a sufficient amount of sample for composite work was very time consuming, especially for scissioned-carbonised short fibre. In fact this is one of the impediments to the use of electrospun fibres in such composite applications [1].

For scissioned-carbonised short fibres, the amount of UV-Ozone treated electrospun fibres that were sonicated for 18 min (full break-up of the web) at one time was only about 30 mg (0.03 g) (with 10 sheets of 1 cm² electrospun web). This process has to be repeated to obtain sufficient short fibre for carbonisation, which is about 1 g. After the carbonisation process, with a 60 - 70 % loss in weight, the amount of scissioned carbonised short fibre left was about 0.4 g. In comparison, the carbonised-scissioned short fibre preparation is more straight forward, where the as-spun web is carbonised immediately, followed by ultrasonication of the whole batch (about 0.4 g) for 30 min. Since the preparation of the carbonised-scissioned short electrospun PAN is much easier than scissioned-carbonised sample, only carbonised-scissioned electrospun PAN were used to investigate the best method to prepare the composite. After the most

suitable method was determined, the scissioned-carbonised/epoxy composites were prepared. The preparation routes to produce the composites can be seen in Figure 3.9.



Figure 3.9 Preparation of carbonised-scissioned short electrospun PAN/epoxy composites.

Both Protocol 1 and 2 was conducted using high speed mixing, whilst Protocol 3 and 4 were performed using a solvent method with a combination of high speed mixing and ultrasonication bath. The formulation of the composite systems is tabulated in Table 3.3.

	Short fibre to	Short fi	ibre	Surfactant	Epoxy	Amine
Method	epoxy	weight		BYK9076	DGEBA	weight
	concentration	(g)		weight	weight	(g)
	Wt %			(g)	(g)	
				(20 wt% of		
				fibre weight		
High speed mixing	2.5	0.123		-	4	0.8
	5	0.246		-	4	0.8
	2.5	0.123		0.0246	4	0.8
	5	0.246		0.0492	4	0.8
Solvent method	2.5	0.123		-	4	0.8
(acetone)	5	0.246		-	4	0.8
High speed mixing	2.5	0.123		0.0246	4	0.8
and Ultrasonication	5	0.246		0.0492	4	0.8
bath						

 Table 3.3 Formulation of the carbonised-scissioned and scissionedcarbonised short electrospun PAN composite component

In the first method (Protocol 1), 4 g of epoxy was added into 0.123 g of dried carbonised-scissioned short electrospun PAN to produce 2.5 wt% composite prior to high speed mixing . The mixing was performed at 2000 rpm for 5 min. The mixture was then placed in the vacuum oven at -100 kPa for 2 days to remove air bubbles, followed by addition of 0.8 g amine at the ratio of 5:1(epoxy to amine) according to manufacturer's recommendations [138]. Speed mixing at 2000 rpm

for 2 min was carried out prior curing. The composite was poured into the silicon mould designed to produce samples intended for a 3 point bending test, with the dimension of 13 (W) mm x 25 (L) mm x1 (t) mm. The mould was clamped on both sides by steel plates covered by Teflon sheets, to hold the sample in place during reaction and allow easy mould release when they were solidified. The curing was performed at room temperature for 48 hr, followed by post curing at 60°C overnight. The composite was demoulded and the edges smoothed using sand grit paper P80.

Due to an unsatisfactory dispersion being obtained using this method, BYK9076 surfactant at 20 wt% (to the short fibre weight) was added to improve the surface wetting of the carbonised PAN in Protocol 2. The surfactant was incorporated into the epoxy prior to speed mixing for 5 min. After degassing at -100 kPa in a vacuum oven, the hardener was added, followed by further speed mixing for 2 min. The curing process was used the same procedure as for Protocol 1. The flowchart for the experimental procedures of Protocol 1 and 2 is shown in Figure 3.10.



Figure 3.10 Flowchart of experimental procedure for Protocol 1 (without BYK9076) and Protocol 2 (with BYK9076).

Protocol 3 (without BYK9076) and 4 (with BYK9076) was performed using the solvent method, with combination of high speed mixing and use of the ultrasonication bath, as summarised in Figure 3.11.



Figure 3.11 Flowchart of experimental procedure for Protocol 3 (without BYK9076) and Protocol 4 (with BYK9076)

In Protocol 3, 0.123 g carbonised-scissioned short electrospun PAN was sonicated in 10 mL acetone for 10 min at 80% amplitude and 2/2 lapsed ON/OFF time.

The inclusion of acetone to aid the dispersion of nanofibers need to be use with caution. It is noted that the acetone is difficult to vaporize [119] and has been shown to alter the epoxy network formation and reduce the mechanical properties [139]. Due to that, excess acetone was removed after acetone and carbonised PAN mixture was sonicated. The mixture was left in the fumehood to allow the excess acetone to evaporate until approximately 1 g of acetone mixture was left in the vessel. Subsequently, 4 g of epoxy was added to the mixture followed by shear mixing for 5 min at 2000 rpm and ultrasonication bath for 30 min. The mixture was weighed before placing it in the vacuum oven at -100 kPa and 60°C for removal of residual acetone and degassing. The weight was monitored every 6 hr to ensure the complete removal of acetone. Following this, 0.8 g amine was added and mixed using the high shear mixer at 2000 rpm for 2 min, followed by moulding at room temperature for 48 hr and post curing at 60°C overnight.

In comparison, Protocol 4 involved the addition of BYK9076 surfactant into the speed mixing vessel containing the epoxy resin, prior to high shear mixing with the short fibres. The rest of the experimental steps were the same as in Protocol 3.

3.4 Characterisation

3.4.1 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is a widely-used technique to study the morphology and microstructure of a solid surface, which is important in understanding the structure property relationship of a material. In this method, the sample surface is scanned by a high energy electron beam where the incident electrons interact with the specimen atoms and cause extensive scattering. Two types of SEM device were used in this study, being the Scanning Electron Microscope, SEM (JEOL840A JEOL Ltd, Japan) and the Field Emission Scanning Electron Microscope FEG SEM (JEOL 7001F, JEOL Ltd, Japan). The short fibre samples were dried overnight in the fumehood, followed by heating at 60°C in vacuum oven for 2 hr prior to platinum coating of the sample (1 nm thickness) using a sputter coater (Cressington 208HR, UK).

3.4.2 Transmission electron microscopy (TEM)

Transmission Electron Microscopy (TEM) was used to characterise the short fibre surface morphology at higher magnifications. It was able to provide a clear image of the surface roughness of the short fibre, and any localised melting present. Furthermore, it was also used to confirm the conversion of the electrospun PAN into carbon fibre after the carbonisation process. To image these samples, the sonicated short fibre (PS and carbonised PAN) were mixed with water, and a drop of the supernatant was placed onto a TEM copper hexagonal grid. The sample was dried in the fumehood prior to imaging using a Philips CM20 TEM.

3.4.3 Turbidity measurements

Comparison between the concentration of short fibres for different types of polymers i.e PS, PMMA, PLLA and PAN were estimated using a turbidity meter Cyberscan TB1000, Eutech Ins, (Singapore) to determine the minimum time required for successful sonication. Squares of approximately 1 cm² were cut from an electrospun web and sonicated in 30 mL of MiliQ water for durations ranging between 10 to 90 s for both the PS and PMMA, whilst the sonication time for PAN and PLLA were extended for durations up to 35 min. Any remaining electrospun web was removed using tweezers prior to the turbidity measurement so that the results largely reflected the concentration of short fibres produced and remaining in the suspension.

3.4.4 Fourier Transform Infrared spectroscopy (FTIR)

In order to better understand the surface and physical properties of the nanofibres, the PS samples were also characterised in transmission mode by Fourier Transform Infrared spectroscopy (FTIR) using a Thermo Scientific Nicolet 6700 with scanning range of 4500 to 400 cm⁻¹ and 4 cm⁻¹ resolution. The sample were pre-mixed with potassium bromide (KBr) powder at 3 wt% and compressed into a disc.

For the post-treated PLLA and PAN webs, the change in chemical structure was investigated using reflection mode by Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR) using a Thermo Scientific Nicolet 6700 with scanning range of 4500 to 400 cm⁻¹ and 4 cm⁻¹ resolution. A small amount of post-treated web was firmly pressed on to the ATR crystal prior to making a measurement.

3.4.5 Raman Spectroscopy

Raman spectroscopy is a powerful tool to study the microstructure of carbonaceous materials [109, 111, 140]. The information on the perfection of crystallinity, for example, can be obtained by analysing Raman spectra where the sp^2 bonded species (graphite) shows in *D*-peak and *G*-peak centered around 1360 cm⁻¹ and 1580 cm⁻¹, respectively, which can be seen in Figure 3.12.



Figure 3.12 Raman spectra of carbonised PAN showing the *D* peak and *G* peak of different carbonisation temperature A,B and C at 1400°C, 1800°C and 2200°C. Adapted from [109].

The ratio, *R* of the intensity of *D*-peak (I_D) and *G*-peak (I_G) is representative of the quality of the carbon produced, with the lower the value of *R* indicating the greater amount of ordered graphitic plane compared to disordered carbon. In our study, the Raman spectra of the carbonised-scissioned and scissioned-carbonised PAN were obtained using a Renishaw Invia Microscope which had a red laser emitting at 633 nm.

3.4.6 X-Ray Diffraction (XRD)

X-Ray diffraction (XRD) is a characterisation technique to determine the sample's crystallinity, to confirm its phase, and measure the average crystal size. From XRD data, the size of crystallite L_c and L_a , along *c*-and *a*-directions (refer to

Figure 3.13) can be calculated from the Bragg and Scherrer equation [109] as follows:

$$L_{c} = \frac{0.9\lambda}{\beta\cos\theta}$$
 Equation 3.3
$$L_{a} = \frac{1.84\lambda}{\beta\cos\theta}$$
 Equation 3.4

where L_c and L_a is the crystallite size attributed to the (002) and (10) crystallographic plane of graphite crystallites which is shown by the diffraction peak around 2θ angle of 24° and 44° respectively. λ is the wavelength of Cu K α X-ray, β is the full width at half the maximum intensity (FWHM) at (002) and (10) peak.



Figure 3.13 An idealized schematic of the carbon structure, showing L_a and L_c which is the thickness and diameter of the carbon layer stack [94].

The XRD spectra were collected using a Phillips 1140 diffractometer with copper target (Cu K α) with wavelength, λ = 0.1541 nm with a scan rate of 2°/min and comprised of discrete 0.02° steps.

3.4.7 Resistivity measurement

Electrical resistivity measurements were carried out using standard 4-point probe (RM3-AR from Jandel Engineering, UK) consisting of four tungsten metal tips with 0.5 mm equal space. For carbonised electrospun PAN measurement, the electrospun web was manually compacted using a mortar and pestle prior to carbonisation, to flatten the sample surface. The instrument was calibrated and tested with the standard material to ensure the reliability and accuracy of the measurement. The bulk resistivity of the sample is given by

$$\rho = 2\pi s \left(\frac{v}{l}\right)$$
 Equation 3.6

where the probe spacing was uniformly s (0.5mm), I is the current applied at the outer two probe tips and V is the voltage generated between the inner two tips. At least 5 different areas on each specimen were measured and the mean values determined.

3.4.8 Tensile testing for electrospun web

Tensile testing was conducted using an Instron 5848 microtester (USA) with 10 N load and displacement rate of 5 mm/min. The electrospun web with the thickness of approximately 0.3 mm was cut at the middle section of the collector using a dogbone shape cutter, with a gauge length of 20 mm, as shown in Figure 3.14.



Figure 3.14 Electrospun sample preparation a) cutting in progress, b) the dogbone shaped electrospun web prepared for tensile testing

The electropun web was peeled from the Al foil prior to thickness measurements obtained using a Mitutoyo Digimatic 293-832. The electrospun web was held in

place using pneumatic grip to avoid pre-failure of the sample. Figure 3.15 shows the experimental set up of the tensile experiment using the Mini Instron.



Figure 3.15 Tensile testing setup using Mini Instron Microtester with pneumatic grips.

The ultimate tensile strength (σ_{UTS}), Young's Modulus (*E*) and % strain to failure (ductility) were determined from five independent samples for each type of electrospun polymer.

3.4.9 3 point bending test for carbonised short electrospun PAN fibre/epoxy composite

The composites were prepared at 2.5wt% and 5 wt%, as detailed in Section 3.3.5. The mixtures were poured into a rectangular mould shaped with the dimension of $13(W) \ge 25(L) \ge 1(t)$ mm in accordance with ASTM Standard D7264 Flexural Testing for polymeric composites. The sample was cured at room temperature in the fumehood for at least 48 hr, followed by post curing at 60° C overnight.

The cured samples were demoulded and trimmed at the edges using sand paper grit P80. The 3 point bend test was perform using Instron 5848 microtester (USA) with 2 kN load and displacement rate of 2 mm/min until fracture. At least 5 samples of each sample were tested in order to obtain the flexural properties of the composite, such as modulus, strength and failure strain.
Chapter 4 - Electrospinning and Ultrasonication of Different Types of Electrospun Fibres

4.1 Introduction

In this chapter, the optimisation of the electrospinning parameters for the four materials primarily studied in this thesis - poly(styrene)(PS), poly(methyl methacrylate) (PMMA), poly(acrylonitrile)(PAN) and poly(*L*-lactic acid)(PLLA) will be discussed. The processing parameters, such as the type of solvent, polymer concentration, working distance, accelerating voltage and flow rate were all varied to obtain an optimum fibre morphology that was beadless, uniform and within an acceptable diameter range. These nanometre/submicron-sized fibres were then subjected to ultrasonication to study their influence on manipulating the scission of electrospun fibre. The results are presented in terms of the visual observation, characterisation on the surface morphology, tensile properties of the as-spun web (prior to sonication) and turbidity measurement of the short fibres supernatant (following sonication).

4.2 Electrospinning

Although electrospinning of PLLA, PMMA, PAN and PS polymers has been reported by others in a range of studies [2, 109, 125, 141, 142], it is clear that using a different apparatus and environmental working conditions will lead to different fibre morphologies, in addition to any changes in processing conditions. For this reason, as a starting position, we have chosen the solvent and processing parameters from the literature as a guideline for our conditions, and then manipulated conditions so that the electospun fibres produced could achieve a surface morphology that is beadless and were of sub-micron diameter size. In general, the polymer was dissolved in the solvent at a specific wt/v % prior electrospinning. The detail method and processing parameters of electrospinning can be found in Section 3.3.1 and Table 3.1.

4.2.1 Poly(*L*-lactic) Acid (PLLA)

The common solvents that have been used to electrospun PLLA include chloroform [143] and a mixture of chloroform and acetone [144]. We initially present results with chloroform alone, with Figure 4.1 showing PLLA electrospun fibres spun from chloroform at 6.5 wt/v% and 8 wt/v% concentration, with a needle feed rate of 2.4 mL/h, through an 18 G gauge needle with a 20 kV voltage, and 15 cm working distance to the collector.



Figure 4.1 SEM images of PLLA in chloroform at a) 6.5 wt/v%, b) 8 wt/v%.

It can be seen in Figure 4.1 that at a 6.5 wt/v % polymer concentration, the fibres produced contained elongated beads. Increasing the concentration to 8 wt/v% lead to beadless, non-uniform fibres, with two distinctive fibre diameters. This bimodal size distribution is due to the secondary jet that erupts from the primary electrospinning jet, producing smaller fibre diameters. These secondary jets arise due to the fibre-solvent interaction and higher voltage used [2]. It has often been suggested that the addition of ionic surfactant can improve electrical conductivity and reduce the surface tension of the polymer solution [2, 145], with the increased conductivity resulting in more charge carried by the electrospinning jet, leading to more fibre stretching and thus a thinner fibre [2]. The results of incorporation of DTAB are shown in Figure 4.2, where the PLLA was electrospun in chloroform with 1 mM DTAB, with the other parameters the same as before for 8 wt/v%, 12 wt/v%, 13.7 wt/v% and 15.3 wt/v% polymer concentrations.



Figure 4.2 Electrospun PLLA fibres in with chloroform as the solvent, with 1mM DTAB at the polymer concentration of a) 8 wt/v%, b) 13.7 wt/v% and c) 15.3 wt/v%.

It can be seen in Figure 4.2 that with the addition of the cationic surfactant DTAB, electrospun fibres produced from chloroform at 8 wt/v% polymer concentration contained some fibres, but predominantly consisted of spherical beads, while at the same concentration without DTAB addition the fibres obtained were beadless (Figure 4.1b). However, it is important to note that although without addition of DTAB addition, the fibres showed no beads, the non-uniform fibre diameter was undesirable. At 8 wt/v% concentration, the inclusion of DTAB in the chloroform polymer solution resulted in a difference in charge distribution on the Taylor cone and generated nanofibres with beads [35]. The addition of a cationic surfactant will increase the charge density, leading to a greater conductivity. If the conductivity level is too high, multi-jets will be produced and lead to fibres with beads [125, 146]. It was previously shown that without DTAB addition, 8 wt/v% results in a bimodal distribution in fibres resulting in distinct fibres diameter due to secondary jets (Figure 4.1b). With the addition of DTAB, an increase in conductivity leads to an unstable jet and causes jet break-ups (electrospraying). It was also found by Kriegel et al [147] that the

addition of DTAB reduced the viscosity of PEO solutions which also might contribute to the beads in our findings. This can be overcome by increasing the concentration to that at which chain entanglements occur to enable continuous stretching of the jet. This was particularly true when the polymer concentration was increased to 12 wt/v% (not shown here), and 13.7 wt/v% (Figure 4.2b), where the beads changed from spindle-like shapes to elongated beads. This shows that by increasing the concentration, the intermolecular force or chain entanglement of the polymer was increased and sufficient for jet stretching. Finally, the optimum fibre morphology for PLLA in chloroform with 1 mM DTAB was obtained at the concentration of 15.3 wt/v% with a feed rate of 1.6 mL/h, 20 kV accelerating voltage and 15 cm working distance. These conditions resulted in an average fibre diameter of 790 \pm 390 nm where no beading was observed, although the uniformity of the fibres was still not satisfactory, as shown in the high standard deviation of fibre diameter.

In order to improve the uniformity and reduce the diameter of the electrospun fibres, PLLA was electrospun with a mixture of chloroform and acetone, with 1 mM DTAB. It has been reported that the addition of acetone to the PLLA in chloroform solution leads to improved continuity of the electrospinning jet [144, 145], likely due to the lower polarity of acetone compared to chloroform, which reduces the interactions between the solvent and polymer molecules [145]. This in turn reduces jet cohesive energy, contributing to a greater ease of spinning and thus more uniform fibre diameters. The electrospinning of PLLA with chloroform and acetone with 1mM DTAB addition

was carried out at the concentration of 13 wt/v%, 13.7 wt/v%, 15 wt/v% and 16 wt/v%, with the other parameters, as stated in Table 3.1. The result showed that increasing the polymer concentration lead to a larger fibre diameter. This is because the greater concentration leads to a higher solution viscosity and an increased molecular entanglement that result in high cohesive forces between the polymer molecules, thus reducing the stretching and thinning of the fibres [41]. For the same concentration of 13.7 wt/v% PLLA, reducing the accelerating voltage from 15 kV to 10 kV leads to a larger fibre diameter (not shown). This reduced electrostatic field results in less polymer stretching and fibres with a larger diameter [2]. For this system, the optimum fibre morphology was obtained at 13.7 wt/v% polymer concentration with the feed rate of 1.2 mL/h, 20 kV accelerating voltage, 18 G needle gauge and 16 cm working distance which obtained the average fibre diameter of 770 ± 240 nm (Figure 4.3a). The larger fibre average diameter was obtained at 16 wt/v%, with an average fibre diameter of 970 ± 400 nm, as shown in Figure 4.3b.



Figure 4.3 Electrospun PLLA in chloroform:acetone with 1 mMDTAB at a)13.7 wt/v% and b)16 wt/v%.

Figure 4.3 shows that the optimum fibre morphology obtained was more uniform for the 13.7 wt/v% PLLA concentration, where the standard deviation of the fibre diameter was about 200 nm. It was thus found that the addition of acetone did improve the electrospinning process of PLLA with the uniformity of the fibres achieved (lower standard deviation of the fibre diameter showing the distribution of the fibres' diameter is more uniform). Meanwhile, the 16 wt/v% PLLA concentration showed that higher concentrations lead to higher viscosities that made maintaining flow difficult, and the resulting fibres had a greater average fibre diameter and were less uniform.

4.2.2 Poly(methyl methacrylate) (PMMA)

PMMA was electrospun using two solvents: DMT and DMF with or without the addition of 1 mM DTAB. PMMA with three different average molecular weight which are 107 000 (lowest), 186 000 (intermediate) and 486 000 (highest) were chosen to study the effect of molecular weight on electrospinning. All were initially electrospun in DMT at 6 wt/v% for the PMMA ($Mw = 107\ 000$), 5 wt/v% for $Mw = 186\ 000$ and 2 wt/v% for the $Mw = 486\ 000$ at same processing condition of 2.4 mL/hr feed rate, 20 kV accelerating voltage, 23G gauged needle and 10 cm working distance on the flat collector. The surface morphology of the electrospinning results are shown in Figure 4.4.



Figure 4.4 SEM images of electospun PMMA in DMT a) Mw = 107 000 at 6 wt/v % b) Mw = 186 000 at 5 wt/v% c)Mw = 486 000 at 2 wt/v%.

Figure 4.4 shows that the PMMA with lowest molecular weight (Figure 4.4a) resulted in an electrospun output with the worst appearance, the fibres were entirely beads, with no significant fibre shape. The PMMA with the intermediate average molecular weight of 186,000 consistently resulted in 'cup-shape' beads with a few fine fibres, whilst the highest molecular weight led to a web of fine fibres with many beads. These results indicate that the molecular weight can also affect the electrospun fibre morphology. This is related to the degree of entanglements of the polymers in the solution, and is also related to viscosity [2, 148]. Too low a molecular weight, as shown in Figure 4.4a and 4.4b resulted in electrospraying, where the electrospinning jet break-up during polymer stretching was due to the low polymer chain entanglement, with the result being spherical particles even when higher concentrations were used. The sample with the highest PMMA molecular weight had a better appearance (even though it was at a lower concentration), producing a morphology of fibres in addition to beads, indicating that although the higher molecular weight encouraged some

entanglement, this concentration was still not sufficient to produce the degree of entanglement required to cause a continuous jet. To ensure sufficient entanglement and production of a stable jet, further electrospinning work with PMMA was conducted using highest molecular weight PMMA. This PMMA (Mw = 486000) was electrospun in DMT with 1 mM DTAB (for more uniformity) at both 8 wt/v% and 10 wt/v% (not shown). However, both concentrations still resulted in beading within the fibres, although the number of beads decreased with increased concentration of polymer solution.

In an effort to obtain a more uniform morphology, PMMA (Mw = 486000) was electrospun using DMF with 1 mM DTAB at the concentration of 5.7 wt/v%, 6.5 wt/v% and 7 wt/v%. The 5.7 wt/v% concentration (image not shown here) resulted in fine fibres with very limited beading, whilst at 6.5 wt/v% concentration, beadless fibres were formed. Further increasing the concentration to 7 wt/v% and 25 kV accelerating voltage lead to a more uniform and larger average fibre diameters, as shown in Figure 4.5.



Figure 4.5 PMMA in DMF with 1mM DTAB at a) 6.5 wt/v% with 20 kV accelerating voltage, b) 7 wt/v% with 25 kV accelerating voltage.

We found that the optimal conditions for electrospnning of high molecular weight PMMA were 6.5 wt/v% polymer concentration, 20 kV accelerating voltage, 18 G gauged needle, 1.6 mL/hr and 15 cm working distance. These conditions led to fibres of 550 ± 160 nm in diameter, whilst larger fibres (800 ± 260 nm) could be produced at the concentration of 7 wt% and 25 kV accelerating voltage with the other parameters the same as before.

4.2.3 Polystyrene (PS)

PS was electrospun in chloroform and DMF with 1 mM DTAB on a flat collector to produce a fibre web consisting of randomly-oriented nanofibres. Webs with fibres in an aligned orientation were also obtained using the rotating cylindrical mandrel collector at 6.3 m/s surface velocity. Both fibres were electrospun at 12 wt/v% concentration. Although this effect was not studied in detail as part of this research, in general the alignment of the fibres depends on the speed of the rotating mandrel [149]. Higher speeds result in more alignment until, at a certain point, no fibres are collected on the mandrel at very high rotation speeds but became dispersed in the air because the velocity of the jet may be slower than the surface velocity of the rotating mandrel [149]. In this study a speed of 6.3 m/s was chosen for the surface of the collector, since higher speeds resulted in the fibres being dispersed at the side of the electrospinner instead of onto the collector.

The fibre morphology for the 12 wt/v% concentration was reasonably uniform and no beads were found for both random and aligned orientation fibres, with similar diameters of 730 ± 310 nm and 775 ± 160 nm for the aligned and random fibres, respectively, as shown in Figure 4.6.



Figure 4.6 SEM images of PS with (a) random and (b) aligned orientation. Both were electrospun at 12 wt/v% concentration.

To investigate the effect of fibre diameter on ultrasonication scission, the PS fibres were produced by varying the concentration to obtain three sizes of fibre diameter. The thinner PS fibres were electrospun at 8 wt/v%, whilst the larger fibre diameter were achieved when electrospun at 16 wt/v%. All the fibres for these comparative purposes were electrospun in the same solvent solution, which was a mixture of chloroform and DMF with 1 mM DTAB, at the same speed of rotating mandrel of 6.8 m/s surface velocity. The other electrospinning parameters were kept the same, being a 1.6 mL/hr feed rate, 20 kV accelerating voltage, 6 cm working distance and 18G gauged needle. Figure 4.7 shows the SEM images of the morphology of the fibres with the respective average fibre diameter.



Figure 4.7 SEM images of PS electrospun fibre at different polymer concentration a) 16 wt/v%, $d = 930 \pm 290$ nm, b) 12 wt/v%, $d = 730 \pm 310$ nm and c) 8 wt/v%, $d = 240 \pm 70$ nm.

It can be seen that by changing the solution concentration, the fibre diameter can be varied, although all the diameters are still in submicron range. The largest diameter fibres were produced at 16 wt/v% concentration, with average diameters of 930 ± 290 nm, and the thinnest fibre diameter in this study being obtained at 8 wt/v%, having an average fibre diameter of 240 ± 70 nm.

4.2.4 Polyarylonitrile (PAN)

PAN was electrospun in DMF at 10 wt/v% polymer concentration, with the feed rate of 1.6 mL/hr, 20 kV accelerating voltage and 16 cm working distance on a flat collector. The SEM images of the surface morphology of the as-spun web are shown in Figure 4.8.



Figure 4.8 SEM image of PAN electrospun in DMF at 10 wt% concentration.

PAN fibres were readily obtained as beadless, uniform nanofibres with an average fibre diameter of 640 ± 165 nm, and a random fibre orientation.

4.3 Comparison of ultrasonication of the different types of electrospun polymers

The electrospun nanofibre webs of the four polymers mentioned in the previous section (Section 4.2) were then used for ultrasonication studies. The electrospun webs chosen were free from artefacts such as beading and broadly within the same average diameter in range of 600 - 800 nm. The 1 cm² areas cut from the webs were then sonicated in MilliQ water. The sonication was performed at 80 % amplitude and 2/2 lapsed ON/OF time with the total run time was varied until the electrospun web was completely broken. The webs and short fibre were characterised using SEM, turbidity measurements and tensile testing.

4.3.1 Scanning electron microscope (SEM)

SEM was performed on the webs and short fibre before and after ultrasonication to compare the surface morphology and to quantify the average fibre length of the short fibres. Figure 4.9 shows the electrospun fibres before and after sonication for what we define in this work as the "minimum sonication time", except for PAN and PLLA, where the fibre web remained intact even after much longer sonication times. We define this minimum sonication time as the first time that the web was visually observed to significantly fragment. This was ca. 40 s for PMMA and 60 s for PS, whilst no such minimum sonication time observed for PAN and PLLA, even after 35 min of sonication, as recorded in Table 3.2.



Figure 4.9 SEM images of the fibres before sonication (left) and after a minimum sonication run time (right), at the point at which fibre webs were visually observed to have significantly fragmented (for PS and PMMA only, at 60 s and 40 s, respectively) whilst for PAN and PLLA the SEM images were taken of the fibre after sonication run time of 35 min. a,b) PLLA at 13.7 wt/v% with the average diameter of 770 ± 240 nm, c,d) PS at 12 wt/v%, average diameter = 775 ± 160 nm, e,f) PMMA at 6.5 wt/v% , average diameter = 550 ± 160 nm and g,h) PAN at 10 wt/v% , average diameter = 640 ± 165 nm.

Figure 4.9 shows that within 40 s for PMMA and 60 s for PS, both were successfully scissioned into smaller lengths of $10.3 \pm 10.8 \ \mu m$ and $15.0 \pm 7.2 \ \mu m$ respectively, whilst for PAN and PLLA the electrospun web remained intact for the entire process (at 35 min sonication was eventually stopped). For the PS and PMMA samples the supernatant turned whitish in colour after the minimum sonication time, highlighting that short fibres were homogenously dispersed within it. However, for PAN and PLLA, the web appeared to have been elongated due to the sonication, largely loosening the dense as-spun fibre web. It is clear that different sonication times are required for the scission of electrospun scaffolds produced from different materials, and for two samples, even very significant energy input were not able to lead to scission. It can also be seen that the sonication process does lead to some slight changes in the fibre morphology in terms of shape, with some 'curling' or 'waviness' introduced into the fibres. It appears that although the ultrasonication forces have not been sufficient to cause significant scission, they have caused bending and buckling (but not failure) of the fibres, due to a range of stresses on the fibres surface [150].

In order to further understand the mechanism of failure, high magnification SEM images of the electrospun fibres before and after sonication were examined (Figure 4.10). Note that the SEM images of PAN and PLLA after sonication run time of 60 s were also recorded for a comparison to PMMA and PS, which did scission at a run time of 40 s and 60 s, respectively.



Figure 4.10 SEM images of the fibres before sonication, t = 0 and after sonication run time with the respective sonication run time shown a) PLLA prior to sonication , b) PLLA at t= 60 s, c) PS prior to sonication , d) PS at t=60 s, e) PMMA prior to sonication f) PMMA at t= 40 s, g) PAN prior to sonication, h) PAN at t = 60 s, i) PLLA at t= 35 min and j) PAN at t = 35 min.

The SEM images of the fibre surface before sonication show some surface roughness. This degree of roughness is common on the surface of electrospun fibres, although it is rarely highlighted or discussed elsewhere in the literature, where there are very few some close-up images presented. It has been reported that such roughness in electrospun fibres arises from solvent-polymer interactions and the rate of solvent removal, which in turn depends on the type of solvents employed, polymer concentration and relative humidity [47, 124, 151]. The sonicated samples, however, show an even greater degree of roughness, particularly the PLLA and PAN samples, at a sonication time of 35 min in Figure 4.10i and j, respectively, indicating that prolonged sonication only roughens the surface without the scissioning effect.

4.3.2 Turbidity measurement

For all samples, an attempt was made to quantify the degree of electrospun fibre scission using a turbidity measurement, where the results reflect the concentration of particles (in our case, short fibres) in the solution (Figure 4.11). For this experiment, webs of the same dimensions and thickness were used to ensure that there was approximately the same concentration of short fibres in the supernatant if all the fibres had been completely scissioned. Large, unbroken portions of the electrospun web were removed using tweezers prior to measurement and thus the turbidity measurement is an indication of the concentration of the short fibres that have been produced at that point in time. The measurement was performed for sonication times ranging from 10 s to 90 s for all types of fibres, although this was extended to 35 min for the PAN and PLLA samples due to reduced success in scissioning.



Figure 4.11 Turbidity measurement for PS (\Box), PMMA (\circ), PAN (Δ) and PLLA(*) after ultrasonication processing. The arrow bar indicates the minimum sonication time from visual observation, indicating substantial break-up (for PS and PMMA).

Figure 4.11 shows that as the sonication time increased, the same trend was observed for the concentration of short fibres in solution. Note that for the PMMA, a small fibre clump (removed prior to turbidity measurement) was present up to the 20 s sonication time point. It was largely fragmented (as judged visually) after 40 s of sonication (when NTU was ca 250 units), whilst for PS substantial fragmentation occurs after 60 s, by which it also reached NTU of ca 250. From this observation, we can conclude that when the turbidity

measurement reaches the ca. 250 NTU range, all PS and PMMA fibres had been broken up into short fibres, correlating to a minimum sonication time of 40 to 60 s (Figure 4.11), which is similar to the minimum sonication time defined earlier. From visual inspection, short fibres begin to become present in supernatant (as the supernatant colour has turned slightly whitish) when the turbidity was greater than 50 NTU. This indicates that in the case of PAN, some limited scission commences after 40 s of sonication, with the concentration of fibres gradually increasing for the full duration of the experiment. In contrast, the PLLA webs essentially remain intact for the first 20 min of sonication, with a limited amount of short fibres increasingly produced at a slow, linear rate after 35 min. This result indicates that the inherent polymer properties influence the scission events, highlighting the need for post-treatment of some of the polymers we may wish to scission to improve short fibre yields, and this is explored in the next chapter.

There are many factors that are likely to contribute to the difference in the sonication times required to reduce the web to discrete fibre lengths such as the electrospun fibre morphology (fibre diameter and alignment), as well as the mechanical properties of the electrospun polymers. Since all the fibres were of broadly similar diameter and randomly aligned orientation, and given that the same ultrasonication experimental parameters were used for all materials (80% amplitude and 2/2 lapsed ON/OFF time), it can be concluded that differences are largely due to material properties of the initial electrospun web, particularly when comparing the materials that can be readily scissioned during sonication (PS, PMMA), to those that cannot be scissioned (PLLA, PAN). When comparing the

PMMA and PS nanofibres that could be scissioned, it can be seen that PMMA was a little thinner, and it also appeared to scission slightly more rapidly than PS when sonicated. In order to make further comparisons, we examined the mechanical properties of the as-spun webs that we obtained by tensile testing.

4.3.2 Tensile testing

Tensile testing of the electrospun web was performed using an Instron desktop tensile tester with a 10 N load cell, and using a crosshead displacement rate of 5 mm/min, as described in Section 3.4.8. This was used to determine mechanical properties of the web such as modulus, tensile strength and strain to failure (ductility). The stress strain curve for the electrospun web can be seen in Figure 4.12, with the key mechanical properties from these curves shown in Table 4.1, in order to assist in the determination as to which of these properties is most relevant to the scissioning process.



Figure 4.12 Stress strain curve of electrospun fibre webs.

Materials	PS	PMMA	PAN	PLLA
Tensile strength (MPa)	0.6 ± 0.2	1.6 ±0.4	2.5 ± 0.1	1.6 ± 0.2
Tensile modulus (MPa)	8.0 ± 0.8	0.4 ± 0.1	12.2 ± 7.7	11.1 ± 2.6
Ductility (%)	16.8 ±1.9	1.9 ± 0.8	86.3 ±22.1	79.2 ±17.9
Initial electrospun fibre diameter (nm)	775 ± 160	550 ± 160	635 ± 165	771±240
Minimum sonication time (s)	60	40	N/A	N/A
Final short fibre length (µm)	15.0 ± 7.2	10.3 ± 10.8	N/A	N/A

Table 4.1 Mechanical properties of electrospun PS, PMMA, PAN and PLLAwebs

It is clear from Figure 4.12 and the data in Table 4.1, that the PAN and PLLA webs are much more ductile than those of the PS and PMMA, whilst the modulus and strength appear, in part, to be somewhat similar for all samples. It should be noted, that whilst determination of modulus and strength are straightforward from an experimental viewpoint for electrospun webs, the nature of how the fibres are folded and stacked within the tensile sample could influence their values. However, with regards the values of ductility, the fibres themselves are stretched to failure when the web is oriented, and thus the ductility of the web is more likely to be related to the ductility of the individual fibres.

When considering the process of the non-woven web being scissioned by sonication, there will likely be aspects of both initially stretching of the web and/or deformation of the individual fibres. Thus from the tensile test data, for nanofibres that are broadly the same diameter, web ductility is likely to have the greatest correlation with the scission time. Note, the PMMA which by visual observation or by using turbidity measurements, showed that it could be scissioned into short fibres most rapidly was also the least ductile (although drawing this conclusion is made more complex because the PMMA has a slightly lower diameter as well). However, it should be noted that PAN fibres have an even smaller fibre diameter compared to the PS, and yet remain unbroken after a comparably longer sonication time. Thus in this work, simple variations in diameter do not explain the different behaviours observed. It therefore appears that materials that are sufficiently ductile and tough are able to resist the stresses imposed by the sonication process. We also note that although neither PAN nor PLLA were able to be scissioned well, PAN appeared to show some limited scissioning, as indicated by the greater turbidity measurement (Figure 4.11), which reflects the fact that more short fibres appeared in the solution as the sonication time was extended up to 35 min. We can see from Table 4.1 that PAN is a slightly more ductile than PLLA, which would be reasonable for reduced scission. However, the ductility between PAN and PLLA are (within error) the same, and the PAN fibre has a slightly lower diameter, and this could be a reason for its greater ability to be scissioned.

4.3.3 Mechanism of scission

A range of possible failure mechanisms have been discussed in the literature [22, 85, 88] for carbon nanotubes and are likely relevant to polymer nanofibres. It is possible that during sonication, the nanofibres are exposed to a range of forces upon bubble collapse, and the way these forces interact, deform or cause ultimate failure of the nanofibres depends on aspects such as the the material properties, as well as its length.

There are three main mechanism that can be adopted in nanofibre scission which are 1) tension failure [22, 85, 87] 2) buckling that leads to fracture [86, 87, 152] and 3) impact of jet from imploding bubbles [55, 89, 90]. In considering the tension and buckling mechanism, the calculation of critical tensional force for nanofibres to break-up (F_c) was adapted from Hennrich et al [22] and the critical compressive force for buckling (F_b) to occur was adapted from Pagani et al [87],

as shown in Equation 2.7 and 2.8, respectively (refer to Section 2.3.2.3). From these equations, the critical tensile force, compressive force and critical curvature are calculated, as shown in Table 4.2 and would determine the possibility of failure of nanofibres by these two mechanisms (tension and buckling).

 Table 4.2 Calculation of critical tensile force, compressive force and critical radius of curvature of electrospun nanofibres.

Material	Average	Tensile	Young	Critical	Critical	Critical radius
	fibre	strength,	Modulus,	tensile	compressive	of curvature in
	diameter	$*\sigma_{m}$	*E	force,	force, Fc	buckling mode,
	*(nm)	(Mpa)	(MPa)	$F_c(\mu$	$(pN, 10^{-12}N)$	$\xi_{c,crit}$ (μ m)
				N)		
PS	775	0.6	8	0.28	0.0242	5.0
PMMA	550	1.6	0.4	0.38	0.00030	0.1
PAN	635	2.5	12.2	0.80	0.0163	1.5
PLLA	771	1.6	11.1	0.75	0.03226	2.7

*experimental results as in Table 4.1

The four types of electrospun materials being used had very similar tensile strengths, and little variation in the fibre diameter. Therefore, approximately the same maximum tensile force, as shown in Table 4.2, was predicted to cause the fibres to fail. This would lead to the scissioning of all types of fibre web (different polymers), which was not found in this work. Therefore, tensile failure during the initial stage of sonication when the fibres are long was unlikely to be a mode of failure.

From Table 4.2, the critical value for compressive force for buckling to occur is very small $(10^{-14} \text{ to} 10^{-16} \text{ N})$, thus leading to some level of bending and buckling in all fibres. It can indeed be seen in Figure 4.9b and 4.9h, that for the PLLA and PAN fibres which do not fail, some degree of bending has occurred,

with the significant amounts of U-shapes and curls supporting this hypothesis. Even in the scissioned PS fibres (Figure 4.9d), where scissioning has been observed, some curvature of the fibres was evident with a radius of curvature ranging from ca. $5 - 15 \mu m$. This is observed to a lesser degree (but is nonetheless apparent) in scissioned PMMA nanofibres (Figure 4.9f). However, bending alone, although able to cause curling and deformation, is not the only, or indeed primary manner, in which these samples are reduced in length. This is because only when the radius of curvature falls below the critical radius of curvature,($\xi_{c,crit}$) will the nanofibes fail, which is very small and ranges from 0.1 µm for PMMA and 5.0 µm for PS (Table 4.2). Furthermore, it can be seen that the ends of the fibres that were scissioned (PMMA and PS) are not seen in Figure 4.10 to be particularly drawn to a tip. Likewise, the resultant scissioned fibres remain bent. It may be that the scissioned fibres, both prior to scissioning and following this event, may undergo bending/buckling, but this is not the cause of failure. Such polymeric materials probably require much higher curvature stresses to fail in this manner.

The electron micrographs in Figure 4.10 show that there is a some degree of pitting and erosion on the surface of the fibres which have been sonicated, compared to those prior to sonication. Samples which are tougher (have greater ductility), such as PAN and PLLA, would thus presumably be more resistive to erosive wear and/or to subsequent deformation of the fibres. This is evident in the surface roughness increment of the post-sonicated PLLA and PAN (Figure 4.10b and 4.10h) which is almost negligible compared to PS with the same sonication time of 60 s and 40 s sonication run time for PMMA. Extending the sonication run time to 35 min for PAN and PLLA only resulting in increment of surface roughness (Figure 4.10i and 4.10j) without scissioning effect. It may be that this is an important part of the mechanism by which these submicron diameter fibres fail. Microjetting resulting from an implosion of a bubble near solid surface (a nanofibre in this case) is able to erosively wear and roughen the surface and the fibres are more likely to fail by subsequent stresses at this weakened zone. Once the nanofibre web is broken, and shorter fibres are achieved, other failure mechanisms may be possible – either further bending or tensile drawing, as well as further pitting and failure, depending on fibre length.

Other mechanisms such as high temperatures resulting from compression of air within the collapsing bubbles are unlikely to occur, as large scale melting was not observed on any of the fibres in Figure 4.9 or Figure 4.10 of the sonicated cut or uncut samples, and this has also been discarded as an option by others [86, 88]

4.4 Summary

In summary, four types of polymers (PLLA, PMMA, PS and PAN) have been successfully electrospun, producing submicron electrospun nanofibres with diameters in the range of 600 to 800 nm. Manipulating the electrospinning parameters allowed the variation of fibre diameter, uniformity and surface morphology. In this chapter, we demonstrate that ultrasonication is a new and effective method to cause the scission of brittle submicron -diameter electrospun polymers such as PS and PMMA. In contrast, generating short fibres from more ductile electrospun polymers such as PAN and PLLA was more difficult. It is likely that there are various combinations of tensile, buckling and impact of jet mechanisms occurring at different times during the sonication process. In the initial sonication of electrospun nanofibre web, the buckling mechanism would lead to deformation (bending and curling) of the fibres, although it would not directly result in the break-up of the nanofibres. It is suggested that pitting and erosion from the microjet during bubble implosion is the primary mechanism for the break-up, with tensile failure dominates the scission mechanism only occurring when the fibre length is sufficiently short.

Chapter 5 - The Effect of Ultrasonication Processing Parameters and Posttreatment of Electrospun Fibres on the Scissioning Process

5.1 Introduction

It has been shown earlier in the thesis that electrospun fibres can be successfully scissioned using the ultrasonication method. It was found to be a process particularly suitable for brittle polymers such as PS and PMMA, whilst more ductile materials require further post-treatment to facilitate the scissioning process. The potential mechanisms involved in scissioning were also discussed and related to bubble cavitation and collapse caused by the ultrasonic probe. These mechanisms ranged from the effect of the impact of the jet resulting from imploding bubbles leading to erosion and pitting which would create point of weakness for crack initiation, to fibre buckling for long fibres that oriented parallel to the bubble surface during bubble growth leading to rotation and buckling of the fibres when the bubble collapsed. The shorter fibres that align normal to the bubble surface will experience a difference in velocity for both fibres' end when the bubble imploded (the highest velocity at the end nearest to the bubble wall compared to the farthest end) that results in tensile failure. There are a number of factors which can influence the cavitation (and thus the scission process), and investigations of these are reported in this chapter. They include processing parameters such as the effect of the type of solvent used during sonication, concentration of dissolve gas in the solvent, sonication amplitude, lapsed time, electrospun fibre orientation, fibre diameter, and processing temperature.

In this chapter, these parameters will be investigated, using either PMMA or PS non-woven webs (mainly PS). The latter part of the chapter investigates how post-treatment of the electrospun fibres can be used to encourage the scissioning of polymers such as PLLA and PAN webs, which proved particularly hard to scission. The post-treatments investigated include UV- Ozone treatment, physical ageing below the glass transition to densify the fibres and annealing above the glass transition temperature to relax the fibres. It is hoped that these methodologies, when applied to the nanofibres, will encourage scissioning.

5.2 Effect of sonication run time on ultrasonication of PS and PMMA electrospun fibre webs

Results of the sonication of PS and PMMA non-woven webs presented before in this work have proven that they can be scissioned in water in a relatively short time. In this section, the ultrasonication time was prolonged to investigate its effect on the resultant short fibre length on the webs of the above-named polymers. The experimental procedure used was as described in Section 3.3.3, where the ultrasonication process was maintained at the amplitude of 80 % and 2/2 lapsed ON/OFF time whilst the running time was varied from 40 s to 4 min. Figure 5.1 shows the difference between the average short fibre length for PS and PMMA for the minimum sonication time (40 s for PMMA and 1 min for PS) to 4 min.



Figure 5.1 The average short fibre length for PS and PMMA electrospun webs averaged from 3 different images and involved the quantification of approximately 50 fibres.

Figure 5.1 demonstrates that as the sonication times were increased, the PS nanofibre fibre length was reduced. The minimum sonication time of 1 min scissioned the web into short fibres with the average length of $15 \pm 7 \mu m$. As the sonication time was increased to 4 min, the short fibre length was reduced to about $6 \pm 3 \mu m$, the scissioned fibre length being inversely proportional to sonication time.

In contrast, it was found in the case of the PMMA electrospun fibres, the electrospun webs were scissioned to its final, achievable length after only 40 s. At this minimum sonication time, the average short fibre length was 10 μ m with a high standard deviation of ± 11 μ m. Increasing the sonication time to 1 min did not change the average short fibre length significantly but reduced the length deviation to ± 4 μ m. However, extending the sonication run time up to 4 min showed no further significant impact on the short fibre length, it remaining at some 10 ± 4 μ m.

This difference in behaviour between PS and PMMA may be due to the difference in mechanical properties, since PMMA is more brittle and thinner in diameter (E= 0.4± 0.1 MPa, ductility = 1.9 ± 0.8 %, diameter = 550 ± 160 nm) compared with PS (E= 8.0 ± 0.8 MPa, ductility = 16.8 ± 1.9 %, diameter = 775 ± 160 nm).

Further investigations on the effect of sonication were carried out using the PS web since the change in the average short fibre length is more pronounced, compared to PMMA which plateau out (Figure 5.1).

5.3 Ultrasonication of polystyrene nanofibres

In order to investigate the scissioning process in more depth, sonication of PS was carried out in water or ethanol using a range of experimental conditions. Factors investigated include: the initial fibre orientation, sonication time, sonication amplitude and lapsed time, the influence of the original nanofibre diameter, the influence of removing or introducing additional gas in the sonication medium to initiate/inhibit microbubble formation and the effect of the temperature of the sonication medium.

5.3.1 Effect of solvent on the ultrasonication of PS

To investigate the effect of the fluid medium on the ultrasonic scissioning of PS, two solvents were used – water (as usual) and ethanol. Both were chosen since they did not cause PS to swell. The ultrasonication was performed for run times of 1, 2, 3, 4 and 8 min with 2/2 lapsed ON/OFF time and 80 % amplitude. The minimum sonication time for both non-solvents is the same ca. 1 min. Figure 5.2 shows the SEM images of PS sonicated in water and ethanol for 1, 2 and 8 min, with the quantification of the short fibre length being presented in Figure 5.3.



Figure 5.2 Sonication of PS a-c) in water for 1, 2 and 8 min, respectively and d-f) in ethanol for 1,2 and 8 min respectively.



Figure 5.3 The average fibre length for PS in water and ethanol, as a function of sonication run time of 2 min to 8 min. The quantification at 1 min is not possible using SEM images due to the single fibres images being too long for PS in ethanol, whilst the SEM images of PS sonicated in ethanol for sonication run times of 4 min or greater was not sufficiently clear to allow determination of fibre length due to observed 'swelling/melting' of fibres, as shown in Figure 5.4b.

Figure 5.3 demonstrates that electrospun PS, when sonicated in either water or ethanol, is able to successfully shorten the fibres, although it is clear that for the same conditions sonication in water is able to produce shorter fibres than sonication in ethanol, where the average short fibre length is $4 \pm 2 \mu m$ and $6 \pm 5 \mu m$ at sonication run time of 2 min. Comparing behaviour with water, a more highly volatile solvent such as ethanol would cause vapour to enter the bubble during the collapse which may cushion the impact, in turn reducing the scission effect. However, after sonication run times of 2 min, the surface morphology of the short fibres produced by sonication in ethanol appear to be deformed (they appear to be curled, swollen and merged together), with this changes becoming

more obvious as the sonication time is increased, as can be seen in Figure 5.2e and 5.2f. This makes it very difficult to perform image analysis on the micrographs, as the edges of the fibres in SEM images become quite indistinct. This is why short fibre lengths can only be quantified for 2 and 3 min sonication run time in ethanol.

Higher magnification of SEM and TEM images of the short fibre sonicated in water and ethanol at sonication run time of 8 min can be seen in Figure 5.4.



Figure 5.4 SEM images of PS short fibres sonicated in a) water , b) ethanol, with higher magnification TEM images from the same samples sonicated in c,e) water and d,f) ethanol.

Figure 5.4a and 5.4c show the rough surface of the short fibres scissioned in water after 8 min of sonication run time. Although the short fibres are overlapping, the features of the fibre surface and edge can readily be observed. In contrast, for the same sonication run time in ethanol, the fibrous structure can barely be seen as some of the fibres have become swollen, apparently leading to gelation of the outer layer making the fibres appeared to be merged (Figure 5.4b and 5.4d). The free end of the scissioning process (Figure 5.4e and 5.4f) of the short fibres in both of these solvents shows a wavy end.

The swelling effect that resulted in deformation of the fibres likely occurs due to the ethanol diffusing in to the nanofibres [153]. When the ethanol diffused in the fibres, gelation commences from the outer layer of the fibres. This deformation appears to be irreversible, because when the short fibres have been dried and heat up to 60° C in vacuum oven prior imaging in SEM and the gelation behaviour still remains (note, this is not observed for fibres that have been dried by the same methodology, and which have been sonicated for reduced times).

To better understand the effect of bulk solvent temperature of the PS fibres in ethanol, the webs were immersed in ethanol in a beaker at 30°C and 60°C for 8 days and 8 min respectively and the SEM images of the study is shown in Figure 5.5.


Figure 5.5 SEM images of PS nanofibre web in ethanol (without sonication) at a,b) 30°C immersed for 8 days c,d) immersed at 60°C for 8 min.

Figure 5.5 shows that no swelling was observed for PS electrospun web immersed in ethanol with a bulk temperature of 30°C, whilst a small amount of localized swelling could be seen in PS in ethanol at 60°C (Figure 5.5d). Comparing these images with the sonicated PS in ethanol for 8 min (Figure 5.4b), a greater degree of swelling (alongside the scissioning of the fibres) was observed for the sonicated PS. This suggests that for a temperature as high as 60°C, ethanol would results in swelling of PS even without sonication. Note that in most of the work described above for sonication in both water and ethanol, the bulk temperature of the solvent was kept below 30°C using an ice-water slurry around the sonication vessel. Swelling of the fibres when sonicated in ethanol suggests that there exist localised hot spot (above 60°C) during sonication due to the bubble implosion that leads to this swelling.

5.3.2 Effect of electrospun fibre orientation

The influence of fibre orientation on the outcomes of ultrasonication processing was undertaken by doing comparative studies on random and aligned PS webs, the latter collected on a spinning mandrel with a surface velocity of 6.3 m/s. The sonication was performed in water at the amplitude of 80 %, 2/2 lapsed ON/OFF time at the run time of 1, 2, 3, 4 and 8 min. The visually-observed minimum sonication time for the two webs of differing levels of fibre alignment appeared broadly the same, ca. 1 min. The SEM images of the as-spun webs before and after sonication run time of 8 min with the quantification of the average fibre length for sonication run time of 2 min to 8 min were shown in Figure 5.6. Note that the quantification of average fibre length for a 1 min sonication run time was difficult from SEM images due to the length that was too great for measurement.



Figure 5.6 SEM images of the as-spun fibres and after a sonication time of 8 min respectively, a-b) aligned fibres, c-d) random fibres and e) average short fibre lengths from above SEM micrographs of sonicated, electrospun fibres for random and aligned orientations.

The SEM images, Figure 5.6a and 5.6c, show that regardless of orientation, both initial electrospun nanofibre diameters were approximately the same - 775 ± 160 nm and 732 ± 312 nm - for the random and aligned fibre webs, respectively. The sonication of webs consisting of fibres of both random and aligned fibres, processed for 1 min to 8 min resulted in electrospun webs being converted to discrete, short fibres. Sonication of the random webs led to longer, average fibre lengths and a higher standard deviation, compared to those produced from the aligned webs, where sonication at run time of 8 min produced fibres of length $6 \pm$ 2 μ m and 3 \pm 1 μ m, respectively. A statistical analysis (Independent T-test) highlighted that there is a significant difference (p < 0.05) in the fibre length between the aligned and random fibre webs for each sonication time (Figure 5.6e). In addition to the overall macroscopic alignment of the fibres, it should be noted that aligning the fibres in an electrospun webs also likely leads to a higher degree of molecular orientation of the polymer chains within those fibres, resulting in a greater strength and reduced elongation at break and ductility [154]. Reduction in ductility would particularly facilitate scission, as discussed above. In addition, the scission of random fibres may be more difficult due to a denser, entangled fibre network having reduced possibilities for bubble infusion and less possibility for flexing of the fibres.

Since the aligned PS webs produced a more uniform, shorter fibre length with a lower standard deviation, all future results presented below in this chapter were obtained using electrospun PS webs with aligned orientations.

5.3.3 Effect of sonication run time

The effect of sonication time was examined for aligned PS nanofibre webs produced on the rapidly rotating mandrel, with a surface velocity of 6.3 m/s. PS electrospun web was sonicated in water at 80 % amplitude, 2/2 lapsed ON/OFF time and varying the sonication run time from 1 min to 8 min. It was found that increasing the sonication run time resulted in shorter fibre lengths, as shown in Figure 5.7 (quantification was performed from t = 2 min onwards).



Figure 5.7 Average short fibre length for PS sonicated in water for run time of 2 min to 8 min.

The initial webs of ca. 1 cm^2 was readily broken into smaller pieces after 1 min of sonication, with longer sonication times resulting in shorter fibre lengths, a significant decrease occurring after 3 min, with even longer processing times showing a reduced effect on fibre length. This is likely due to the fact that the

microjets formed are not as effective at causing failure in the already-scissioned fibres, as they are more dispersed and it is statistically less likely that microjets will impinge on the surface of a fibre (unless that surface itself nucleates bubbles which do not move away from that surface before they collapse). In further support of a jetting mechanism as the mechanism for fibre scission, it is found that increasing the sonication time also caused an increased in surface roughness, as shown in Figure 5.8.



Figure 5.8 PS fibres surface morphology a) before-sonication b-f) after sonication in water for sonication run time of 1, 2, 3, 4 and 8 min respectively. Eroded and pitted surface of the fibres is more pronounced as the sonication run time is increased.

Figure 5.8 shows an erosion and pitting become more visible on the surface at sonication run time of 2 min onwards, especially in the case of sonication run times of 8 min (Figure 5.8f), with some of the short fibres severely eroded with multiple holes on its surface, due to impingement of high velocity microjets on the surface [56, 57]. This can also be observed in TEM micrographs (Figure 5.9) which show extensive pitting and indentations on the fibre surface after 8 min of sonication time. The indents evident in Figure 5.9 demonstrate that the microjets do not necessarily cause direct failure, but rather may be responsible for initiating failure and/or points of weakness and it may take several cavitation cycles – including the application of tensile forces on the fibres to cause complete fibre scission.



Figure 5.9 TEM images of PS sonicated in water for 8 min a) short nanofibres at lower magnification, b) indentations which are probably due to mirojetting and could act as weak points from which final failure of the short nanofibres is initiated.

5.3.4 Effect of amplitude

The amplitude refers to the distance of up and down movement of the probe tip and normally expressed in percentage,% of amplitude. Higher amplitude would means that higher electrical energy is delivered to the probe which is directly related to the energy delivered to the sample (comprised of the viscosity of sample including solvent and fibres), if the sonicator probe size and the depth of the probe immersed in the sample are kept constant. Thus, the greater the resistance to the movement of the probe due to higher viscosity samples and the deeper immersion of the probe into the sample, then, the greater the amount of energy required by the probe to reach the specified amplitude [155]. The effect of ultrasonication amplitude of the polystyrene electrospun fibre web was carried in water for a run time of 3 min and 2/2 lapsed ON/OFF time, with the amplitude varied from 40 % to 80 %. As much as possible, parameters that could contribute to the amount of energy to the probe were maintained constant. It was ensured, for example, that the amount of water and electrospun fibre was the same and that the position of the probe (how much it immersed in water) and the cleaning of the probe prior to usage (to reduce the amount of debris that might contribute to the bubble nucleation effect) were kept the same.

During the experiment, it was observed that at 40 % amplitude, the electrospun web did not fully break-up. For that reason, the ultrasonication was only performed at amplitudes above 50%. The quantification of the short fibre length from three different SEM images for the sonication run time of 3 min at amplitude of 50 % to 80 % is shown in Figure 5.10.



Figure 5.10 The effect of changing the amplitude of the sonication probe on the average short fibre length for a sonication run time of 3 min.

From Figure 5.10, no significant changes to the short fibre length are observed for the amplitudes of 60 % to 80 %, although the standard deviation for the short fibre of the 80 % amplitude is lower compared to the other amplitudes whilst longer short fibre length was produced at 50 % amplitude. It was also visually observed that if the amplitude was reduced to 40 %, no scissioning was possible, even after 3 min of sonication run time. This therefore suggests that the minimum amplitude for scissioning the PS electrospun fibre for 3 min sonication time is 50 %.

5.3.5 Effect of lapsed time

The lapsed time with regards the sonication process refers to the length of time the probe operates in the ON state. An OFF period occurs between the ON times and is included to let the heat generated dissipate to the surrounding solvent, thus allowing maintenance of a broadly constant temperature. During the lapsed ON time, the bubble will expand and implode violently [50, 156]. Sometimes, larger bubbles may not be able to fully collapse, which will reduce the energy produce during the implosion. The 'OFF' time thus represents an opportunity for the bubbles to coalesce and those bubbles that formed during 'ON' time to implode. When the probe is switched 'ON' once more, new bubbles will be produce, expand and implode. The effect of the lapsed time was varied; 0 lapsed time, 2/2 (2 s ON and 2 s OFF), 2/6 and 5/5, whilst the amplitude and run time were kept constant at 80 % and 3 min, respectively. A sonication time of 3 min was chosen to allow the nanofibres to be scissioned completely. Before the start of the experiment, the temperature of the sample (water in the vial) was cooled until it reached 5° C. The final temperature was measured manually immediately after sonication was completed. SEM images of the short fibres at a different lapsed times are shown in Figure 5.11, with the corresponding average short fibre length presented in Figure 5.12.



Figure 5.11 SEM images of PS short fibres at different lapsed ON/OFF time a,b) zero lapsed time, c,d) 2/2, e,f) 2/6, g,h) 5/5. ON time refers to the duration of the probe in the ON state before it is switched off for a period (OFF time), over the whole period of the set run time.



Figure 5.12 Effect of lapsed ON/OFF time on the a) average short fibre length and b) final bulk water temperature.

Figure 5.11 shows that the SEM images of zero lapsed time have a significantly longer fibre length (the quantification shown in Figure 5.12). The surface morphology for the short fibre with a longer lapsed ON time of 5 s showed greater surface roughening due to sonication, compared with a short lapsed ON time, the latter presenting significantly less damage to the fibre surface. The average short fibre length, with their different final temperatures, for different lapsed ON/OFF times shown in Figure 5.12, demonstrate that without an OFF time included in the setting, the short fibre length is significantly longer and has a broader length distribution, the average and distribution being some $9.3 \pm 5.0 \,\mu\text{m}$,

when compared with other settings. Without an OFF time between sonication mode (zero lapsed time), the sonicator runs continuously, leading to a high final temperature due to the heat not having sufficient time to dissipate to the surroundings (Figure 5.12b). This can also be observed for longer lapsed ON times of 5 s, although the final temperature here is slightly lower than for no OFF times. The reduction in the final temperature would be due to the 5 s OFF time, since during this time period, the generation of new bubbles ceases and the solution cools. However, the final temperature still remains high, compared to the 2/2 and 2/6 lapsed time, due to a long ON time. This demonstrates that the ON time is clearly a greater determinant of final solution temperature compared with the OFF (lapsed) time. In the case of the 2/2 and 2/6 lapsed time sequences, there is little difference in temperature and short fibre length, demonstrating that 2 s ON time requires only a 2 s OFF time to allow sufficient cooling due to heat dissipation. Extending the OFF time to 6 s for these shorter ON times did not significantly lower the final temperature, or decrease the short fibre length.

5.3.6 Effect of initial fibre diameter

To investigate the influence of fibre diameter on scission events, aligned PS webs with an average fibre diameter of 240 ± 70 nm, 730 ± 310 nm and 930 ± 290 nm, were electrospun. This variation in diameter was obtained by increasing the electrospining polymer concentrations from 8 wt/v% to 16 wt/v%, with the more concentrated polymer solutions producing nanofibres of greater diameter.

The electrospun fibres were sonicated at 80 % amplitude, 2/2 lapsed ON/OFF time, and the sonication run time was varied from 1 min to 8 min. The minimum sonication time for all the electrospun PS with these different initial diameters was found to be the same i.e 1 min. The short fibres lengths were quantified for the sonication run time of 2 min onwards, as shown in Figure 5.13.



Figure 5.13 a) Effect of sonication on PS fibre at different initial fibre diameters and b-d) SEM images of polystyrene prior to sonication for different concentrations of 8 wt/v%, 12 wt/v% and 16 wt/v % respectively.

Figure 5.13 indicates that large fibre diameter samples were reduced in length to a lesser degree, for all sonication times. In particular, at very short sonication times (2 min), the fibres with the greatest diameter were significantly greater in length (albeit with a greater size distribution). The webs with the largest diameter fibres

(930 ± 290 nm) resulted in longer scissioned fibres, compared to the other two webs for each of the sonication times, as determined using ANOVA analysis, with p<0.05. No significant difference in terms of the short fibre length was observed between webs with fibres of diameter 730±310 nm and 240 ±70 nm webs (p>0.05).

Given that, in an approximate sense, all of the PS fibres of different diameter have similar ductility and strength, the force required for failure during bubble collapse is greater for the thicker fibre. Equation 2.7 indicates that the force required to break the fibre would be proportional to the fibre diameter. Assuming the tensile strength for all the fibre webs is the same, the tensile force required to break the fibre as a function of diameter (from the largest to smallest diameter) should be greater than 300 nN, 200 nN and 30 nN, respectively (Equation 2.7). However, as mentioned above, fibre scission is not due to tensile forces alone. Failure may arise due to other modes of deformation, including from the impact of jetting and being exposed to a buckling deformation. If it is assumed that the erosive depth caused by an impinging jet is the same for all fibres, this represents a reduced relative penetration of those fibres with a larger diameter, and the strain generated by collapsing bubbles may likely be insufficient to cause the impinged, thicker fibre to fail, and thus the length of scissioned, thicker fibres could be expected to be slightly greater. This must be balanced with the larger diameter fibres (with greater surface area) presumably having a greater statistical likelihood of bubbles becoming attached to their surface.

Note that this discussion also makes the assumption that the molecular morphology, including the chain orientation, between different diameter fibre samples is the same, which may not be the case. However, if molecular orientation was the important factor, one may expect that the chains in the thicker fibres to be less oriented and thus show more ductile behaviour on deformation. This would also contribute to the outcome that fibres with greater diameter are more ductile, harder to scission and result in longer scissioned fibres. It is not clear at this point which of the above possibilities is the most influential.

5.3.7 Effect of bubble nucleation due to different types of gas dissolved in the solvent

Previous studies on carbon nanotubes have suggested that most sonication effects are due to bubble cavitation behaviour [90, 157] and thus modifying the cavitation properties of the solution should also influence the scission events. One of factors that influence cavitation is the presence and/or concentration of dissolved gases in the solvent. The effect of degassing equilibrated water, and the incorporation of additional helium to the degassed sample for PS sonicated in water, is shown in Figure 5.14.



Figure 5.14 Effect of degassing on the nanofibre length after sonication of the water sonication medium (\Box), and the effect of the introduction of helium (\circ) into the water,. A control experiment (Δ) was carried out with water equilibrated at room temperature and pressure, whilst the degassed sample (Vac) was achieved by degassing water in vacuum oven for 12 hr.

For shorter sonication times (less than 4 min) degassing of the water increased the resultant fibre length, compared to sonication in water with equilibrium concentrations of dissolved air (control) or water with additional helium added, with the latter two showing no significant difference (p>0.05) in the final length of the scissioned fibres. Whilst dissolved gases can act as nucleating sites, they can also diffuse into the growing bubble and cushion the collapse of the bubble [51], reducing its potential impact on fibre deformation. However, the use of helium, which is less soluble in water than air, would reduce this cushioning effect, and yet still ensure availability of gas for nucleation. Conversely, degassing the water should theoretically reduce the bubble nucleating sites,

resulting in less cavitation (and thus fibre scission). However, in this instance there would also be less gas that can diffuse into the bubbles and thus the severity of any collapse of bubbles formed would be greater, with the balance of these properties related to the gas type.

In previous work by others, the effects of sonication on single polymer chains in solution have been found to be enhanced for systems saturated with monatomic gas (such as Ar and He) where cavitation is easier, compared to diatomic gases (O₂, H₂, N₂ and air) and polyatomic gases (eg CO₂) [49, 51]. The different behaviour is due to differences in specific heat capacity ratio of the monatomic gases, which are higher compared to diatomic and polyatomic gases. The specific heat ratio influences the maximum heat and maximum pressure of the bubble implosion sites, thereby affecting the sonochemical process. Equations 2.1 and 2.2 show the relationship of the ratio of specific heat with the maximum pressure and temperature, indicating that the greater the specific heat, the greater the pressure and thus the more energy released to the surrounding upon implosion, directly leading to a greater sonochemical effect [63, 158]. This indicates that sonication in water equilibrated with helium (monatomic gas) which has a lower solubility and higher specific heat ratio compared to air (diatomic gas) would produce a greater cavitation effect, due to greater bubble nucleation and subsequent bubble collapse, leading to a greater scission rate.

However, the findings in this work show that scission of the PS nanofibres is not greatly affected by the type of dissolved gas. The gas, regardless of type, appears to act as a nucleation site for bubbles leading to collapse and the formation of microjets, explaining the rapid shortening of fibres compared to the degassed sample. This effect appears to dominate the two possible mechanisms (nucleation vs. cushioning), with the role of gas in the cushioning effect of collapsing bubbles appearing to be less. As sonication time increases (more than 3 min), the average fibre length for all conditions becomes statistically the same, attributable to equilibrium amounts of air becoming entrained in the initially-evacuated sample at longer sonication times.

5.3.8 Effect of temperature on scission of PS nanofibre by sonication in water

The effect of temperature was investigated by comparing low temperature sonication (initial temperature of about 5°C, achieved by cooling the vessel with an ice-water slurry) to that of an ice pack cooling vessel only, which resulted in high temperature processing of about 25°C (initial temperature) and up to 90°C (final temperature). The study on the effect of temperature processing was performed for the run time of 1 min to 8 min with 80 % amplitude and 2/2 lapsed ON/OFF time. The sonication starts when the water initial temperature was 5°C (for low temperature processing study) and about 25°C for high temperature processing. The water temperature was manually measured immediately after the sonication process (final temperature), and the results shown in Figure 5.15.



Figure 5.15 The effect of sonication process in water for high temperature (HT, Δ) and low temperature processing (LT, \bullet) a) final water temperature as function of sonication time b) average short fibre length as a function of length of the sonication process c) average fibre length as a function of energy.

The recorded temperature (Figure 5.15a) for both samples after sonication for various times indicates that the maximum, final temperature of the low temperature sonication process was approximately 30°C, whilst high temperature processing (using an ice pack only) was in the range of 70°C to 90°C. Although the temperature of processing is different, the post sonication short fibre length

remained statistically the same (Figure 5.15b). It has been found previously that when the temperature of the sonication media was lower, cavitation processes increased, leading to a greater extent of the sonochemical reaction [64]. This phenomenon is related to solvent properties such as viscosity and vapour pressure. A lower temperature, and thus a higher solvent viscosity, will lead to greater cohesive forces between solvent molecules which will increase the threshold of cavitation, thereby making scission more difficult [158]. If sufficient energy were delivered to overcome these forces and cause cavitation, upon the bubbles ultimate collapse, the hydrodynamic shear force exerted on the fibres would be greater [64, 159]. It has been reported that when sonication is used to scission individual polymer chains, the solvent viscosity must usually be optimised to ensure the shear force between the solvent molecule is sufficient to cause the breakage of chemical bonds [65], showing that a viscosity that is too high or low is undesirable for effective cavitation (and thus scission). In addition, the higher viscosity makes displacement more difficult, leading to higher energy inputs recorded for lower temperature processing (Figure 5.15c).

Any increase in temperature would lead to an increase in vapour pressure, encouraging more vapour entering the cavitation bubble and cushioning its implosion [64]. However, we did not observe such differences, probably because the difference in materials that were sonicated (electrospun fibre as in our work vs polymer solutions) and the range of the temperature differences that could be achieved with our experimental set up was not sufficiently large to cause a significant influence on cavitation, when compared to work from others who varied the temperature from -10° C to 61° C [160].

5.3.9 Characterisation via Fourier Transform Infrared spectroscopy (FTIR) and Differential Scanning Calorimetry (DSC)

Both infrared spectroscopy and thermal calorimetry were used to determine if any molecular changes to the polymers bulk and surface properties occurred due to the scissioning process. The FTIR spectra shown in Figure 5.16a demonstrate that there is no chemical change of the bulk sonicated electrospun PS fibres in water, where it can be seen that the absorption bands peaks for all conditions are similar to those of neat PS.



Figure 5.16 Comparison between the chemical and physical properties of PS as received, electrospun fibre and sonicated short fibre in water a) FTIR spectra and b) DSC results, showing the glass transition temperature, T_g

There was also no change in the glass transition temperature (approximately 100° C) as a result of the process, although the region was found to be broader for

the sonicated sample. This may be due to some mild plasticisation of the PS with water. Therefore, it appears the sonication process does not adversely affect the chemical structure or physical properties of the electrospun polystyrene nanofibers, as judged by these two techniques.

5.4 Effect of electrospun web post-treatment on ultrasonication

From previous chapter, it was noted that ductility is one of the factors that most determine whether scission of the nanofiber web by sonication is possible. The ductile polymers in this study, PLLA and PAN, were not able to be scissioned after sonication run times as long as 35 min. For this reason, post-treatment of the electrospun web may be required so that intrinsically ductile fibres can be scissioned. The method that chosen for this work was UV irradiation, in combination with ozone treatment, using a UV Ozone ProcleanerTM UV PC 220 device. This apparatus provides UV irradiation using a mercury lamp at 254 nm wavelength and ozone gas excitation exposure. UV-Ozone treatments are widely used for removing organic contamination, such as from silicon wafers, and can also be used to counteract low wettability and hydrophobicity of organic materials through the introduction of polar groups [161, 162]. UV irradiation also has been shown to lower the mechanical properties of some polymers by itself causing some individual molecular chain scissioning [161].

5.4.1 UV-Ozone treatment of PLLA and PAN fibres

Both PLLA and PAN electrospun webs were irradiated for 12 min using the UV-Ozone device with the intensity of 14.75 mW/cm² at a distance of approximately 1 cm. SEM images in Figure 5.17 show the irradiated PLLA and PAN webs prior to sonication, at different magnification.



Figure 5.17 SEM images of UV-Ozone irradiated electrospun webs at different magnification a,b) PLLA, c,d) PAN

Figure 5.17 shows that the UV-Ozone treatment has changed the surface morphology of PLLA electrospun webs, where etching on the fibres surface can be observed. In contrast, the PAN electrospun webs surface morphology remains the same as for the untreated webs. The effect of UV-Ozone irradiation depends on the chemical nature of the polymer and the UV wavelength and it has been reported that the carbonyl group (C=O) bond can be cleaved at the wavelength of

225 nm [161], whilst the UV-Ozone cleaner used in this work has a wavelength of about 254 nm. In contrast, homolysis of alkane (C=C) PAN fibres occurs at the wavelengths greater than 300 nm, an indication that the UV wavelength that was used in this experiment is not sufficient to cause chain scission.

Tensile testing of the UV-Ozone irradiated and untreated electrospun PAN and PLLA was performed to study the effect of UV-Ozone on the mechanical properties. Figure 5.18 shows the stress-strain curves of the untreated and UV-Ozone irradiated electrospun webs, and a summary of these mechanical properties is presented in Table 5.1.



Figure 5.18 Stress strain curve of the untreated and UV-Ozone irradiated PAN and PLLA.

	Elastic Modulus,	Tensile strength, σ	Elongation at
Material			
	E (GPa)	(MPa)	break (%)
PLLA (untreated)	11.1 ± 2.6	1.6 ± 0.2	79.2 ± 17.9
PLLA (UV-Ozone	15.4 ± 2.8	1.2 ± 0.3	56.1 ± 16.9
,			
irradiated)			
·····			
PAN (untreated)	12.2 ± 7.7	2.5 ± 0.1	86.3 ± 22.3
PAN (UV irradiated)	21.7 ± 6.9	3.2 ± 0.3	50.2 ± 13.5
````			

Table 5.1 Mechanical properties of the untreated and UV-Ozone irradiatedelectrospun PLLA and PAN.

It can be seen from Figure 5.18 and Table 5.1 that the UV-Ozone treatment increased the elastic modulus of both electrospun PLLA and PAN webs by some 39 % and 78 %, respectively. The tensile strength of PAN webs increased by 29 % and showed a reduction in ductility of about 40 %. However, for PLLA both the tensile strength and ductility decreased by 23 % and 30 %, respectively. It has previously been reported that the effect of UV irradiation varies depending on the polymer exposed [163]. The effect of UV irradiation on polymers includes discoloration, scission of the main chain, photoinduced crystallisation and crosslinking [161, 163, 164]. The UV-Ozone treatment of PLLA is also likely to degrade the PLLA macromolecules, as it reduces its strength and the elongation to failure, initiating the degradation of polymer molecules and reducing the molecular weight [162]. This could occur at either the surface (since the introduction of surface flaws through exposure would change mechanical

properties), as well as within the bulk. Any increase in modulus observed could be due to some limited crosslinking. Most importantly, it can be seen from these results that the UV-Ozone treatment leads to a decrease in ductility, resulting in the desired electrospun fibre embrittlement.

The effect of UV-Ozone treatment on a subsequent ultrasonication process involved performing ultrasonication on both irradiated PLLA and PAN electrospun webs. Both were sonicated in water at 2/2 lapsed ON/OFF time and 80 % amplitude. The minimum sonication time was taken, as before, to be the minimum time where significant fibre break-up could be visually observed. It was found to be 29 min for PLLA and 18 min for PAN. The untreated electrospun webs for PLLA and PAN were also sonicated at the same time (minimum sonication time for irradiated webs) for comparative purposes. The SEM images of the sonicated webs can be seen in Figure 5.19.

The PLLA and PAN webs (Section 4.3), which previously could not produce short fibres post sonication, were now able to be fragmented into short fibres of  $5.2 \pm 5.4 \,\mu\text{m}$  in length and  $10.6 \pm 5.1 \,\mu\text{m}$  (Figure 5.19) after 29 min and 18 min of sonication, respectively. Note that this still required a significantly longer scission time compared to PS and PMMA. As observed previously with the untreated PLLA webs, the surface of sonicated fibres that were subjected to UV-Ozone treatment had a rougher, pitted surface compared with the presonicated sample (Figure 4.10a (as-spun) and Figure 5.17b (as-spun UV-Ozone irradiated), but this change was not as significant as for the untreated sample following sonication (Figure 5.19b). This surface morphology change is also observed in sonicated untreated PAN (Figure 5.19f), when compared with sonicated UV-Ozone treated PAN (Figure 5.19h). This supports the hypothesis that ductility and toughness represent the most important mechanical properties of the electrospun nanofibres in terms of the ability of sonication to cause scissioning. It is most likely that it is the manifestation of this toughness, which is reduced due to pitting and tensile and bending deformations, that lead to the final failure.



Figure 5.19 SEM images of sonicated a,b) as-spun PLLA t= 29 min, , c,d) UV-Ozone irradiated PLLA t= 29 min, e,f) as-spun PAN, t = 18 min and g,h) UV-Ozone irradiated PAN, t = 18 min.

The chemical characterisation of the untreated, pre and post sonication UV-Ozone irradiated webs were performed using reflection mode by Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR) with the spectra as shown in Figure 5.20.



Figure 5.20 ATR -FTIR spectrum for as received, as-spun, as-spun with UV-Ozone treatment and sonicated PLLA (UV-Ozone treated web) in water.

It was observed that the as-received PLLA, UV-Ozone treated electrospun PLLA and sonicated UV treated webs show a similar asymmetric and symmetric bending vibration of methyl groups at 1456 and 1383 cm⁻¹ with ester linkages appeared at 1747, 1180, 1126 cm⁻¹ corresponding to C=O, C-O-C and O-C-C vibration for all types of PLLA sample. However, the as-spun PLLA webs showed a new band of methyl group at 2973 cm⁻¹, whilst for other conditions, only asymmetric and symmetric stretching vibration of methyl group at 2997 and 2947 cm⁻¹ were seen. This new peak was probably due to the solvent residue of chloroform, CHCl₃. It was noted that chloroform has a peak at 2976 cm⁻¹ which appeared in the as-spun spectrum. After UV-Ozone treatment this peak disappears, likely due to removal of the residual solvent during UV-Ozone exposure.

The ATR-FTIR spectra of the PAN fibre before and after UV-Ozone treatment are shown in Figure 5.21.



Figure 5.21 ATR-FTIR Spectra of PAN as received, as-spun, as-spun with UV-Ozone irradiation and sonicated PAN (UV-Ozone treated web) in water

Figure 5.21 shows that the as received and sonicated electrospun webs PAN have a similar peak ,where the methylene group stretching vibrations appear at 2923

and 2867 cm⁻¹. The strong peak at 2240 cm⁻¹ is the characteristic vibration of the nitrile group (-CN). The stretching vibrations of carbon-carbon double bonds are shown at 1660 and 1630 cm⁻¹. The peaks at 1452 cm⁻¹ and 1361 cm⁻¹ are assigned to the bending vibrations of methylene and methane group, respectively. The 1253 cm⁻¹ peak is due to vibration of methane group. However, there is an additional weak band at 2356 cm⁻¹ and 2321 cm⁻¹ appearing in the as-spun and asspun (UV-Ozone) treated webs spectra which is due to CO₂ (could be originated from environment and contaminant) and can be neglected. UV-Ozone irradiation for both PLLA and PAN thus did not seem to change the chemical structure of the surface and bulk polymer.

## **5.4.2** Effect of heat treatment

The effect of heat treatment study was conducted using PS which scissions readily, and PLLA which is difficult to scission by sonication. Three types of heat treatment were undertaken, all of them targeting a different effect and change in property. They were: ageing below  $T_g$  to improve densification (for both amorphous PS and semi-crystalline PLLA), annealing nanofiber webs above  $T_g$  to reduce built in stresses (for amorphous PS only), and annealing between the glass transition temperature and the melting point to increase crystallinity (for semicrystalline PLLA only). The physical ageing of polymers (densification) is considered to be a reversible change of polymers in which the packing of the polymer chains is improved as the non-equilibrium glassy state bare driven towards greater equilibrium. It occurs due to physical changes, without chemical modification of the structure [126]. The optimal ageing temperature which must be below the glass transition is usually some 5°C to 25°C below  $T_g$  [126, 128-130]. Due to reduced chain mobility, a decrease in ductility results, thus assisting the ultrasonication scission.

Conversely, annealing above  $T_g$  was also performed for PS which is intended to reduce the built up stresses that would likely exist within the fibres as they are rapidly electrospun and formed by evaporation of the solvent. To achieve this stress relaxation effect in PS, the web was heated in a vacuum oven  $10^{\circ}$ C above  $T_g$ .

Recrystallisation of PLLA was performed to increase the crystallinity of the electrospun web because the degree of crystallinity would affect the structure and mechanical properties of polymers. This is achieved by annealing the sample in the cold crystallisation region which is discussed in the next section.

### 5.4.2.1 Polystyrene

Physical ageing of PS nanofibers was undertaken by ageing at a temperature below its glass transition temperature, which first had to be determined. A DSC scan was used to determine the  $T_g$  of PS, using the mid-point of the step change in heat capacity. The ageing temperature must be less than this

value to densify the sample. The glass transition temperature,  $T_g$  was found to be 103°C (ca 100°C), and thus a range of ageing temperatures were used from 75°C to 90°C in steps of 5°C - 10°C for 12 hr to investigate the best ageing temperature for PS. The best ageing temperature can be determined from the greatest amount of excess enthalpy overshoot which obtained directly from DSC. This overshoot area is a measure of the densification that occurs during ageing. The experimental procedure for sample preparation was described in Section 3.3.2.2.

The DSC thermograms are shown in Figure 5.22 and the effect of the ageing temperature on the thermal enthalpy, in particular the overshoot, can be clearly seen.



Figure 5.22 Effect of ageing temperature on thermal enthalpy overshoot (the value in the bracket shows the excess enthalpy of the overshoot from DSC).

From the Figure 5.22, it can be seen that the different ageing temperatures lead to a range of excess enthalpy overshoots. The unaged curve shows a slight endothermic annealing peak due to a small degree of relaxation which occurs during cooling and heating. The height, area and temperature of the endothermic peak of the isothermal ageing is greatest at 85°C which is about 15°C below  $T_g$ (100°C) with the excess of enthalpy overshoot of 4.2 J/g. The enthalpy was lowest at 75°C and 95°C, where at this temperature only small changes in structural relaxation took place. Ageing at temperatures very close to  $T_g$  would mean that only a short time is required to reach equilibrium and densification is not great, whilst at a very low temperature (greater than 25°C below the glass transition), the equilibrium state would require a longer time to reach equilibrium, thus in both cases, a small change in enthalpy is recorded.

Thus, in this work 85°C was chosen for the ageing temperature, with the effect of ageing time being investigated by varying it from 3 hr to 14 hr. The DSC scan of the endothermic curve for the respective ageing times is shown in Figure 5.23.



Figure 5.23 The effect of ageing time on enthalpy change for samples aged at 85°C (the value in the bracket shows the excess enthalpy at the overshoot obtained from DSC).

It can be seen that the best ageing time is 12 hr and 14 hr, where the excess of enthalpy is highest at follows by 7, 4 and 3 hr. A low enthalpy changes reflects that the densification process is less, with longer ageing times increasing the amount of densification. From this results, three ageing time were selected based on the greatest, medium and low ageing enthalpies, which were 14, 7 and 3 hr respectively.

The surface morphology of the electrospun fibre aged at 85°C for 14, 7 and 3 hr were examined using SEM (Figure 5.24), and no difference in the morphology could be observed between pre and post-aged fibres, where the fibres
appears to be similarly wrinkled and rough, as observed earlier in the unaged sample.



Figure 5.24 SEM images of PS a) unaged and aged fibres at 85°C for b) 14 hr, c) 7 hr and d) 3 hr

The other heat treatment performed for PS is annealing above  $T_g$ . For this study, the annealing temperature used was 110°C which is about 10°C above  $T_g$  (ca 100°C). The annealing process is meant for stress relaxation of the chain that would affect the mechanical properties of PS.

The annealing of PS as-spun fibre above the glass transition temperature to reduce inbuilt stresses after electrospinning was performed at  $110^{\circ}$ C for 10 min, 30 min and 60 min and the SEM images of the annealed samples can be seen in Figure 5.25.



Figure 5.25 SEM images of electrospun PS annealed above  $T_g$  at 110°C for a,d) 10 min, b,e) 30 min and c,f) 60 min

Annealing above  $T_g$  was found to lead to a smoother fibre surface, where the wrinkling in the fibres appeared to be reduced. This is in agreement with the work by Pai et al [151] where annealing at 110°C for 2 hr was found to smoothen the PS microfibres surface due to the molecules have sufficient mobility to rearrange and result in reduced surface energy. However, in our study, the fibres also seemed to have been locally "melted" to the degree where the fibres become fused to neighbours, this effect becoming more pronounced as the annealing time was increased to 30 min and 60 min. The densification of the electrospun web itself (the distance between fibres appeared to be reduced, not to be confused with the densification of the individual fibres by annealing samples below the glass transition, as described in the preceding paragraphs) also occurs after annealing at prolonged time (30 min and 60 min). After 60 min of above- $T_g$  annealing, the

SEM images indicate that plasticisation and densification of the fibres is more obvious as shown n Figure 5.25c and 5.25f.

The mechanical testing of all of the heat-treated electrospun fibres (by physical ageing below  $T_g$ , or annealing above  $T_g$ ) was undertaken to determine the elastic modulus, tensile strength and ductility of the webs at a deformation rate of 5 mm/min. The results of these tests are presented in Figure 5.26 and 5.27.



Figure 5.26 Stress-strain curve of the various heat treated electrospun PS – either aged at 85°C below  $T_g$ , or annealed and relaxed at 110°C above  $T_g$ .



Figure 5.27 Tensile properties of heat treated electrospun PS , A) control, B) aged 85°C for 14 hr, C) aged 85°C for 7 hr, D) aged 85°C for 3 hr, E) annealed at 110°C for 10 min, F) annealed at 110°C for 30 min, G) annealed at 110°C for 60 min.

In general, Figure 5.26 and 5.27 show that ageing and annealing leads to different effects on the mechanical properties. Both heat treatments result in a decrease in ductility, with a greater reduction in ductility resulting from the process of annealing above the glass transition temperature. Ageing below  $T_g$  causes no significant difference to the elastic modulus but does lead to a reduction in tensile strength. In contrast, both elastic modulus and tensile strength is higher when the webs were annealed above  $T_g$ .

A longer ageing time (14 hr) which led to the greatest highest excess of enthalpy overshoot leads to the greatest reduction in both tensile strength and ductility, compared to the untreated webs which are at  $0.25 \pm 0.13$  MPa and 9.75

 $\pm$  0.5 %. The ageing of the samples for only 3 and 7 hr led to a lesser reduction of ductility of about 6 % and 10 %, respectively.

Annealing the electrospun fibres above  $T_g$  show an increase of between 100 % to 400 % in the elastic modulus, and an increment in tensile strength with a reduction of ductility from 70 % to 80 %, in agreement to what has been observed in the literature where the annealed PS electrospun microfibres exhibit an increment of modulus and strength with a reduction in ductility compared to the as-spun fibre [151]. It was suggested the strength and modulus improvement of the web was due to the shrinkage of voids in the fibres leading to stronger and less ductile materials [151].

The effect of ageing and annealing on ultrasonication scission was performed by sonicating the electrospun webs for 10 s up to 240 s, and was carried out at time steps of 10 s until the minimum sonication time was determined. The average fibre lengths for the all treated and untreated samples are given in Figure 5.28.



Figure 5.28 Effect of PS heat treatment on ultrasonication scission. The quantification of the short fibres was undertaken by commencing at the minimum sonication time, 20 s for samples aged below  $T_g$  sample, and 60 s for the control and samples annealed above  $T_g$ .

From Figure 5.28, it can be seen that ageing below  $T_g$  (irrespective of ageing time) has reduced the minimum sonication time to 20 s, compared to the control sample where the minimum sonication time was 60 s. After the minimum sonication time was reached, the difference in the short fibre length is no longer significant. Ageing, which leads to a reduced ductility of the fibre, assisted scission during the sonication process. The sample aged to the greatest degree (14)

hr) had the shortest average fibre length at the minimum sonication time (20 s), compared to the other samples aged for 3 and 7 hr.

In contrast, annealing the fibres above  $T_g$  at 110°C for 10 min and 30 min did not affect the scission process during sonication, with the minimum scission time still 60 s, similar to the untreated fibre. Meanwhile, annealing above  $T_g$  for 60 min resulted in no scission even when the sonication time was extended for times up to 20 min. Although fibres annealed above the glass transition showed reduced ductility compared to those which had not been annealed, shorter scission times were not observed. It can be seen from the surface morphology that the annealed fibre webs appeared to be densified (fibres closer together) and in some cases fused with neighbouring fibres, this latter effect becoming more pronounce as the annealing time is increased. This surface morphology affects scission since in this case the fibres became thicker (bundling) resulting in more impact required to fail the sample with the ductility reduction has no effect on minimum sonication time. At the longest annealing time (60 min), the fibrous structure has not really been maintained and the as-spun webs almost form a film which cannot be readily scissioned. Note that even though the temperature of annealing is below what may usually be used to process these materials (such as by fibre extrusion or injection moulding), the high surface energy of the nanofibers (due to their curved surfaces) may help drive these materials to clump together or form films, to lower the amount of surface area, and thus surface energy.

#### 5.4.2.2 Poly-*L*-lactide Acid

A study on the effect of heat treatment on PLLA fibres was carried out by conducting a range of treatments such as physical ageing at below  $T_g$ (densification) and annealing at cold crystallisation temperature region (between  $T_g$  and  $T_m$ ) to encourage crystallisation.

For physical ageing below  $T_g$ , the DSC scan was done, and from the midpoint of the step change in heat capacity the  $T_g$  for PLLA was found to be 55°C. Heating at 15°C below  $T_g$  (40°C) was thus used to densify the fibres. Note that for PLLA, the ageing temperature was not optimised since the  $T_g$  for PLLA is quite low and it is difficult to maintain a temperature below 40°C using a normal vacuum oven. An ageing temperature of 40°C and an ageing time of 14 hr were thus used. The DSC thermograms of the as-spun and aged fibres can be seen in Figure 5.29.



Figure 5.29 DSC thermograms of as-spun and aged PLLA at 40°C for 14 hr.

Figure 5.29 shows that ageing of PLLA at 40°C for 14 hr resulted in the excess of the enthalpy overshoot to 2.1 J/g, compared with the unaged webs of 1.5 J/g, an increase of some 43 % and evidence that ageing and the sample for this time and temperature has effectively aged the sample.

A variation in the degree of crystallinity is another way in which a semicrystalline polymer such as PLLA can be manipulated to influence its structure and mechanical properties. Isothermal annealing at the cold crystallisation temperature of PLLA is a controlled method to increase the final degree of crystallinity of the polymer. A DSC heating scan was performed on as-spun PLLA to determine the initial percentage of crystallinity. From the DSC thermogram, the cold crystallisation temperature could also be seen to be around 75°C (Figure 5.30). Isothermal heating at this temperature for 15 min showed that the amorphous region has crystallised and thus the degree of crystallinity was increased. This is reflected in the second heating run curve, where the exothermic crystallisation curve is no longer apparent (Figure 5.30).



Figure 5.30 DSC curve showing the disappearance of cold crystallisation peak compared to as-spun spectrum when the fibre was reheated to 75°C for 15 min.

From Figure 5.30, the crystallinity of the PLLA can be determined by taking the difference between enthalpy at cold crystallisation and melting temperature and using Equation 3.1, the as-spun PLLA having a crystallinity of 34.2 % (with  $\Delta H_m$  = 51.2 J/g,  $\Delta H_c$ =19.7 J/g), with the annealed fibre at 75°C for 15 min possessing a crystallinity of 64.1 % ( $\Delta H_m$ = 60.08 J/g), some 30 % increase. Note that in this calculation, the enthalpy of 100 % crystalline PLLA was taken to be 93 J/g [165].

The SEM images of the heat-treated PLLA electrospun webs can be found in Figure 5.31.



Figure 5.31 SEM images of the heat treated PLLA ,a,b) aged at 40°C for 14 hr, c,d) annealed at 75°C for 15 min (recrystallised).

Figure 5.31 show that there is no obvious change in surface morphology of the heat-treated PLLA nanofibres, for the aged or recrystallised webs. Tensile testing of the electrospun webs was performed to study the effect of heat treatment on mechanical properties and the results are presented in Figure 5.32 and Figure 5.33 (note that the UV-Ozone treated PLLA results also shown in these figures for comparison purpose).



Figure 5.32 Stress strain curve of the heat-treated electrospun PLLA.



Figure 5.33 Effect of heat treatment on PLLA mechanical properties, A) asspun, B )aged at 40°C for 14 hr, C) annealed at 75°C for 15 min (recrystallised) and D)UV-Ozone irradiated.

Figure 5.32 and 5.33 show that ageing and annealing for recrystallisation leads to an increase in modulus and strength, with a reduction in ductility. The improvement in mechanical properties was more pronounced for the recrystallised sample annealed at  $75^{\circ}$ C for 15 min, where the tensile strength and modulus increased by some 130 % and 180 %, respectively, with a reduction in ductility of some 60 %.

The heat-treated electrospun PLLA webs were sonicated to investigate its effect on ultrasonication scission. Note that the as-spun PLLA was not able to be scissioned directly without UV-Ozone treatment. It was hoped that using the heat treatment method would facilitate the scission process, since the heat treatment involved here has a reduced likelihood of changing the chemical structure, as compared with UV-Ozone treatment. The heat treated, as-spun PLLA was sonicated until full break-up is observed. The SEM images of the sonicated fibre at the minimum sonication time can be seen in Figure 5.34.



Figure 5.34 SEM images of the sonicated heat treated electrospun fibre at the minimum sonication time from left to right, a) aged at 40  $^{\circ}$ C, t= 35min and b) crystallised at 75 $^{\circ}$ C, t= 35 min.

Clearly the heat treatment (either ageing or crystallisation) has successfully improved the ability of sonication to scission the PLLA nanofibres. The ductility of the aged and recrystallised webs is broadly similar, leading to the same minimum sonication time. It can be seen that both sonicated heat treatments resulted in short fibres that still consist of lengthy, curled short fibres, making it difficult to measure the length from SEM images.

Due to this complexity, the only comparison between the methods is made based on their ability to enable scissioning, and on the comparison of the minimum sonication time. The minimum sonication time for the heat-treated webs is slightly longer (35 min) compared to UV-Ozone irradiation treatment (29 min). Although the ductility of UV-Ozone irradiated web is very similar to that of the recrystallised and aged PLLA webs, it was found to be able to be scissioned faster due to the morphology of the fibre (etched surfaces) that contain many defects which contribute to the ease of scission.

## 5.5 Summary

This chapter discussed how ultrasonication processing parameters can influence the average length and surface morphology of the short fibres. It was found that webs comprised of smaller diameter fibres produced slightly reduced length fibres on sonication, likely due to the lower force being required to elongate the fibres to failure. Increasing the alignment of the fibres in the original web, achieved by increasing the rotation speed of the drum collector during electrospinning, also led to smaller fibres upon scissioning. This is probably because of the greater orientation of the polymer chains and reduced ductility within the fibres, as well as differences in the non-woven web morphology.

Other processing variables such as temperature and dissolved gas did not appear to significantly change the cavitation/scission process, and thus did not greatly influence the final length. It was found that the sonication process itself did not affect the chemical or physical structure of the fibres or their constituent polymers.

It was found that UV-Ozone irradiation and various heat treatments of the electrospun fibres could also be used to influence the ultrasonication scission process. This is particularly useful in the case of electrospun polymers such as PAN and PLLA which are intrinsically hard to scission. The ability to scission the webs can be related to the mechanical properties of the treated fibres, where a reduction in ductility of the sample or roughening of the surface made scissioning by sonication possible. However, care was necessary not to degrade or distort the webs too much, in order that the fibrous nature of the web was maintained. Heat treating the fibres for too long, for example, led to a compromise in web quality due to clumping of the fibres.

# **Chapter 6 - Production and Application of Carbonised Electrospun Poly(acrylonitrile) (PAN) Short Fibres in Composite Systems**

## 6.1 Introduction

One of the applications of short fibres, such as those produced by scission using sonication and discussed in this thesis, would be as additives in composite systems. The use of electrospun fibres in composite systems in the past has either involved the impregnation of the entire non-woven web in resin and reacting the matrix, or has used ball milling of the web to convert it into short fibres which are then mixed with the reactive resin. Short fibres scissioned from the web by ultrasonication thus provide a new method of producing discrete fibres with a nanoscale diameter to use in composites.

In this chapter we will present detailed studies involving the production of short poly(acrylonitrile) (PAN) fibres which can be electrospun and subsequently carbonised into potentially rigid, conducting fibres. There are two different ways in which this can be achieved, either by applying the scissioning before or after carbonisation. Regardless of the precise route by which these short fibres are made, they will be incorporated into epoxy resin in this work to determine if they can act as a reinforcing phase in that system. The challenge is to disperse such short nanofibres well, and this will be studied by varying the processing technique (including the use of surfactant) and characterising the final system in terms of its morphology and mechanical properties.

## 6.2 Carbonisation of polyacrylonitrile (PAN) short fibres

PAN is one of the most widely-used precursors for the production of carbon fibres due to a high carbon yield and good economic viability [96, 136]. Such carbon fibres are used in numerous applications such as membrane filters, electronic devices, and as composite reinforcement in polymers to improve mechanical properties and electrical conductivity [136].

To date, the incorporation of carbonised electrospun PAN into composites has been undertaken by milling the carbonised PAN, thereby converting it into short fibres prior to incorporation into resin [9]. To our knowledge, no research has been conducted to scission the electrospun PAN into short fibres *prior* to carbonisation process which would be beneficial in terms of reducing the effect of potential fusion of neighbouring fibres during carbonisation. Any process in which already-carbonised electrospun webs are milled would potentially induce damage on the fibre surface and may lead to a loss of the individual fibrous structure. In this work the use of ultrasonic scissioning of PAN *prior* carbonisation may prevent such fibre degradation.

Our previous work (as presented in Chapter 4 and 5) has shown that the electrospun web of some polymers can be directly scissioned using the ultrasonication method alone. We found that this method appeared to work best with brittle polymers, as compared to more ductile materials which required some post-treatment of the as-spun web to cause it to be weakened and be more susceptible to ultrasonic scissioning. The preliminary work on sonication of electrospun PAN shown earlier found that PAN is quite a ductile polymer, and UV-Ozone post-treatment on the PAN was required to encourage scission due to sonication. In this work we have investigated the effect of the scissioning of electrospun PAN webs *prior to* and *after* carbonisation.

## 6.2.1 Preparation of carbonised short electrospun PAN fibres

In this work, the carbonised short electrospun PAN fibres produced can be categorised into two which are "scissioned-carbonised" and "carbonised-scissioned" short electrospun PAN fibres, the two word descriptor indicating in a temporal sense the order that the materials were scissioned or carbonised i.e. scissioned-carbonised means the web was scissioned first and the resultant short fibres carbonised. "Carbonised-scissioned" means that the web was carbonised first and the carbonised web was scissioned"). Note that the scissioned-carbonised electrospun PAN fibres were prepared by sonicating the UV-Ozone treated web for 18 min (full break up) prior carbonisation. The carbonisation process was conducted in the tube furnace, and involved stabilisation and carbonisation stages, as discussed in Section 2.5. Stabilisation involved a heat treatment of electrospun PAN up to 280°C in air (oxygen), holding it at 280°C for 1 hr to allow oxidation taken place, whilst carbonisation was performed from 280°C to 1200°C in high purity argon, with both stages were conducted using a heating rate of 2°C/min. The details of the preparation of the samples can be found in Section 3.3.4. The images of the

physical electrospun PAN web and the dried UV-Ozone treated short electrospun PAN fibre before and after carbonisation can be seen in Figure 6.1.



Figure 6.1 a) Electrospun PAN before carbonisation b) Electrospun PAN after carbonisation, c) dried UV-Ozone treated short electrospun PAN fibre before carbonisation d) UV-Ozone treated short electrospun PAN fibre after carbonisation, in alumina crucible showing the white color of electrospun PAN changing to black, carbonised PAN with shrinkage and densification of the webs also observed.

Figure 6.1 shows that the originally white electrospun webs become black, in addition to showing considerable shrinkage of the webs when they are carbonised. The color change was due to the structural changes where nitrile group ( $C \equiv N$ ) converts into imine double bonds (C = N), forming a ladder structure as in Figure 2.9 and 2.10 [97].

Further tests were undertaken directly on the scissioned-carbonised PAN after the carbonisation, whilst the carbonised scissioned PAN had to be sonicated prior to use. The sonication for carbonised-scissioned sample was performed in water for 30 min run time with 80% amplitude and 2/2 lapsed ON/OF time, followed by drying the sample under the fumehood to remove excess water for about 3 days and vacuum oven dried at 100°C with -100 kPa until constant weight. The surface morphologies of the carbonised-scissioned and scissioned-carbonised short elecrospun PAN made in this way were compared, and this is shown in Figure 6.2.

Figure 6.2 shows that in general the carbonisation process of the asspun web leads to a smoother surface morphology (Figure 6.2d), where the roughness of the original surface (Figure 6.2b) is reduced. In addition, the structure of the carbonised fibre (Figure 6.2c) is wavy in shape, compared to the straight, long as-spun fibres (Figure 6.2a) [140]. The waviness is due to the unbalanced inner stress around the outer surface during shrinkage as the dehydrogenation reaction proceeds [166], where volatile substances such as water are released that result in diameter shrinkage. The shrinkage causes the outer region of the fibre to be under compression, whilst the inner core is in tension, creating unbalanced stresses [94].



Figure 6.2 SEM images of the relevant fibres at different levels of magnification 3000x (left) and 50 000x (right), a,b) as-spun PAN web (before carbonisation) c,d ) carbonised as-spun PAN, e,f) sonicated carbonised short fibres (carbonised-scissioned), g,h) sonicated UV-Ozone treated electrospun web (before carbonisation) i,j) scissioned-carbonised short fibre (carbonisation of sonicated UV-Ozone treated web).

The carbonised as-spun web shows that some of the nanofibres demonstrate a slight fusion with the neighbouring fibres (Figure 6.2c and 6.2d), and some fibres thus become bundled together. This fusion is not observed for the scisssioned-carbonised short fibres (Figure 6.2i and 6.2j), although the same carbonisation procedure was performed in both samples. Some slight fusion was also reported in the study of Zussman [167], where SEM images showed some fusion of carbonised fibres that were lying on top of each other, as shown in Figure 6.3. Note that few papers to date in this area have discussed in any detail the surface morphology of the carbonised PAN, with most of them only reporting the shrinkage aspect and claiming smooth surfaces [166, 168].



Figure 6.3 SEM images adapted from Zussman [167] showing the PAN fibres a) before and , b) after carbonisation. The superimposed arrow indicates the slight fusion of the carbonised PAN.

In this work, the modest fusion observed is dependent on the arrangement of the fibres, where fibres that are in close proximity to neighbouring fibres have a high tendency to fuse to the outer surface of these neighbouring fibres, and can be observed in Figure 6.2d. The carbonised fibre fusion (Figure 6.2c and 6.2d) leads to an agglomeration of the carbonised-scissioned short fibres, as seen in Figure 6.2e and 6.2f.

In contrast, fibre fusion and bundling was not observed for the scissioned-carbonised short fibres, as can be seen in Figure 6.2i and 6.2j. The surface morphology of the carbonised short fibres again appears to be smoother (Figure 6.2) when compared to that of the pre-carbonised short fibres (Figure 6.2h). Although the same stabilisation and carbonisation procedure was performed for both samples (either the non-woven web or the short fibres), such differences in fusion and bundling would likely be due to the nature of the long continuous fibres web being in close proximity to other parts of the web, as compared with carbonisation of 'free flowing' short nanofibres. In addition, external tension was not applied during stabilisation stage (heat treatment up to 280°C in oxygen), which may contribute to some fusion of the fibres. Some studies reported the use of tension to maintain molecular orientation and avoid shrinkage [95]. External tension can be applied by wrapping the electrospun webs tightly around a glass rod so that they are under tension during the stabilisation stage [109]. In our work, the external tension was not applied to the as-spun web prior carbonisation, since the aim of this work was to compare the difference between the product of scissioning before carbonisation (scissioned-carbonised) and after carbonisation (carbonised-scissioned) using ultrasonication. Clearly, in such comparative studies, applying tension to the short fibres (scissionedcarbonised) is not feasible.

#### 6.2.2 Structural characterisation

The carbonised-scissioned and scissioned-carbonised short fibres were characterised using Thermal Gravimetric Analysis (TGA), Transmission electron microscopy (TEM), Raman spectroscopy, X-ray Diffraction (XRD) and 4 point probes to determine electrical resistivity.

## 6.2.2.1 Thermal Gravimetric Analysis (TGA)

TGA analysis was used to investigate thermal degradation of the asspun PAN and scissioned electrospun PAN short fibres (UV-Ozone treated electrospun PAN) during the carbonisation process. The experiment was conducted using the same carbonisation steps as described previously, where the sample was heated in air up to 280°C, followed by isothermal heating for 1 hr at a heating rate of 2°C/min. A further carbonisation process was subsequently performed by heating up the sample from 280°C to 1200°C in argon, at the same heating rate. Figure 6.4 shows the TGA curves for the carbonisation of as-spun PAN web and the scissioned electrospun PAN short fibres.



Figure 6.4 TGA curves for A) as-spun PAN web (--), B) UV-Ozone treated, short PAN nanofibres (...)

From the TGA results, it can be seen that the thermal degradation of both samples is clearly apparent at between 270°C to 300°C. This thermal degradation has previously been described by others as being due to the exothermic cyclisation reaction [169, 170]. The cyclisation involves the reaction of the nitrile groups -C=N- linear structure, forming a -C=N- ladder structure that results in shrinkage. An oxidation reaction that causes dehydrogenation also occurs during the stabilisation stage, concurrently with cyclisation, leading to the release of volatile materials such as water (H₂O), hydrogen cyanide (HCN), ammonia (NH₃) and carbon dioxide  $(CO_2)$ contributing to the weight loss [168, 171, 172]. The cyclisation and dehydrogenation chemistry as discussed by Rahaman et al can be seen in Figure 2.9 (Section 2.5). The weight loss of the UV-Ozone treated PAN

during the exothermic reaction (270°C to 300°C) is some 9 % lower, as compared to as-spun PAN. This is probably due to the pre-existing oxidation that results during UV–Ozone treatment. Recall, that in this study, the UV– Ozone pre-treatment was intended to make the fibres able to be scissioned more readily.

It has previously been reported by others that photo-irradiation also leads to the formation of a ladder structure for PAN, similar to that of the thermal stabilisation effect where the linear chemical structure of PAN converted into ladder structure [173, 174]. In these studies, the PAN meltspun fibres were photo-irradiated by UV light prior to heat treatment, to assist the stabilisation process due to the inadequate crosslinking in the fibre core (when only conventional stabilisation heat treatment was conducted), resulting in defects within the fibre.

However, it should be noted that the difference in the weight loss at the end of exothermic reaction is less than 10 %, which indicates only a marginal oxidation effect from the photo-irradiation. The oxidation of the UV-Ozone treated fibre was also not shown in the FTIR spectrum, where the peaks of both as-spun and UV-Ozone treated fibre are the same, as discussed in Section 5.4.1.

Further weight loss is due to the evolution of volatile substances that continue to be evolved as the carbonisation process continues (heating in argon of up to  $1200^{\circ}$ C) with additional gases being emitted such as methane (CH₄), carbon monoxide (CO) and hydrogen (H₂). The relationship between the amount of gases evolved with respect to temperature, has been studied by others and is shown here in Figure 6.5 [97, 175]. It is likely that the evolution of these volatile substances contributes to the total weight loss of carbonised PAN, which is about 60 %, in agreement with studies by others [97, 175].



Figure 6.5 Evolution of non-carbon elements from PAN fibre during carbonisation [97]

The final weight loss after completion of the carbonisation process of UV-Ozone treated fibre is less by only about 3 %, compared to the as-spun fibre loss. The weight loss due to the carbonisation process also results in the decrease in the diameter of the carbonised as-spun and UV-Ozone treated PAN, as presented in Figure 6.6.



Figure 6.6 The effect of carbonisation on fibre diameter, A) as-spun web B) carbonised as-spun web, C) UV-Ozone treated short fibre, D) carbonised UV-Ozone treated short fibre (n = 50).

From Figure 6.6, it can be seen that carbonisation of the web leads to a reduction in diameter from  $620 \pm 123$  nm to  $580 \pm 178$  nm, some 7 %. Meanwhile the UV-Ozone treated short fibre carbonisation results in shrinkage of fibre diameter by about 20 %, from  $680 \pm 179$  nm to  $520 \pm 194$  nm. Although the average fibre diameter suggests that the UV-Ozone treated short fibres shrink more compared to shrinkage of the as-spun web, taking into consideration the error bar in Figure 6.6, the difference is minimal. The shrinkage of the carbonised fibre is due to the formation of carbon basal planes that lead to the arrangement and compactness of structures along the fibre axis, that also lead to an increase in density [166, 176].

The morphology and structure of the carbonised short electrospun PAN was analysed using TEM and is shown in Figure 6.7.



Figure 6.7 TEM images of a, c) carbonised-scissioned and b, d) scissioned-carbonised PAN short fibre.

Figure 6.7 shows that the carbonised-scissioned and scissioned-carbonised short electrospun fibre have a similar carbonaceous, turbostratic structure, where the sheets of carbon atoms are haphazardly folded, or crumpled together (Figure 6.7c and 6.7d) with several sheath layers across the edge (Figure 6.7a).

It is likely that this skin-core heterogeneity, also discussed by others, is due to the temperature difference at the skin to the core of the fibre during carbonisation [109, 167]. The micrographs appearances are consistent with what is found in conventional turbostratic carbon microstructures [94].

Further confirmation of the conversion from a polymeric fibre to a carbon-based one was obtained using Raman spectroscopy and XRD measurement.

### 6.2.2.3 Raman spectroscopy

Raman spectroscopy of the carbonised-scissioned and scissionedcarbonised short fibre was performed using Renishaw Invia Microscope with red laser of 633 nm to obtain the information on the perfection of crystallinity as shown by the *D*-peak and *G*-peak centered around 1360 cm⁻¹ and 1580 cm⁻¹, respectively. From the spectrum, the *R*-ratio, which is the ratio between the intensity of *D*-peak ( $I_D$ ) and *G*-peak ( $I_G$ ) can be obtained and represents the concentration of disordered (*D*-peak) and ordered (*G*-peak) carbon species [140]. The Raman spectrum is presented in Figure 6.8, with the *R*-ratio calculated using the Lorentzian fitted curve provided in OriginPro 8.5 software.



Figure 6.8 Raman spectroscopy of a) carbonised-scissioned and b) scissioned-carbonised short electrospun PAN showing the *D*-peak and *G*-peak of the Lorentzian fitted curve.

Both the carbonised-scissioned and scissioned-carbonised short fibre PAN show the appearance of the *D* and *G* peak at 1342-1360 cm⁻¹ and 1580-1600cm⁻¹, respectively (Figure 6.8) which demonstrate that the as-spun PAN has been converted into a less ordered carbon materials (indicated by the magnitude of the *D*-peak) and more ordered graphitic crystallites (*G* peak). The relative intensity ratio of the *D*-peak to *G*-peak (the *R*-ratio) for the scission-carbonised short fibre, as shown in Figure 6.8(b), is slightly higher compared to carbonised-scission (Figure 6.8a), being 1.07 and 0.97, respectively. The lower the value of *R*-ratio, the better the quality of carbon is achieved since the ordered graphitic plane is greater than the disordered

carbon [140]. The lower value of R of the carbonised-scissioned sample shows that it has a slightly higher degree of graphitisation and alignment of the graphitic planes, compared with the scissioned-carbonised sample, with a lower value of R meaning a greater the amount of  $sp^2$  (graphite) clusters in the sample [140]. However, the difference between the *R*-ratio of the scissionedcarbonised and carbonised-scissioned samples did not vary significantly (1.07 vs 0.97), with both values much lower than reported elsewhere. For example, values of 1.39 were reported by Kim et al and 1.48 by Lee et al [140, 175] due to a higher carbonisation temperature used in our experiments which was 1200°C and the purge gas used was argon (compared to Kim et al carbonised in argon up to 1000°C and Lee at al carbonisation temperature is 1200°C with  $N_2$  as purging gas). It is known that the higher the carbonisation temperature, the more ordered graphitic structures that result [140]. Argon gas is also a better inert atmosphere at high temperatures for carbonisation compared to  $N_2$ , due to the higher density and viscosity of argon [94]. It is likely that any slight difference in R ratio between the carbonised-scissioned and scissionedcarbonised sample obtained in this study (0.97 and 1.07, respectively), is probably due to the flaws resulting from the UV-Ozone treatment process that lead to a slightly lower quality of carbon produced by the scissionedcarbonised route [173].

#### 6.2.2.4 X-ray Diffraction (XRD)

In this research, XRD characterisation was performed by Dr Jana Habsuda on the carbonised-scissioned and scissioned-carbonised short fibre using Phillips 1140 diffractometer with copper target (Cu K $\alpha$ ) with wavelength,  $\lambda$ = 0.1541 nm with the rate of 2°/min and 0.02° step, to further investigate and compare the structures of the different carbonised electrospun PAN, and the results are shown in Figure 6.9.



Figure 6.9 XRD curves of samples A) carbonised-scissioned and B) scissioned-carbonised PAN short fibre

Figure 6.9 shows two diffraction peaks at  $2\theta$  scattering angles of about  $25^{\circ}$  and  $44^{\circ}$ , which are close to those previously reported for the graphitic structure [113], and were similar for the carbonised-scissioned and scissioned carbonised short fibre. Using this XRD data, the size of crystallite  $L_c$  and  $L_a$ , along *c*-and *a*-directions (refer to Figure 3.13), respectively, can be calculated by using Equation 3.3 and 3.4 with  $\lambda = 0.154$  nm,  $\beta = 0.08$  rad and  $\theta = 0.21$  rad  $(2\theta = 24.5^{\circ})$ , the crystallite size at (002) plane,  $L_c$  is 1.77 nm for both carbonised-scissioned and scissioned-carbonised sample. The crystallite size at (10) plane,  $L_a$  is 5.10 nm for carbonised-scissioned with  $\beta = 0.06$  rad and  $\theta = 0.39$  rad  $(2\theta = 44.2^{\circ})$ , and for scissioned-carbonised  $L_a$  is 4.38 nm with  $\beta =$ 

0.07 rad and  $\theta = 0.39$  rad ( $2\theta = 43.7^{\circ}$ ). The result shows that the crystallite size for carbonised-scissioned sample is the same for (002) plane, and is slightly bigger compared to scissioned-carbonised sample for the (01) plane. This is in agreement with Raman spectroscopy results, where the *R-ratio* for carbonised-scissioned is lower compared to the scissioned-carbonised sample, with *R-ratio*'s of 0.97 and 1.07, respectively. Both XRD and Raman results thus indicate that the UV-Ozone treatment prior to carbonisation leads to a slightly lower order of carbon structure.

Compared with literature, the  $L_c$  value obtained in this study is within the range obtained by others where Zhou et al [109] obtained 0.882 nm and 1.17 nm (carbonisation temperature of 1000°C and 1400°C), whilst Ji et al [176] produced an average of 1.76 nm crystallite size (carbonisation temperature of 1280°C - 1400°C). Kim et al [140] found a higher  $L_c$  size of 2.15 nm (carbonisation temperature 1000°C in argon) and  $L_a$  size is 3.36 nm. The difference in the crystallite size for this study and that reported in the literature is likely due to the difference in carbonisation parameters such as temperature (larger crystallite size with increasing temperature), purge gas used, stabilisation steps used and the initial fibre diameter.

#### 6.2.2.5 Electrical resistivity measurements

The resistivity measurements of carbonised-scissioned and scissionedcarbonised electrospun PAN were performed using standard 4-point probe and consisted of four tungsten metal tip with 0.5 mm equal space. The electrospun PAN web was compacted with mortar and pestle prior to carbonisation, to produce a compact and flat sample of carbonised PAN to allow the direct measurement of resistivity. From these measurements, the voltage and current values were obtained and using Equation 3.5 with a probe spacing of 0.5 mm, the bulk resistivity calculated for the carbonised-scissioned sample and scissioned-carbonised sample and found to be  $0.07 \pm 0.00 \ \Omega$ .cm and  $0.16 \pm 0.02 \ \Omega$ .cm, respectively. The conductivity of the sample is the reciprocal of bulk resistivity, and can thus be determined to be  $14.2 \pm 0.04 \ S \ cm^{-1}$  and 6.20  $\pm 0.8 \ S \ cm^{-1}$ . This is similar to the conductivity of the carbon fibre mat obtained by Kim et al and Liu et al, which is  $1.9 \ S \ cm^{-1}$  [140] and 55.41 S cm⁻¹ [95] for the carbonisation temperatures of  $1000^{\circ}$ C and  $2000^{\circ}$ C, respectively.

In this study, the conductivity for the carbonised-scissioned electrospun PAN fibres was greater than that of the scissioned-carbonised web, in agreement for the lower amount of *R-ratio* and larger crystallite size  $(L_a)$  observed for the carbonised-scissioned sample. This is in agreement with the findings by Kim et al whereby an increase in carbonisation temperature (from 700°C to 1000°C) resulted in an increased in conductivity, with a decrease in *R-ratio* and larger crystallite size  $(L_a \text{ and } L_c)$  [140]. The higher conductivity of the carbonised-scissioned sample compared to scissioned-carbonised sample was due to the higher degree of graphitisation and alignment of the graphitic planes produced in carbonised-scissioned sample. However, this difference is small, which suggests that the UV-Ozone post-treatment method does not significantly reduce the conductivity and graphite quality of the carbonised short fibre PAN.

## 6.3 Carbonised PAN short fibre/epoxy composites

The incorporation of PAN nanofibres into a crosslinked matrix such as an epoxy represents an important potential use of scissioned fibres as additives, both to potentially improve mechanical properties, as well as rendering the composites conductive. A number of processing methods and additives will be described, which were used to improve the nanofibre dispersion and remove the air bubbles in the composite systems. In addition, we will compare the mechanical properties of the carbonised-scissioned and scissioned-carbonised short fibre as reinforcements for epoxy resin systems.

### **6.3.1** Effect of sample preparation

To determine the optimal sample preparation method, only the carbonised-scissioned short electrospun PAN was used for composite reinforcement, due to the simplicity in preparing the short nanofibres in this manner, as highlighted in Section 3.3.5.

The composites were prepared by the addition of 2.5 wt% and 5 wt% of carbonised-scissioned short fibre to the epoxy resin, using the high speed mixing method or solvent method (acetone), with or without the addition of surfactant alkylammonium salt, BYK9076 (BYK Inc, US) which has previously been used as a dispersant for carbon nanofibres/nanotubes in composite systems [119-122].

For the high speed mixing method, the dried carbonised-scissioned short fibre were added to epoxy resin and mixed in the high speed mixer for about 5 min. This was followed by vacuuming of the mixture in the vacuum
oven for 2 days to remove the air bubbles, and was followed by the addition of hardener (at the manufacturer's recommended concentration). Following addition of the hardener, high speed mixing was again performed for 2 min. Finally, moulding, curing and post-curing of the composite were performed prior to further testing. Meanwhile, for the composite with surfactant addition, 20 wt% (compared to the short fibre weight) of BYK9076 surfactant was added to the epoxy resin prior to incorporating the carbonised-scissioned short fibre in to the high speed mixer. The rest of the procedure was the same as that used for high speed mixing without surfactant use.

The SEM images of the carbonised-scissioned short fibre/epoxy composite prepared at the concentration of 2.5 wt% and 5 wt % using the high speed mixing method, without and with surfactant addition, can be seen in Figures 6.10 and 6.11, respectively.



Figure 6.10 SEM images of the composite based on the addition of the carbonised-scissioned nanofibres in the epoxy composite for a-c) 2.5 wt %, d-f) 5 wt % concentrations. These are produced without the addition of surfactants, and show an agglomeration of the fibres. Small air bubbles (as circled) in the 5 wt% sample can also be observed, but not in the 2.5 wt% composite.



Figure 6.11 SEM images of the epoxy composite containing carbonisedscissioned PAN nanofibres for concentrations of a-c) 2.5 wt %, d-f) 5 wt% using the high speed mixing technique and the incorporation of surfactant BYK9076 showing no improvement on agglomeration of the short fibre.

Comparing Figures 6.10 and 6.11, which are both samples prepared using the high speed mixing method, the latter images where there was an addition of surfactant, did not demonstrate a significantly improved dispersion of the carbonised PAN short fibre, with high agglomeration of the fibres still apparent. This likely demonstrates that the processing technique (high shear mixing) is not suitable for this application.

It should be noted that no air bubbles were observed in the 5 wt% composite when the surfactant was added, as can be seen in Figure 6.11d, when compared to the Figure 6.10d (no surfactant addition). This could be due to a change in the viscosity of the mixture and increasing ease of bubble removal by vacuuming or a change in polarity of the mixture.

The solvent method of sample preparation to aid dispersion was also used. The addition of a solvent in which the monomer is soluble reduces the viscosity of the mixture, thus making dispersion of the short fibres in resin easier. In this method, the carbonised-scissioned short fibre were sonicated in acetone using probe sonicator for 10 min at 80 % amplitude and 2/2 lapsed ON/OFF time. The mixture was placed in the fumehood to remove excess acetone, followed by the addition of epoxy resin which was then mixed using the high speed mixer for 5 min. To ensure a better dispersion of epoxy with the short fibres, the mixture in a beaker was placed in an ultrasonic bath for 30 min. Subsequently, degassing was performed in a vacuum oven at 60°C. Finally, amine was added to the mixture prior high speed mixing was performed for 2 min. Moulding and curing was performed at room temperature for 48 hr, with post-curing at 60°C overnight. For the sample prepared with surfactant, the surfactant was added together at the same time as the epoxy resin was incorporated, whilst the rest of the procedure follows the same step.

The SEM images of the carbonised-scissioned /epoxy composite using the solvent method with and without surfactant can be seen in Figure 6.12.



Figure 6.12 Carbonised-scissioned/epoxy composite prepared by the solvent method, a,b) 2.5 wt% nanofibres without surfactant, c,d) 2.5 wt% nanofibres with surfactant, e,f) 5 wt% nanofibres without surfactant, g,h) ) 5 wt% nanofibres with surfactant

The SEM images of the carbonised-scissioned samples with and without surfactant in Figure 6.12 show that dispersion of the short fibres using the solvent method leads to a much improved dispersion, compared with the high speed mixing technique, alone with large agglomeration of short fibre being observed in the latter technique (Figure 6.11b and 6.11e). The overall rougher fracture surface and reduced resin-rich area, compared with high speed mixing method, demonstrates that the degree of the dispersion of the short fibres is better using solvent method. However, when comparing Figure 6.12f and 6.12h where both materials were produced using the solvent method, whether they are made with or without surfactant does not lead to a significant difference. Clearly, this result shows that the solvent methodology is more important than whether or not a dispersant is used, when trying to maximise dispersion.

Flexural mechanical testing was performed on the resulting composites to compare the deformation properties of the carbonised-scissioned epoxy composite using high speed mixing and solvent method, either with surfactant or without surfactant addition, and the results can be seen in Figure 6.13 and the results are tabulated in Table 6.1.



Figure 6.13 The effect on flexural mechanical properties of high speed mixing without surfactant (XHSP) and with surfactant (SHSP) and the solvent method without surfactant (XSSOL) and the solvent method with surfactant (SSOL) for carbonised-scissioned PAN /epoxy composite at 2.5 wt % and 5 wt % concentrations, compared with neat epoxy resin (control, no fibre additive).

Figure 6.13 shows that when comparing the high speed mixing and solvent methods of producing blends, the solvent method leads to greater flexural modulus and strength - with or without surfactant addition. In contrast, the strain-to-failure (ductility) was reduced, regardless of the method used. The reduction in ductility of samples produced by the high speed mixing technique is greater compared to samples made by the solvent method, either with or without surfactant. At 2.5 wt% carbonised-scissioned/epoxy concentration, an increase of some 40% of the flexural modulus, from 1.8 GPa to 2.5 GPa (compared with neat epoxy resin) is found if the solvent method is used with

surfactant addition, whilst using the solvent method without surfactant addition results in an increase from 1.8 GPa (epoxy) to 2.2 GPa (ca. a 22 % increase in flexural modulus).

The solvent method has the effect of reducing the viscosity of the short fibre-epoxy mixture whilst being mixed, which enables better dispersion of the short fibres [119]. The addition of the surfactant aids dispersion by introducing steric repulsive forces between the short carbon fibres [177]. Their inclusion should also improve adhesion between fibre and matrix in the solid state. Although this was not clearly observed in the SEM images, there was some improvement in the flexural properties. However, the addition of surfactant alone in the high speed mixing technique did not significantly increase the modulus and strength, with the high viscosity of the mixture making good dispersion difficult. Hence, the short fibre aggregation results in large resin-rich areas, with the clustering of fibres leading to a reduction in mechanical properties.

Based on this work, the solvent method was used to prepare the remaining samples, in which the effect of nanofibres produced by the carbonised-scissioned protocol, compared to reinforcement produced by the scissioned-carbonised methodology, will be compared.

## 6.3.2 The effect of PAN nanofibre preparation (carbonisedscissioned vs. scissioned-carbonised) on epoxy composite reinforcement

The samples in this section were prepared using the same steps as in carbonised-scissioned/epoxy composite where scissioned-carbonised short fibre was sonicated in acetone using sonicator probe for 1 min (for the purpose of short fibre dispersal only). After removal of excess acetone, the epoxy resin was added (note that for samples prepared with surfactant, the surfactant was also added at this time point), prior to shear mixing for 5 min and followed by further agitation by placing the beaker in an ultrasonication bath for 30 min. The amine hardener was added in the mixture after degassing was performed, followed by 2 min shear mixing. The sample was subsequently characterised after the moulding and curing process.

The SEM images of the scissioned-carbonised/epoxy composite with and without surfactant, using the solvent method, are shown in Figure 6.14.



Figure 6.14 Scissioned-carbonised/epoxy composite prepared by solvent method ,a,b) 2.5 wt% nanofibres without surfactant, c,d) 2.5 wt% nanofibres with surfactant, e,f) 5 wt% without surfactant, g,h) ) 5 wt% nanofibres with surfactant.

The SEM images of the scissioned-carbonised/epoxy composite, as shown in Figure 6.14, demonstrate that short fibre dispersion is better compared to the carbonised-scissioned/epoxy composite (Figure 6.12), especially for the 5 wt% concentration (Figure 6.14e and 6.14g). Although clusters of short fibres are still visible, the fusion of fibres that leads to higher clusters of fibres is not apparent, when compared to the carbonised-scissioned/epoxy composite (Figure 6.12f and 6.12h).

Comparison between the flexural properties of carbonisedscissioned/epoxy composite with scissioned-carbonised/epoxy composite using the solvent method, and with or without surfactant addition, is shown in Figure 6.15 and summarised in Table 6.1.



Figure 6.15 Flexural properties for carbonised-scissioned/epoxy without surfactant (XSCS) and with surfactant (SCS) and scissionedcarbonised/epoxy without surfactant (XSSC) and with surfactant (SSC) at 2.5 wt % nanofibres and 5 wt % nanofibres concentration with neat epoxy (0 wt%) as control.

### Table 6.1 Flexural properties of the carbonised PAN/epoxy composites

			Flexural Modulus	Flexural	Failure strain
Samples	Method	Weight %	(GPa)	Strength(MPa)	(%)
Ероху	High speed mixing	0	$1.82 \pm 0.20$	$68.80 \pm 7.01$	$10.29 \pm 1.06$
Carbonised-scissioned/epoxy without surfactant	High speed mixing	2.5	2.11 ± 0.25	$65.07 \pm 12.87$	2.95 ± 1.21
		5	1.70 ± 0.13	51.75 ± 2.75	3.29 ± 1.16
	Solvent method	2.5	2.24 ± 0.18	68.70 ± 8.53	5.03 ± 1.72
		5	2.31 ± 0.27	$59.89 \pm 9.91$	3.90± 0.57
Carbonised-scissioned/epoxy with surfactant	High speed mixing	2.5	1.77 ± 0.16	$62.15 \pm 7.34$	4.03 ± 1.09
		5	$1.66 \pm 0.01$	$49.18 \pm 10.11$	4.35 ± 2.62
	Solvent method	2.5	2.53 ± 0.14	$73.02\pm7.79$	$5.20 \pm 2.80$
		5	2.41 ± 0.12	$63.07 \pm 8.66$	$3.30 \pm 0.42$
Scissioned-carbonised/epoxy without surfactant	Solvent method	2.5	$2.40 \pm 0.23$	$75.17\pm0.01$	5.43 ± 2.03
		5	2.62 ± 0.05	82.75 ± 0.39	7.60 ± 1.41

Scissioned-carbonised/epoxy with surfactant	Solvent method	2.5	2.46 ±0.16	$76.13 \pm 0.0$	8.50 ± 2.45
		5	2.73 ± 0.08	79.77± 0.12	6.45 ± 1.77

Using the solvent blending method, both the scissioned-carbonised and carbonised-scissioned epoxy composite showed an increase in flexural modulus and strength, when compared with the neat resin. When comparing both the carbonised-scissioned and scissioned-carbonised sample results, it can be seen that for the 2.5 wt% fibre concentration, no significant difference can be observed between samples in the flexural modulus and strength. However, a greater difference in properties is evident at 5 wt% nanofibre concentration, with a higher modulus and strength obtained for the scissionedcarbonised/epoxy samples (with or without surfactant addition). At this concentration, the modulus of the scissioned-carbonised composite without surfactant addition (when compared to the property of the neat resin) was increased by 46 %, with the carbonised-scissioned composite gave an increase of ca 28%. The improvement in flexural strength is lower, some 80 MPa for scissioned-carbonised/epoxy compared with 60 MPa for the carbonisedscissioned/epoxy and neat resin's value of 69 MPa. The addition of surfactant did not seem to improve the properties significantly for both carbonisedscissioned and scissioned-carbonised composite.

The fusion effect of the carbonisation process which contributes to the agglomeration of short fibres in the carbonised-scissioned/epoxy sample was, as previously discussed, eliminated by performing the carbonisation process of the short fibres after ultrasonic scissioning of the electrospun web to produce the scissioned-carbonised samples. This in turn improves the flexural modulus and strength of the composite, due to the better dispersion and interfacial adhesion of the fibre-matrix interface.

It can be seen that the failure strain for both scissioned-carbonised and carbonised-scissioned composite is still lower than the neat resin. However, the scissioned-carbonised/epoxy samples have a higher failure strain value (7 %), compared with carbonised-scissioned/epoxy (4 %) for 5 wt% short fibre This reduction in ductility is a common result in concentration. nanocomposites when carbon nanotubes are incorporated in a thermosetting matrix, where the failure strain is either reduced or shows no improvement, due to the defects in the samples such as air bubbles and nanoparticulate agglomeration in some part of the composite which becomes the point of defects [177]. For instance, although the samples were kept in the vacuum oven for a prolonged time, all air bubbles may not be completely removed leading to reduced properties [177]. The fact that there is a broad distribution of results is also indicative of the nature of the failure due to induced flaws. The SEM images of the fracture surface of the carbonised-scissioned/epoxy and scissioned-carbonised/epoxy at 5 wt% nanofibres concentration with surfactant are shown in Figure 6.16.



Figure 6.16 SEM images of the fracture surface of a) carbonisedscissioned/epoxy and b) scissioned-carbonised/epoxy composite, both at 5 wt % nanofibres with BYK9076 surfactant addition.

The SEM images of the fractured surface of the composite samples after the flexural testing show that the mechanism of failure involves fibre pull-out, and the smooth surface of the extracted nanofibers demonstrate that there is a poor interfacial fibre-matrix interface, leading to the reduced ductility.

#### 6.4 Summary

In this chapter it is demonstrated that the ultrasonication method can be used to produce short electrospun PAN after the UV-Ozone irradiation of the electrospun web. This work showed that the structures of both carbonisedscissioned and scissioned-carbonised nanofibre samples are slightly different, with the quality of the carbonised-scissioned short fibre being slightly better compared to scissioned-carbonised. This is due to the possible flaws in the latter sample, resulting from UV-Ozone treatment necessary to allow scissioning of the neat PAN web required as part of the process to produce the scissioned-carbonised sample. These flaws are apparent from the examination of Raman spectra and X-ray diffraction results of the nanofibres. Further work is required to improve the carbonisation procedure for the scissionedcarbonised sample in order to obtain a higher degree of graphitisation and value of conductivity. The scission of the electrospun PAN prior to carbonisation has been shown to assist in overcoming the fusion and bundling that occurs if the web is first carbonised. This issue leads to clusters of carbonised, fused fibres that further adversely influence dispersion of the short carbon fibres in the resin.

The short fibres produced were incorporated in to epoxy resins to produce composite systems. It was found that the solvent method is superior in terms of nanofibre dispersion (where the resin is diluted with a miscible solvent), when compared to high speed mixing technique where the nanofibres are directly incorporated into the high viscosity resin. The solvent method, with its lower viscosity allowed samples to be briefly sonicated in solution to encourage dispersion, and short fibre agglomeration is reduced, and this remains in the viscous resin once the solvent is removed. Using this solvent blending method, the mechanical properties of the scissioned-carbonised composite at low concentration (2.5 wt%) showed no significant improvement compared to the properties of carbonised-scissioned composite. At 5 wt% concentration, the modulus and strength of the scissioned-carbonised composite increased modestly by ca. 13 % and 30 %, respectively.

# **Chapter 7 - Conclusions and Suggestions for Future Work**

#### 7.1 Conclusions

The focus of the research in this thesis has been the investigation into the possibility to use ultrasonication to convert electrospun webs into individual short fibres, as well as elucidating some of the effects of varying the processing parameters and the incorporation of some of the short fibres (carbonised) produced in to an epoxy resin to form composites.

This research involved electrospinning of four types of polymer materials, being poly(styrene) (PS), poly(methyl methacrylate) (PMMA), poly(acrylonitrile)(PAN) and poly(L-lactic) acid (PLLA). It was found that the materials behaved differently when exposed to an ultrasonic probe. It was found that for non-woven webs that had roughly similar fibre diameters, as well as similar tensile strength and elastic modulus, it was the ductility of the polymers that were the main determinant as to whether the web was able to be scissioned using an ultrasonic probe. It was thus shown that ultrasonication is a new and effective method to cause the scission of sufficiently brittle submicron/nanometre-diameter electrospun polymer nanofibres, in this work for the PS and PMMA samples. Although generating short fibres from more ductile electrospun polymers such as PAN and PLLA was more difficult (regardless of the length of time for which the samples were sonicated), posttreatment of these ductile polymers, such as by using UV-Ozone treatment and heat treatment was able to induce flaws and embrittle the material. These imperfections then act as points for the initiation of failure, facilitating the scissioning of these more ductile materials.

In terms of understanding the process, by observing the nature of the surface morphology and effects of the various processing parameters, it was suggested that the mechanism of this scissioning method was related to the formation of cavitation bubbles which, upon collapse, can lead to a range of deformations on the fibres, including bending, fibre compression, erosion and pitting of samples. If the fibres are short enough, tensile deformation can also occur. It is likely that there are various combinations of these mechanisms at different times during the sonication process. In the initial catastrophic event, where a portion of the non-woven, electrospun web is reduced to fibres, both flexing and microjet erosion are likely to be the primary mechanisms acting on the fibres which are drawn tangentially to the bubble edge. The attainment of curled fibres (whether the web was scissioned or not) and greater roughening of the surface, are all indicative of bending and erosion mechanisms, respectively. Once the fibres are smaller than a certain length, they can potentially be drawn into the collapsing bubble, with the particles long axis oriented in a radial manner to the bubble surface, and become subjected to a high rate of tensile deformation.

Based on these understandings of the scission mechanism, other variables such as the morphology (diameter, orientation) of the initial electrospun fibres were investigated. It was found that webs comprising smaller diameter fibres resulted in slightly smaller length fibres after sonication, likely due to the lower force being required to elongate the fibres to failure. Increased alignment of the fibres in the original web, achieved by increasing the rotation speed of the drum collector during electrospinning, also led to smaller fibres upon scissioning. This is probably because of the greater orientation of the polymer chains and reduced ductility within the fibres, as well as differences in the non-woven web morphology. Other processing variables such as temperature and dissolved gas did not appear to significantly change the cavitation/scission process, and thus did not greatly influence final length. It was found that the sonication process itself did not affect the chemical or physical structure of the fibres or their constituent polymers.

The effect of scissioning the PAN fibres before and after carbonisation was also investigated with comparison between the morphology, carbonaceous quality, electrical conductivity and the mechanical properties of the carbonised fibres when reinforced with epoxy resin were conducted. Carbonising the PAN short fibres (scissioned-carbonised) demonstrated a better surface morphology of the carbonised sample, as the limited fusion and bundling effect observed in the carbonised as-spun PAN web (carbonised-scissioned) does not occur. It was also found that the chemical and electrical properties of the scissioned-carbonised short fibres appear to be similar to the carbonisedscissioned short fibres, showing the potential of carbonising the short fibres.

In preparation of the composite, it was found that the solvent blending method is was able to produce better mixtures, compared to high speed mixing technique which allowed a better dispersion of the short fibres. The mechanical properties of the scissioned-carbonised short electrospun PAN/epoxy appear to be superior compared to the carbonised-scissioned short fibre PAN/epoxy due to the effect of fibre's fusion during carbonisation for the carbonised-scissioned sample.

### 7.2 Suggestions for future work

Numerous areas can be explored in this research to further understand and broaden the application of this research. Development of numerical modelling of the ultrasonic scissioning of the electrospun fibres would be beneficial to understand the process. Such modelling would benefit from a better real time view of the process, such as using a high quality high speed camera to monitor the scission process. The bubble cavitation occurs at about 20 kHz, which suggest the speed of the camera would be at the range of at least 20 000 frames per secs.

It was shown earlier that post-treatment can be used to enhance the ability of ductile webs to be scissioned. Other treatment methods could also be explored, with treatments such as sodium hydroxide (NaOH) and amine treatments that would modify the surface and encourage failure. As noted earlier, the short fibres have a wide potential in biomedical field where they can be use as vessels for the containment of drugs or in tissue engineering as injectable fibrous scaffolds, for example in anisotropic cavities such as neural pathways. It may also be beneficial to have short fibres in hydrogel systems, where they can act as tissue scaffolds or as slow drug release vehicles. The anisotropic, high aspect ratio of the fibres means that they could have the effect of structurally reinforcing the hydrogel, in addition to their functional properties. The ultrasonication method also can be used to produce composite electrospun fibres, especially with nanoparticles decorating the nanofibres of the electrospun web. Normally in such composite systems, the nanoparticles are premixed during polymer solution preparation and are then electrospun to produce nanoparticle/electrospun fibre composite (nanoparticles within the nanofibres). This is unfortunate, because if they are contained inside the nanofibres, their functionality may not be readily available. We have done some initial work where a PS electrospun web was scissioned using sonication, whilst at the same time including Fe₂O₃ nanoparticles in the sonicating fluid with the web. This was sonicated for 2 min and the SEM images (Figure 7.1) shows that the nanoparticles become embedded on the surface of electrospun fibres.



Figure 7. 1 SEM images showing PS sonicated in water with magnetic maghemite Fe₂O₃ nanoparticles, potentially producing a short electrospun fibre composite.

Further research on optimising the concentration of the nanoparticles is required that depends on the intended applications, such as enhancement of electrical conductivity of the electrospun fibres or their magnetic properties. These could be applied in a range of applications, and is a relatively facile method for incorporating such nanoparticles on to the surface of the scissioned fibres.

### **List of References**

- 1. Huang, Z.-M., et al., *A review on polymer nanofibers by electrospinning and their applications in nanocomposites.* Composites Science and Technology, 2003. 63(15): p. 2223-2253.
- 2. Ramakrishna, S., et al., An Introduction to Electrospinning and Nanofibers 2005, Singapore: World Scientific Pub.
- 3. Bhardwaj, N. and S.C. Kundu, *Electrospinning: A fascinating fiber fabrication technique*. Biotechnology Advances, 2010. 28(3): p. 325-347.
- 4. Nisbet, D.R., et al., *Neurite infiltration and cellular response to electrospun polycaprolactone scaffolds implanted into the brain.* Biomaterials, 2009. 30(27): p. 4573-4580.
- 5. Nisbet, D.R., et al., *Review Paper: A Review of the Cellular Response* on Electrospun Nanofibers for Tissue Engineering. Journal of Biomaterials Applications, 2009. 24(1): p. 7-29.
- 6. Nisbet, D.R., et al., Interaction of embryonic cortical neurons on nanofibrous scaffolds for neural tissue engineering. Journal of Neural Engineering, 2007. 4(2): p. 35.
- Li, D., Y. Wang, and Y. Xia, *Electrospinning of polymeric and ceramic nanofibers as uniaxially aligned arrays.* Nano Lett., 2003 (3): p. 1167.
- 8. Jalili, R., M. Morshed, and S.A.H. Ravandi, *Fundamental parameters* affecting electrospinning of PAN nanofibers as uniaxially aligned fibers. Journal of Applied Polymer Science, 2006. 101(6): p. 4350-4357.
- 9. Sancaktar, E. and D. Aussawasathien, *Nanocomposites of Epoxy with Electrospun Carbon Nanofibers: Mechanical Behavior*. The Journal of Adhesion, 2009. 85(4-5): p. 160-179.
- 10. Deniz, A.E., et al., *Electrospun polymeric nanofibrous composites containing TiO2 short nanofibers*. Materials Chemistry and Physics, 2011. 129(3): p. 701-704.
- Kim, J.S. and D.H. Reneker, *Mechanical properties of composites* using ultrafine electrospun fibers. Polymer Composites, 1999. 20(1): p. 124-131.
- 12. Verreck, G., et al., *Preparation and Characterization of Nanofibers Containing Amorphous Drug Dispersions Generated by Electrostatic Spinning*. Pharmaceutical Research, 2003. 20(5): p. 810-817.
- 13. Kriha, O., et al., Connection of Hippocampal Neurons by Magnetically Controlled Movement of Short Electrospun Polymer Fibers—A Route to Magnetic Micromanipulators. Advanced Materials, 2007. 19(18): p. 2483-2485.
- Mark, S.S., et al., Bioconjugation of Alkaline Phosphatase to Mechanically Processed, Aqueous Suspendible Electrospun Polymer Nanofibers for Use in Chemiluminescent Detection Assays. Macromolecular Bioscience, 2008. 8(6): p. 484-498.

- 15. Stoiljkovic, A. and S. Agarwal, *Short Electrospun Fibers by UV Cutting Method*. Macromolecular Materials and Engineering, 2008. 293(11): p. 895-899.
- 16. Tungprapa, S., et al., *Electrospun cellulose acetate fibers: effect of solvent system on morphology and fiber diameter.* Cellulose, 2007. 14(6): p. 563-575.
- 17. Fathona, I.W. and A. Yabuki, *A simple one-step fabrication of short* polymer nanofibers via electrospinning. Journal of Materials Science, 2014: p. 1-10.
- 18. Luo, C.J., et al., *Electrospinning short polymer micro-fibres with average aspect ratios in the range of 10–200.* Journal of Polymer Research, 2011. 18(6): p. 2515-2522.
- 19. Watmough, D., *Role of ultrasonic cleaning in control of cross-infection in dentistry*. Ultrasonics, 1994. 32(4): p. 315-317.
- 20. Suslick, K.S., ed. Ultrasound : Its Chemical, Physical and Biological Effects. 1988, VCH Publishers Inc: New york.
- 21. Brenner, M.P., S. Hilgenfeldt, and D. Lohse, *Single-bubble sonoluminescence*. Reviews of Modern Physics, 2002. 74(2): p. 425-484.
- Hennrich, F., et al., *The Mechanism of Cavitation Induced scission of Single-Walled Carbon Nanotubes*. J.Physical Chemistry B, 2007. 111: p. 1932-1937.
- 23. Chen, H., et al., *Effect of dispersion method on tribological properties* of carbon nanotube reinforced epoxy resin composites. Polymer Testing, 2007. 26(3): p. 351-360.
- 24. Kim, T.G. and T.G. Park, *Biodegradable Polymer Nanocylinders Fabricated by Transverse Fragmentation of Electrospun Nanofibers through Aminolysis.* Macromolecular Rapid Communications, 2008. 29(14): p. 1231-1236.
- 25. Kim, T.G., et al., *Hierarchically Assembled Mesenchymal Stem Cell Spheroids Using Biomimicking Nanofilaments and Microstructured Scaffolds for Vascularized Adipose Tissue Engineering.* Advanced Functional Materials, 2010. 20(14): p. 2303-2309.
- 26. Hsieh, A., et al., *Hydrogel/electrospun fiber composites influence neural stem/progenitor cell.* Soft Matter, 2010. 6: p. 2227-2237.
- 27. Thieme, M., et al., *Electrospinning and cutting of ultrafine bioerodible poly(lactide-co-ethylene oxide) tri- and multiblock copolymer fibers for inhalation applications.* Polymers for Advanced Technologies, 2011. 22(9): p. 1335-1344.
- 28. Cooley, J.F., *Apparatus for electrically dispersing fluids*, 1902: US Patents.
- 29. Formhals, A., *Process and Apparatus for Preparing artificial threads*, U. Patent, Editor 1934.
- 30. Sun, Z., et al., *Compound Core–Shell Polymer Nanofibers by Co-Electrospinning*. Advanced Materials, 2003. 15(22): p. 1929-1932.
- 31. Bazilevsky, A.V., A.L. Yarin, and C.M. Megaridis, *Co-electrospinning* of core-shell fibers using a single-nozzle technique. Langmuir, 2007. 23(5): p. 2311-2314.

- He, C.L., et al., *Coaxial electrospun poly(L-lactic acid) ultrafine fibers* for sustained drug delivery. Journal of Macromolecular Science, Part B: Physics, 2006. 45 B(4): p. 515-524.
- 33. He, C., et al., *Core-shell ultrafine electrospun fibers for drug release applications*. Gaojishu Tongxin/Chinese High Technology Letters, 2006. 16(9): p. 934-938.
- 34. He, J.-H., et al., *Electrospun Nanofibers and Their Applications*. 2008, Shawbury,UK: iSmithers.
- 35. Huang, Z.M., et al., *A review on polymer nanofibers by electrospinning and their applications in nanocomposites.* Composites Science and Technology, 2003. 63(15): p. 2223-2253.
- 36. Fong, H., I. Chun, and D.H. Reneker, *Beaded nanofibers formed during electrospinning*. Polymer, 1999. 40(16): p. 4585-4592.
- 37. Zong, X., et al., *Structure and process relationship of electrospun bioabsorbable nanofiber membranes.* Polymer, 2002. 43(16): p. 4403-4412.
- Yu, D.G., et al., Coaxial electrospinning with sodium dodecylbenzene sulfonate solution for high quality polyacrylonitrile nanofibers. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2012. 396: p. 161-168.
- 39. Jia, L. and X.h. Qin, *The effect of different surfactants on the electrospinning poly(vinyl alcohol) (PVA) nanofibers.* Journal of Thermal Analysis and Calorimetry, 2012: p. 1-11.
- 40. Frenot, A. and I.S. Chronakis, *Polymer nanofibers assembled by electrospinning*. Current Opinion in Colloid and Interface Science, 2003. 8(1-2): p. 64-75.
- 41. Deitzel, J.M., et al., *The effect of processing variables on the morphology of electrospun nanofibers and textiles.* Polymer, 2001. 42(1): p. 261-272.
- 42. Baji, A., et al., *Electrospinning of polymer nanofibers: Effects on oriented morphology, structures and tensile properties.* Composites Science and Technology, 2010. 70(5): p. 703-718.
- 43. Inai, R., M. Kotaki, and S. Ramakrishna, *Deformation behavior of electrospun poly*(*L*-*lactide-co-ε-caprolactone*) nonwoven membranes under uniaxial tensile loading. Journal of Polymer Science, Part B: Polymer Physics, 2005. 43(22): p. 3205-3212.
- 44. Xu, C.Y., et al., Aligned biodegradable nanofibrous structure: A potential scaffold for blood vessel engineering. Biomaterials, 2004. 25(5): p. 877-886.
- 45. Theron, A., E. Zussman, and A.L. Yarin, *Electrostatic field-assisted alignment of electrospun nanofibres*. Nanotechnology, 2001. 12(3): p. 384-390.
- 46. Ashammakhi, N., et al., Advancing tissue engineering by using electrospun nanofibers. Regenerative Medicine, 2008. 3(4): p. 547-574.
- 47. Casper, C.L., et al., *Controlling surface morphology of electrospun polystyrene fibers: Effect of humidity and molecular weight in the electrospinning process.* Macromolecules, 2004. 37(2): p. 573-578.
- 48. Casper, C.L., et al., Understanding the effects of processing parameters on electrospun fibers and applications in tissue

engineering, in ACS Symposium Series, D.H. Reneker and H. Fong, Editors. 2006. p. 205-216.

- 49. Mason, T.J., ed. *Chemistry with Ultrasound*. 1990, Elsevier Applied Science: New York. 195.
- 50. Mason, T.J. and J.P. Lorimer, *Applied Sonochemistry: The uses of power ultrasound in chemistry and processing*. 2002, Germany: Wiley-VCH, Verlag GmBH.
- 51. Price, G.J., ed. *Current Trends in Sonochemistry*. 1992, The Royal Society of Chemistry: Cambridge.
- 52. Margulis, M.A., *Sonoluminescence and sonochemical reactions in cavitation fields. A review.* Ultrasonics, 1985. 23(4): p. 157-169.
- 53. Margulis, M.A., *Fundamental aspects of sonochemistry*. Ultrasonics, 1992. 30(3): p. 152-155.
- 54. Margulis, M.A., *Fundamental problems of sonochemistry and cavitation*. Ultrasonics Sonochemistry, 1994. 1(2): p. S87-S90.
- 55. Suslick, K.S. and G.J. Price, *Application of Ultrasound to Materials Chemistry*. Annual Review of Materials Science, 1999. 29(1): p. 295-326.
- 56. Philipp, A. and W. Lauterborn, *Cavitation erosion by single laser*produced bubbles. Journal of Fluid Mechanics. 361: p. pp 75-116
- 57. Shima, A., Studies on bubble dynamics. Shock Waves, 1997. 7(1): p. 33-42.
- 58. Suslick, K.S., et al., *Effects of high intensity ultrasound on inorganic solids*. Ultrasonics, 1987. 25(1): p. 56-59.
- 59. Chukwumah, Y.C., et al., *Effect of frequency and duration of ultrasonication on the extraction efficiency of selected isoflavones and tans resveratrol from peanuts ( Arachis hypogaea).* Ultrasonics sonochemistry, 2009. 16(2): p. 293-299.
- 60. Portenlänger, G. and H. Heusinger, *The influence of frequency on the mechanical and radical effects for the ultrasonic degradation of dextranes.* Ultrasonics Sonochemistry, 1997. 4(2): p. 127-130.
- 61. Yamaguchi, T., et al., *Effects of frequency and power of ultrasound on the size reduction of liposome*. Chemistry and Physics of Lipids, 2009. 160(1): p. 58-62.
- 62. Dezhkunov, N., *Multibubble sonoluminescence intensity dependence* on liquid temperature at different ultrasound intensities. Ultrasonics sonochemistry, 2002. 9(2): p. 103-106.
- 63. Luche, J.-L., *Synthetic Organic Sonochemistry*. 1998, New York: Plenum Press.
- 64. Vijayalakshmi, S.P. and G. Madras, *Effect of temperature on the ultrasonic degradation of polyacrylamide and poly(ethylene oxide)*. Polymer Degradation and Stability, 2004. 84(2): p. 341-344.
- 65. Vijayalakshmi, S.P. and G. Madras, *Effects of the pH, concentration, and solvents on the ultrasonic degradation of poly(vinyl alcohol).* Journal of Applied Polymer Science, 2006. 100(6): p. 4888-4892.
- 66. Chakraborty, J., et al., *Ultrasonic degradation of polybutadiene and isotactic polypropylene*. Polymer Degradation and Stability, 2004. 85(1): p. 555-558.

- 67. Kuijpers, M.W.A., et al., *The mechanism of cavitation-induced polymer scission; experimental and computational verification.* Polymer, 2004. 45(19): p. 6461-6467.
- 68. Kuijpers, M.W.A., et al., Influence of the CO2 Antisolvent Effect on Ultrasound-Induced Polymer Scission Kinetics. Macromolecules, 2005. 38(4): p. 1493-1499.
- 69. Vane, L.M., V.V. Namboodiri, and T.C. Bowen, *Hydrophobic zeolite-silicone rubber mixed matrix membranes for ethanol-water separation: Effect of zeolite and silicone component selection on pervaporation performance.* Journal of Membrane Science, 2008. 308(1–2): p. 230-241.
- 70. Dang, F., et al., A new effect of ultrasonication on the formation of *BaTiO3 nanoparticles*. Ultrasonics Sonochemistry, 2010. 17(2): p. 310-314.
- 71. Kuijpers, M.W.A., et al., *Cavitation-Induced Reactions in High-Pressure Carbon Dioxide*. Science, 2002. 298(5600): p. 1969-1971.
- 72. Wang, M., et al., *Field-responsive superparamagnetic composite nanofibers by electrospinning*. Polymer, 2004. 45(16): p. 5505-5514.
- 73. Ye, H., et al., *Reinforcement and rupture behavior of carbon nanotubes--polymer nanofibers*. Applied Physics Letters, 2004. 85(10): p. 1775-1777.
- 74. Friedrich, K., S. Fakirov, and Z. Zhang, *Polymer Composites: From Nano- to Macro-Scale*. 2005, USA: Springer. 373.
- 75. Liu, J., et al., Fullerene Pipe. Science, 1998. 280: p. 1253-1256.
- 76. Zorbas, V., et al., *Preparation and Characterization of Individual Peptide-Wrapped Single Walled carbon Nanotubes*. Journal of American Chemical Society, 2004. 126: p. 7222-7227.
- 77. Li, H., J.R. Friend, and L.Y. Yeo, *A scaffold cell seeding method driven by surface acoustic waves*. Biomaterials, 2007. 28(28): p. 4098-4104.
- 78. Wang, Y., J. Wu, and F. Wei, A treatment method to give separated multi-walled carbon nanotubes with high purity, high crystallization and a large aspect ratio. Carbon, 2003. 41(15): p. 2939-2948.
- 79. Islam, M.F., et al., *High Weight Fraction Surfactant Solubilization of Single-Wall carbon Nnaotubes in Water*. Nanoletters, 2003. 3(2): p. 269-273.
- 80. Li, J. and Y. Zhang, *Cutting of multi walled carbon nanotubes*. Applied Surface Science, 2006. 252(8): p. 2944-2948.
- Madni, I., et al., Mixed surfactant system for stable suspension of multiwalled carbon nanotubes. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2010. 358(1-3): p. 101-107.
- 82. Yudasaka, M., et al., *Effect of an organic polymer in purification and cutting of single walled carbon nanotubes*. Applied Physics A: Materials Science processing, 2000. 71: p. 449-451.
- 83. Ma, R., et al., *The effects of UV/ozone treatments on the electrical transport behavior of single-walled carbon nanotube arrays.* Chemical Physics Letters, 2009. 474(1-3): p. 158-161.

- 84. Li, M., et al., Oxidation of single-walled carbon nanotubes in dilute aqueous solutions by ozone as affected by ultrasound. Carbon, 2008. 46(3): p. 466-475.
- 85. Lucas, A., et al., *Kinetics of Nanotube and Microfiber Scission under Sonication*. The Journal of Physical Chemistry C, 2009. 113(48): p. 20599-20605.
- 86. Chew, H.B., et al., *Compressive dynamic scission of carbon nanotubes under sonication: fracture by atomic ejection.* Proceedings of the Royal Society A: Mathematical, Physical and Engineering Science, 2011. 467(2129): p. 1270-1289.
- 87. Pagani, G., et al., *Competing mechanisms and scaling laws for carbon nanotube scission by ultrasonication*. Proceedings of the National Academy of Sciences, 2012.
- Ahir, S.V., Y.Y. Huang, and E.M. Terentjev, *Polymers with aligned carbon nanotubes: Active composite materials*. Polymer, 2008. 49(18): p. 3841-3854.
- 89. Guo, Z., et al., *High-speed observation of the effects of ultrasound on liquid mixing and agglomerated crystal breakage processes.* Powder Technology, 2007. 171(3): p. 146-153.
- 90. Wagterveld, R.M., et al., *Visualization of acoustic cavitation effects on* suspended calcite crystals. Ultrasonics Sonochemistry, 2011. 18(1): p. 216-225.
- 91. Martel, R., H.R. Shea, and P. Avouris, *Rings of single-walled carbon nanotubes*. Nature, 1999. 398(6725): p. 299-299.
- 92. Jo, J.-H., et al., *In vitro/in vivo biocompatibility and mechanical properties of bioactive glass nanofiber and poly*(ε*-caprolactone) composite materials*. Journal of Biomedical Materials Research Part B: Applied Biomaterials, 2009. 91B(1): p. 213-220.
- 93. Sutti, A., T. Lin, and X. Wang, Shear-Enhanced Solution Precipitation: A Simple Process to Produce Short Polymeric Nanofibers. Nanoscience and Nanotechnology, 2011. 11: p. 8947-8952.
- 94. Morgan, P., *Carbon fibers and their composites*, 2005, CRC Press: Boca Raton. p. 1131.
- 95. Liu, C.K., et al., *Preparation of carbon nanofibres through electrospinning and thermal treatment*. Polymer International, 2009. 58(12): p. 1341-1349.
- 96. Nataraj, S.K., K.S. Yang, and T.M. Aminabhavi, *Polyacrylonitrile*based nanofibers—A state-of-the-art review. Progress in Polymer Science, 2012. 37(3): p. 487-513.
- 97. Rahaman, M.S.A., A.F. Ismail, and A. Mustafa, *A review of heat treatment on polyacrylonitrile fiber*. Polymer Degradation and Stability, 2007. 92(8): p. 1421-1432.
- 98. Duan, Q., B. Wang, and H. Wang, *Effects of Stabilization Temperature* on Structures and Properties of Polyacrylonitrile (PAN)-Based Stabilized Electrospun Nanofiber Mats. Journal of Macromolecular Science Part B: Physics, 2012. 51: p. 2428–2437.
- 99. Bergshoef, M.M. and G.J. Vancso, *Transparent Nanocomposites with Ultrathin, Electrospun Nylon-4,6 Fiber Reinforcement.* Advanced Materials, 1999. 11(16): p. 1362-1365.

- 100. Neppalli, R., et al., *Poly([epsilon]-caprolactone) filled with electrospun nylon fibres: A model for a facile composite fabrication.* European Polymer Journal, 2010. In Press, Corrected Proof.
- 101. Jiang, S., et al., *Short electrospun polymeric nanofibers reinforced polyimide nanocomposites*. Composites Science and Technology, 2013. 88(0): p. 57-61.
- 102. Jiang, S., A. Greiner, and S. Agarwal, *Short nylon-6 nanofiber reinforced transparent and high modulus thermoplastic polymeric composites.* Composites Science and Technology, 2013. 87(0): p. 164-169.
- 103. Li, G., et al., Inhomogeneous toughening of carbon fiber/epoxy composite using electrospun polysulfone nanofibrous membranes by in situ phase separation. Composites Science and Technology, 2008. 68(3-4): p. 987-994.
- 104. Chen, G. and H. Liu, *Electrospun cellulose nanofiber reinforced* soybean protein isolate composite film. Journal of Applied Polymer Science, 2008. 110(2): p. 641-646.
- 105. Tang, C. and H. Liu, Cellulose nanofiber reinforced poly (vinyl alcohol) composite film with high visible light transmittance. Composites Part A: Applied Science and Manufacturing, 2008. 39(10): p. 1638-1643.
- 106. Liao, H., et al., Aligned electrospun cellulose fibers reinforced epoxy resin composite films with high visible light transmittance. Cellulose, 2012. 19(1): p. 111-119.
- 107. Lin, S., et al., *Electrospun nanofiber reinforced and toughened composites through in situ nano-interface formation*. Composites Science and Technology, 2008. 68(15-16): p. 3322-3329.
- 108. Chen, L.-S., et al., *Development of a transparent PMMA composite reinforced with nanofibers.* Polymer Composites, 2009. 30(3): p. 239-247.
- 109. Zhou, Z., et al., Development of carbon nanofibers from aligned electrospun polyacrylonitrile nanofiber bundles and characterization of their microstructural, electrical, and mechanical properties. Polymer, 2009. 50(13): p. 2999-3006.
- 110. Wang, Y., S. Serrano, and J.J. Santiago-Aviles, *Conductivity measurement of electrospun PAN-based carbon nanofiber*. Journal of Materials Science Letters, 2002. 21(13): p. 1055-1057.
- 111. Wang, Y., et al., *Raman characterization of carbon nanofibers* prepared using electrospinning. Synthetic Metals 138, 2003 p. 423– 427.
- 112. Aussawasathein, D., Electrospun Conducting Nanofiber-based Materials and Their Characterisations: Effects of Fiber Characteristics on Properties and Application, 2006, The University of Akron: USA.
- 113. Sutasinpromprae, J., et al., *Preparation and characterization of ultrafine electrospun polyacrylonitrile fibers and their subsequent pyrolysis to carbon fibers*. Polymer International 2006. 55 p. 825–833.
- 114. Meyyapan, M., ed. *Carbon nanotubes: science and application*. 2005, CRC Press LLC: Florida,USA.

- 115. Gupta, B., N. Revagade, and J. Hilborn, *Poly(lactic acid) fiber: An overview.* Progress in Polymer Science, 2007. 32(4): p. 455-482.
- 116. Kriegel, C., et al., *Electrospinning of chitosan–poly (ethylene oxide) blend nanofibers in the presence of micellar surfactant solutions.* Polymer, 2009. 50(1): p. 189-200.
- 117. Lin, T., et al., *Effects of polymer concentration and cationic surfactant on the morphology of electrospun polyacrylonitrile nanofibres.* Journal of materials science & technology, 2005. 21(Supplement 1): p. 1-4.
- Yang, D., et al., Control of the morphology of micro/nanostructures of polycarbonate via electrospinning. Chinese Science Bulletin, 2009. 54(17): p. 2911-2917.
- 119. Liao, Y.-H., et al., *Investigation of the dispersion process of SWNTs/SC-15 epoxy resin nanocomposites*. Materials Science and Engineering: A, 2004. 385(1–2): p. 175-181.
- 120. Zhu, Y., C.E. Bakis, and J.H. Adair, *Effects of carbon nanofiller* functionalization and distribution on interlaminar fracture toughness of multi-scale reinforced polymer composites. Carbon, 2012. 50(3): p. 1316-1331.
- 121. Xia, H. and M. Song, *Preparation and characterization of polyurethane–carbon nanotube composites*. Soft Matter, 2005. 1(5): p. 386-394.
- Nouranian, S., et al., Dynamic mechanical analysis and optimization of vapor-grown carbon nanofiber/vinyl ester nanocomposites using design of experiments. Journal of Composite Materials, 2011. 45(16): p. 1647-1657.
- 123. Dong, Y., et al. Distinctive degradation behaviors of electrospun PGA, PLGA and P(LLA-CL) nanofibers cultured with/without cell culture. in Advanced Materials Research. 2008. Hong Kong, P.R.
- 124. Megelski, S., et al., *Micro- and Nanostructured Surface Morphology* on Electrospun Polymer Fibers. Macromolecules, 2002. 35(22): p. 8456-8466.
- 125. Wang, C., C.-H. Hsu, and J.-H. Lin, *Scaling Laws in Electrospinning* of Polystyrene Solutions. Macromolecules, 2006. 39(22): p. 7662-7672.
- 126. Hutchinson, J.M., *Physical aging of polymers*. Progress in Polymer Science, 1995. 20(4): p. 703-760.
- 127. Van Melick, H., et al., *Kinetics of ageing and re-embrittlement of mechanically rejuvenated polystyrene*. Polymer, 2003. 44(4): p. 1171-1179.
- 128. Brunacci, A., et al., *Structural relaxation in polystyrene and some polystyrene derivatives*. Macromolecules, 1996. 29(24): p. 7976-7988.
- 129. Celli, A. and M. Scandola, *Thermal properties and physical ageing of poly (l-lactic acid)*. Polymer, 1992. 33(13): p. 2699-2703.
- 130. Simon, S., J. Sobieski, and D. Plazek, *Volume and enthalpy recovery of polystyrene*. Polymer, 2001. 42(6): p. 2555-2567.
- 131. Chen, S.Z.D., ed. *Handbook of Thermal and Calorimetry : Application to polymer and plastics.* Vol. 3. 2002, Elsevier Science Amsterdam, Netherlands.
- 132. Wang, Y. and J.F. Mano, *Effect of structural relaxation at physiological temperature on the mechanical property of poly (L-lactic*

acid) studied by microhardness measurements. Journal of applied polymer science, 2006. 100(4): p. 2628-2633.

- 133. Ho, C.H. and T. Vu-Khanh, *Effects of time and temperature on physical aging of polycarbonate*. Theoretical and Applied Fracture Mechanics, 2003. 39(2): p. 107-116.
- 134. D'Amico, T., C.J. Donahue, and E.A. Rais, *Thermal Analysis of Plastics*. Journal of Chemical Education, 2008. 85(3): p. 404.
- 135. Wangxi, Z., L. Jie, and W. Gang, *Evolution of structure and properties* of *PAN precursors during their conversion to carbon fibers*. Carbon, 2003. 41(14): p. 2805-2812.
- 136. Yusof, N. and A.F. Ismail, Post spinning and pyrolysis processes of polyacrylonitrile (PAN)-based carbon fiber and activated carbon fiber: A review. Journal of Analytical and Applied Pyrolysis, 2012. 93(0): p. 1-13.
- 137. Zhao, Z., et al., The relationship between the structures of polyacrylonitrile carbon fibers and the stabilized fiber precursors. Beijing Huagong Daxue Xuebao (Ziran Kexueban)/Journal of Beijing University of Chemical Technology (Natural Science Edition), 2013. 40(2): p. 44-48.
- 138. Anonymous. Dalchem Epoxy 521 Technical Datasheet.
- 139. R.Loos, M., L.A. F.Coelho, and S. H.Pezzin, *The effect of acetone addition on the properties of epoxy*. Polímeros,2008. 18: p 76-80
- 140. Kim, C., et al., *Raman spectroscopic evaluation polyacrylonitrilebased carbon nanofibers prepared by electrospinning*. Journal of Raman Spectroscopy, 2004. 35: p. 928-933.
- 141. Lin, T., et al., *The charge effect of cationic surfactants on the elimination of fibre beads in the electrospinning of polystyrene.* Nanotechnology, 2004. 15(9): p. 1375.
- 142. Chen, Y.Z., et al., *Poly(methyl methacrylate)/silica nanocomposite fibers by electrospinning*. Journal of Polymer Science, Part B: Polymer Physics, 2009. 47(12): p. 1211-1218.
- 143. You, Y., et al., *In vitro degradation behavior of electrospun polyglycolide, polylactide, and poly(lactide-co-glycolide).* Journal of Applied Polymer Science, 2005. 95(2): p. 193-200.
- 144. Zeng, J., et al., *Biodegradable electrospun fibers for drug delivery*. Journal of Controlled Release, 2003. 92(3): p. 227-231.
- 145. Zeng, J., et al., *Ultrafine Fibers Electrospun from Biodegradable Polymers*. Journal of Applied Polymer Science, 2003. 89(4): p. 1085-1092.
- 146. Angammana, C.J. and S.H. Jayaram, Analysis of the effects of solution conductivity on electrospinning process and fiber morphology. Industry Applications, IEEE Transactions on, 2011. 47(3): p. 1109-1117.
- 147. Kriegel, C., et al., Influence of surfactant type and concentration on electrospinning of chitosan-poly (Ethylene Oxide) blend nanofibers. Food Biophysics, 2009. 4(3): p. 213-228.
- 148. Gupta, P., et al., *Electrospinning of linear homopolymers of* poly(methyl methacrylate):exploring relationships between fiber formation, viscosity, molecular weight and concentration in good solvent. Polymer, 2005. 46: p. 4799-4810.

- 149. Teo, W.E. and S. Ramakrishna, A review on electrospinning design and nanofibre assemblies. Nanotechnology, 2006. 17(14).
- 150. Lu, K.L., et al., *Mechanical damage of carbon nanotubes by ultrasound*. Carbon, 1996. 34(6): p. 814-816.
- 151. Pai, C.-L., M.C. Boyce, and G.C. Rutledge, *Morphology of Porous and Wrinkled Fibers of Polystyrene Electrospun from Dimethylformamide*. Macromolecules, 2009. 42(6): p. 2102-2114.
- 152. Fakhri, N., et al., *Diameter-dependent bending dynamics of single-walled carbon nanotubes in liquids*. Proceedings of the National Academy of Sciences, 2009. 106(34): p. 14219-14223.
- 153. Wypych, G., Handbook of Solvents, 2001, ChemTec Publishing.
- 154. Inai, R., M. Kotaki, and S. Ramakrishna, *Structure and properties of electrospun PLLA single nanofibres*. Nanotechnology, 2005. 16(2): p. 208-213.
- 155. Anonymous. User's Guide Autotune Series High Intensity Ultrasonic Processor. [cited 2011 15 March].
- 156. Suslick, K.S., Sonochemistry, in Comprehensive Coordination Chemistry II, J.A. McCleverty and T.J. Meyer, Editors. 2003, Pergamon: Oxford. p. 731-739.
- 157. Jambrak, A.R., et al., *Ultrasound effect on physical properties of corn starch*. Carbohydrate Polymers, 2010. 79(1): p. 91-100.
- 158. J.Mason, T. and J.P. Lorimer, *Applied Sonochemistry*. 2002, Verlag GmbH, Weinheim Wiley-Vch
- 159. Grönroos, A., P. Pirkonen, and O. Ruppert, *Ultrasonic depolymerization of aqueous carboxymethylcellulose*. Ultrasonics Sonochemistry, 2004. 11(1): p. 9-12.
- 160. Price, G.J. and P.F. Smith, Ultrasonic degradation of polymer solutions: 2. The effect of temperature, ultrasound intensity and dissolved gases on polystyrene in toluene. Polymer, 1993. 34(19): p. 4111-4117.
- 161. Sakai, W. and N. Tsutsumi, *Photodegradation and Radiation Degradation*, in *Poly(Lactic Acid)*. 2010, John Wiley & Sons, Inc. p. 413-421.
- 162. Yixiang, D., et al., Degradation of electrospun nanofiber scaffold by short wave length ultraviolet radiation treatment and its potential applications in tissue engineering. Tissue Engineering Part A., 2008. 14(8): p. 1321-1329.
- 163. Guillet, J., Fundamental processes in the UV degradation and stabilization of polymers. Pure Appl. Chem, 1972. 30(1-2): p. 135-144.
- 164. Stowe, B.S., R.E. Fornes, and R.D. Gilbert, *UV degradation of Nylon* 66. Polym Plast Technol Eng, 1974. v: p. 159-197.
- 165. Mano, J.F., et al., *Glass transition dynamics and structural relaxation* of *PLLA studied by DSC: Influence of crystallinity.* Polymer, 2005. 46(19): p. 8258-8265.
- 166. Zhu, J., et al., *Magnetic polyacrylonitrile-Fe@FeO nanocomposite fibers - Electrospinning, stabilization and carbonization.* Polymer, 2011. 52(13): p. 2947-2955.
- 167. Zussman, E., et al., *Mechanical and structural characterization of electrospun PAN-derived carbon nanofibers* Carbon 2005. 43: p. 2175-2185.

- 168. Gupta, A. and I.R. Harrison, *New aspects in the oxidative stabilization of pan-based carbon fibers: II.* Carbon, 1997. 35(6): p. 809-818.
- 169. E.Fitzer and D.J. Muller, *The influence of oxygen on the hemical reactions during stabilization of PAN as carbon fiber precursor*. Carbon, 1974. 13: p. 63-69.
- 170. Wang, B., et al., *Effect of the aggregation structure on the thermal shrinkage of polyacrylonitrile fibers during the heat-treatment process.* Journal of Applied Polymer Science, 2012. 125(5): p. 3545-3551.
- 171. Nielsen, M., et al., Formation of toxic gases during pyrolysis of polyacrylonitrile and Nylon. Journal of Analytical and Applied Pyrolysis, 1995. 35: p. 43-51.
- 172. Saiyasombat, C. and S. Maensiri, *Fabrication, morphology, and structure of electrospun pan-based carbon nanofibers.* Journal of Polymer Engineering, 2008. 28(1-2): p. 5-18.
- 173. Paiva, M.C., et al., UV stabilization route for melt-processible PANbased carbon fibers. Carbon, 2003. 41(7): p. 1399-1409.
- 174. Naskar, A.K., et al., UV assisted stabilization routes for carbon fiber precursors produced from melt-processible polyacrylonitrile terpolymer. Carbon 2005. 43 p. 1065–1072.
- 175. Lee, S., et al., *Structural evolution of polyacrylonitrile fibers in stabilization and carbonization*. Advances in Chemical Engineering and Science, 2012. 2: p. 275-282.
- 176. Ji, M., et al., Structural Evolution of Polyacrylonitrile Precursor Fibers during Preoxidation and Carbonization. Polymer Bulletin 2007. 59,: p. 527–536.
- Wladyka-Przybylak, M., et al., Functionalization effect on physicomechanical properties of multi-walled carbon nanotubes/epoxy composites. Polymers for Advanced Technologies, 2011. 22(1): p. 48-59.