CHAPTER I

INTRODUCTION

1.1 Background

The fabrication of materials with one-dimensional nanoscale structure is of great promise for the fundamental understanding of the roles of dimensionality and size in an optical, electrical, and mechanical properties with reference to applications in semiconductor, mechanical, and chemical industries. Polymer nanofibres are of considerable interest for various kinds of applications including filters, reinforcing agents, biomedical materials and fibre templates to prepare nanotubes. Recently, there has been a growing interest in one-dimensional, inorganic nanosized materials such as carbon nanotubes, carbon nanorods, silica and titania nanofibres/nanotubes. These one-dimensional nanomaterials exhibit some novel physical and chemical properties due to their peculiar structure and size effect, and are of great importance in nanodevices and mesoscopic theoretical research. Hence, it is very interesting to conduct the research in this field. From this point, it comes to a very important question of the how nanofibres are fabricated.

From various types of spinning technique, electrospinning technique is an effective method for producing nanofibres. Previously, there are two routes for making ultra-fine fibres commercially that are direct spinning and conjugate spinning. In direct spinning method, the conditions of conventional spinning are optimised so as to be suitable for the production of ultra-fine fibres. In the conjugate spinning, ultra-fine fibres are produced by extrusion of polymer components arranged alternately such as in the islands-in-a-sea, separation or splitting, and multi-layer types, and then splitting these components into fibres.

In recent years, due to further understanding and continuing development of the technique, electrospinning offers to be a new method that can make ultra-fine fibres with diameters in the nanometre range. In this process, it involves the application of a strong

electrostatic field between capillary connected with a reservoir containing a polymer solution or melt and a collection screen. Under the influence of the electrostatic field, a pendant droplet of the polymer solution at the capillary tip is destabilised into a conical shape (Taylor cone). If the voltage surpasses a threshold value, electrostatic forces overcome the surface tension, and a fine charged jet is ejected. The jet moves towards a grounded collection plate. Due to the extensional viscosity of the polymer solution and the presence of entanglements, the jet remains stable and does not transform into spherical droplets as expected for a liquid cylindrical thread. The solvent begins to evaporate immediately after the formation of the jet. The result is the deposition of a thin polymer fibre on a substrate located above the counter electrode.

The formation of fibres from this spinning process can be divided into two parts.

(1) The initiation of the jet.

(2) The continuous flow of the jet

The initiation of the jet

In electrospinning, initiation and formation of the jet are complex and interesting processes. The initiation is less important than the maintenance of a stable jet, but it is an essential step to the technique.

Before the electric field is applied to the polymer solutions, and when the capillary tube or nozzle is in a vertical position and carries a drop to the tip of nozzle, the relation between the surface tension and the height of the column of liquid under equilibrium conditions is given by

$$2\gamma(1/R + 1/r) = \rho gh \qquad (1)$$

where γ is the surface tension of the liquid of density ρ, h is the height of the column of liquid above the lowest surface of the drop, R is the radius of curvature of the liquid at the upper liquid surface and r is the radius of curvature of the liquid at the lower surface

of the liquid. The drop formation can be observed without an applied electric field. If the hydrostatic pressure is high enough, a jet is formed instead of a drop (Michelson, 1990).

Consider a droplet of polymer solutions that is applied to a high electric field. Charges are present in the liquid repel one another. The repulsion forces are opposed to the forces of surface tension of the liquid molecules. The polymer droplet becomes unstable when repulsive force from charged surface becomes large enough to overcome the stabilising force of surface tension. The conditions that are necessary for a charged surface to become unstable can be described by considering a force equilibrium equation,

$$V_* = (4\pi r \gamma)^{1/2}$$

where V_* is the critical potential, r is the droplet radius, and γ is the surface tension of the solution. For the droplets subjected to a higher potential, $V > V_*$ the droplet elongates into a cone-like shape that was described mathematically by Taylor and often referred to as a Taylor cone.

The charge per unit area at the tip of this Taylor cone becomes higher as the radius near the tip of the cone decreases. As the potential is increased, beyond the stability limit, a jet of liquid ejected from the tip of the cone. After jet initiation, the cone shape cannot be maintained if the flow of solution to the capillary or nozzle tip does not match the rate at which the solution is being removed by the jet. However, the electrostatically driven jet may continue to flow after the collapse of the cone, even though the shape of the surface from which the established jet originates is radically different from the conical shape seen at the time of the jet initiation.

The continuous flow of the jet

Originally, the mechanism of the appearance of a stable electrospinning jet separates into four regions as shown in figure 1.1. The jet emerges from the charged surface at the base region, travels through the jet region, divides into many fibres in the splaying region, and stops in the collecting region.
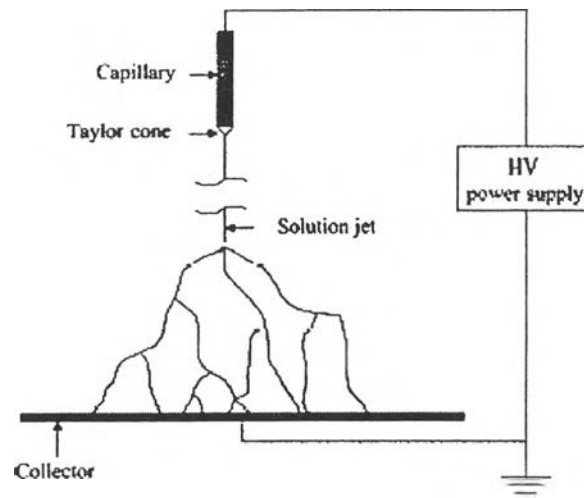
Figure 1.1 Schematic drawing of an electrospinning set-up.

After observation of the jet formation through the high speed electronic camera which recorded up to 2000 frames per second with a time resolution of approximately 0.0125 ms, the mechanism is altered from previous mechanism (Reneker *et al*, 2000). After a charged jet is ejected from the droplet, it will flow continuously under the influence of the electric field. There are two kinds of electrical forces that act on the jet. One force is from the external field that tries to pull the jet toward collector. Another force is the self-repulsion between the charges carried by adjacent segments of the jet that try to push each other apart. The self-repulsion can also cause different types of instability such as bending instability and splitting instability.

In electrically driven bending instability, alternatively referred to as instability, the jet rotates in a conical region, whose vertex is the end of the straight jet. The other end of the jet, which is highly stretched, and reduced in diameter, is deposited on the collector as a result of the fast whipping motions. Previous observations at coarser time resolution led to the mechanism where, instead of a single whipping fiber, a large number of smaller diameter fibres are formed at the end of the initial straight jet under

the action of charges present, and are deposited independently on the collector (Shin *et al*, 2001).

The jet followed a bending, winding, spiraling and looping path in three dimensions. The jet in each loop grew longer and thinner as the loop diameter increased. After some time, segment of a loop suddenly developed a new bending instability, but at a smaller scale than that of the first one. Each cycle of bending instability can be described in three steps (Reneker *et al*, 2000).

Step 1: A smooth segment that was straight or slightly curved suddenly developed an array of bends.

Step 2: The segment of the jet in each bend elongated and the array of bends became a series of spiraling loops with growing diameters.

Step 3: As the perimetre of the loops increased, the cross-sectional diameter of the jet forming the loop grew smaller; the conditions of the first step were established on a smaller scale, and the next cycle of bending instability began.

This cycle of instability was observed to repeat in a smaller scale. It was inferred that a larger number of cycles occurred resulted in a decrease in the jet diameters, hence a decrease in the diameter of the obtained fibres. The fluid jet solidifies as it dried and electrospun nanofibres were collected some distance below the envelope cone.

By applying a secondary external field of the same polarity as the surface charge on the jet, it is possible to control or eliminate the bending instability (Deitzel *et al*, 2001). This mechanism allows for greater control over the deposition of electrospun fibre on a surface and for collection of electrospun fibres in other forms besides non-woven mats.

Another instability of the charged jet is the splitting instability. It occurs when the charged jet increases as the solvent evaporates. The elongation of the jet can reduce charge per unit surface area since elongation increases the surface of a particular mass. The charged jet can reduce its charge per unit surface area by ejecting a smaller jet from the surface of the primary jet, or by splitting apart to form two smaller jets. This

instability of the jet is also observed in the previous mechanism, which is in part of splaying region.

However, there are some problems which must be overcome; e.g., what should be the best precursor for producing silica nanofibres? Silatrane complexes stand as a very good candidate for this process. Silatrane complexes are one of a family of organosilicon compounds, these compounds are derived from trialkanolamine such as triethanolamine, triisopropanolamine. They have silicon-nitrogen coordination in the structure. These are hydrolytically stable and have unique physical properties. They can be stable in air (moisture) for periods of up to several weeks in their bulk forms. With these reasons the silatrane complexes can be served as precursors in electrospinning process by a sol-gel technique.

In sol-gel method, this has widely been used as an alternative technology for the preparation of a wide variety of forms including monoliths, powders, coatings, and fibres because the conventional method requires high temperature which often limits the control of the microstructure, properties, shape, and surface features obtained. The goal of this method is to use low temperature chemical process to produce net-shape, net-surface objects, or composites that can be used commercially after a minimum of additional processing step.

Sol-gel technology is the preparation of ceramic, glass, or composite materials by the preparation of a sol, gelation of the sol, and removal of the solvent. Potential advantages of the sol-gel process include:

(1) The ability to maintain high purity

(2) The ability to vary compositional homogeneity at a molecular level

(3) Low temperatures of processing that lead to saving in energy

(4) Preparation of new crystalline phases and new noncrystalline solids

(5) The ability to produce samples in different physical forms

(6) Ultrastructure control of materials by manipulating network formation from early stages of sol formation

(7) Preparation of materials having improved physical properties

On the other hand, this technique holds some drawbacks which are the shrinkage of the ceramics from removal of the solvents and the need for expensive high-purity alkoxides. This tends to limit the use of the process for bulk ceramics, but is a minor for special applications or those cases where conventional technology fails.

The handling of precursor by heat treatment is an important factor needed to be considered. Generally, the sol-gel process is the synthesis of an inorganic network at low temperature by a chemical reaction in solution. This technique involves a transition characterised by a relatively rapid change from a liquid (solution or colloidal solution) into a solid (gel-like state).

Sol-gel technology can be divided into two types. Firstly, colloidal method involves the suspension of solid particles in a liquid to form a sol. Secondly, polymeric method involves polymerisation of organometallic compounds, such as alkoxides that provide a convenient source for inorganic monomers to form a gel with three-dimensional network structure. The metal alkoxides, $M(OR)_n$, generally consist of metal atom, M, bonded through oxygen atom to one or more alkyl groups, when n is the valence of the cation.

Generally, the precursor is dissolved in a suitable organic solvent in order to obtain a solution. The solvent must be carefully selected so that a solution with high concentration of the required component is obtained.

Sol-gel processing involves the following steps:

1. Hydrolysis of precursor
2. Polycondensation
3. Gel formation
4. Organic pyrolysis by heat treatment

The first step, starting materials (metal alkoxides) are mixed in a selected solvent system to form a solution. In the gelation process, the transition from a solution into solid, involves simultaneous hydrolysis and polycondensation of metal alkoxide precursor. Many factors influence the rate of hydrolysis and condensation because both processes often occur simultaneously. The most important variables are temperatures,

nature and concentration of electrolyte, nature of solvent, and types of alkoxide precursor. The following step, pyrolysis, is necessary to convert gel into a useful form.

Sol-gel process can be done at the ambient condition (vacuum is not needed). Another advantage of this process is inexpensive as compared to other deposition techniques. Materials can be produced in a variety of forms, such as fine powders, thin films, monoliths and fibres. However, some drawbacks of the sol-gel process are excessive shrinkage that can cause cracking.

At present, metal alkoxides are exploited as precursors for polymeric gel in sol-gel processing. These precursors are readily used with a suitable organic solvent, which is usually alcohol. The metal alkoxide bond is in general extremely susceptible to hydrolytic reaction leading to metal hydroxides or hydrated oxide. The choice of an alkoxide can be considered by many factors including metal content, reactivity, availability, cost, and sensitivity to moisture and decomposition temperature.

A compound with less organic content and high metal content is always a proper precursor. Less organic solvent causes in less volumetric shrinkage during drying and annealing. Therefore, film has fewer tendencies to crack. Although, a compound with high metal content is usually much more reactive, it may be difficult to prepare a stable solution. For alkoxides with different alkyl groups, the reactivity usually increases in the order of methyl>ethyl>propyl>butyl>higher order alkyl groups.

In the gelation step, there are two important reactions in polymeric gel formation. These reactions are partial hydrolysis, followed by condensation polymerisation. Polymerisation steps via hydrolysis and condensation reaction are depicted in the reaction scheme 1.1;

Reaction 1 (Hydrolysis)

$$M(OR)_n + H_2O \longrightarrow M(OR)_{n-1}(OH) + ROH$$

Reaction 2 (Condensation)

$$M(OR)_n + M(OR)_{n-1}(OH) \longrightarrow M_2O(OR)_{2n-2} + ROH$$

Reaction 3 (Condensation)

$$M(OR)_{n-1}(OH) + M(OR)_{n-1}(OH) \longrightarrow M_2O(OR)_{2n-2} + H_2O$$

The M-O-M network product is formed by polycondensation reactions as in reactions 2 and 3, in which alcohol and water are produced as the by-products. There are many applications of controlled hydrolysis to obtain a desired molecular structure.

Other parameters that need to be considered are the aging of gel, removal of solvent, and heat treatment.

Aging represents the time between the formation of a gel and the removal of solvent. As long as the pore remains in the matrix, a gel can undergo many transformations. For alkoxide derived gels, condensation between surface functional groups continue to occur after the gel point. This process can actually be desirable because it leads to a more cross-linked network that is mechanically stronger and easier to handle.

Drying is a process of evaporating solvent from a gel network. Similar to aging, a gel is not static during drying and, for that reason, drying can be viewed as part of the overall aging process. The properties of product are thus depended on the drying method and condition.

Calcination/Sintering often is done in the presence of a reactive gas (e.g. flowing air, oxygen, or hydrogen) in order to burn off any organic residues or to oxidize (or reduce) the sample. Exposing the sample to a high temperature over an extended period of time leads to sintering and consequently a less surface area. The process can also cause the material to crystallise into different structural forms. Thus, the physical characteristics of the product depend on various parameters, such as temperature, heating rate, time and gaseous environment.

From the work on the electrospun silica nanofibres via sol-gel process, the electropsun silica nanofibres were prepared by sol-gel technique. The sol precursors are prepared from tetraethylorthosilicate (TEOS), $Si(OCH_2CH_3)_4$. In recent years, there have been efforts to synthesise metal oxide (silica or titania) nanofibres and nanotubes by the sol-gel template method. Meanwhile, preparation of micron-sized silica fibres have been achieved by extruding spinnable sol through an orifice.

In this work, silica nanofibres will be prepared by electrospinning technique from silatrane precursors.

1.2 Objectives

The objectives of this research work are :

1. To prepare electrospun silica fibres from silatrane precursors
2. To characterise structures, morphologies, and properties of the obtained electrospun fibres