CHAPTER I
INTRODUCTION

The production of ultra-fine fibers has been developed continuously. To manufacture finer and finer fibers has always been challenging for the researcher in academic institute and fiber companies for decade. Different ultra-fine fibers are designed to provide the interesting characteristics such as very large surface area to volume ratio, large aspect ratio, flexibility in surface functionalities, good interpenetrating capacity in other materials and superior mechanical performance (Nakajima, 1994). Previously, there are two routes to make continuous ultra-fine fibers commercially that are direct spinning and conjugate spinning. In direct spinning method, the conditions of conventional spinning are optimized so as to be suitable for the production of ultra-fine fibers. While in the conjugate spinning, ultra-fine fibers are produced by extrusion of polymer components arranged alternately such as islands-in-a-sea-type, separation type or splitting type, and multi-layer type, and then splitting these components into fibers (Hongu and Phillips, 1997).

In short recent years, the fabrication of ultra-fine fibers with diameters being in sub-micron down to nanometer range by the technique known as electrostatic spinning or electrospinning has been much development and exploration. This process is different from the conventional spinning by the applied of high electrostatic fields to the polymer melts or solutions, whereas the mechanical forces are applied in the conventional spinning. Naturally, the ultra-fine fibers from this process are obtained as a non-woven fabric, which exhibits several interesting characteristics, such as small pore sizes between adjacent fibers, high porosity, and high specific surface area. These characteristics can be of tremendous uses in some applications such as filters or the separation of sub-micron particles, as reinforcing fillers in composite materials, as wound-dressing and tissue scaffolding materials for medical uses and as controlled release materials for agricultural and pharmaceutical uses (Huang *et al.*, 2003).

Set-up of the electrospinning process is very simple. The three major components are a high-voltage power supply, a container for a polymer solution or melt with a small opening to be used as a nozzle, and a conductive collection device.

An emitting electrode of the high-voltage power supply charges the polymer solution or melt by either directly submerging the electrode in the polymer solution or melt or by connecting the electrode to a conductive nozzle. The other or grounding electrode of the high-voltage power supply is connected to the conductive collection device to complete the circuit. Other set-ups are also possible (Hongu and Phillips, 1997).

The basic principles of the electrospinning process are concerned with the application of a high electrostatic potential from an emitting electrode of a high-voltage power supply to the polymer solution or melt across a finite distance between a conductive nozzle and a grounded collective screen (Reneker and Chun, 1996). The Coulombic repulsion force between charges of the same polarity produced in the polymer solution or melt by the emitting electrode destabilizes the hemi-spherical droplet of the polymer solution or melt located at the tip of the nozzle to finally form a droplet of a conical shape (i.e. the Taylor cone). With further increase in the electrostatic field strength beyond a critical value, the Coulombic repulsion force finally exceeds that of the surface tension which finally results in the ejection of an electrically charged stream of the polymer solution or melt (i.e. the charged jet).

There are six major forces acting on an infmitestimal segment of the charged jet: they are 1) body or gravitational force; 2) electrostatic force which carries the charged jet from the nozzle to the target; 3) Coulombic repulsion force which tries to push apart adjacent charged species being present within the jet segment and is responsible for the stretching of the charged jet during its flight to the target; 4) viscoelastic force which tries to prevent the charged jet from being stretched; 5) surface tension which also acts against the stretching of the surface of the charged jet; and 6) drag force from the friction between the charged jet and the surrounding air (Wannatong *et al.*, 2004). Due to the combination of these forces, the electrically charged jet travels in a straight trajectory for only a short distance before undergoing a bending instability, which results in the formation of a looping trajectory (Reneker *et al.*, 2000). During its flight to the collector, the charged jet thins down and, at the same time, dries out or solidifies to leave ultrafine fibers on the collective screen.

In the electrospinning process of a polymer solution, a number of parameters can influence the morphology of the obtained fibers. These governing

parameters can be categorized into three main types: 1) solution (e.g. concentration, viscosity, surface tension, and conductivity of the polymer solution); 2) process (e.g. applied electrostatic potential, collection distance, and feed rate); and 3) ambient parameters (e.g. temperature, relative humidity, and velocity of the surrounding air in the spinning chamber) (Doshi and Reneker, 1995). Baumgarten (1971) was one of the early researchers who recognized the effects of some of these parameters on the morphological appearance of as-spun acrylic fibers. He found that an increase in the solution viscosity (as a result of an increase in the solution concentration) was responsible for an increase in the average fiber diameter, while an increase in the flow rate of the acrylic solution did not appreciably affect the fiber diameters. He also found that the spinning drop tended to dry out in dry air (<5% R.H.), while fibers did not dry properly and tangled on the collecting screen in humid air (>60% R.H.), and spinning could not be performed in helium atmosphere.

Larrando and Manley (1981) found that the diameter of molten polyethylene and polypropylene electropun fibers decreased with an increase of electric field intensity. Under the same electric field intensity, increasing the temperature of the molten polymer lead to the formation of smaller fibers. The orifice diameter was found to have no effect on fiber diameter. Fong *et al.* (1999) investigated the formation of minute beads along the electrospun poly(ethylene oxide) (PEO) fibers by relating the phenomenon to the properties of the solutions. They found that the number of beads decreased with increasing viscosity and net charge density, while it decreased with decreasing surface tension coefficient, of the solutions.

Deitzel *et al.* (2001) studied the effects of two of the most important processing parameters: spinning voltage and solution concentration, on the morphology of the electrospun PEO polymer. They found that spinning voltage was strongly correlated with the formation of bead defects in the fibers, whereas solution concentration was the most strongly affect fiber size that fiber diameter increased with increasing solution concentration according to a power law relationship. Buchko *et al.* (1999) found the dependence of process parameters (i.e. solution concentration, applied potential, collection distance, and collection time) on morphology of electrospun webs obtained. Demir *et al.* (2002) observed that the diameters of as-spun polyurethaneurea increased as the third power of solution concentration. They

also found that the morphology of these as-spun fibers correlated strongly with the solution viscosity. Zong *et al.* (2002) also found strong influence of the solution concentration and salt addition on diameters of as-spun poly(D,L-lactic acid) (PDLLA) and poly(L-lactic acid) (PLLA). Addition of pyridinium formate into PLA solutions (Jun *et al.*, 2003) helped increase solution conductivity values and, in turn, helped decrease the possibilities for bead formation. Choice of the solvent system used also found to have a strong influence on the morphology and diameters of the as-spun cellulose acetate (Liu and Hsieh, 2002), poly(ε-caprolactone) (PCL) (Lee *et al.*, 2003), and poly(vinyl chloride) (PVC) (Lee *et al.*, 2002) fibers, respectively.

Although various aspects of electrospun fibers have been intensely explored and reported in the open literature in the past years, a number of fundamental aspects of the process for different polymer-solvent systems are still worthy of further investigation in order to gain a thorough understanding of the process. Since, in this work, the effects of solution and process parameters on the resulting electrospun polyamide-6 fibers were focused. Polyamide-6 was also spun by conjugate spinning method to produce ultra-fine fibers (Nakajima, 1994), and it has been used commercially in the textile industry, which has excellent properties (e.g. high strength, high modulus, flexibility, toughness, chemical resistance and a low coefficient of friction) (Mark *et al.*, 1992).

The objective of this research work was to study the effect of solution and process parameters on the morphological characteristics and the diameter of the electrospun polyamide-6 fibers using optical scanning (OS) and scanning electron microscopy (SEM) techniques. For the solution parameters, various influencing parameters were investigated, i.e. solution concentration, molecular weight of polyamide-6, solution temperature, addition of ionic salt, and solvent systems. The solution properties (i.e. viscosity, surface tension, conductivity) of all those solutions were measured to describe the influencing of solutions parameters on the obtained electrospun fibers. For the process parameter, electrostatic field strength and the emitting electrode polarity (either positive or negative) were varied.

The content of this dissertation divided in 6 chapters; some theoretical backgrounds with literature surveys of the electrospinning process and objective of this research work are in chapter I. Some resulting of solution parameters including

process parameter (i.e. solution concentration, solvent type, salt addition, and emitting electrode polarity) are described in Chapter 2, which is the format of a manuscript published in Macromolecular Symposia (216, p.293-299, 2004). Chapter 3 focused on the effect of solution parameters (i.e. solution concentration, molecular weight of polyamide-6, solution temperature, solvent systems, and salts addition), this chapter is the format of a manuscript published in Macromolecular Chemistry and Physics (205, p. 2327-2338, 2004). The effect of emitting electrode polarity, the one of process parameter, was investigated combining with some influencing solution and process parameters (i.e. polyamide-6 concentration, molecular weight of polyamide-6, electrostatic field strength, solution temperature, solvent type, and addition of an inorganic salt), are contained in Chapter 4. Chapter 5 focused on the effect of various solvent systems. Finally, Chapter 6 is the overall conclusions of this research and recommendation for the further work.

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