

CHAPTER II

LITERATURE SURVEY

2.1 Electrospinning

2.1.1 Experimental Set-up

In general, the experimental set-up can be divided into two types based on direction of polymer supplying nozzle including horizontally and vertically. The two kinds of polymer supplying nozzle are glass pipette and metal needle. For the experimental set-up where glass pipette is used, the external potential was supplied by directly inserting a metal electrode to the capillary tube filled with a polymer solution (Reneker, 1995). Schematic drawing of this is shown in Fig. 2.1. In case of the metal needle set-up, the external potential was attached outside of the metal needle (Baumgarten, 1971, Norris, 2000).

Screens of different geometry were used as collecting devices for the charge fibers such as metal sieve, even metal screen. Recently, Warner *et al.* (2000) developed a novel rotor electrospinning unit to produce the first yarns (see Fig. 2.2). This unit is capable of spinning from multiple spinners simultaneously. A rotating collector provides a mechanism for continuous removal of the non-woven fabric as a yarn.

2.1.2 Polymer Types

Many kinds of polymer have been successfully produced by electrospinning process from polymer solution and melts (Lorrando, 1981). At least 20 polymers have been electrospun in laboratory of Reneker *et al.* (1996). These are polyethylene oxide (PEO), which is the most often used to study parameters influencing the process, textile fiber polymers such as nylon, high performance polymers such as polyimide, and biopolymers including DNA (Fang, 1997). In addition, liquid crystal polymers such as polyaramid and polyaniline which is an electrically conducting polymer have also been successfully electrospun by this group. Moreover, polymer blends, for example, polyaniline/polyethylene oxide (Norris, 2000), can be produced by this process as well.

The list of other polymers that have already been electrospun are as follows: polyethylene, polypropylene (Lorrando, 1981), polyamid acid, poly-gamma-benzyl-glutamate, polyethylene terephthalate, Nylon 6-polyimide, polyhydroxybutyratevalerate, polyetherimide, polyferrocenyldimethylsilane, polyacrylonitrile, poly (*p*-phenylene terephthalamide) (Reneker, 2000), Nylon6-montmorillonite nanocomposite (Fong, 2002), and poly (D, L-lactic acid)(Zong, 2002).

Baumgarten (1971) spun fibers measuring less than 1 μm in diameter by electrostatic means from dimethyl formamide (DMF) solution of acrylic resin. High-speed photographs showed that a single fiber was drawn out from the electrically charged drop, which was suspended from a metal capillary. The effects on diameter and jet length of solution viscosity, surrounding gas, flow rate, voltage, and geometry were determined. With pure DMF, fine droplets were formed. Fiber formation started with a 7.5 wt% solution (1.7 poise) and continued to 20 wt% (215 poise). With 17.5 and 20 wt%, however, drying of the fiber was incomplete, and the fiber began to stick to itself in mid air. Fiber diameter increased with solution viscosity.

2.1.3 Pathway of Charged Jet

In 1995, Doshi and Reneker proposed that the charged polymer jet was due to the forces from the increase in surface charge density as the diameter is reduced by evaporation. Five years later, year 2000, Reneker *et al.* submitted a new idea of charged jet pathway to explain the formation of bending instability of polymer solution charged jet. They show that the electrically charged jet traveled for a few centimeters in a straight line. At the end of the straight line, it bent to be a diaphanous shape, also conical, with its vertex at the end of the straight segment. This cone is the envelope, in space, of the complicated set of paths. This notion was also emphasized by the images obtained with short exposure times by Baumgarten (1971) and by Warner *et al.* (1998) and Hohman *et al.* (2001).

2.1.4 Microstructure and Morphology

The microstructure and morphology of electrospun fiber were investigated by scanning electron microscope (SEM), differential scanning calorimetry (DSC), synchrotron wide-angle X-ray diffraction/small angle X-ray scattering (Zong, 2002), atomic force microscopy (AFM) (Jeager, 1996), TEM (Buchko, 1999), and wide-angle X-ray scattering (WAXS) (Buchko, 1999). Baumgarten (1971) electrospun polyacrylonitrile from solution but did not characterize the molecular orientation of fiber. Thus this present work investigated his data.

In 1996, Jeager *et al.* observed the surface morphology of electrospun PEO by using AFM and also optical microscope to investigate the birefringence. They reported that, at the molecular level, the electrospun PEO fibers possess a highly ordered surface layer and the chain direction of the molecules was parallel to the fiber direction.

This property was also found in other electrospun fibers, for instance, semi-crystalline poly (D, L-lactic acid) exhibited non-crystalline but highly oriented chain when characterized by DSC and XRS (Zong, 2002), nylon displayed molecular orientation along the fiber axis but it was not uniform (Buchko, 1999), while electrospun SLPF thin films were not well orientated. In addition, Buchko *et al.* (1999) suggested that thermal and solvent annealing could be a method for increasing the crystallinity of electrospun fibers.

2.1.5 Applications

Almost 90 years ago, the process that generates ultrafine fibers by using electrostatical field ("electrospinning") was discovered by Zeleny (1914). However, this process has just received a great deal of attention in the last decade. Because of the small fiber diameters, electrospun textiles inherently possess a very high specific surface area and small pore size. These properties make electrospun fabrics interesting candidates for a number of applications. They are high performance filters i.e., dust collecting system and air filter (Emig, 2002), soldier protective clothing (Gibson, 1999), biomedical application including scaffolding for tissue growth (Vyakarnam, 2001), drug delivery system and wound dressing

materials (Doshi, 1995; Huang, 2001), electronic applications (Norris, I.D., 2000), composite reinforcement (Dzenis, 2001; Doshi, 1995), the design of solar sails, light sails, and mirrors for use in space, the application of pesticides to plants and as structural elements in artificial organs (Reneker, 20000). Some of the applications mentioned previously have been used and already patented such as dust filter containing nano non-woven tissue which was patented by Emig (2002).

2.2 Carbon fiber

To utilize the unique characteristics of the high specific surface provided by electrospun fibers. Carbon nanofibers made from polymeric precursors make it possible to expand the list of possible uses for nanofibers from electrospinning technique.

In 1999, Chun *et al* produced carbon nanofibers from both polyacrylonitrile and mesophase pitch by electrospinning technique. Stabilization and carbonization were used to convert as-spun nanofibers to carbon fibers. The nanofibers are arbitrarily long, although a way to make nanofibers less than a millimeter long with high aspect ratios was found. The diameters of typical carbon nanofibers are in the range from 100 nanometer to a few microns. The carbon nanofibers were observed by wide angle X-ray diffraction. Nanofibers provide a higher ratio of surface to mass than ordinary used in composite. Carbon nanofibers can be useful in filters, as a support for catalysts in high temperature reactions, in composites to improve mechanical properties, or for thermal management in semiconductor devices. Nanopores in carbon fibers were produced using nitrogen gas saturated water vapor. However, the conductivity of carbon nanofiber was not reported.

MacDiarmid *et al.* (2001) has similarly converted, as Chun's work, polyacrylonitrile fibers (diameter 750 nm) to a carbon fibers by first heating at 200°C in air for 20 minutes followed by heating at 800°C for 2 hours under nitrogen. A current per voltage curve was obtained for a 600 nm diameter carbon fiber.

The knowledge for producing carbon fibers from precursor that has very small diameter is still lacking. Thus, the carbon fiber manufacturing technique for

the typical carbon fiber will be adopted for the preparation of carbon nonofibers.

The composition structure, and quality of PAN precursors predetermine carbon fiber manufacturing conditions, and to a large extent the quality and mechanical properties of the resulting carbon fiber. The exact composition of PAN polymer used for carbon fiber precursor varies from company to company and is commonly considered to be a trade secret. Gupta *et al.* (1991) suggested that copolymer with greater than 90% acrylonitrile (AN) with small amounts of comonomer such as methyl acrylate, methyl acrylate, or itaconic acid are predominately used. The comonomer serves two purposes. Firstly, the comonomer increases thermal reactivity and broadens the stabilization rates, and provides better thermal control of the process. Secondly, it tends to reduce the strong intermolecular bonding that occurs in PAN homopolymer because of the polar nitrile group, consequently, increases fiber stretchability.

Liu *et al.* (1994) reported a variation in tensile mechanical properties and morphological structure along the carbonization by following the progressing of continuous carbonization (300-1250°C) of polyacrylonitrile (PAN)-base oxidized fibers. The tensile strength and Young's modulus of the fibers generally increase throughout the carbonization stage. Meanwhile, the fiber diameter displays a significant decrease. The preferred orientation of carbon layer planes was observed to increase remarkably for temperatures over 400°C. In a similar manner, the stacking size increases significantly but reaches saturation around 600°C, a changing point corresponding to that observed for the variation of the Young's modulus.