

## CHAPTER II

### LITERATURE SURVEY

#### 2.1 Experimental Set-up

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 needle, and a conductive collector screen. In the electrospinning process the power supply is used to create an electrically-charged jet of polymer solution or melt. Mutual charge repulsion causes a force directly opposite to the surface tension (Huang *et al.*, 2003). As the strength of the electric field increases, the hemispherical shape of a pendant drop at the tip of the needle elongates to form a conical shape, known as the Taylor cone (Taylor, 1964). With further increasing the field strength, a critical value is attained when the repulsive electrostatic forces overcome the surface tension and a charged jet of fluid is ejected from the tip of the needle. The discharged polymer solution jet undergoes a whipping process wherein the solvent evaporates, leaving behind a charged polymer fiber, which lays itself randomly on a grounded conductive collector screen, which is connected to the grounding electrode of the power supply (Deitzel *et al.*, 2001).

In general, the experimental setup can be divided into two types based on the direction of polymer-supplying nozzle, which is horizontal or vertical. The two kinds of polymer-supplying nozzle are used: glass syringe and metal needle. For the experimental setup where a glass syringe is used, the external potential was supplied by directly inserting a metal electrode to the needle filled with a polymer solution (Reneker *et al.*, 1996).

Nanofibers obtained are in the form of non-woven webs because the polymer jet trajectory is in a very complicated three-dimensional “whipping” fashion caused by bending instability rather than in a straight line. Up to date, there is no continuous long nanofiber yarn obtained and the publications related to aligned nanofibers are very limited. Nevertheless, there are some possible means which has been used to prepare aligned electrospun nanofibers such as the use of a cylinder

collector with a high rotating speed (Boland *et al.*, 2001), an auxiliary electrode/electrical field (Berry, 1990), a thin wheel with a shape edge (Theron *et al.*, 2001), a framed collector (Fong *et al.*, 2001), and the multiple field technique (Deitzel *et al.*, 2001).

## 2.2 Polymer Types

Electrospinning (also called electrostatic spinning) is a process that utilizes electrical force to produce polymer fibers from polymer solutions or melts. Although the behaviour of electrically driven liquid jets and electrically charged liquid drops have been of interest since the late 1800's, electrospinning was paid attention only during the recent several decades.

The earliest patent on electrospinning of polymer fibers was issued by Formhals (1934), followed by the first scientific study by Baumgarten (1971), in which the fiber diameter was in the range between 500-1,100 nm. Later, Larrondo *et al.* (1981) described the electrospinning of polyethylene and polypropylene fibers from the melts in air. Recently, it has been shown that the electrospinning process is capable of producing fibers with submicron-scale diameters (Doshi *et al.*, 1995), and these diameters are at least one order of magnitude smaller than those obtained by the conventional fiber spinning. To date, over 30 synthetic or natural polymers have been electrospun, with research interest focussing primarily on the structure and the morphology of the electrospun fibers.

In electrospinning, unexpected phenomenon and experimental results such as the formation of beads, necklace, ribbon-like and branched jet, etc. have been observed. The formation of beads within electrospun fibers has been observed often by Baumgarten (1971). He was one of the early researchers who recognized the effects of a number of parameters on the morphological appearance of as-spun acrylic fibers. He found that an increase in the solution viscosity was responsible for the observed increase in the average fiber diameter, while an increase in the flow rate of the acrylic solution did not appreciably affect the fiber diameters.

Entove *et al.* (1997) reported that the bead formation occurred as a result of instability of the polymer solution jet. Fong *et al.* (1999), on the other hand,

indicated that solution viscosity, surface tension and net charge density induced by the electrospinning are the main factors contributing to the formation of beads during the formation of the fibers. They found that the number of beads decreased with increasing viscosity and net charge density and decreasing surface tension coefficient of the solutions.

Wannatong *et al.* (2004) used six solvent (i.e. acetic acid, acetonitrile, m-cresol, toluene, THF, and DMF) with different properties (e.g. boiling point, density, dipole moment, dielectric constant, and solubility parameter) to prepare electrospun polystyrene fibers. Fiber diameters were found to decrease with increasing density and boiling of the solvents. A large difference between the solubility parameter of PS and solvent was responsible for the bead-on-string morphology observed. Productivity of the fibers (the numbers of fiber webs per unit area per unit time) was found to increase with increasing dielectric constant and dipole moment of the solvents. Among the solvent investigated, DMF was the best solvent that provided PS fibers with highest productivity and optimal morphological characteristic. The beadless, well-aligned from 10% (w/v) PS solution in DMF at an applied electrostatic field of 15kV/10cm, a N<sub>2</sub> flow rate of 101 ml/min, and a rotational speed of the collector of 1,500 rpm.

Choice of solvent or a combination of solvents used was also found to have a significant effect on the morphology of the electrospun fibers. Lee *et al.* (2002) found that electrospun poly(vinyl chloride) (PVC) fibers from PVC solutions in tetrahydrofuran (THF) showed broad range of diameters from 500 nm to 6  $\mu$ m, while those from PVC solutions in DMF showed diameters in the vicinity of 200 nm and those from PVC solutions in mixed THF and DMF showed diameters of less than 1  $\mu$ m. Lee *et al.* (2003) electrospun poly( $\epsilon$ -caprolactone) (PCL) from the PCL solutions in a mixture of methylene chloride and dimethylformamide (DMF). They found that the spinnability and the diameter of the obtained fibers dramatically decreased with increasing DMF content, due possibly to the increased conductivity dielectricity of the resulting solutions.

In order to produce nanometer-sized fibers in the industrial scale, the productivity of the fibers is important. The higher amount of fiber produced within a

specified time period implies the greater chance for the polymer solution to be spinnable.

Jarusuwannapoom *et al.* (2005) reported that only the PS solutions in 1,2-dichloroethane (DCE), *N,N*-dimethylformamide (DMF), Ethylacetate (EA), methylethylketone (MEK), and tetrahydrofuran (THF), among the eighteen individual solvents investigated, could produce fibers with high enough productivity. Based on quantitative observation of the results obtained, the important factors determining the productivity of the as-prepared PS solutions are high enough values of both the dipole moment of the solvent and the conductivity of both the solvent and the resulting solutions, high enough boiling point of the solvent (in order for the hanging droplets not to drying out during electrospinning), and not-so-high values of both the viscosity and the surface tension of the resulting solutions.

The best solvent with the highest solubility are not always the best solvent for electrospinning, since the production rate of the fibers depends not only on the process conditions, but also on the solvent properties of the fluid itself (Hongrojjanawiwat *et al.*, submitted). The spinnability of the solution depends on chemical structure and size of solvent molecules. They found that solvents with linear molecular structure tended to have higher spinnability than those with cyclic or aromatic structures. This finding could be useful in choosing an appropriate solvent for electrospinning of polystyrene nanofibers at a high enough production rate.

### 2.3 Microstructure and Morphology

Geometric properties of nanofibers such as fiber diameter, diameter distribution, fiber orientation and fiber morphology (e.g. cross section shape and surface roughness) can be characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM) (Li *et al.*, 2002). The use of TEM does not require the sample in a dry state as compared to that of SEM. Hence, nanofibers electrospun from a polymer solution can be directly observed under TEM. An accurate measurement of nanofiber diameters with AFM requires a rather precise procedure. The fibers appear larger than their actual diameters because of the AFM tip geometry (Puygranier *et al.*, 2001).

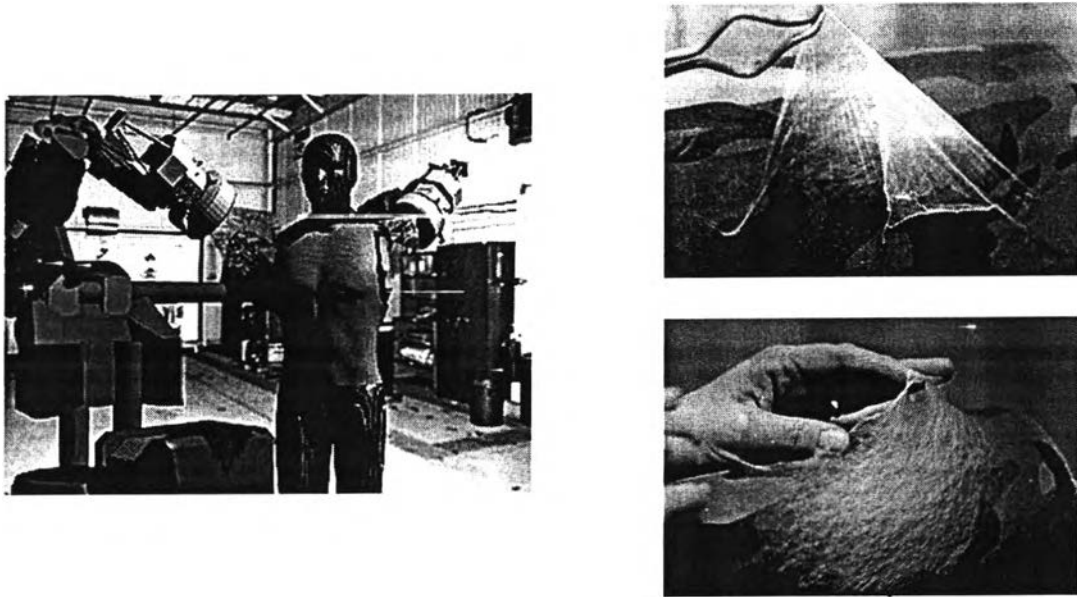
Molecular structure of nanofibers can be characterized by Fourier-transformed infrared (FT-IR) (Grählert *et al.*, 1999) and nuclear magnetic resonance (NMR) techniques (Bourbigot *et al.*, 2000). Supermolecular structure describes the configuration of the macromolecules in nanofibers and can be characterized by optical birefringence (Buchko *et al.*, 1999), wide angle X-ray diffraction (WAXD), small-angle X-ray scattering (SAXS) and differential scanning calorimetry (DSC) (Zussman *et al.*, 2002).

The conductivity, i.e. the electrical transport properties, of the electrospun nonwoven ultra-fine mat of polyaniline doped with camphorsulfonic acid blended with poly(ethylene oxide) (PEO) has been measured and reported (Norris *et al.*, 2000). As the non-woven mat was highly porous and the fill factor of the fibers was less than that of a cast film, the measured conductivity seemed to be lower than that of the bulk.

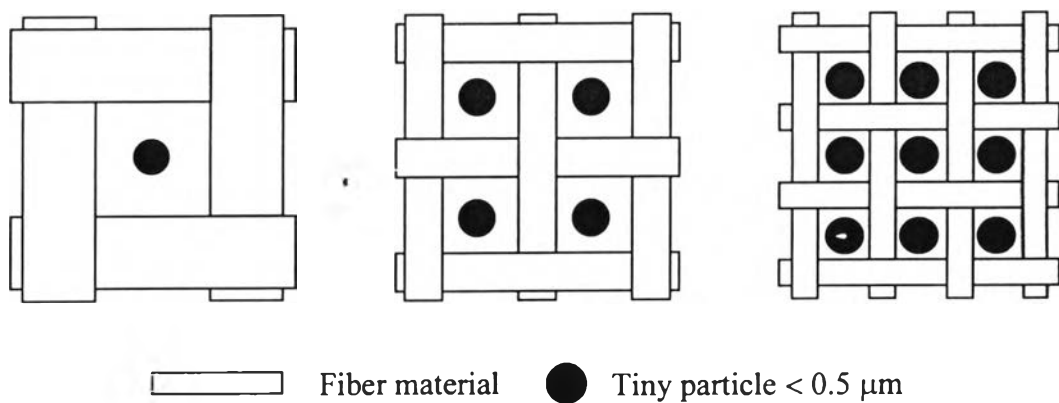
## 2.4 Applications

Electrospun fibers are typically collected in the form of non-woven mats of ultrafine fibers that exhibit small pore size and huge surface-to-volume ratio, which have great potentials uses in many fields. This fabric show great promise for exploitation as soldier protective clothings (see Figure 2.1) and as mesoporous filters (Gibson *et al.*, 1999) as shown in Figure 2.2. Other applications that are being explored include fibrous reinforcement in composite materials (Doshi *et al.*, 1995), optical and electronic applications (Norris *et al.*, 2000), and biomaterials for wound dressing, drug delivery system, and scaffolding for tissue engineering (Buchko *et al.*, 1999).

It should be realized that most of these applications have not reached their industrial level just yet, but being more of a laboratorial curiosity. Reasons that prevent actual utilization of the electrospun fibers is the inherent low throughput of the process, broad distribution of fiber diameters produced, and the difficulty to produce fibers having excellent mechanical properties. However, their promising potential is believed to attract greater attentions and investments from academia, governments, and industries alike.



**Figure 2.1** Proposed use of nanofibers that have high porosity with very small pore sizes as military protective clothings that could provide good resistance to the penetration of chemically harmful aerosols ([www.sbccom.army.mil/products/cie/electrospinning](http://www.sbccom.army.mil/products/cie/electrospinning)).



**Figure 2.2** Proposed use of nanofibrous materials as filtering media with excellent filtration efficiency (Z. M. Huang *et al.*, 2003).