CORE-SHELL NANOFIBER ASSEMBLIES CONTAINING IONIC SALTS

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CORE-SHELL NANOFIBER ASSEMBLIES CONTAINING IONIC SALTS

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ABSTRACT

It is well known that core-shell fibers offer more advantages compared to conventional single component fibers. The core-shell structure provides a convenient way to achieve better mechanical, biological, and electrical properties. Their outstanding properties make core-shell fibers promising materials for applications such as agents for drug release, drug delivery, tissue engineering, and ion conducting batteries. In this research, polyethylene oxide (PEO) – polyvinyl acetate (PVAc) core-shell nanofibers were prepared by the Gas Jet nano-Fibers (GJF) gas jet spinning technique. Sodium chloride (NaCl) was added in solution of PEO to form the core of the fibers. The morphology was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Thermal characterization was performed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Solubility of NaCl in the core solution was determined a priori. The crystallinity of PEO core was detected by DSC and polarized optical microscope (POM). The viscosity of the core solution was determined by Advanced Rheometric Expansion System (ARES) G2 rheometer. The conductivity of core-shell nanofiber was tested by a pH meter. The factors that influenced the fabrication process were the concentration of polymer/ionic salt, solvent and solvent ratio, pressure of the gas jet, and the rate of solution injection
through the nozzle. The diameter and diameter distribution of the resultant fibers were obtained. The average fiber diameters were smaller and the diameter distribution became narrower at higher gas jet pressure and higher rates of liquid injection. PVAc is proved to be a promising material for the shell. The core-shell structure of nanofibers with diameters smaller than 200 nm was confirmed by TEM. It was revealed that NaCl decreased the crystallinity of the PEO core and created a conductive medium. The study revealed that the amount of inorganic salt in the core should be controlled to at certain value to obtain consistent core-shell structure.
DEDICATION

This thesis is dedicated to my beloved parents (Jianguo Zhao and Xiumin Cao) for their forever support and love, and the special one in my life for his encouragement and patience.
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CHAPTER I
INTRODUCTION

Gas-jet spinning is a new, simple, and practical technique for the production of polymer fibers with diameters ranging from a few hundred nanometers to several micrometers. This method of mass production of fibers can be widely used in industry, as it is user-friendly, less costly, and may offer higher production rates. Electrospinning has been reported to be the preferred method to produce nanofibers from polymeric solutions and generally can produce a narrower fiber diameter distribution compared to other methods. However, a relatively low production rate of nanofibers, typically less than 0.3 g/h per jet, and the requirement of high voltage limit the application of electrospinning [1,2]. Due to high voltage usage and the requirement of certain dielectric constant, polymer systems that can be studied by electrospinning are also limited [3,4]. Some other processes have been attempted for production of nanofibers, including Gas Jet nanofibers (GJF), melt blowing [5], solution blowing spinning [6], centrifugal spinning, and the rotary jet spinning (RJS) methods [7,8].
Nanofibers differ from the large diameter fibers in that they have a large surface per unit mass. This unique characteristic can be combined with some other properties of polymers and inorganic compounds, such as crystallinity, biocompatibility, and conductivity. In recent years, core-shell nanofibers show growing interest over conventional single component nanofibers due to some unique mechanical and electrical properties and applications [9]. One application involves formation of hollow fibers by spinning core-shell fibers followed by removal of the core [10]. Naim et al. fabricated hollow fiber membranes by wet-spinning and applied them in gas separation to remove carbon dioxide [11]. In core shell structure, the shell isolates the core from the external space. Therefore, the core is protected until it is time for its release. Materials that cannot be fabricated by other means such as fibers of inorganic materials or low molecular weight polymers can now be fabricated in the core with a spinnable shell. It can be used in drug delivery and drug release after removal of the shell [12-15]. Core-shell nanofibers can also be used in the field of tissue engineering [16,17]. Geoghegan et al. spun sodium alginate/poly (ethylene oxide) core-shell nanofibers used as scaffolds for tissue engineering applications [18]. Nanofibers considered as promising materials for batteries have been widely reported. Gu et al. reported that such nanostructures would improve the electrochemical properties [19]. Core-shell structure fibers were prepared to obtain better stability and relatively high capacity as electrochemical cathode [20]. Lithium ion batteries enjoy high market use and are well known for their high capacity. Sodium chloride was used in this work due to concerns over safety and cost.
Core-shell fiber formation by spinning of polymer solutions has been reported in terms of physical properties of solution, feeding rates of solution, solution concentrations, and the viscosity and tip-to-collector distance [21-23]. Nguyen et al. reported core-shell nanofiber spinning with constant feed rate for the shell and variable feed rate for the core. With an increase of the core feed rate, the core expands to maximum diameter followed by fracturing of the shell fiber into two side-by-side fibers [21].

Gas-jet spinning of PEO/PVAc core-shell fibers has not been reported in literature except for one study by Benavides et al [36]. Multiple factors should be taken into account. These include the rate of solvent evaporation, surface free energy difference between the polymers, polymer viscosity, and flow rate [24]. An accepted way to spin core-shell structure is to put the lower surface energy polymer solution in the shell and the higher surface energy polymer solution in the core [25]. Early in 2001, Duan et al. [26] concluded that a more homogenous surface of polymer blend will form by increasing the extent of hydrogen bonding. However, the controlling factors of the above method are too complicated to realize. Since we tried to use a system with the core and shell polymer dissolved in different solvents, self-stratification was not important.

In this research, poly(ethylene oxide) (PEO) with appropriate amounts of sodium chloride were mixed in a mixture of deionized water and ethyl alcohol to form the
core solution. Polyvinyl acetate (PVAc) was used to form the shell solution in a mixture of ethyl acetate and ethyl alcohol. PEO was chosen for its solubility in water, low toxicity, biocompatibility, and biodegradable properties [27]. PVAc was selected for its insolubility in water. PEO was chosen to form the core due to its solubility in an aqueous solution of sodium chloride. The study attempted to prepare core-shell nanofibers by the GJF method with a liquid core for ion conductivity. Sodium chloride added into the core was considered to study how salts affect the structure, crystallinity, and diameter of the core shell nanofibers. In this thesis, the preliminary work with sodium chloride was carried out. However, appropriate applications may require salts other than sodium chloride.

The morphologies of the fabricated nanofibers were detected by scanning electron microscopy (SEM). Transmission electron microscopy (TEM) was used to verify the core-shell structure and to determine the diameters of both the core and the shell. The amount of remaining solvent in the fiber was determined by thermal gravimetric analysis (TGA). The effect of sodium chloride on the crystallinity of PEO was studied by differential scanning calorimetry (DSC). Ionic conductivity of the core was detected by a pH meter. In the study, several factors were considered, such as the flow rate of polymer solution, the amount of sodium chloride, the amounts of ethyl alcohol and ethyl acetate solvent, polymer concentration, and the pressure of the gas jet.
The thesis is organized as follows: Chapter II presents the background knowledge of the study, literature review, and a statement of the key problems. Chapter III presents the experimental details of the research, including materials, equipment, and spinning conditions. Previous work on fabrication PVAc fibers and conditions for fabrication of core-shell nanofibers are discussed in Chapter IV. Chapter V presents a discussion on how NaCl affects core-shell nanofibers. Chapter VI provides the overall summary of the work and recommendations for further studies.
CHAPTER II
BACKGROUND AND LITERATURE SURVEY

In textile industry, the conventional fiber-spinning technologies produce fibers with diameters no less than 2 µm. Most commercial fibers have diameters much greater than that. However, fiber mechanical properties and other characteristics show improvement with a decrease in fiber diameter. With smaller diameters, fibers present larger surface areas, smaller pore sizes, and unique surface roughness. Figure 1(a) shows annual number of publications on the subject of electrospinning from 1994 to 2006. Publication distribution in Figure 1(b) demonstrates research interests in nanofiber electrospinning by country [28].

Figure 1. (a) Annual number of publications on the subject of electrospinning, as provided by the search engine of SciFinder Scholar. (b) Publication distribution by nation based on the SciFinder Scholar search system with the term
‘electrospinning’ searched. Adapted from [28].

2.1. Nanofibers

Nanofibers are defined as fibers with diameters on the order of 100 nanometers, but less than 1000 nanometers [29]. Nanofibers offer small pore sizes and large surface areas with improved mechanical, chemical, electrical and biological properties due to the nanoscale diameter. Several techniques have been used to produce polymer nanofibers, including gas jet nanofibers, melt blowing, solution blow spinning, and electrospinning.

2.1.1. Electrospun nanofibers

The usage of electrostatic force to produce micrometers diameter fibers was first presented by Anton Formhals’s series of patents published from 1934 to 1944 [30]. However, electrospinning was not considered as the primary technique to produce nanofibers until the 1990s. An example for electrospinning is work done by Shao et al. on the electrospinning process of PAN nanofibers [31]. These PAN nanofibers were used as substrates and zinc oxide was deposited on the top of the fiber membranes by sol-gel technique. A high-voltage power supply is needed to provide an electric-field for electrospinning. This may require anywhere from several thousand volts to a hundred thousand volts. Flow rate of spinning fluid managed by a flow control pump is used to adjust productivity and diameters. Single spinneret or multispinnerets are used for flow of polymer solution or melt. Different collectors can be designed depending on the desired fiber assemblies.
An electrospinning setup is presented in Figure 2 [32]. This process produces fibers with diameters ranging from 1 to 2000 nm [33]. Solution electrospinning offers a quick way for producing nanofibers. However, some widely used polymers such as PE and PP cannot be spun at room temperature [34]. Melt electrospinning is used instead in this case.

Figure 2. Schematic of electrospinning setup. Used with permission from Ref [32].

Although electrospinning has been the primary method over other nanofiber preparation processes, the productivity of electrospinning still cannot meet the requirements of large-scale production demand. The flow rate of a single jet, normally less than 0.3 g/h, has limited the application of electrospinning [35]. Also, the high voltage of electrospinning can lead to large fiber diameters and
bead formation in some cases. Electrospinning narrows the choice of polymer systems used in nanofiber formation process [36]. More production methods have drawn attention with large-scale production ability in recent years including gas jet fiber method (GJF).

2.1.2. Nanofibers by gas jet (GJF)

The nanofiber by gas jet (NGJ) process was first reported in a series of patents by Reneker [37-39]. The GJF process setup, similar to electrospinning, consists of a syringe pump to control flow rate, a spinneret, and a collector. Compressed high velocity gas is applied to stretch the liquid jet. During the stretching, the solvent evaporates to form nanofibers. Benavides et al. presented nanofibers with core-shell and side-by-side arrangements and different ways for polymer solution in contact with gas jet by GJF process [36]. We will discuss more about this work later in this chapter.

Nanofibers produced by GJF alone have yet to be studied. More details about GJF will be stated in the other part of Chapter II. Gas-jet/electrospinning in combination presents another method. Lin et al. prepared poly(ether sulfone) (PES) nanofibers by gas-jet/electrospinning and reported parameters such as concentration of polymeric solution by varying the voltage, the tip-collector distance (TCD), inner diameter of the nozzle, and gas flow rate [40]. However, the flow rate in this case is still very low (6.0ml/h) compared to GJF. Figure 3 shows the schematic of the gas-jet/electrospinning, adapted from ref [40].
2.1.3. Nanofibers by other methods

Other methods for formation of nanofibers have been reported including melt spinning, bicomponent spinning, and rotary jet spinning (RJS). Bicomponent spinning commonly follows two steps. First, spin islands-in-the-sea (INS) fibers as bicomponent fibers as produced due to their cross-sectional appearance. Second, the “sea” polymer is dissolved to obtain the smaller diameter “island” polymers. This process is limited to certain polymers since the island polymer is generally a polyester and the sea polymer is commonly a water-soluble polymer [41]. Melt spinning with a rather high production rate is also limited to a few polymer systems. Polymer melt is extruded through dies, blown with high velocity, and spun into fibers. Polymers that have been successfully melt-blown into fibers, are polyethylene, poly(methyl methacrylate), polypropylene, poly(ethylene terephthalate), polyamides, polystyrene, and poly(butylene terephthalate) [42].
The fibers produced by melt spinning are typically short, discontinuous fibers with diameters ranging from 2 to 6 µm [43]. Centrifugal spinning, or rotary jet spinning, is a simple, efficient, and nozzle-free spinning process to produce nanofibers with diameters as low as 25 nm. Droplets of polymer solution were applied onto a spin coater and the chuck was rotated fast. Nanofibers formation starts when the spin-coated liquid becomes unstable due to a combined action of the centrifugal force and the Laplace force induced by the surface curvature. However, defects, such as beads, are difficult to control and avoid in this case. Figure 4 shows schematic of RJS and morphology of the nanofiber produced by RJS [44].

Figure 4. Schematic of rotary jet spinning and morphology of nanofiber produced by rotary jet spinning, adapted from [44].

2.2. Core-shell nanofibers

A growing interest in multicomponent nanofibers over conventional single component nanofibers has been increasing due to the desire for novel properties derived from a combination of various components. Core-shell nanofibers allow
nonfabricated or noneasy spinnable materials to spin with a spinnable sheath surrounding them. The shell generally plays as a protective layer to the core until the two materials are separated. A core-shell structure leads to some functional enhancements and improvements in mechanical and electrical properties compared to single component fibers. In recent years, core-shell nanofibers prepared by one-step electrospinning process have attracted much attention. Coaxial dual nozzle and emulsion electrospinning are two typical methods for producing core shell nanofibers. Coxial electrospinning technology was inspired by electrospinning of core shell fibers [45] and fabrication of core shell glass fibers [46]. Details about coaxial electrospinning is discussed in the following sections.

2.2.1. Coaxial dual nozzle and emulsion electrospinning

Coaxial electrospinning or co-electrospinning of core-shell nanofibers was first presented in 2003 as a branch of nanotechnology [47]. The novel core-shell structure of nanofibers was introduced by co-electrospinning. Similar to electrospinning, when high voltage is applied on polymeric solutions, a Taylor cone forms, resulting in stretching of polymer jets with a pulling force and electrically driven perturbations [48,49]. As a result, the core-shell polymer jet solidifies and core-shell fibers are deposited on the collector. The two components in co-electrospinning can be two polymeric solutions or one polymer solution as the shell and one nonspinnable Newtonian fluid or powder as the core.
Post-processing of core-shell fibers allows for the production of hollow structured nano- or microfibers. The encapsulation and release of biological-core in core-shell fibers has applications in drug delivery, drug release, tissue engineering, and sensors. Because of this, co-electrospinning attracted much attention and was studied by several groups [50-55].

Conventional coaxial dual nozzle electrospinning technology requires a dual nozzle for both core and shell materials, shown in Figure 5 [56]. Inner and outer solutions can be delivered into each nozzle separated by two syringe pumps. Individual syringe pumps easily control the rate of inner versus outer solutions.

Figure 5. Schematic of coaxial electrospinning for core shell nanofibers. With permission from References [56].

Poly(dodecylthiophene)-poly(ethylene oxide) (PDT-PEO) solutions can be co-electrospun into relatively smooth surface core-shell nanofibers with an
average outer diameter of 1000 nm and an average inner diameter of 200 nm. It is worth noting that PDT is nonspinnable since it has rather low molecular weight. The high molecular weight PEO acts as a higher viscosity and lower surface tension sheath around the PDT [57]. Common electrospun fibers include chitosan, cellulose, collagen, elastin, gelatin, hyaluronic acid, and silk fibroin [58]. Poly(lactic acid)-chitosan (PLA-CS) were fabricated by co-electrospinning process with PLA being the core and CS being the shell. Figure 6 shows TEM images of co-electrospun core shell nanofibers fabricated at different core feed rate. PLA was fully encapsulated by the shell CS at core feed rates of 1.0 and 2.0 µL/min and shell feed rate of 5.0 µL/min as shown in Figure 6(a) and (b). When the core feed rate increased to 4.0 µL/min with the same shell feed rate, side by side fibers were observed in TEM images rather than core shell fibers, as shown in Figure 6(c). As the core feed rate increased, the core size went from about 120 nm to 360 nm and the shell diameters increased from 270 nm to 480 nm. A reduction of the shell feed rate led to instability of Taylor cone and formation of side-by-side fibers [59].
Figure 6. TEM pictures of the coaxially electrospun composite nanofibers of the PLA/CS fabricated at shell feed rate of 5.0 μL/min and core feed rate of (a) 1.0 μL/min, (b) 2.0 μL/min and (c) 4.0 μL/min. With permission from Ref [59].

Emulsion electrospinning is also a novel process in the preparation of core-shell nanofibers with two polymer solutions used as a working liquid [60]. The Taylor cone is generated from the emulsion and electrospinning jets are stretched into nano- or microfibers. Emulsion electrospinning is a single-nozzle electrospinning process. The dispersed drops become the core of the electrospun fiber during stretching and evaporation, and the continuous phase turns into the shell part of the fiber. In reference [60], PAN in DMF and PMMA in DMF solutions were blended and allowed to sit for 24 hours. After one day, the solution phase separated into PMMA/DMF droplets with average diameter of 100 μm dispersed in a PAN/DMF continuous matrix. The prepared solution was then electrospun by
a single-nozzle traditional electrospinning setup. Outer diameters in the range of 0.5-5 μm were observed and core-shell structure was captured by TEM. The fiber diameter was similar to that of fibers produced by dual-nozzle co-electrospinning.

Chitosan (CS) had also been electrospun as the shell with PEO as the core by emulsion electrospinning. With different blend ratio of PEO/CS, the inner diameter varied from about 120 nm to 490 nm and the outer diameter from around 140 nm to 600 nm, as shown in Table 1 [61].
Table 1. Summary of Fiber Diameter Data Obtained from TEM Images. With permission from Ref [61].

<table>
<thead>
<tr>
<th>component</th>
<th>blend ratio</th>
<th>mean diameter of core layer (nm)</th>
<th>mean diameter of nanofiber (nm)</th>
<th>diameter ratio of core to fiber</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO/CS (Mw=3000 g/mol)</td>
<td>3/1</td>
<td>492.97</td>
<td>597.08</td>
<td>0.826</td>
</tr>
<tr>
<td>PEO/CS (Mw=10 000 g/mol)</td>
<td>1/3</td>
<td>123.48</td>
<td>177.92</td>
<td>0.694</td>
</tr>
<tr>
<td>PEO/CS (Mw=10 000 g/mol)</td>
<td>1/1</td>
<td>122.34</td>
<td>145.88</td>
<td>0.837</td>
</tr>
<tr>
<td>PEO/CS (Mw=10 000 g/mol)</td>
<td>3/1</td>
<td>199.12</td>
<td>216.05</td>
<td>0.922</td>
</tr>
<tr>
<td>PEO/CS (Mw=50 000 g/mol)</td>
<td>3/1</td>
<td>288.72</td>
<td>341.74</td>
<td>0.845</td>
</tr>
<tr>
<td>PEO/CS (Mw=200 000 g/mol)</td>
<td>3/1</td>
<td>432.70</td>
<td>495.37</td>
<td>0.837</td>
</tr>
</tbody>
</table>
However, the emulsion electrospinning, in many cases, did not result in core-shell structure nanofibers, but instead formed individual droplets embedded in the matrix polymer. Here we only discussed the cases, which resulted in core-shell structures with a continuous core and matrix shell.

Co-electrospinning allows non-spinnable polymers, metal salts, powders, nanoparticles, liquid crystals, and proteins to be encapsulated in the fiber core. This leads to an array of interesting applications. One such application is embedding drugs or biological agents in the core for drug delivery [62-77]. This method prevents a burst release and both controls the release rate through the membrane of the shell and protects the core from outside elements [78]. Hydrophilic or biodegradable polymers are preferred as shell materials. The desorption ability of the shell exposed to the surrounding water allows for the release of the core materials [76,79,72,74]. This principle of choosing polymers for the shell also works for applications in cell and tissue engineering or any other biological usage. Some nanofibers can be used as separators of Li-ion batteries, producing a nano-scale porous structure which leads to an increase of ionic conductivity for the membrane in liquid electrolyte. Polyvinylidenedifluoride (PVDF), polyacrylonitrile (PAN) and their derivatives are polymers widely used in this field. In addition to drug delivery, core shell nanofiber with a conductive core further enhances the ionic conductivity. Also, aligned fibrous membranes can provide higher mechanical properties such as tensile strength and modulus [80,81].
Core-shell nanofibers can be used as electrodes in batteries since a core shell structure is able to extend the cycle life for a normal electrode. PMMA Silica/PAN core-shell nanofibers were prepared by dual nozzle electrospinning. Silica is a promising material for anodes since it is capable of large-scale energy storage. However, silica has a short cycle life and is susceptible to pulverization via unstable contacts between silica and carbon conductors during operation. This core-shell structure solves this problem by protecting silica in the core. Figure 7 shows electrochemical test results for the PMMA Silica/PAN core-shell nanofibers, denoted as SiNP@C [82].
Figure 7. Electrochemical tests for SiNP@C. (A) Potential profiles during the first cycle at a C/10 rate. (B) Charge–discharge potential profiles of SiNP@C at different cycles. The cell was measured at 2.75 A/g. (C) A rate capability test for SiNP@C. (D) Potential profiles for the cases whose specific capacities are displayed in (C). The C rates in (C) and (D) are based on the actual charge–discharge rates, not on the theoretical capacities. (E) Discharge capacities of SiNP@C as a function of Si weight portion, when measured at 0.1C rate. With permission from Ref [82].
2.3. Composite functional nanofibers

The development of new composite nanofibers has gained much attention because composite nanofibers enhance physical and chemical properties. Polymer composite functional nanofibers usually consist of two or more composites and can be polymer/polymer, polymer/nanoparticles, or polymer/inorganic salts in composition.

2.3.1. Polymer/polymer composite nanofibers

Polymer/polymer composite nanofibers consist of two or more polymers. Polymer/polymer core/shell nanofibers belong to polymer/polymer composite nanofibers. Similarly, polymer/polymer composite nanofibers can be fabricated by two methods. One method is single-nozzle one-step spinning, such as emulsion electrospinning. Two or more polymers are dissolved in solvents separately and then mixed together for period of time before being spun into nanofibers. Biopolymers are frequently used in polymer/polymer composite nanofibers because biopolymers are biodegradable, biocompatible, nontoxic, and are relatively inexpensive. As mentioned before, blends of chitosan with other polymers such as polyethylene oxide (PEO) and poly(vinyl alcohol) (PVA) are widely studied by several groups [83-90].

The other widely used method for fabrication of polymer/polymer composite nanofibers is dual- or multi-nozzle spinning, such as co-electrospinning. In this
case, two or more polymers are dissolved in different solvents before spinning. The method can produce hybrid core-shell and side-by-side nanofibers.

2.3.2. Polymer/nanoparticle composite nanofibers

Polymer/nanoparticle composite nanofibers consist of nano-scale inorganic fillers and a polymer matrix. The idea for polymer/nanoparticle composite nanofibers originated from a desire to combine the flexibility of lightweight polymers with the high mechanical strength, chemical stability, and heat stable inorganic particles [91,92]. Polymer/nanoparticle nanofibers can be applied as membranes, as storage systems, and for energy conversion due to enhanced mechanical, optical, electrical and thermal properties without losing transparency [92-94]. Methods of producing polymer/nanoparticles composite nanofibers include polymer template procedure, one-step electrospinning, electroless deposition and in situ reduction, and sol-gel [95].

Polymer template procedure forms polymer nanofibers by electrospinning or other methods, and then prepares the polymer/nanoparticle nanocomposites by melt blending through a twin screw extruder [96-100]. The polymer nanofibers are immersed in a nanocomposites solution to attach nanoparticles on the fiber surface. In order to get good fiber-particle adhesion, further thermal or chemical treatment is sometimes needed [101]. Typical nanoparticles used in this method include Si$_3$N$_4$ [99], layered silicate clays [96-98], and multiwalled carbon nanotubes [102].
One-step spinning method is a simpler, user-friendly, fast, and low cost technique to produce the polymer/nanoparticle composite nanofibers. Nanoparticles and polymer solution were prepared separately and mixed together before electrospinning in a process similar to emulsion electrospinning. Silicate clays [103-106], SiO$_2$ [107-109], TiO$_2$ [110], and Fe$_3$O$_4$ [111] are the most commonly used nanoparticles in this technique.

Sol-gel process has been widely used to produce functional coatings. This technique has the advantages such as ease of production, smooth surface, good homogeneity, and ease of control. This process is also safe, able to produce large scale coatings, requires low temperatures to operate, and is cost-effective [112]. Nanoparticles like TiO$_2$ [113-115] and ZnO [116] are widely used in this method.

Electroless deposition and in situ reduction method refers to a kind of nanoparticles - metal ions. This method is a two-step process. First, polymer/metal ions composite nanofibers are electrospun into fibers, then the metal ions are reduced within the nanofibers.

2.3.3. Polymer/inorganic salt composite nanofibers

Polymer/inorganic salt nanofibers have applications in photographic and optical materials, ionic conductors, sensors, and lithium-ion batteries. 1D TiO$_2$ or
TiO$_2$/Ag composite hollow fibers were prepared by co-electrospinning and were applied as anodes of lithium-ion batteries without binders and additives. The polymer substance, PVP, was removed after the nonwoven fibers were calcined at 500 °C for 1h in air [117].

2.4. Recent work on Gas-Jet Nanofibers [36]

As mentioned earlier, GJF is a simple, easy to operate, high production process to fabricate nanofibers. This section focuses on recent work on the scalable gas jet process developed by Benavides et al [36].

The GJF process is similar to the electrospinning process starting with polymeric solutions fed into the nozzle and constantly extruded out of the needle by a syringe pump. Multiple syringe pumps may be used depending on different structures needed for the nanofibers. In this process, polymeric solutions are brought in contact with the gas jet. Three nozzle setups are used in the process - wall-anchored nozzle shown in Figure 8 (b), needle-tip nozzle presented in Figure 8 (c), and pendant drop shown in Figure 8 (d). A liquid jet is formed by stretching due to the force of the gas. Evaporation and stretching continues until the viscosity of the liquid jet is greater than the stretching force of the gas or the velocity of the solidified liquid jet equals to the velocity of the gas jet. The fibers are collected at far enough distance away from the nozzle.
Figure 8. (a) presents a schematic for NJF process. Figure 10. (a) Schematic setup of the GJF process with wall-anchored nozzle. (b–d) Images of polymeric liquid jet emanating from (b) wall-anchored nozzle, (c) needle-tip nozzle, and (d) pendant drop. With permission from Ref [36].
Table 2. Effect of Processing Variables on Fiber Diameter and Morphology

Obtained by GJF Process\textsuperscript{a}. With permission from Ref [36].

<table>
<thead>
<tr>
<th>polymer and mol wt</th>
<th>conc wt %</th>
<th>air pressure (psi); air flow rate (m\textsuperscript{3}/min)</th>
<th>collection distance (m)</th>
<th>mean fiber diameter (µm)</th>
<th>nozzle type</th>
<th>fiber characteristics</th>
<th>solid polymer feeding rate (g/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO 1 M</td>
<td>3.5</td>
<td>10; 0.1556</td>
<td>1.8</td>
<td>3.6</td>
<td>needle-tip</td>
<td>fiber</td>
<td>1.7</td>
</tr>
<tr>
<td>PEO 1 M</td>
<td>3.5</td>
<td>20; 0.1339</td>
<td>1.8</td>
<td>1.7</td>
<td>needle-tip</td>
<td>fiber</td>
<td>1.7</td>
</tr>
<tr>
<td>PEO 1 M</td>
<td>3.5</td>
<td>30; 0.12</td>
<td>1.8</td>
<td>1.2</td>
<td>needle-tip</td>
<td>fiber</td>
<td>1.7</td>
</tr>
<tr>
<td>PEO 1 M</td>
<td>3.5</td>
<td>40; 0.1081</td>
<td>1.8</td>
<td>0.8</td>
<td>needle-tip</td>
<td>fiber</td>
<td>1.7</td>
</tr>
<tr>
<td>PEO 300 K</td>
<td>3</td>
<td>15; 0.1422</td>
<td>1.8</td>
<td>0.2</td>
<td>wall-anchored</td>
<td>fiber</td>
<td>1.4</td>
</tr>
<tr>
<td>PEO 300 K</td>
<td>3</td>
<td>15; 0.1422</td>
<td>1.8</td>
<td>0.2</td>
<td>wall-anchored</td>
<td>fiber</td>
<td>1.4</td>
</tr>
<tr>
<td>PEO 1 M</td>
<td>3</td>
<td>10; 0.1556</td>
<td>1.8</td>
<td>0.2</td>
<td>pendant drop</td>
<td>fiber</td>
<td>0.09</td>
</tr>
<tr>
<td>PEO 1 M</td>
<td>6</td>
<td>10; 0.1556</td>
<td>1.8</td>
<td>0.2</td>
<td>wall-anchored</td>
<td>fiber</td>
<td>2.9</td>
</tr>
<tr>
<td>PEO 1 M</td>
<td>6</td>
<td>20; 0.1339</td>
<td>1.8</td>
<td>0.4</td>
<td>wall-anchored</td>
<td>fiber</td>
<td>5.7</td>
</tr>
<tr>
<td>PEO 1 M</td>
<td>6</td>
<td>30; 0.12</td>
<td>1.8</td>
<td>0.6</td>
<td>wall-anchored</td>
<td>fiber and bead</td>
<td>8.6</td>
</tr>
<tr>
<td>PEO 1 M</td>
<td>2</td>
<td>20; 0.1339</td>
<td>1.8</td>
<td>0.1</td>
<td>wall-anchored</td>
<td>fiber and bead</td>
<td>0.9</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Polymer molecular weight 1 M = 1000000; 300 K = 300000, 1.3 M = 1300000.

Needle-tip nozzle diameter \( \Phi = 0.83 \) mm. Air flow rate is in cubic meter per minute at 20 °C at pressures indicated in the table.

Table 2 presents the effects of some processing parameters on fiber diameter and fiber characteristics. Little change is observed between the fibers produced by a wall-anchored nozzle and those produced by a needle-tip nozzle with other
parameters being the same. However, the pendant drop nozzle configuration gives
the fibers smaller mean fiber diameters at low gas jet pressure (10 psi). At higher
gas jet pressure, the pendant drop becomes unstable.

Side-by-side and core-shell nanofibers were fabricated by GJF process with
custom-built nozzles. As shown in Figure 9 (a), a modified wall-anchored nozzle
system was used to produce side-by-side nanofibers by gathering two polymeric
solution streams. Polymer solution A (red color) on the top flows down the wall
due to gravity and covers the polymer solution B (blue color) to form a two layer
liquid before meeting with the gas jet and turning into a liquid jet. Figure 9 (c) and
(d) shows side-by-side nanofibers with different groups of polymers in SEM
images.
Figure 9. (a, b) Schematic of wall-anchored nozzles to produce fibers with (a) side-by-side and (b) core–shell morphology. (c–f) SEM images showing various morphological forms of fibers. (c) Side-by-side using 6% w/w PEO in ethanol and PVP 6% w/w in ethanol. (d) Side-by-side from PVAc 6% w/w in ethyl acetate, and PEO 6% w/w in ethanol. (e) Blend of PEO and trisilanol isobutyl POSS in ethanol. (f) Core and shell using blend of PEO and trisilanol isobutyl POSS in core and PVAc in shell. (g) Transmission electron micrograph showing PVP core and PEO shell in a section of the fiber. The diameter of the nozzle tip was 0.83 mm. The distance between the centerlines of the two nozzles in (a) was kept at 18 mm to produce side-by-side fibers. With permission from Ref [36].

The setup for the production of core-shell nanofibers by GJF is similar to dual nozzle coaxial electrospinning. With coaxial dual nozzles, core and shell polymer solutions were brought together as shown in Figure 9 (b). The conformation of the core shell structure were detected in two ways, one way is to mix trisilanol
isobutyl POSS with core polymer solution (PEO) and observe SEM images of this nanofibers before fabricating the core shell nanofiber with POSS in the core and examining if the rough surface become smooth surface due to the polyvinyl acetate (PVAc) shell fully encapsulate the core, as shown in Figure 9 (e) and (f). Another method is to detect core shell structure directly through transmission electron microscopy (TEM), as presented in Figure 9 (g).
CHAPTER III
EXPERIMENTAL

3.1. Materials
The materials used in the study are presented in detail below. Figure 10 shows the chemical structures of all the polymers used in this work.

3.1.1. Polyethylene oxide (PEO)
Polyethylene oxide (PEO), as stated in Chapter I, is a unique water-soluble biopolymer. Some of the excellent properties of PEO include biodegradability, biocompatibility, and low toxicity [18]. This polymer is widely used as polymer electrolytes and as separators in lithium batteries.

For our study, PEO powder was purchased from Alfa Aesar with molecular weight of 1,000,000 g/mol and was used without further purification. Figure 10 (a) shows the structure of PEO.

3.1.2. Polyvinyl acetate (PVAc)
Polyvinyl acetate (PVAc) is a water-insoluble thermoplastic. PVAc emulsions in water are used as adhesives for porous materials and PVAc can also be used in coating applications.
In this research, PVAc was purchased from Wacker Chemie AG, grade UW10, with a viscosity of 35.0-55.0 mPa s at 10% polymer solution in ethyl acetate. PVAc UW10 is completely soluble in ethyl acetate and partially soluble in ethanol (94%). The structure of PVAc is shown in Figure 10 (b).

3.1.3. Sodium chloride (NaCl)

Sodium chloride is a very commonly used ionic compound. In our study, NaCl was purchased from Aldrich and used without further purification.

![Chemical structure of (a) PEO and (b) PVAc](image)

Figure 10. Chemical structure of (a) PEO and (b) PVAc

3.2. Preparation and Processing of Materials

3.2.1. Preparation of PEO and PVAc Solutions

Different ratios of PEO/NaCl were dissolved in solvents to prepare solutions for the core liquid. The amount of sodium chloride was varied from 0 to 1 gram per 100 ml solvent. The solvents were mixtures of 50 ml ethanol and 50 ml water, 80
ml ethanol and 20 ml water, or 100 ml water. The amounts of polymer and solvent used in each group are presented in Table 3. The viscosity and surface tension were adjusted by the concentration of the polymer and the salt and the ratio of the two solvents.

Solutions of PEO/NaCl with different concentrations and ratio of solvents were prepared. Water used in our research was deionized water. PEO was added several times separately in the solvent for better dissolution. Generally, the solvent was added into a container before adding the polymer and sodium chloride. The composites and the solvents were stirred overnight at 60°C with magnetic stirrer, or for 40 minutes with a high intensity mixer to obtain homogenous solutions. The mixer was rested every 10 - 15 minutes to prevent overheating.

Three groups of PVAc solutions were prepared in our research. A mixture of ethyl acetate and ethanol was used as the solvent for PVAc. The reason why a two solvent system was chosen will be explained in the following chapter. The amounts of polymer and solvent in each group are presented in Table 4.
Table 3. Amount of solute and solvent in PEO solution$^b$

<table>
<thead>
<tr>
<th>Group Name</th>
<th>PEO (g)</th>
<th>NaCl (g)</th>
<th>H₂O (ml)</th>
<th>Ethanol (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5PEO-100</td>
<td>2.5</td>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>2.5PEO-0.1-100</td>
<td>2.5</td>
<td>0.10</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>2.5PEO-0.5-100</td>
<td>2.5</td>
<td>0.50</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>2.5PEO-50/50</td>
<td>2.5</td>
<td>0</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>2.5PEO-0.25-50/50</td>
<td>2.5</td>
<td>0.25</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>2.5PEO-0.5-50/50</td>
<td>2.5</td>
<td>0.50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>2.5PEO-0.75-50/50</td>
<td>2.5</td>
<td>0.75</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>2.5PEO-1-50/50</td>
<td>2.5</td>
<td>1</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>2.5PEO-0.5-20/80</td>
<td>2.5</td>
<td>0.5</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>2.5PEO-0.75-20/80</td>
<td>2.5</td>
<td>0.75</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>1.5PEO-0.5-20/80</td>
<td>1.5</td>
<td>0.5</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>1.5PEO-0.25-20/80</td>
<td>1.5</td>
<td>0.25</td>
<td>20</td>
<td>80</td>
</tr>
</tbody>
</table>

$^b$PEO MW in Table 3 is 1,000,000 mol/g.

Table 4. Amount of solute and solvent in PVAc solution

<table>
<thead>
<tr>
<th>Group Name</th>
<th>PVAc (g)</th>
<th>Ethyl acetate (ml)</th>
<th>Ethanol (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5PVAc50/50</td>
<td>5</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>9PVAc50/50</td>
<td>9</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>9PVAc75/25</td>
<td>9</td>
<td>75</td>
<td>25</td>
</tr>
</tbody>
</table>
3.2.2. Fiber Spinning by GJF

Polymer solutions were converted into nanofibers with different morphologies by the GJF method. A general schematic of the GJF process is presented in Figure 11. The process begins with feeding polymeric solutions into one/multiple customized syringe(s) and set it/them on the syringe pump. The polymer solutions were extruded at a constant rate by control of the syringe pump. Again, more than one syringe pump can be used to obtain various structures of nanofibers. While extruding, the liquid at the tip of the nozzle was brought in contact with the gas jet to form a liquid jet. As the liquid jet travelled along with the gas jet, the solvents evaporated, and the liquid jet stretched due to force exerted by the gas jet. This evaporation and stretching lasted until either the velocity of the liquid jet equaled that of the gas jet or the increasing viscosity of the liquid jet prevented further stretching. The nozzle-to-collector distance was adjusted to collect fully stretched nanofibers. Figure 12 presents digital photos of the GJF fiber spinning setup.

Figure 11. A schematic of the GJF process for fabrication of one component nanofibers.
Figure 12 (a) presents the collector box used to keep all nanofibers inside during the fabrication process. At the end of the box, a mat was attached to the paperboard to collect the final fibers. Needle tip to gas nozzle distance shown in Figure 12 (b) is generally set as 1.5 cm to 3 cm depending on the choice of polymer and pressure of the gas jet. As shown in Figure 12 (c), a customized syringe pump is used to control the injection rate of polymeric solution. The set up has two syringe holders. Therefore, two syringes can be operated at the same time when the same extrudate rate from both syringes is needed. A pressure regulator presented in Figure 12 (d) shows the pressure of the gas jet. The gas in our case was air. Generally, the pressure of the gas was varied from 10 psi to 30 psi to produce nanofibers. With higher pressure, stretching forces induced by the gas jet can be too large for the liquid jet, which may result in instabilities. With lower pressure, the diameter of the fibers are quite large (several micrometers) and a longer nozzle to collector distance is needed.
3.2.2.1. PEO nanofibers and PVAc nanofibers by GJF

The PEO or PVAc solution was fed into a 20 ml plastic syringe (BD) or a 10 ml plastic syringe (HSW) with a delivery tube attached to the head of the syringe. Bubbles inside the syringe were carefully removed to make sure that the injection rate was accurate. This way, the injection rate could be calculated from the diameter of the plastic syringe. The syringe was placed in an automatic syringe pump (Fusion 200) and fixed. The other end of the pipe was connected to a 3 ml plastic syringe (BD) by a bolt with one hollow end and one screw end. The 3 ml syringe was equipped with a steel needle (JG17-0.5X, Jensen Global). The syringe setup can also be simplified to one syringe filled with PEO or PVAc solution with a steel needle equipped on the top. Gas jet was fixed on a solid frame and the pressure was controlled through a pressure regulator. Gas jet pressure applied for one component nanofiber include 10 psi, 20 psi, and 30 psi. The distance between the needle and the gas jet nozzle was kept at 1.5 – 2.0 cm in this case. In our study, a box (shown in Fig. 12 (a)) was built for collecting the fibers.

3.2.2.2. PEO/PVAc core-shell nanofibers by GJF

GJF process has several unique features. Using the gas as a driving mechanism, the process is easy to operate, user-friendly, quality controllable, and provides high production rates. The GJF process for nanofiber fabrication, however, has many variables to control, such as the extrusion rate of polymer solution,
operating temperature, and gas pressure. The conditions need to be carefully adjusted especially with core-shell nanofibers.

Similar to coaxial electrospinning, core-shell nanofibers fabricated by GJF process require a dual nozzle. The self-made dual nozzle syringe made from a 3 ml plastic syringe is shown in Figure 13 (b). A small diameter needle bent to 90 degree was fitted into the hole to deliver the core fluid. Superglue (Krazy®) was used to hold the needle firmly to the syringe. Superglue was applied on the surrounding of the bent needle at least once per hour for five to six hours to make sure no leakage of the core fluid would occur. Figure 13 (a) shows the placement of the PEO/NaCl core solution and the PVAc shell solution. Another syringe attached to the bent needle was used to extrude the PEO/NaCl solution. PEO/NaCl solution was fully encapsulated by PVAc solution. Both syringes containing polymer solutions were set on one syringe pump and the extrusion rate was chosen to be the same extrusion rate for the shell solution. For smooth operation and for obtaining core-shell structure morphology, the concentric position of the core needle should be guaranteed from the front and the side. Fig. 13 (b) shows the self-made dual nozzle syringe assembly. The dual nozzle assembly was tested by pushing water through the upper syringe. The dual nozzle worked if the water came out in the center without any leakage in the system.
Figure 13. Dual nozzle assembly for production of core-shell nanofibers by GJF process. (a) schematic diagram of dual nozzle assembly, (b) digital picture of self-made dual nozzle syringe.

PEO/NaCl and PVAc solutions were filled into a 20 ml plastic syringe and a 60 ml plastic syringe, separately. These syringes were connected separately to two plastic pipes. The 60 ml syringe containing PVAc solutions was connected to the end of the dual nozzle syringe by the pipe. The 20 ml syringe containing PEO/NaCl solutions was connected to the end of another 3 ml plastic syringe and the head of the 3 ml syringe was fitted into the top needle of the dual nozzle syringe. Two syringes carrying solutions were placed in the same automatic syringe pump and fastened firmly. Gas jet pressure was controlled by the pressure regulator. The distance between the needle of the dual nozzle syringe and gas jet nozzle was fixed at 2.5 cm to 3 cm. The extrusion rate of PVAc solution was 0.5 or 0.8 ml/min. The pressure of gas-jet applied was 20 psi or 30 psi for fabrication of core-shell nanofibers. Figure 14 presents the schematic of core-shell nanofibers fabrication with a dual nozzle by GJF process.
3.3. Characterization

The single component nanofibers (PEO and PVAc fibers) produced by GJF process were analyzed for their thermal properties and morphology. The thermal and morphological properties of core-shell nanofibers were also analyzed. The conductivity of the core solution was evaluated by a pH meter.

3.3.1. Thermal analysis

3.3.1.1. Thermogravimetric analysis (TGA)

The thermal stability and the amount of remaining solvent in the nanofibers were investigated by a TGA Q50 device from TA Instruments (New Castle, DE). Sample specimens of ca. 8 mg were subjected to thermal scans from room temperature...
temperature up to 600 °C, with a scan rate of 20 °C/min and a continuous nitrogen purge of 50 ml/min. The amount of solvent in the fibers was determined from the weight loss prior to 200 °C. The temperature at the maximum rate of mass loss, T1 was obtained from the plot of the first derivative of mass versus temperature.

3.3.1.2. Differential scanning calorimetry (DSC)

The melting behavior of PEO nanofibers, PEO nanofibers containing NaCl, was investigated by differential scanning calorimetry (DSC) using a DSC Q200 from TA Instruments. The thermal properties such as melting temperature Tm, glass transition temperature Tg, and enthalpy change ΔHm were determined from the heat flow versus temperature plot by heating the specimen from room temperature to 100 °C then cooling down to -20 °C and heating to 100 °C again at a heating rate of 10 °C/min.

Equation (3-1) was used to determine the percentage of crystallinity by comparing the enthalpy of fusion of the polymer to the enthalpy of fusion of a 100 % crystalline polymer.

\[
\text{Crystallinity (\%) = } \frac{\Delta H_m}{\Delta H_0} \times 100\% 
\]

(3-1)

\(\Delta H_m\) in equation (3-1) was obtained from the area under the melting peak of PEO in DSC traces or mixture of PEO and NaCl, and can be used to characterize the crystallinity of polymers.
3.3.2. Rheological analysis

An Advanced Rheometric Expansion System (ARES) G2 from TA Instruments, operated with stainless steel DIN concentric cylinders, was used to test the viscosity of solutions of PEO and PEO/NaCl. A bob of 27.682 mm in diameter and 41.604 mm in length, and a cup of diameter 30 mm were used. The operating gap was set at 5.85 mm. The temperature for rheological testing was maintained at 25 °C and the shear rate was set to at 1 s⁻¹ to 250 s⁻¹.

3.3.3. Morphological analysis

Three microscopic analysis techniques were used to analyze the morphology of different one-component and core-shell nanofibers. The images of nanofiber surfaces, nanofiber diameter, and diameter distribution, were obtained from the microscopy analysis.

3.3.3.1. Scanning electron microscopy (SEM)

The surface properties, diameter, and diameter distribution of one-component nanofibers and core-shell nanofibers were examined by high resolution scanning electron microscopy (SEM) using JEOL JSM5310 scanning electron microscope at an accelerating voltage of 5 - 10 kV. Samples were collected on metal mounts using one double-sided carbon tape and coated with a silver sputtering layer using Sputter Coater, Model ISI 5400 under argon gas atmosphere. The average fiber diameter and diameter distribution were determined by measuring diameters of 500 fibers for each sample. For this purpose, SEM images were analyzed using Image J analysis software (Image J, National Institutes of Health, USA).
3.3.3.2. Transmission electron microscopy (TEM)

TEM technique is based on an electron beam interacting with a thin specimen while transmitting through it. The interaction between the beam and the specimen were magnified and adjusted to focus on an imaging device.

In our study, TEM was used to determine the structure of core-shell nanofibers and in some cases, the crystal size of NaCl inside the core-shell nanofibers. The core-shell structure was characterized by transmission electron microscopy (TEM, TACNAI-12, FEI) working at 120 kV. The samples for TEM observation were prepared as follows. First, the nanofibers were collected on a glass slide ensuring that fibers were fluffily placed on the glass slide instead of winding firmly. Second, the carbon-coated copper grids were gently held with delicate tweezers on the collector to directly obtain a thin layer of fibers while rubbing back and forth on it.

3.3.3.3. Polarized optical microscopy (POM)

The crystal formation during core solution drying process and how NaCl affects the crystallinity of PEO were visually determined by polarized optical microscopy. A polymer solution droplet was placed on a glass slide and the crystallization process was observed under POM. A BX60 Olympus optical microscope equipped with an EOS 5D Mark II Cannon camera was used to observe the crystal formation process. The crystal growth from solutions of NaCl and PEO were investigated in the same manner. The final spherulites of PEO were observed under polarized mode.
3.3.4. Ionic conductivity test

The ionic conductivity of the core solution was determined by a Corning Pinnacle 530 pH meter in mV mode. PEO and NaCl solutions were prepared and their conductivity was determined as function of drying time in air. A 476296 premium rugged bulb glass electrode was used in this case since it is ideal for organic or aqueous samples.
CHAPTER IV

FABRICATION OF CORE-SHELL STRUCTURE NANOFIBERS

This chapter mainly focuses on core-shell nanofiber production. The nanofibers morphology was examined by usual scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

The following details are discussed in this chapter. The conditions to produce fibers with smooth surface and ideal diameter nanofibers were investigated first to make sure that PVAc fibers were good enough to make up the shell in core-shell fibers. The fiber morphology was characterized by SEM. The core-shell structure was confirmed by TEM.

The capillary number represents the relative effects of viscous and interfacial forces acting across an interface between a liquid and a gas or between two immiscible liquids [118]. It is defined as

\[
Ca = \frac{\text{viscous forces}}{\text{capillary forces}} = \frac{\mu \bar{v}}{\gamma} \quad (4-1)
\]

where \( \mu \) is the viscosity of the solution, \( \bar{v} \) represents the characteristic velocity of the flow and \( \gamma \) is the surface tension of the liquid. The larger the capillary number, the longer and smoother the fibers that we can get. This leads to three basic variables
to be considered in fiber spinning by GJF process. In order to minimize the role of interfacial force, the viscosity can be increased by increasing the concentration of the solution. Also, a low surface tension solvent can be used. The velocity of the gas jet can be increased by increasing the pressure of the gas jet. Note, however, that the pressure of the gas jet should not be too high so as to obtain stable fiber formation.

4.1. Polyvinyl acetate (PVAc) nanofibers

Factors taken into account in our study for fabrication of PVAc solution were (1) concentration of PVAc in solutions, (2) pressure of the gas jet, and (3) ratio of the solvents - ethyl acetate and ethanol. A needle tip nozzle was used with a distance of 2 cm from the air jet. The nozzle-to-collector distance was fixed at 1.8 m. The morphology of four groups of PVAc fibers are presented in Figure 15. A 5 g/100ml PVAc solution with 1:1 ratio of the solvents was fabricated at a gas jet pressure of 20 psi. The first attempt led to formation of many beads, as shown in Figure 15 (a). The beads form due to lack of polymer chain entanglement [119]. One of the possible ways to promote the formation of fibers with less defect is to increase the concentration of PVAc solution. This was done by increasing the concentration to 0.09 g/ml. A 0.09 g/ml PVAc solution with 1:1 solvent ratio was spun at 20 psi, the same gas-jet pressure as in the previous attempt. The pressure of the gas jet was changed as a factor. An increase of the pressure of the gas jet increases the velocity of air flow and in turn leads to an increase of capillary number. The pressure of the gas jet was adjusted at 20 and 30 psi for most of the work reported here. A pressure of 40 psi was also used but an unstable liquid jet formed and did not yield fibers. The third factor studied was the surface tension of the solvents. The value of the surface tension of the solvent varies with temperature (T) in a linear relation:
\[ y = a - bT \quad (4-2) \]

where \( T \) is the temperature (°C). Table 5 lists the values of \( a \) and \( b \) for ethyl acetate and ethanol.

<table>
<thead>
<tr>
<th>Name</th>
<th>Vapor Pressure(KPa) (at room temperature)</th>
<th>Boiling point(°C)</th>
<th>Surface Tension a (dyn/cm)</th>
<th>Surface Tension b (dyn/(cm·°C))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl acetate</td>
<td>9.7</td>
<td>78</td>
<td>26.29</td>
<td>0.1161</td>
</tr>
<tr>
<td>Ethanol</td>
<td>5.5</td>
<td>77</td>
<td>24.05</td>
<td>0.0832</td>
</tr>
</tbody>
</table>

PVAc is completely soluble in ethyl acetate and partially soluble in ethanol. We chose a mixture of the two solvents for PVAc. Ethyl acetate and ethanol has similar boiling points as shown in Table 5. At room temperature (20 °C), the surface tension of ethyl acetate is 23.39 dyn/cm and that of ethanol is 21.97 dyn/cm. As indicated in equation (4-1), lower surface tension is preferred for fabrication of fibers. The surface tension of ethanol is slightly lower than ethyl acetate. Vapor pressure of ethyl acetate at room temperature is higher than that of ethanol. This means that evaporation rate of ethyl acetate is higher than that of ethanol. One more issue for consideration is the miscibility of the core and the shell solutions. If the same solvent is used for the core and shell solutions, the liquid-liquid interfacial tension is adjusted by the two polymers and is small. This promotes formation of smooth core-shell structures [120]. In view of this, ethanol was chosen as a solvent for both the core and shell solutions.
Figure 15 shows SEM images of PVAc fibers fabricated with the following conditions. (a) a 0.05 g/ml PVAc with 1:1 solvent mixture spun at 20 psi; (b) a 0.09 g/ml PVAc with 1:1 solvent mixture spun at 20 psi; (c) a 0.09 g/ml PVAc with 1:1 solvent mixture spun at 30 psi; (d) a 0.09 g/ml PVAc with 4:3 solvent mixture (ethyl acetate/ethanol) spun at 20 psi. As shown in Fig. 15 (a) and (b), bead formation reduced when the concentration of the solution was increased. The primary reason why beads form at low polymer concentration is relatively low value of viscous force compared to interfacial force. An additional reason might be lesser polymer chain entanglements at lower polymer concentration. Comparing Figure 15 (b) and (c), it can be seen that beads appeared as the pressure of the air jet was increased from 20 psi to 30 psi. At higher pressure, the degree of turbulence increases, which causes instability of the liquid flow and promotes beads formation. On the other hand, a larger fraction of smaller diameter fibers were obtained at 30 psi air pressure than at 20 psi. Also note that at 30 psi pressure, the instability of the liquid jet led to some larger diameter fibers. The effect of solvent make up, e. g., 1:1 ethyl acetate and ethanol versus 4:3 ethyl acetate and ethanol, are not really apparent in Figure 15 (b) and 15 (d). The boiling point of ethyl acetate and ethanol are very close to each other and the evaporation rates of the two solvents are not different. Also the values of surface tension of the two solvents are close to each other. In view of this, a ratio of 1:1 (ethyl acetate/ethanol) was used in core-shell nanofibers fabrication.
Figure 15. SEM images of different PVAc fibers fabricated at various concentration, pressure of gas-jet and ratio of solvent (ethyl acetate/ethanol) (a) 5%, 20psi, 1:1 (b) 9%, 20psi, 1:1 (c) 9%, 30psi, 1:1 (d) 9%, 20 psi, 4:3.
4.2. Formation of core-shell structure nanofiber

Figure 16. The SEM images of 0.025 g/ml PEO, 0.001 g/ml NaCl (water as solvent)/0.09 g/ml PVAc core-shell nanofibers prepared at (a) 0.4 ml/min, 20 psi (b) 0.8 ml/min, 20 psi (c) 0.8 ml/min, 30 psi by the GJF process.

The core-shell nanofibers shown in Figure 16 were prepared with a 0.025 g/ml PEO, 0.001 g/ml NaCl (in water) solution and a 0.09 g/ml PVAc (solvent ratio 1:1 as stated before) solution. Note that the extrusion rate of solutions is the same for the core and the shell solution. The variables considered in this case were extrusion rate and the pressure of gas jet. Three groups of nanofibers were fabricated. Comparing Figure 16 (a) with (b), it is seen that when the extrusion rate was increased, larger liquid jets were formed leading to larger diameter fibers, up to 20 µm. The pressure was increased to 30 psi with other conditions being the same. Such fibers are shown in Figure 16 (c). It is apparent that fiber diameter reduced and the fibers showed
narrower distribution of diameter. It is also noted that flat fibers were formed as shown in Figure 16. This was due to low viscosity of the core solution. This was alleviated by using a mixture of solvents for preparation of the core solution.
Figure 17. The SEM images and diameter distribution diagrams of 0.025 g/ml PEO, 0.005 g/ml NaCl (4:1 ethanol/water as solvent)/9%PVAc core-shell nanofibers
prepared at (a) 0.5 ml/min, 20psi (b) 0.8 ml/min, 20psi (c) 0.5 ml/min, 30psi (d) 0.8 ml/min by the GJF process.

The weight percent of sodium chloride was increased to 0.005 g/ml to obtain better resolution in TEM images. In addition, to avoid the formation of flat-shaped fibers and to decrease the surface tension of the core liquid, ethanol was used as one of the solvents for preparation of PEO/NaCl solution. This also aided reduction of the value of interfacial tension between core and shell solutions. Figure 17 shows SEM images and diameter distribution diagrams of core-shell nanofibers from a core liquid of 0.025 g/ml PEO, 0.005 g/ml NaCl in 4 : 1 ethanol/water and 0.09 g/ml PVAc as the shell liquid. The increase of viscosity and lowering of surface tension, resulted in core-shell nanofibers with close to circular cross-section. In Figure 17 (a) and (b), the extrudate rate was increased from 0.5 to 0.8 ml/min at the same gas-jet pressure (20 psi). This led to an increase of liquid jet diameters. The diameter distribution of the core-shell fibers became narrower and the average diameter became smaller although an increase of liquid extrudate rate led to higher liquid jet diameter. This can be explained as follows. At the higher extrude rate, gas jet was not able to evaporate all the solvent. As a result, the liquid stretched more before being fixed solid. The core-shell fibers spun at 30 psi have smaller diameters and narrower diameter distribution since the stretching force increased with the increase of gas-jet pressure. As shown in Figure 17 (d), the core-shell fibers with smaller diameters and narrower diameter distribution were obtained at 0.8 ml/min and 30 psi air jet pressure also due to higher stretching forces of the air jet. It was obtained at 0.8 ml/min and 30 psi. The average diameter of around 500 nm and narrower diameter distribution fibers.
Figure 18. TEM images of core-shell nanofibers of PEO/NaCl/PVAc at rate of 0.8 ml/min for both the core and the shell liquid and gas-jet pressure of (a) 20psi (b) 30psi.

Figure 18 shows TEM images of the core-shell structure of the PEO/NaCl/PVAc nanofibers fabricated at different gas jet pressures. The contrast between the core and the shell in TEM images was obtained due to the electronic density difference between the core and the shell materials was augmented by NaCl. However, the core-shell structure can only be recognized around and below 200 nm diameter in our experiments. As shown in Figure 18 (b), the shell is lighter and the core is darker as expected. In other cases, if the diameter is larger than 300 nm, the electron beams cannot pass through the fibers easily to offer desired contrast. This is evident in Figure 18 (a) - the core-shell nanofiber appeared dark due to a larger diameter of 500 nm.
4.3. Solvent in the core of core-shell nanofibers

The conductivity of the core relies on the amount of remaining solvent after fibers are formed. This was examined by monitoring the weight loss using a TGA. The weight loss of the fibers before the first degradation was considered as the weight of solvent remaining in the core. We assumed that the solvent evaporated completely in the shell after fabrication. Figure 19 shows TGA result of PEO powder, PVAc solids, a mixture of PEO powder and PVAc solid, and NaCl/PVAc core-shell nanofibers. The mixture of two polymers prepared at 9:1 PVAc/PEO ratio, imitates the weight ratio of the two polymers in the final fibers.

In this study, only the weight loss of the solvent remaining in the core was considered. As shown in Figure 19, the difference between the red curve (mixture of two polymers) and blue curve (core-shell fibers) before 300 °C was due to the core solvent evaporation from the fibers. It is apparent that a 3 – 6 wt% solvent remained in the core.
Figure 19. TGA curve of PEO powder (black), PVAc solid (green), mixture of PEO and PVAc (red) and core-shell fibers (blue).
CHAPTER V
EFFECT OF SODIUM CHLORIDE ON CORE-SHELL NANOFIBERS

In the previous chapter, it was established that PEO/NaCl/ PVAc core-shell structure nanofibers were fabricated and the morphology of core-shell nanofibers was detected. This chapter will focus on the effect of inorganic salt (sodium chloride) on viscosity, crystallinity of PEO, morphology, and conductivity of the core-shell nanofibers.

5.1. Solubility of sodium chloride
The solubility of sodium chloride in the core fluid defines the limit of the amount of sodium chloride that can be added into the core solution without precipitation and formation of crystals upon evaporation of water from the core solution. The solubility of NaCl in water at 25 °C is 360 g/1 kg. NaCl barely dissolves in ethanol with a solubility of 0.65 g/1 kg at 25 °C [121]. Thus the presence of ethanol in the core liquid was expected to decrease the solubility of NaCl compared to that of NaCl in water.

An experiment was designed to determine the solubility of NaCl in the core liquid. The unit of solubility is changed to g/100 ml from g/1 kg. Two groups of core liquid were tested, one is with 1:1 ethanol/water as the solvents. 7.2 g NaCl was added into 20 ml ethanol and 20 ml water. A second group contained 4:1
ethanol/water as solvents. In this case, 7.2 g NaCl was added into 80 ml ethanol and 20 ml water. The solutions were prepared by stirring the ingredients for 30 min. The clean solution was collected with a syringe and placed in an empty bottle. The amount of salt in the solution was determined by drying the solution in an oven at 100 °C until all the solvents evaporated. Equation (5-1) was used in calculation of solubilities of NaCl in the core liquid.

\[
\frac{\text{weight of solid}}{\text{weight of saturated solution}} = \frac{s}{100 + s} \quad (5-1)
\]

The solubility of NaCl in the core solutions are presented in Table 6.
At 20 °C, the solubility of NaCl in 1:1 ethanol/ water core liquid is 12.2 g/ 100 ml while in 4/1 ethanol/ water is 1.9 g/ 100 ml. Therefore, five groups of core liquid with amounts of NaCl - 0, 0.25 g, 0.50 g, 0.75 g, 1.00 g were prepared. For simplicity, these five concentrations of NaCl were marked as 0, 0.25 %, 0.5 %, 0.75 % and 1% in the rest of the discussion.

5.2. Effect of sodium chloride on viscosity of core liquid

The viscosity of the core liquid is a key factor in core-shell fiber fabrication process. Lower viscosity of the core liquid may allow higher surface tension forces to rupture the core-shell structures. Therefore, it was worth to investigate the effect of sodium chloride concentration on the viscosity of PEO solution. Five groups of core liquid with 2.5 g PEO in 50 ml water and 50 ml ethanol were prepared with 0, 0.25 %, 0.5 %, 0.75 %, 1% NaCl. The viscosity of these five groups of core solutions was determined by ARES G2 rheometer with stainless steel bob and DIN concentric cylinders. The shear rate was varied from 1 s$^{-1}$ to 250 s$^{-1}$. The temperature was kept at 25 °C. Figure 20 shows plots of viscosity versus shear rate for the five groups of core solutions.

Table 6. NaCl solubility in core liquid

<table>
<thead>
<tr>
<th></th>
<th>Empty bottle (g)</th>
<th>Bottle + saturated solution (g)</th>
<th>Bottle + NaCl solid (g)</th>
<th>Saturated solution (g)</th>
<th>NaCl solid (g)</th>
<th>S (20 °C) (g/ 100 ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4:1 ethanol/water</td>
<td>12.9713</td>
<td>26.1281</td>
<td>13.2146</td>
<td>13.1568</td>
<td>0.2436</td>
<td>1.8864</td>
</tr>
</tbody>
</table>
Figure 20. Plots of viscosity versus shear rate of 0.025 g/ml PEO solutions with five different NaCl concentrations (0, 0.25 %, 0.5 %, 0.75 %, 1 %).

As shown in Figure 20, the viscosity of 2.5 % PEO solution without NaCl is apparently higher than other core solutions containing NaCl. However, an increase of the concentration of NaCl from 0.25 % to 1 % did not show significant reduction of the solution viscosity. It was established in the last section that in PEO solution with 1/1 ethanol/water solvent ratio, the NaCl solubility at 20 °C is about 12 g. At 25 °C, the NaCl solubility did not change much. Therefore, 0.25 g to 1 g NaCl can be easily dissolved in the core liquid. It is also seen in Figure 20 that the core liquid exhibited shear thinning behavior eventhough the liquid contained only 0.025 g/ml PEO.
5.3. Effect of sodium chloride on crystallinity of core

PEO is a highly crystalline polymer. The formation of crystals reduces the mobility of long chain polymer. This can reduce ionic mobility and result in low conductivity. Therefore, an estimate of polymer crystallinity is essential for assessing the conductivity of the core liquid in the nanofiber.

Differential scanning calorimeter (DSC) was used to determine the crystallinity of the core polymer component. 2.5 g PEO, 1 g NaCl in 80 ml ethanol and 20 ml water solution was prepared and dried out in an oven at 100 °C. This process was designed to simulate the solvent evaporation process during fiber formation and also to make sure the ratio of PEO/NaCl was the same as in the core of nanofibers. Figure 21 shows the DSC curve of the dried PEO/NaCl solid and pure PEO powder, separately.
Figure 21. DSC scans (exo up) of (a) PEO/NaCl dried out from 2.5 % PEO, 1% NaCl with 4:1 ethanol/water and (b) PEO powder. The enthalpy of fusion of the corresponding melting transition is given as J/g.

As shown in Figure 21 (a) and (b), the melting point of PEO is 67 °C for PEO powder and 68 °C for dried PEO/NaCl solid. The melting point is quite high for inorganic salt (801 °C for NaCl). Thus NaCl did not have any effect on crystalline melting point of PEO. The enthalpy of fusion ($\Delta H_m$) is 145 J/g for PEO powder and 103 J/g for dried PEO/NaCl mixture. A reduction of $\Delta H_m$ indicates that with NaCl mixed with PEO, crystal growth of PEO was hindered. This also indicates that a large fraction of PEO chains remained in amorphous forms. This is expected to increase the conductivity of the core in the nanofibers.
Polarized optical microscope (POM) was used to investigate how crystals formed during drying of the core liquid. Figure 22 (a) – 22 (d) shows how the crystals grew as PEO/NaCl solution droplet was allowed to dry. The PEO crystal presented in Figure 22 (e) is a beautifully oriented spherulite. The crystal formation process shown in Figure 22 (a) to (d) indicates that the crystals of PEO were smaller and not so oriented as in PEO spherulite when crystallized in the pressure of NaCl.

Figure 22. (a)-(d) PEO crystal formation during drying of PEO/NaCl solution (e)
Spherulite of PEO under polarized optical microscope.
5.4. Effect of sodium chloride concentration on core-shell structure

Figure 23. 2.5 % PEO, 0.75 % NaCl (solvent ratio 1:1 ethanol/water)/9% PVAc
core-shell nanofiber fabricated at (a), (e) 0.5 ml/min, 20 psi; (b), (f) 0.5 ml/min, 30 psi; (c), (g) 0.8 ml/min, 20 psi; (d), (h) 0.8 ml/min, 30 psi. (a)-(d) are TEM images and (e)-(h) are SEM images.

The concentration of NaCl in the core was also important for fabricating smooth core-shell nanofibers. A 0.025 g/ml PEO, 0.75 % NaCl (solvent ratio 1:1 ethanol/water)/0.09 g/ml PVAc core-shell nanofiber was prepared at four extrusion conditions: 0.5 ml/min, 20 psi; 0.5 ml/min, 30 psi; 0.8 ml/min, 20 psi; 0.8 ml/min, 30 psi. The morphology was investigated by TEM and SEM, as shown in Figure 23 (a)-(d) and (e)-(h), separately. In Figure 23, the presence of 0.75 % NaCl led to NaCl crystals. In some cases, NaCl crystals protruded from the surface of the nanofibers. Therefore, in this case, core-shell nanofiber morphology was not formed. - 0.75 % NaCl concentration was too high for formation of core-shell structures.
Figure 24. TEM images of 0.015 g/ml PEO, 0.5 % NaCl (4:1 ethanol/water)/ 0.09 g/ml PVAc nanofibers, (a) a broken fiber; (b) a core-shell structure fiber with NaCl crystals.

Another group of nanofibers were obtained with 0.015 g/ml PEO, 0.5 % NaCl (4:1 ethanol/water)/ 9% PVAc. As shown in Figure 24 (a), NaCl crystals broke the cross section of some the fibers. Other fibers showed smooth core-shell structures. A number of fibers showed some NaCl crystals in the shell. This endorsed the notion that the concentration of NaCl should be chosen carefully to obtain smooth core-shell fibers.

5.5. Voltage of the core solution

A pH meter was used to obtain the voltage of a 2.5 % PEO and 1 % NaCl (1/1 ethanol/water) core solution. High voltage means high conductivity of the core. The voltage as a function of time was plotted. It was found that the voltage of the
core liquid with time could be simulated to follow equation (5-2), as shown in Figure 25.

\[ y = -75.059 + 11.153 \exp\left(\frac{-x}{8.4}\right) + 28.929 \exp\left(\frac{-x}{39.65}\right) \quad (5-2) \]

From equation (5-2), we can estimate that voltage is about -75 mV in the conducting core of core-shell nanofibers.
CHAPTER VI
OVERALL SUMMARY AND RECOMMENDATIONS

This study focused on fabrication of core-shell structure nanofibers by the GJF process where the core liquid contained an ionic salt. The factors that led to nanofibers smooth surfaces are discussed. The morphology of PVAc fibers and core-shell nanofibers was analyzed by SEM and TEM. The effect of inorganic component, NaCl, on viscosity of the core liquid, crystallinity of PEO, core-shell structure formation and voltage of the core was studied.

Capillary number was introduced to discuss the conditions under which different morphology nanofibers can be produced. It was confirmed that viscosity of the solution, flow rate of the liquid jet and surface tension are three key factors in fiber formation. These factors were varied by changing the concentration of the polymer, concentration of the inorganic salt, extrudate rate of solution, gas-jet pressure, and solvent composition. PVAc fibers with smooth surface and relatively small diameter with narrow diameter distribution were fabricated when proper conditions were used. It was found that ribbon shaped nanofibers resulted core-shell when low viscosity core liquid was used. Core-shell nanofibers with close to circular cross-sectional shape resulted when the viscosity of the core liquid was increased.
The effect of inorganic salt on the properties of core-shell nanofibers was tested in terms of the solubility of NaCl in the core liquid. It was found that smooth core-shell nanofibers resulted when NaCl did not form large crystals due to precipitation. The weight loss data indicated that in some cases, solvent remaining in the core might not dissolve all NaCl. As a result, NaCl crystals were formed. It was found that NaCl crystals were distributed in both the core and the shell polymer of the fiber. In cases, where smooth core-shell fibers were formed, NaCl made the core conductive. The conductivity of core solution increased when the core was dried and the concentration of NaCl was below the solubility of NaCl in the core liquid.

The following summary conclusions can be made from the work reported in this thesis.

First, concentration of polymer, concentration of NaCl, solvent composition, gas-jet pressure and extrudate rate of the solution are five key parameters in the GJF process for fabrication of core-shell nanofibers.

Second, the core-shell structure of nanofibers could be detected by TEM only when the fiber diameter was smaller than 300 nm. The presence of NaCl enhanced the contrast between the core liquid and the shell polymer.

Third, the solubility of NaCl in the core liquid affects the ionic conductivity of the core and the structure of nanofibers. Structure of core-shell nanofibers can be broken by NaCl crystals if the solvent remaining in the core is not enough and the
amount of NaCl is beyond solubility limit of NaCl in the core liquid. The viscosity of the core solution is reduced slightly with additional NaCl, but remains insensitive to the amount of NaCl up to 0.01 g/ml.

This work formed a preliminary study of core-shell nanofiber fabrication by the GJF method. We focused on the effect of sodium chloride on the core-shell nanofibers. The research results are also useful for other inorganic salts, like lithium salts. By changing the inorganic salt, this work can be applied to other problems involving electrolytes.
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