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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

EFFECTS OF PROCESSING AGENTS ON BEAD FORMATION OF ELECTROSPUN
POLY(ETHYLENE OXIDE) NANOFIBERS



Miss Kunawan Arayanarakul

สถาบันวิทยบริการ

จุฬาลงกรณ์มหาวิทยาลัย

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 5 เส้นใยที่ได้จะปราศจากปม การเติมพอลิเอทิลีนไกลคอลที่น้ำหนักโมเลกุลอยู่ในช่วงระหว่าง
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 เอทิลีนออกไซด์ที่ได้จะเรียบ ในหมู่เกลืออนินทรีย์ที่ทดสอบ (ได้แก่ LiCl NaCl KCl MgCl₂ และ
 CaCl₂) เฉพาะเกลือ NaCl เท่านั้นที่ได้เป็นเส้นใย โดยมีค่าเฉลี่ยของขนาดเส้นผ่านศูนย์กลางอยู่
 ในช่วงระหว่าง 73 และ 205 นาโนเมตร การเติม SDS ในปริมาณที่มากขึ้นทำให้เส้นใยพอลิ
 เอทิลีนออกไซด์ที่ได้มีขนาดใหญ่ขึ้น สุดท้ายนี้พบว่าการเติมแอลกอฮอล์ชนิดต่างๆได้แก่เมทานอล
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 ON BEAD FORMATION OF ELECTROSPUN POLY(ETHYLENE OXIDE)
 NANOFIBERS. THESIS ADVISOR : ASSISTANT PROFESSOR
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Electrospun fiber often have beads as “by products”. This research is therefore aimed at investigating the effects of processing agents, i.e. solution concentration, addition of poly(ethylene glycol) (PEG) of different molecular weight (M_w), addition of inorganic salts, addition of sodium dodecyl sulfate (SDS), and solvent system on bead formation of electrospun poly(ethylene oxide) (PEO) nanofibers. First, PEO solutions of varying concentration ranging from 3 to 7% w/v were electrospun to produce fibers with the average diameter ranging from 72 to 242 nm. Only when the concentration of the solution was greater than 5% w/v, no beads were found. Addition of low M_w PEGs (i.e. 1,000-4,600 g/mol) resulted in the formation of beaded fibers, while higher ones (i.e. 8,000-35,000 g/mol) produced smooth fibers. Among the various inorganic salts investigated (i.e. LiCl, NaCl, KCl, $MgCl_2$, and $CaCl_2$), only NaCl salt resulted in smooth fibers, with the average diameter of the fibers ranging between 73 and 205 nm. Increasing amount of SDS resulted in the formation of large fibers. Lastly, addition of various alcohols (i.e. methanol, ethanol, and isopropanol) as the second solvent did not result in the formation of smooth fibers as originally expected.

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CHAPTER I

INTRODUCTION

1.1 Background

The literature about electrostatic spraying contain many helpful insights into the electrospinning process. Electrospinning of the solutions of macromolecules can be traced back to 1934, when Formhals invented a process for making polymer fibers by using electrostatic force. Electrospinning is a straightforward method that produces polymer nanofibers.

The principle of electrospinning process are the use of electrostatic force as the main driving force for fiber formation. In the process, a high voltage power supply is used to charge a polymer solution or melt through a metal contact, e.g. a needle, across a metal collection screen. The applied potential is in the range of 5 to 30 kV, depending on the collection distance. A reservoir containing a polymer solution or melt is attached to the metal contact with a small opening. When the polymer solution or melt is charged, the coulombic repulsion force destabilizes the hemispherical pendant droplet located at the tip of the small opening. At a critical condition, the destabilized, hemispherical droplet changes into a conical shape, which normally terms " the Taylor's cone". Further increase in the applied potential causes a charged jet to be ejected from the tip of the cone. At right conditions, fibers are formed as a result.

Polymer nanofibers have potential uses in filtration, protective clothing, and biomedical applications including wound dressing and drug delivery system. Nanofibers offer advantages for the application of pesticides to plants, as structural elements in artificial organs, as supports for enzymes of catalysts that can promote chemical reactions, and as reinforcing fillers in composites. Ceramic or carbon nanofibers made from polymeric precursors extend the use of nanofibers, due mainly to their high service temperature and high modulus. Flexible fibers are needed on a scale commensurate with micro- or nano- electrical mechanical and optical systems. The use of electrical forces in fabricating materials may lead to new ways of producing micro- or nanoscale devices.

Electrospun fibers often have beads as “by products”. The beads are formed during the processing. An electrically-driven jet of low molecule weight liquid would form droplets, as occurs in electrospraying. The formation of such droplets is due to the capillary breakup of the jet by surface tension. For polymer solutions, the pattern of the capillary breakup was changed radically. Instead of breaking completely in response to the capillary instability, the jets between the droplets formed nanofibers, and the contraction of the radius of the jet, which was driven by surface tension, caused the remaining solution to form beads.

This work can be divided into three main experimental parts. The first is the electrospinning of poly(ethylene oxide). In this part, the effect of concentration on morphological appearance of as-spun fibers was thoroughly investigated by way of scanning electron microscopy. The second part is to study the bead formation of poly(ethylene oxide) in its blends with poly(ethylene glycol). Poly(ethylene oxide) and poly(ethylene glycol) are the same polymer but they are different in the molecular weight, i.e. poly(ethylene glycol) having a low molecular weight, while poly(ethylene oxide) having a high molecular weight. The effects of poly(ethylene glycol) molecular weight and concentration on morphological appearance of as-spun fibers were investigated. The last part is to study the reduction in the bead formation of poly(ethylene oxide) nanofibers. In this part, the effect of certain processing variables (e.g. salt addition, surfactant addition, and solvent system) on bead formation of electrospun poly(ethylene oxide) nanofibers.

1.2 Objectives

The objectives of this research work are:

1. To investigate the bead formation of poly(ethylene oxide)nanofibers; and
2. To investigate the reduction in the bead formation on poly(ethylene oxide) nanofibers.

CHAPTER II

LITERATURE REVIEW

2.1 Electrospinning

2.1.1 History of electrospinning

Electrospinning (also known as electrostatic spinning) is a process that utilizes electrical force to produce polymer fibers from polymer solutions or melts. Although the behavior 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. Lord Raleigh [1] studied the condition of instability in electrically-charged liquid droplets. He showed that when the electrostatic force overcomes the surface tension that acts in the opposite direction of the electrostatic force, liquid is thrown out in the form of fine jets.

An early patent on electrospinning of polymer fibers was issued by Formhals [2] in 1934. In his patent, cellulose acetate was used as the model polymer. Fibers were formed between two electrodes that are in opposite polarities. One electrode was placed into the polymer solution, and another was attached to a conductive collector. The applied potential depended on the properties of the solution, such as molecular weight of the polymer and viscosity of the solution. The small opening used as the spinneret was constructed by drilling a fine hole in a metal alloy.

In 1969, Taylor [3] studied the disintegration of water droplets deformed by an electrostatic field. At the onset of the instability, the droplet elongates to form a conical shape, called Taylor's cone, of which the semi-vertical angle was shown to be 49.3° .

In 1971, Buamgarten [4] was successful in producing acrylic microfibers by the electrostatic spinning process. Dimethyl formamide was used as the solvent. The obtained fiber diameters were in the range of 0.05 to 1.1 microns based on the applied potentials in the range of 5 to 20 kV. The relationships between fiber diameter, fiber jet, solution viscosity, solution feed rate and surrounding gas were observed. He found that fiber diameter increased when the solution viscosity increased. The effect of solution

flow rate on fiber diameters was very small and the effect of surrounding gas depended on the humidity.

Later, Larrondo and Manley [5-7] described the electrospinning of polyethylene and polypropylene fibers from the melts in the air.

During the recent few years, extensive investigations on electrospinning process have been conducted in the aspects of theoretical simulation [8], fiber formation mechanism, influencing factors for fiber size and morphology [9] and so on. Nanofibers of various materials have been fabricated, including ordinary polymers, conducting polymers [10], carbon [11], spider silk, protein [12-13], and DNA. The as-spun fibers have diameters ranging from as small as a few nanometers to several micrometers and therefore possess huge surface-to-volume ratios, resulting in their great potentials in a broad range of fields, such as separation, filtration [14-15], catalysis, fiber-reinforced composites [16], tissue engineering [17], drug delivery system [18], protective textile [19], and as fiber templates for preparation of nanotubes [20].

2.1.2 Principle

It has been reported in the open literature that more than 50 different polymers have been successfully spun into ultrafine fibers. The obtained fibers were reported to range between less than 3 nanometers to over 1 micrometer in diameter. In the electrospinning processing, fibers are spun under a high voltage electrical field. The setup is shown in Fig. 2.1. A polymer solution or melt is contained in a syringe equipped with a piston and a stainless steel capillary serving as an electrode. A grounded counter electrode (a round aluminium plate) is placed down against the capillary and a high voltage is applied between the capillary and the counter electrode.

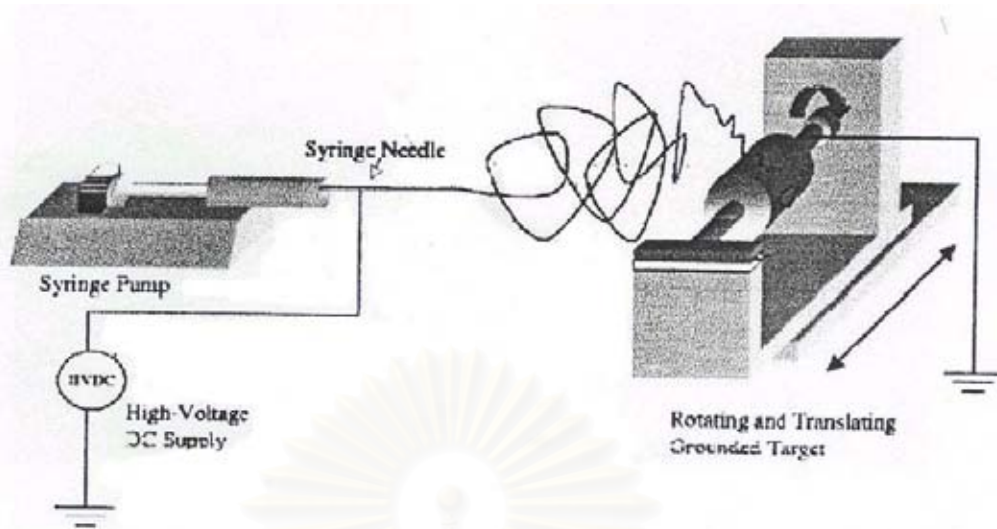


Figure 2.1 Setup for Electrospinning

Under controlled velocity, the piston on the syringe was driven down by a motor and a droplet of polymer solution is suspended by its surface tension at the tip of the capillary. If the free surface of the solution is subjected to an electrical field, charge and/or dipolar orientation will be induced at the air-solution interface. The charge (or dipolar) repulsion causes a force that opposes the surface tension. If the voltage surpasses a threshold value, electrostatic force overcomes the surface tension, resulting in jets being ejected from the solution and moving towards the counter electrode. During the travelling to the counter electrode, the solvent in the jets evaporates and the solidified fibers are deposited on substrate located above the counter electrode.

After a charged jet is ejected from the droplet of conical shape, it flows continuously under the influence of the electrostatic field. There are two kinds of electrostatic forces acting on a jet segment. One is from the external field that reacts with charges present in a jet segment and the other from the coulombic repulsion between adjacent charges of similar polarity. The first force is responsible for carrying the charged jet towards the conductive collector and the second is responsible for the stretching of the charged jet. The coulombic repulsion can cause different types of instability such as bending and splitting instability, viz. the jet followed a bending, winding, spiraling and looping path in three dimensions. The jet in each loop grew longer and thinner as the loop diameter increased, a direct result of the longer path length. After some time, segment of a loop suddenly developed a new bending

instability, but at a smaller scale than that of the first one. Each cycle of bending instability can be described in three steps.

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

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

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

This cycle of instability was observed to repeat in a smaller scale. It was inferred that a larger number of cycles occurred resulted in the decrease in the jet diameters, hence a decrease in the diameter of the obtained fibers. The fluid jet solidifies as it dries and the electrospun nanofibers are collected some distance below the envelope cone [21].

So far, fibers with diameters ranging from as low as 5 nm to several microns have been produced. It is found that the morphology and dimension of the electrospun fibers are dependent on the process parameters, including solution concentration and viscosity, electrical conductivity of the solution, surface tension of the solution, polymer molecular weight, molecular weight distribution of the polymers, vapor pressure and boiling point of the solvent, flow rate, intensity of electrical field, distance between the capillary and the substrate, temperature, humidity and atmosphere etc.

2.1.3 Beaded Nanofibers

Electrospun fibers sometimes have beads of polymer that formed during the process. An electrically-driven jet of a low molecular weight liquid would form droplets, as occurs in the electrospraying process. The formation of such droplets is due to the capillary breakup of the jet by surface tension [22]. For polymer solution, the pattern of the capillary breakup was changed radically. Instead of breaking completely

in response to the capillary instability, the jets between the droplets formed nanofibers, and the contraction of the radius of the jet, which was driven by surface tension, caused the remaining solution to form bead [23].

2.2 Poly(ethylene oxide)

The polymeric derivatives of ethylene oxide are divided into two classes which are defined by the molecular weights. This division is based on methods of production, commercial nomenclature, and properties and uses. Low molecular weight polymers with an average molecular weight of 200 to 20,000 Da are called poly(ethylene glycol)s (PEGs). They are used in ceramics, cosmetics, lubricants, metal working, pharmaceuticals, urethanes, rubber chemicals, electronics, and other applications. The upper molecular weight limit is imposed by base-catalyzed side reactions occurring during the polymerization reaction. Polymeric derivatives with molecular weight of 1×10^5 to 5×10^6 Da called ethylene oxide polymers or poly(ethylene oxide) resins. They are used in flocculation, packing films, acid cleaners, denture adhesives, lubricants, friction reduction, and other applications where water solubility and high viscosity are desired [24].

Poly(ethylene oxide) (PEO) is a water-soluble, thermoplastic polymer produced by the heterogeneous polymerization of ethylene oxide. The white, free-flowing resins are characterized by the following structural formula:



Heterogeneous Catalytic Polymerization

The preparation of polymers of ethylene oxide with molecular weights greater than 100,000 was first reported in 1933. The polymer was produced by placing ethylene oxide in contact with an alkaline-earth oxide for extended periods. In the 1950s, the low yield and low polymerization rates of the early work were improved upon the use of alkaline-earth carbonates as the catalysts. Further improvements in reaction rates and

polymerization control have led to the commercial availability of poly(ethylene oxide) of varying molecular weight.

The polymerization of ethylene oxide to produce high molecular weight polymers involves heterogeneous reaction with propagation at the catalyst surface. The polymerization can involve anionic or cationic reactions of ethylene oxide that generally produce lower molecular weight products. The mechanism for production of extremely high molecular weight polymers is thought to involve a coordinate anionic reaction where ethylene oxide is coordinated with a metal atom of the catalyst and is then attacked by an anion. The various polymerization mechanisms have been described.

Catalysts capable of polymerizing ethylene oxide to high molecular weight polymers include many metal compounds. These are, for examples, alkaline-earth carbonates and oxide, alkyl zinc compounds, alkyl aluminum compounds and alkoxides, and hydrates of ferric chloride, bromide, and acetate. Other catalysts include various alkyls and alkoxides of aluminum, zinc, magnesium, and calcium, and mixtures of these materials with various other inorganic salts. The preparation and utilization of the various catalysts have also been described. The molecular weight of the polymer appears to be controlled by the catalyst systems as well as by polymerization conditions. Rigid control of catalyst preparation and raw material quality appear to be mandatory for successful laboratory preparation of high molecular weight poly(ethylene oxide) [25]. The mechanism of polymerization poly(ethylene oxide) can be shown in Figure 2.2.

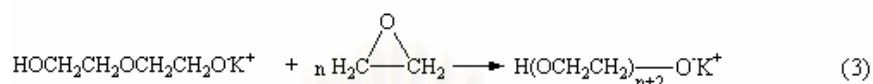
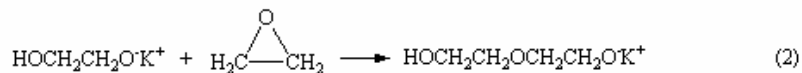
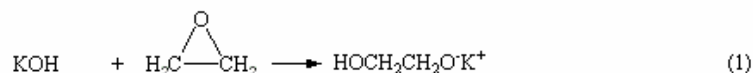


Figure 2.2 Mechanism of polymerization poly(ethylene oxide)

Physical Properties

Density: Although the polymer unit cell dimensions imply a theoretical density of 1.33 g/cm^3 at 20°C and the extrapolation of melt density data indicates a density of 1.13 g/cm^3 at 20°C for the amorphous phase, the density actually measured covers the range of 1.15 to 1.26 g/cm^3 , which indicates the presence of numerous voids in the structure.

Solubility: Poly(ethylene oxide) is completely soluble in water at room temperature. However, at elevated temperatures ($> 98^\circ\text{C}$) the solubility decreases. It is also soluble in several organic solvents, particularly chlorinated hydrocarbons. Aromatic hydrocarbons are better solvents for poly(ethylene oxide) at elevated temperatures. Solubility characteristics are listed in Table 2.1.

Chemical Properties

Oxidation: Because of the presence of weak C-O bonds in the backbone, high molecular weight polymers of ethylene oxide are susceptible to oxidative degradation in bulk, during thermoplastic processing, or in solution. During thermoplastic processing at elevated temperatures, oxidative degradation is manifested by a rapid decrease in melt viscosity with time. In aqueous solution at ambient temperature, the decay of solution viscosity also is an indication of oxidative degradation, and the rate of decay is increased by the presence of traces of chlorine, peroxides, permanganate, or persulfate and certain transition-metal ions such as Cu^+ , Cu^{2+} , Cu^{3+} , Fe^{3+} , and Ni^{2+} . A combination of these agents can lead to severe viscosity losses.

Table 2.1 Solubility of Poly(ethylene oxide)^a in Several Solvents^b

Solvent ^{c,d}	Temperature	
	Resin dissolves on heating >25°C, °C	Resin precipitates on cooling, °C
dissolves at room temperature in		
water		< 0
carbon tetrachloride		< 0
acetonitrile		< 0
ethylene dichloride		< 0
trichloroethylene		< 0
methylene dichloride		< 0
benzene		2
2-propanol (91 wt %)		2
dimethylformamide		14
tetrahydrofuran		18
methanol		20
methyl ethyl ketone		20
dissolves with heating in ^e		
toluene	30	20
xylene	30	20
acetone	35	20
Cellosolve ^f acetate	35	25
anisole	40	0
1,4-dioxane	40	4
ethyl acetate	40	25
ethylenediamine	40	26

Table 2.1 Solubility of Poly(ethylene oxide)^a in Several Solvents^b (Continue)

Solvent ^{c,d}	Temperature	
	Resin dissolves on heating >25°C, °C	Resin precipitates on cooling, °C
dimethyl Cellosolve ^f	40	27
Cellsolve ^f solvent	45	28
ethanol (dry)	45	31
Carbitol ^f solvent	50	32
n-butanol	50	33
butyl Cellosolve ^f	50	33
n-butyl acetate	50	34
2-propanol (dry)	50	36
methyl Cellosolve ^f	50	46

^aMol wt (1-50) × 10⁵

^bRef. 4.

^cSolution concentration = ca 1 wt %.

^dAll solvents except 2-propanol (91 wt %) were carefully dried before testing.

^eThe polymer was insoluble in 1,3-butanediol, ethylene glycol, diethylene glycol, and glycerol at all temperatures.

^fRegistered trademark of Union Carbide Corp.

2.3 Salts

2.3.1 Lithium Chloride

Lithium Chloride [26], LiCl, is produced from the reaction of lithium carbonate or hydroxide acid. The salt melts at 608°C and boils at 1382°C. The 41-mol % LiCl-59-mol % KCl eutectic (melting point, 352°C) is employed as the electrolyte in the molten salt electrolysis production of lithium metal. It is also used, often with other alkali halides, in brazing flux eutectics and other molten salt applications such as electrolytes for high temperature lithium batteries. The salt is extremely hygroscopic and is used in dehumidification applications. It is very soluble in water.

2.3.2 Sodium Chloride

Salt producers classify sodium chloride [27], NaCl, also known as common salt, by the three methods used for its production: mechanical evaporation of solution-mined brine, i.e., evaporated-granulated salt; underground mining of halite deposits, i.e., rock salt; and solar evaporation of seawater, natural brine, or solution-mined brine, i.e., solar salt. Salt in brine is a fourth classification, for solution-mined brine that is typically used as feedstock for chemical production. Salt is a readily available, inexpensive bulk commodity, and a basic requirement for all life. It is found throughout the world in natural underground deposits as the mineral halite and, in some locations, as mixed evaporites in saline lakes. Sodium chloride, as a compound, is the largest component of dissolved solids found in seawater. Sodium chloride precipitates in cubic, crystalline form. When pure, it is colorless and consists of 60.663 wt%Cl and 39.337 wt%Na. Sodium chloride in commercial form can appear as discrete crystals in various size ranges, fine granules of powder, and compressed pellets or blocks. If viewed with magnification, all sodium chloride is crystalline. Depending on gradation and commercial form, salt can be white, grayish, or sometimes brownish. Large crystals of apparently recrystallized halite found in some salt mines are colorless and transparent, clearly showing the mineral's characteristic cubic cleavage. Sodium chloride is readily

soluble in water and insoluble or only slightly soluble in most other liquids. It is an ionic compound, being made up of equal numbers of positively charged sodium and negatively charged chloride ions. When it is melted or dissolved in water the ions can move about freely, so that dissolved or molten sodium chloride is a conductor of electricity; it can be decomposed into sodium and chlorine by passing an electrical current through it.

2.3.3 Potassium Chloride

Potassium Chloride [28], KCl, is a colorless or white, cubic, crystalline compound that closely resembles common salt (sodium chloride). It is soluble in water, alcohol, and alkalis. Potassium chloride occurs pure in nature as the mineral sylvite and is found combined in many minerals and in brines and ocean water. The chief use of potassium chloride is in the production of fertilizers; it is also used in chemical manufacture. For agricultural use it is often called muriate of potash; the concentration of potassium chloride in muriate of potash is expressed as a corresponding concentration of potassium oxide (K_2O), i.e., the concentration of potassium oxide that there would be if the potassium were present as its oxide instead of as its chloride. Thus, muriate of potash that contains (typically) 80% or 97% KCl by weight is said to contain 50% or 60% K_2O , respectively. Manure salts contain some potassium chloride.

2.3.4 Calcium chloride

Calcium chloride [29], $CaCl_2$, is a white, crystalline salt that is very soluble in water. Solutions containing 30-45 wt % $CaCl_2$ are used commercially. Of the alkaline-earth chlorides it is the most soluble in water. It is extremely hygroscopic and liberates large amounts of heat during water absorption and on dissolution. It forms a series of hydrates containing one, two, four, and six moles of water per mole of calcium chloride. Another hydrate, $CaCl_2 \cdot 0.33H_2O$, has been identified, molecular weight 116.98; 94.8 wt % $CaCl_2$; heat of solution in water to infinite dilution, -71.37 kJ/mol. Commercial

applications of calcium chloride and its hydrates exploit one or more of its properties with regard to aqueous solubility, hygroscopic nature, the heat gained or lost when one hydrated phase changes to another, and the depressed freezing point of the eutectic solution at a composition of about 30% by weight calcium chloride.

2.3.5 Magnesium chloride

Magnesium chloride [30], MgCl_2 , is one of the primary constituents of seawater and occurs in most natural brines and salt deposits formed from the evaporation of seawater. It occurs infrequently in nature as the mineral bischofite, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. Large deposits of oceanic origin contain the mineral carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. Magnesium chloride, one of the most commercially important magnesium compounds, is available in the anhydrous and hexahydrate forms. Both are deliquescent and form saturated solutions on standing in a moist atmosphere. Magnesium chloride also forms hydrates containing 8 and 12 molecules of water of hydration.

2.4 Surfactant

2.4.1 Sodium dodecyl sulfate

Sodium dodecyl sulfate [31], SDS, is an anionic surfactant used in a wide range of nonparenteral pharmaceutical formulations and cosmetics. It shows as a detergent and wetting agent effective in both alkaline and acidic conditions. Sodium dodecyl sulfate consists of white or cream to pale yellow-coloured crystals, flakes or powder having a smooth feel, a soapy, bitter taste and a faint odor of fatty substances.

Empirical Formula : $\text{C}_{12}\text{H}_{25}\text{NaO}_4\text{S}$

Molecular weight : 288.38

Sodium dodecyl sulfate is freely soluble in water, giving an opalescent solution and practically insoluble in chloroform and ether. pH of 1% w/v aqueous solution is 7.0 - 9.5. The melting point has been reported as 204 – 207 °C (for pure

substance). At 20°C, critical micelle concentration is 8.2 mmol/L (0.23g/L). Sodium dodecyl sulfate is stable under normal storage conditions. However, in solution, under extreme conditions, i.e. pH 2.5 or below, it undergoes hydrolysis to lauryl alcohol and sodium bisulfate. The bulk material should be stored in a well-closed container away from strong oxidizing agents in a cool, dry place.

2.5 Solvent

2.5.1 Methanol

Methanol [32] (methyl alcohol), CH_3OH , is a colorless liquid at ambient temperatures with a mild, characteristic alcohol odor. Originally called wood alcohol since it was obtained from the destructive distillation of wood, today commercial methanol is sometimes referred to as synthetic methanol because it is produced from synthesis gas, a mixture of hydrogen and carbon oxides, generated by a variety of sources. Methanol has traditionally been used as a solvent and as a feedstock for bulk organic chemicals (primarily formaldehyde), with modest growth potential. However, after 1990, demand for methanol as a feedstock for methyl *tert*-butyl ether (MTBE) accelerated when the latter became a significant oxygenated component in motor fuels. As a result, methanol has evolved into a globally produced and traded commodity with expected future growth in the alternate and oxygenated fuel sectors, driven by both strategic and environmental considerations. Methanol is miscible with water, other alcohols, esters, ketones, ethers, and most organic solvents. Methanol has a particular affinity for carbon dioxide and hydrogen sulfide, which is the basis for its use as the solvent in the Rectisol gas sweetening process. Being polar in nature, methanol often exhibits nonideal behavior with hydrocarbons, forming azeotropes with many compounds. Methanol depresses the formation temperature of natural gas hydrates, leading to its use as an antifreeze in pipelines. Methanol undergoes reactions that are

typical of alcohols as a chemical class. Dehydrogenation and oxidative dehydrogenation to formaldehyde over silver or molybdenum oxide catalyst are of particular industrial importance.

2.5.2 Ethanol

Ethanol [33] or ethyl alcohol, $\text{CH}_3\text{CH}_2\text{OH}$, is one of the most versatile oxygen-containing organic chemicals because of its unique combination of properties as a solvent, a germicide, a beverage, an antifreeze, a fuel, a depressant, and especially as a chemical intermediate for other organic chemicals. The use of fermentation-derived ethanol as an automotive fuel additive to enhance octane and reduce emission has been explosive growth over the last 12 years. Ethyl alcohol under ordinary conditions is a volatile, flammable, clear, colorless liquid. Its odor is pleasant, familiar, and characteristic, as is its taste when suitably diluted with water. The most amazing property of ethanol is the volume shrinkage that occurs when it is mixed with water, or the volume expansion that occurs when it is mixed with gasoline. One volume of ethanol plus one volume of water results in only 1.92 volumes of mixture. The physical and chemical properties of ethyl alcohol are primarily dependent upon the hydroxyl group. This group imparts polarity to the molecule and gives rise to intermolecular hydrogen bonding. These two properties account for the differences between the physical behavior of lower molecular weight alcohols and hydrocarbons of equivalent weight. Infrared spectrographic studies have shown that, in the liquid state, hydrogen bonds are formed by the attraction of the hydroxyl hydrogen of one molecule and the hydroxyl oxygen of a second molecule. This bonding makes liquid alcohol behave as though it were largely dimerized. This behavior is analogous to that of water, which, however, is more strongly bonded and appears to exist in liquid clusters of more than two molecules. The association of ethyl alcohol is confined to the liquid state; in the vapor state it is monomeric.

2.5.3 Isopropyl alcohol

Isopropyl alcohol [34], also known as isopropanol, 2-propanol, dimethylcarbinol, and *sec*-propyl alcohol, is a colorless, volatile and flammable liquid having a molecular weight of 60.09 and a slight odor resembling a mixture of ethyl alcohol and acetone. Isopropyl, the lowest member of the class of secondary alcohols, is generally known as the first petrochemical. Of the lower (C_1 - C_5) alcohols, isopropyl alcohol is third in commercial production, behind methanol and ethyl alcohol. Isopropyl alcohol is used for the manufacture of agricultural chemicals, pharmaceuticals, process catalysts, and solvent. Physical properties of isopropyl alcohol are characteristic of polar compounds because of the presence of the polar hydroxyl, -OH, group. Isopropyl alcohol is completely miscible in water and readily soluble in a number of common organic solvents such as acids, ester, and ketones. It has solubility properties similar to those of ethyl alcohol. There is a competition between these two products for many solvent application. Isopropyl alcohol has a slight, pleasant odor resembling a mixture of ethyl alcohol and acetone, but unlike ethyl alcohol, isopropyl alcohol has a bitter, unpotable taste. Physical and chemical properties of isopropyl alcohol reflect its secondary hydroxyl functionality. For example, its boiling and flash points are lower than *n*-propyl alcohol, whereas its vapor pressure and freezing point are significantly higher. Isopropyl alcohol boils only 4°C higher than ethyl alcohol. Chemical properties of isopropyl alcohol are determined by its functional hydroxyl group in the secondary position. Except for the production of acetone, most isopropyl alcohol chemistry involves the introduction of the isopropyl or isopropoxy group into other organic molecules by the breaking of the C-OH or the O-H bond in the isopropyl alcohol molecule. Isopropyl alcohol undergoes reactions typical of an active secondary alcohol. It can be dehydrogenated, oxidized, esterified, etherified, aminated, halogenated, or otherwise modified at the OH moiety more readily than primary alcohols such as *n*-propyl or ethyl alcohol.

2.6 Literature review

The effects of solution viscosity, charge density carried by the jet, and solution surface tension on the formation bead-on-string morphology were investigated by Fong and co-workers [35]. Beads and beaded fibers were less likely to be formed in fibers spun from highly viscous solutions and in jets with high net charge density. Increasing net charge density favored the formation of smaller fibers. Decreasing the surface tension coefficient of the solution favored the formation of larger fibers.

Deitzel and co-workers [36] studied the effects of applied potential and solution concentration on morphology of electrospun poly(ethylene oxide) fibers. They found that the applied potential correlated strongly with the formation of beaded fibers. Changes in solution concentration contributed mostly to the diameters of the obtained fibers, with the fiber diameters increasing with increasing solution concentration following a power law relationship. In addition, electrospinning of solutions of high concentration produced fibers having a bimodal distribution of the diameters.

In 2003, Lee and co-workers [37] produced electrospun polystyrene fibers by using the mixture of tetrahydrofuran (THF) and *N,N*-dimethyl formamide (DMF) as solvents. They studied different bead dimensions and shapes. They found that the electrospun polystyrene fibers produced contained irregular beads and electrospinning certainly was enhanced with increasing DMF content. The bead concentration was also controlled by DMF content. The aspect ratio of the formed beads and diameter of fibers increased with increasing solution concentration. When polystyrene was dissolved in only THF, unexpected half hollow spheres (HHS) structure appeared.

Jing and co-workers [38] examined the influences of surfactants and medical drugs on the diameter size and uniformity of electrospun poly(L-lactic acid) (PLLA) fibers by adding various surfactants (i.e. cationic, anionic, and nonionic) and typical drugs into the PLLA solution. They found that addition of all the three kinds of surfactants, triethyl benzyl ammonium chloride (TEBAC), sodium dodecyl sulphate (SDS), and aliphatic PPO-PEO ether (AEO10), can reduce the diameter and distribution of electrospun fibers.

Won and co-workers [39] studied the effect of solution properties and polyelectrolyte on the electrospinning of poly(ethylene oxide) (PEO). Ultrafine PEO fibers without beads were electrospun from 3, 4, 7 and 7 wt% PEO solutions in chloroform, ethanol, dimethyl formamide (DMF) and water, respectively. At the concentrations of PEO/DMF solution, the values of $[\eta]C$ were ~ 10 for all solutions. The average diameters of PEO fibers were ranged from 0.36 to 1.96 μm . The higher the dielectric constant of solvent was, the thinner PEO fiber was. The average diameters of electrospun PEO fibers from PEO/water solutions decreased and their distributions were narrower by adding 0.1 wt% poly(allyamine hydrochloride) (PAH) and poly(acrylic acid sodium salt) (PAA) due to the increased charge density in solutions. The addition of PAH and PAA lowered the minimum concentration of electrospinning of a PEO/water solution to 6 wt%.

The effect of polymer weight average molecular weight (M_w) on the fiber structure of electrospun poly(vinyl alcohol) (PVA) has been studied by Koski and coworkers [40]. PVA with a degree of hydrolysis of 98-99% and with molecular weights ranging from 9,000 to 186,000 g/mol was dissolved in water. They found that the molecular weight of PVA and the solution concentration have a significant effect on the structure of the electrospun polymer. It was observed that for each molecular weight, a fibrous structure was stabilized above a minimum concentration, generally corresponding to $[\eta]C > 5$. The average fiber diameter was between 250 nm and 2 μm . The fiber diameter increased with M_w and concentration. At low M_w and or concentration ($[\eta]C > 9$), the fibers exhibited a circular cross-section. Flat fibers were observed at high M_w and concentration ($[\eta]C > 9$).

CHAPTER III

EXPERIMENTAL

This work can be divided into 3 main parts. The first is to investigate the effect of polymer concentration on morphological appearance of electrospun poly(ethylene oxide) (PEO), in order to obtain the optimal conditions for achieving fibers of uniformed shape and size. The conditions were chosen and used for further investigation on the effect of molecular weight of poly(ethylene glycol)s (PEGs) on the morphological of electrospun fibers, in order to investigate the mechanism for bead formation. The last part is to investigate the effects of SDS addition, salt addition, and mixed solvent on morphological appearance of the resulting fibers.

3.1 Materials and Chemicals

Poly(ethylene oxide) (PEO): PEO with its molecular weight of 600,000 g/mol was purchased from Aldrich, Germany.

Poly(ethylene glycol) (PEG): Low molecular weight PEGs (1,000, 1,500, 2,000, 4,600, and 8,000 g/mol) were purchased from Aldrich, Germany, whereas high molecular weight PEGs (10,000, 20,000, and 35,000 g/mol) were purchased from Fluka, Switzerland.

Sodium chloride (NaCl): Sodium chloride (Unilab grade) was purchased from Lab Scan Analytical Sciences, Thailand.

Lithium chloride (LiCl): Lithium chloride (Unilab grade) was purchased from Asia Specialty Chemical Ltd., Australia.

Potassium chloride (KCl): Potassium chloride (Unilab grade) was purchased from Ajax Co. Ltd., Australia.

Magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$): Magnesium chloride (Unilab grade) was purchased from Ajax Co. Ltd., Australia.

Calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$): Calcium chloride (Unilab grade) was purchased from Ajax Co. Ltd., Australia.

Sodium dodecyl sulfate (SDS): Sodium dodecyl sulfate used as an anionic surfactant was purchased from Fluka, Switzerland. The chemical formula is $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OSO}_3\text{Na}$ ($M_w = 288.38$).

Methanol (CH_3OH): Methanol was purchased from Italmar, Co., Ltd., Thailand.

Ethanol ($\text{C}_2\text{H}_5\text{OH}$): Ethanol was purchased from Italmar, Co., Ltd., Thailand.

Isopropanol ($\text{C}_3\text{H}_7\text{OH}$): Isopropanol was purchased from Italmar, Co., Ltd., Thailand.

3.2 Instruments

Table 3.1 lists all the instruments used in this research.

Table 3.1 Instruments used in this experiment

Instrument	Model
1. High Voltage Power Supply	Gamma High Voltage Research D-ES30PN/M692
2. Viscometer	Brookfield DV-III
3. Tensiometer	KrÜss K10T
4. Conductivity meter	Orion 160
5. Scanning Electron Microscope	JEOL JSM-6400
6. Ion Sputtering	Balzers Union SCD 040

3.3 Experimental Procedure

Figures 3.1 and 3.2 display the experimental procedure in this research.

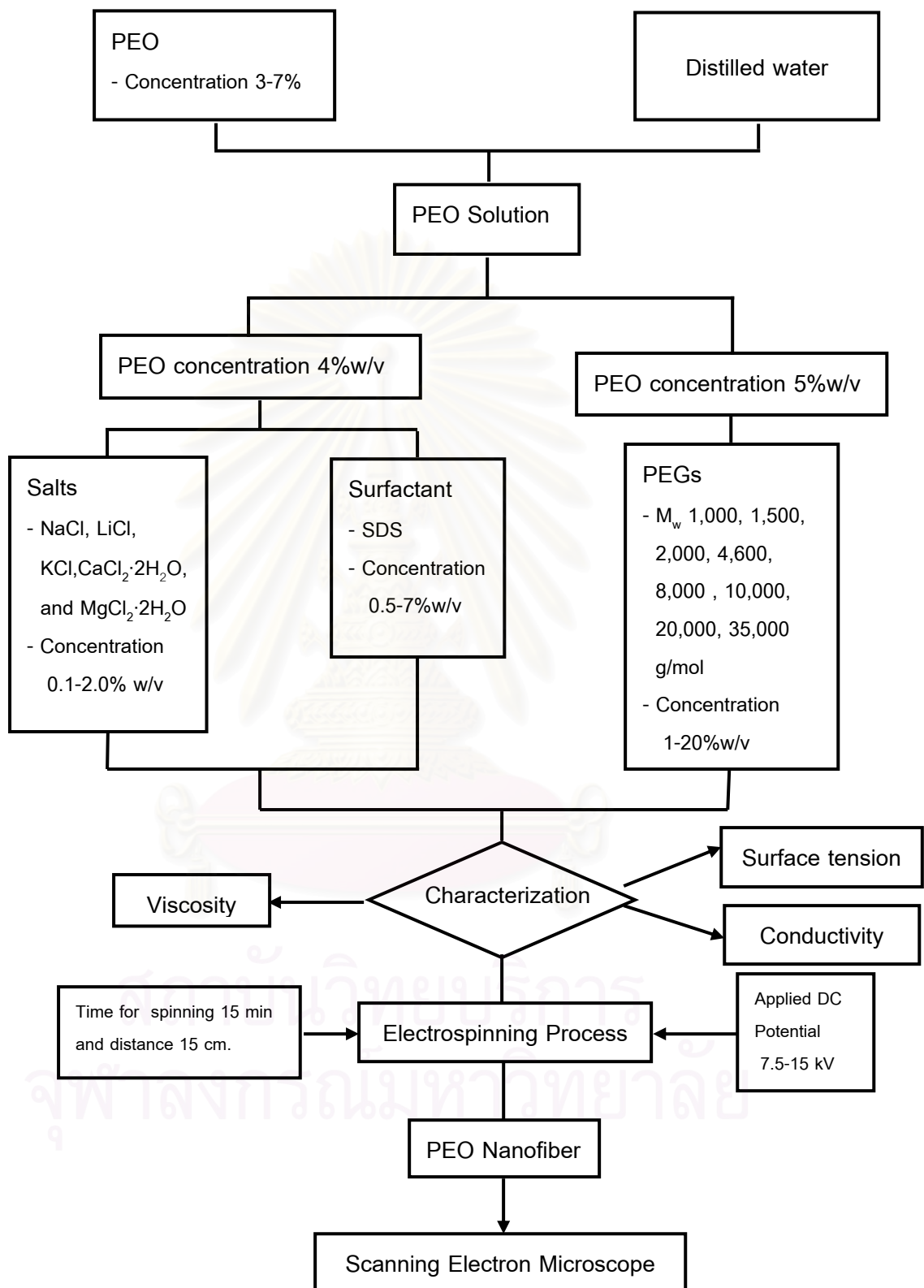


Figure 3.1 Flow chart of the experimental procedure (1).

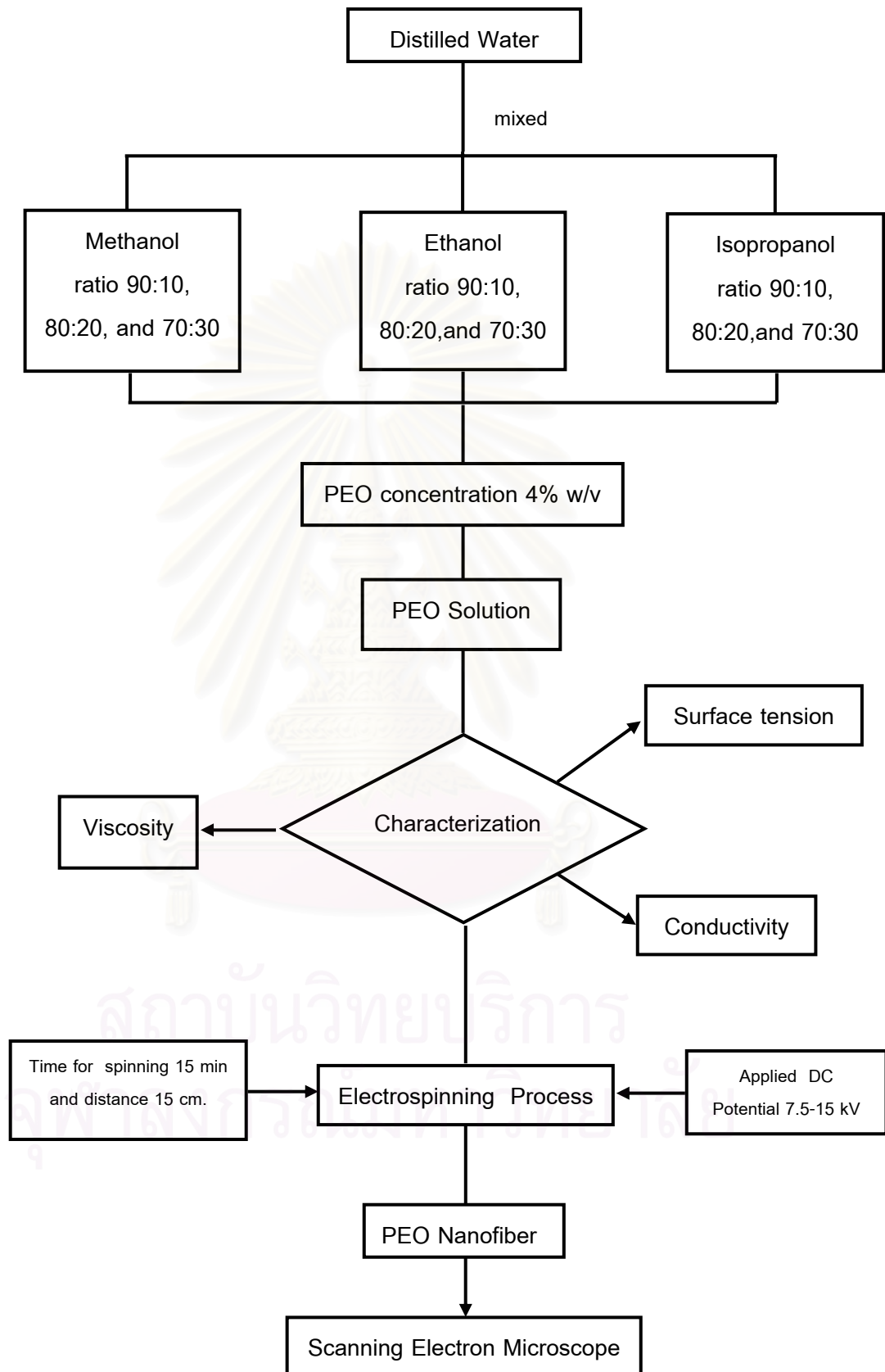


Figure 3.2 Flow chart of the experimental procedure (2).

3.3.1 Effect of poly(ethylene oxide) concentration

In the first part, solutions of PEO were prepared in distilled water in the concentration range of 3 to 7 % w/v.

3.3.2 Effect of PEG molecular weight

A 5% w/v PEO solution was mixed with PEG of various molecular weights and concentrations. Similar to PEO solution, PEGs were dissolved in the PEO solution to prepare the PEO/PEG blend solution with the concentration of PEG ranging between 1 and 20% w/v.

3.3.3 Effect of salts

Various ionic salts (i.e. NaCl, LiCl, KCl, MgCl₂ and CaCl₂) in different concentrations were added into a 4 % w/v PEO solution in order to investigate the effect of ionic salt addition on morphological appearance of the as-spun PEO fibers. The concentration of salts was varied between 0.1 and 2.0% w/v.

3.3.4 Effect of anionic surfactant

Sodium dodecyl sulfate (SDS), used as anionic surfactant in this work, was added into a 4% w/v PEO solution. Its concentration was varied between 0.5 and 7% w/v.

3.3.5 Effect of solvent system

As shown in Figure 3.2, a 4% w/v PEO solution was dissolved in three mixed solvent systems of distilled water with methanol, ethanol, and isopropanol. The ratio of the mixed solvent in each system was 90:10, 80:20, and 70:30 v/v. Some properties of the solvent used are shown in the Table 3.2

Table 3.2 Properties of solvents used in this work.

Solvent	Chemical Formula	Molecular Weight (g/mol)	Boiling point (°C)	Density (g/cm ³)	Solubility parameter (MPa) ^{1/2}	Surface tension (mN/m)
Methanol	CH ₃ OH	32.042	64.6	0.792	14.5	22.1
Ethanol	C ₂ H ₅ OH	46.070	78.5	0.793	12.7	23.1
Isopropanol	C ₃ H ₈ OH	60.100	82.1	0.785	11.9	21.32

3.4 Characterization of PEO Solution

As-prepared solutions were determined for their viscosity using a Brookfield DV-III programmable viscometer (see Figure 3.3). The temperature of the solutions was controlled at 25°C. The surface tension of the solutions was measured using a Krüss K10T tensiometer (see Figure 3.4). The measurement was carried out at 25°C and the atmosphere in the measuring chamber was saturated with vapor of the solvent to limit evaporation of the solvent from the pendant drop samples. The conductivity of the solutions was also measured using an Orion 160 conductivity meter (see Figure 3.5) at 25°C.



Figure 3.3 Brookfield DV-III programmable viscometer



Figure 3.4 Krüss K10T tensionmeter



Figure 3.5 Orion 160 conductivity meter

3.5 Electrospinning Process

Each of the as-prepared solution was placed in a 5 ml syringe with a stainless steel needle of gauge no. 20 (the outside diameter = 0.91 mm.). A Gamma High Voltage Research D-ES30PN/M692 DC power supply (Florida, USA.) was connected to the needle and a grounded collective screen. The polarity of the emitting electrode was positive. These solutions were electrospun under various applied potentials in the range of 7.5 to 15 kV over a fixed collection distance and collection time of 15 cm and 15 minutes, respectively. Figure 3.6 displays the electrospinning setup employed in this research.

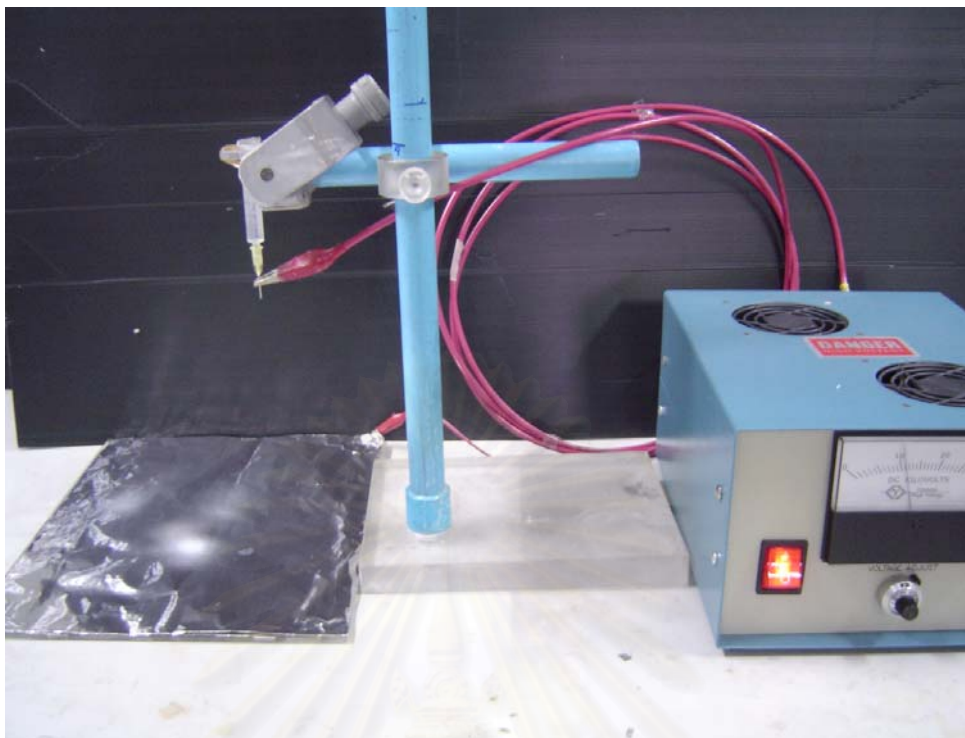


Figure 3.6 The electrospinning setup employed in this research.

3.6 Characterization of As-spun Fibers

To investigate morphology and size of the obtained as-spun fibers, a JOEL JSM-6400 scanning electron microscope (SEM) was used. The samples were coated with gold by an ion-sputtering device for 4 minutes prior to SEM analysis. For each fiber sample, its shape and size were analyzed, in particular, the size of the as-spun fibers was determined using a SemAfore program.

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CHAPTER IV

RESULTS AND DISCUSSION

4.1 Effect of poly(ethylene oxide) concentration

It has been shown to some extent that solution properties play an important role in the morphology of the obtained electrospun polymeric fibers. PEO solutions with concentration ranging between 3 and 7 % w/v were characterized for their viscosity, surface tension, and conductivity values. These values are summarized in Table 4.1.

Table 4.1 The characterization of the PEO solutions.

Sample	Viscosity (cp)	Conductivity (μ S/cm)	Surface tension (mN/m)
PEO 3% w/v	206	17.74	61.39 \pm 0.10
PEO 4% w/v	662	50.05	59.49 \pm 0.05
PEO 5% w/v	1639	57.6	58.42 \pm 0.02
PEO 6% w/v	4748	62.3	58.04 \pm 0.06
PEO 7% w/v	10173	72.5	57.13 \pm 0.06

Clearly, both the viscosity and the conductivity of the solutions were found to increase monotonically with increasing PEO concentration, while the surface tension was found to slightly decrease with increasing PEO concentration.

These PEO solutions were electrospun into fibers, with a representative SEM image for each condition is shown in Figure 4.1. The effect of polymer concentration on morphological appearance of the as-spun fibers could be explained as follows. Figure 4.1 shows the effect of polymer concentration on morphological appearance of the as-spun fibers. At a concentration lower than 3% w/v, electrospinning of such a solution resulted in discrete droplets. The formation of beaded and smooth fibers could be explained based on the interplay between the three major forces, that are coulombic (stretching) forces, viscoelastic (anti-stretching) forces and surface tension [41]. Solutions of low concentrations did not have enough chain entanglement to

withstand both of the electrostatic and coulombic repulsion forces acting on an ejected, charged jet.

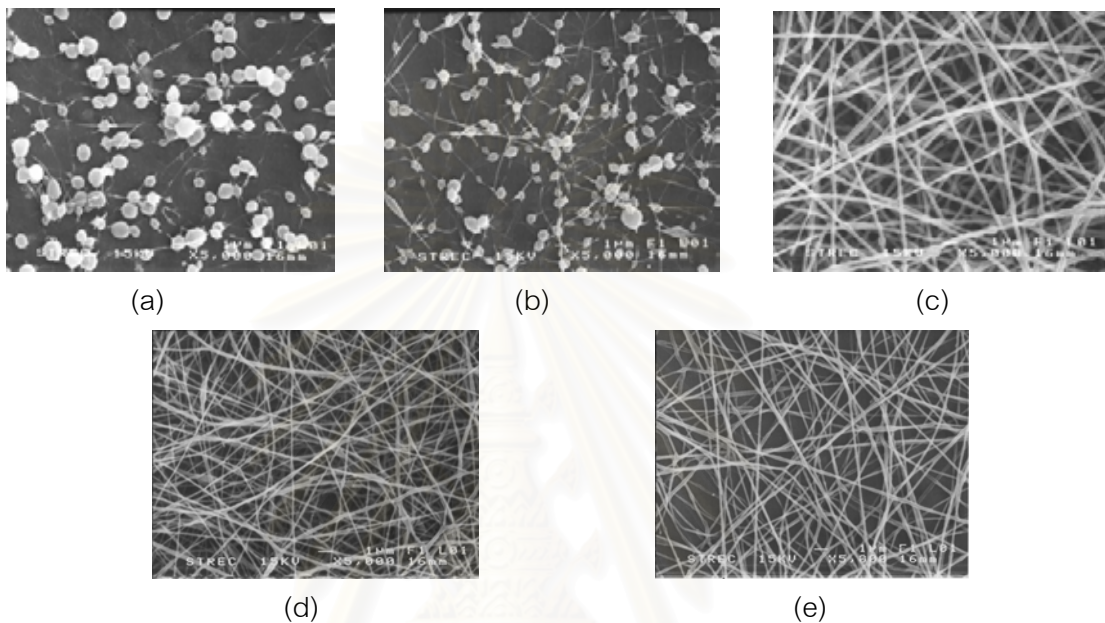


Figure 4.1 SEM images of as-spun PEO fibers from PEO solutions of various concentrations (a) 3, (b) 4, (c) 5, (d) 6, and (e) 7% w/v in distilled water.

An increase in the polymer concentration to 3 and 7% w/v resulted in the formation of beaded fibers. At 3 to 4% w/v, the chain entanglement was high enough to prevent the charged jet from breaking up into droplets. Further increase in the polymer concentration to 5 to 7% w/v resulted in smooth fibers, because of high enough chain entanglement to completely prevent the breaking up to the charged jet. At high viscosities, the viscoelastic force was larger in comparison with the coulombic forces. The increase in the viscoelastic force was sufficient to prevent a charged jet from breaking up into small droplets and to allow the electrostatic stress to further elongate the jet which finally thins down the diameter of the jet tremendously. The formation of beads and beaded fibers is thought to be driven by the surface tension. Surface tension

tries to make the surface area per unit mass smaller, by transforming the broken jets into spheres, while the coulombic forces from adjacent charge species try to increase the surface area of the jet, thus favoring the formation of thinner jets.

Figure 4.2 shows the average fiber diameter of the as-spun PEO as a function of the concentration of PEO solutions. The average fiber diameter was found to range between 75 and 242 nm.

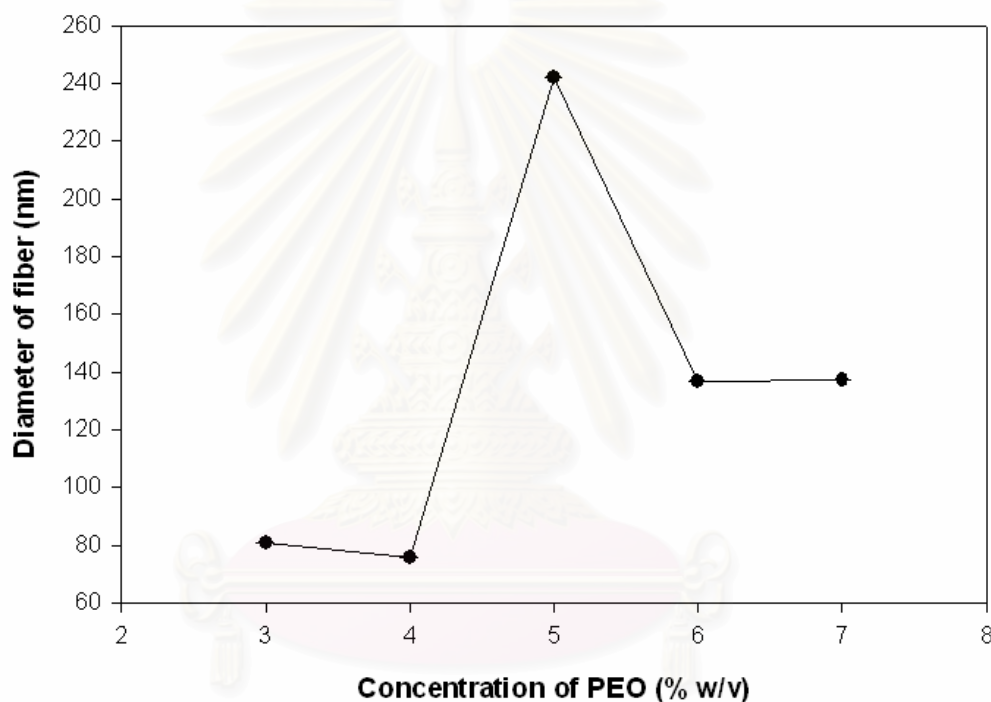


Figure 4.2 Average diameter of as-spun PEO fibers plotted as a function of the concentration.

4.2 Effect of poly(ethylene glycol)

It is now well accepted that electrospinnability of a polymer solution depends on its concentration or more correctly its viscosity. Electrospinning of a polymer solution with high enough concentration of viscosity resulted in a fine charged jet with high enough viscoelastic force that could counter the coulombic repulsion, preventing the fine, charged jet from breaking up into fine droplets. Thus, fine as-spun

fibers resulted. The viscoelastic properties are closely related to the molecular weight of the polymer. Here, the mechanism for the formation of beaded fibers is interesting. If the viscoelastic force was not high enough to counter the coulombic repulsion occurring within an ejected, charged jet, the jet would break up into discrete fragments and, under the work of the surface tension, these discrete fragments would round up to form discrete spherical drops. Another possibility explains the bead formation as a result of the axi-symmetric type of instability that occurs due to the unbalance between the coulombic repulsion and the viscoelastic properties of the ejected, charged jet. This explanation is evidently based on the theoretical ground. Here, we would like to offer another possibility with the notion that migration of the low molecular weight polymeric molecules (in the case of polydispersed polymeric materials) to the liquid (polymeric solution)/air interface could occur and, as a result of the much shorter relaxation times of these small molecules, bead formation could easily occur.

To verify such a hypothesis, a model PEO concentration chosen was 5% w/v, since the solution of this particular concentration produced smooth with very low occurrence of the beads. The model smaller molecular weights are poly(ethylene glycol) of various molecular weights, ranging between 1,000 and 35,000 g/mol. The concentration of these PEGs in the model PEO solution varied between 1 and 20% w/v.

4.2.1 Effect of poly(ethylene glycol) molecular weight

PEG of varying molecular weight (i.e. 1,000, 1,500, 2,000, 4,600, 8,000, 10,000, 20,000, and 35,000 g/mol) was added into the model PEO solution (5% w/v) at the concentration ranged between 1 and 20% w/v. Table 4.2 summarizes some of the property values of these solutions.

According to Table 4.2, the viscosity of the resulting solutions was found to be quite comparable to that of the model solution, with an exception to that containing PEGs of 20,000 and 35,000 g/mol. The obvious increase in the viscosity of the resulting solutions containing PEGs of 20,000 and 35,000 g/mol could be a result of the increase

in the chain entanglement which is caused by the addition of PEGs having rather high enough molecular weights. Similarly, the surface tension of the resulting solutions was also found to be very comparable with that of the model solution. Only the viscosity of the resulting solutions was found to be much greater than that of the model solution, but the property value was, in general, not found to depend on the molecular weight of PEGs if it exceeded 1,000 g/mol.

Table 4.2 Viscosity, surface tension, and conductivity of 5% w/v PEO concentration blended with PEGs by various molecular weight of PEGs.

Sample	Viscosity (cp)	Conductivity ($\mu\text{S/cm}$)	Surface tension (mN/m)
PEO 5% w/v	1639	57.6	58.42 \pm 0.02
PEO 5%w/v + PEG 5%w/v M_w 1,000 g/mol	1616	97.8	56.71 \pm 0.02
PEO 5%w/v + PEG 5%w/v M_w 1,500 g/mol	1687	112.6	57.59 \pm 0.02
PEO 5%w/v + PEG 5%w/v M_w 2,000 g/mol	1563	111.8	57.05 \pm 0.08
PEO 5%w/v + PEG 5%w/v M_w 4,600 g/mol	1823	115.2	56.99 \pm 0.04
PEO 5%w/v + PEG 5%w/v M_w 8,000 g/mol	1639	116.9	57.30 \pm 0.08
PEO 5%w/v + PEG 5%w/v M_w 10,000 g/mol	1923	104.2	57.14 \pm 0.01
PEO 5%w/v + PEG 5%w/v M_w 20,000 g/mol	2367	109.5	57.34 \pm 0.08
PEO 5%w/v + PEG 5%w/v M_w 35,000 g/mol	2791	100.8	57.14 \pm 0.04

Figure 4.3 shows a series of scanning electron micrographs portraying the effect of the molecular weight of PEGs on the morphological appearance of the as-spun materials obtained from eight solutions of different molecular weight PEGs. Obviously, at M_w 1,000-4,600 g/mol mixture of beaded fibers, smooth fiber was present in micrographs (see Figure 4.3 a-d), while only smooth fibers were observed in the case of M_w of PEGs 8,000-35,000 g/mol. It is apparent, based on the micrographs shown in Figure 4.3 e-h, that, for a given PEG resin, the tendency for the observation of beaded

fibers was found to decrease. The mostly likely explanation for such an observation is to much greater increase in the viscoelastic force as a result of the large increase in the degree of chain entanglements due to the increase molecular weight of PEG in the PEO solution and hence the increase the solution viscosity in comparison with the coulombic force.

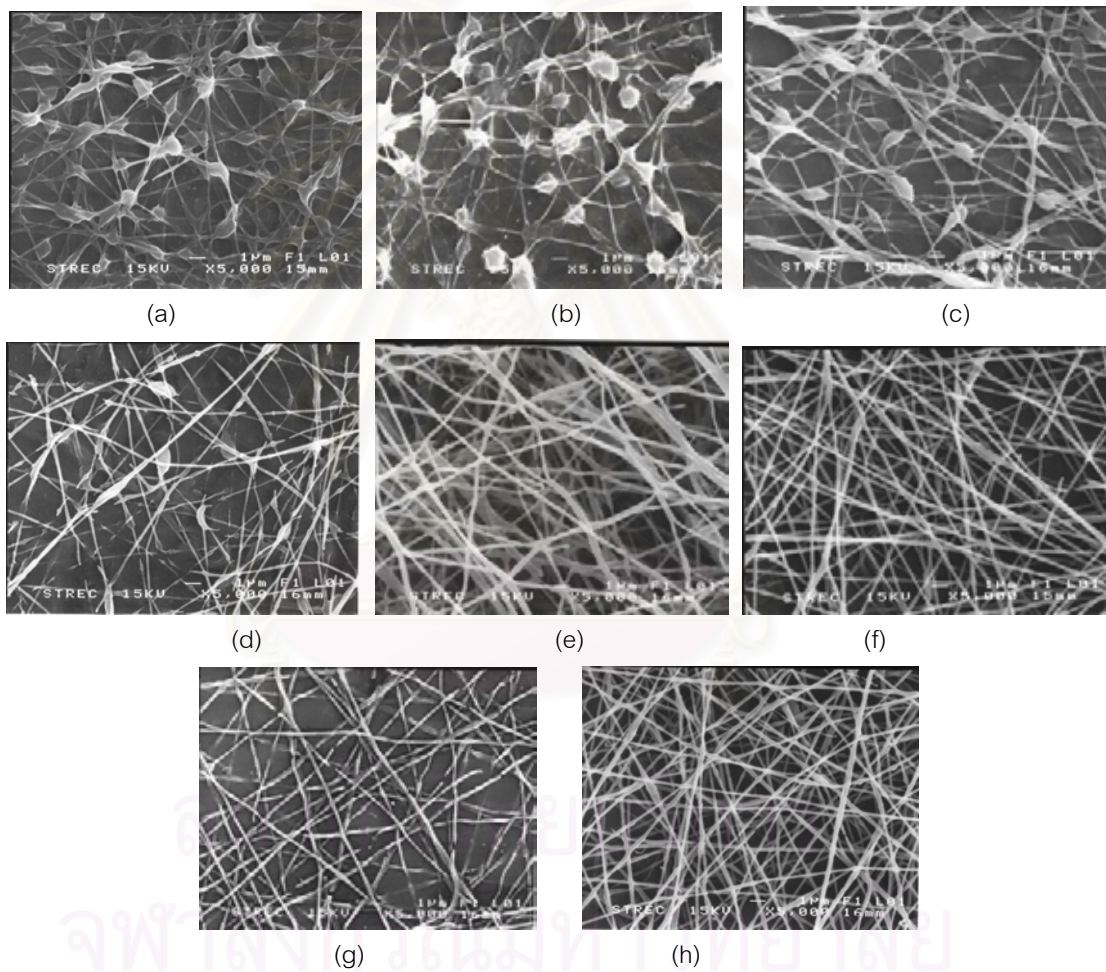


Figure 4.3 Scanning electron micrographs of eletrospun materials obtained of PEO 5% w/v blended PEGs concentration 5% w/v in various molecular weight (a) M_w 1,000 g/mol, (b) M_w 1,500 g/mol, (c) M_w 2,000 g/mol, (d) M_w 4,600 g/mol, (e) M_w 8,000 g/mol, (f) M_w 10,000 g/mol, (g) M_w 20,000 g/mol, and (h) M_w 35,000 g/mol, respectively.

Table 4.3 illustrate the average diameter of bead and fibers of the as-spun PEO blended with PEG fibers. It should be noted that the diameter of the obtained fibers were measured from micrographs showing the as-spun fibers with a small amount of beads present or no beads at all. The average diameter of the as-spun fibers were found to range between about 91 nm to about 230 nm. For the average diameter of bead were found to monotonically increase when increasing the molecular weight of PEGs. It increased from about 1375.54 nm at molecular weight of PEG 1,000 g/mol to about 1545.22 nm at molecular weight of PEG 4,600 g/mol. At high molecular weight of PEG (M_w 8,000-35,000 g/mol), only smooth fibers were observed.

Table 4.3 Diameters of beaded fibers (measured separately between the beads and fibers) were measured from the as-spun of PEO blended with PEG fibers by various molecular weight of PEGs.

Sample	No. Bead	Diameter of bead (nm)	No. Fiber	Diameter of fiber (nm)
PEO 5% w/v + PEG M_w 1,000 g/mol	63	1375.54 \pm 0.36	90	172.27 \pm 0.09
PEO 5% w/v + PEG M_w 1,500 g/mol	29	1429.57 \pm 0.24	47	120.37 \pm 0.05
PEO 5% w/v + PEG M_w 2,000 g/mol	27	1505.70 \pm 0.32	70	162.87 \pm 0.07
PEO 5% w/v + PEG M_w 4,600 g/mol	18	1545.22 \pm 0.64	74	143.01 \pm 0.05
PEO 5% w/v + PEG M_w 8,000 g/mol	0	0	102	226.62 \pm 0.07
PEO 5% w/v + PEG M_w 10,000 g/mol	0	0	94	169.77 \pm 0.04
PEO 5% w/v + PEG M_w 20,000 g/mol	0	0	109	153.12 \pm 0.04
PEO 5% w/v + PEG M_w 35,000 g/mol	0	0	121	230.64 \pm 0.05

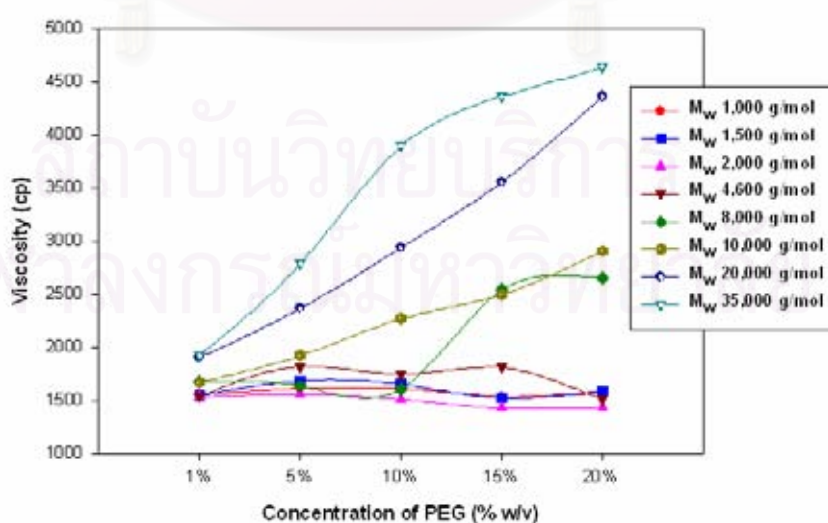
The PEG and PEO were the same polymer but they were different the molecular weight. The PEG have low molecular weight and PEO have high molecular weight. The molecular weight distribution of polymers have broad. In an electrospinning

process, a strong electrostatic field was applied to a polymer solution held in a syringe with a capillary outlet. A pendent droplet of the polymer solution from the capillary outlet deformed into a Taylor's cone by the electrostatic field. When the voltage surpasses a threshold value, the electric force overcomes the surface tension of the droplet and a charged jet of the solution is ejected from the tip of the Taylor's cone during the jet moves toward a collecting aluminium foil, it have time for the low molecular weight of polymers were relaxation, occurred the beaded fibers.

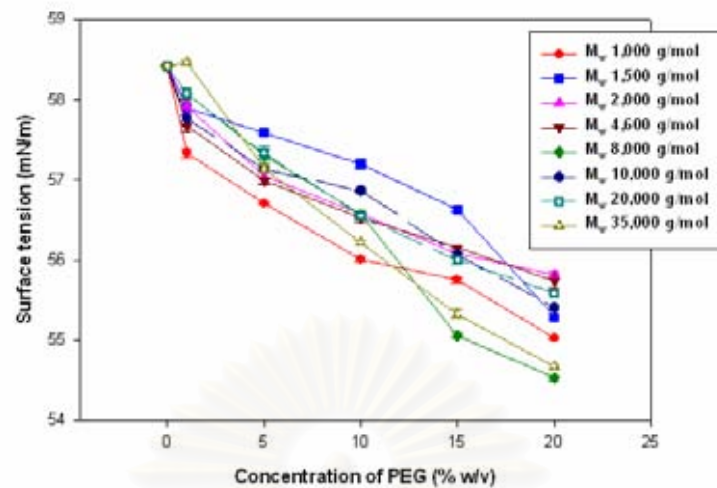
4.2.2 Effect of PEG concentration

Solution of PEO blend with PEG were prepared at various concentrations, ranging from 1 to 20 % w/v.

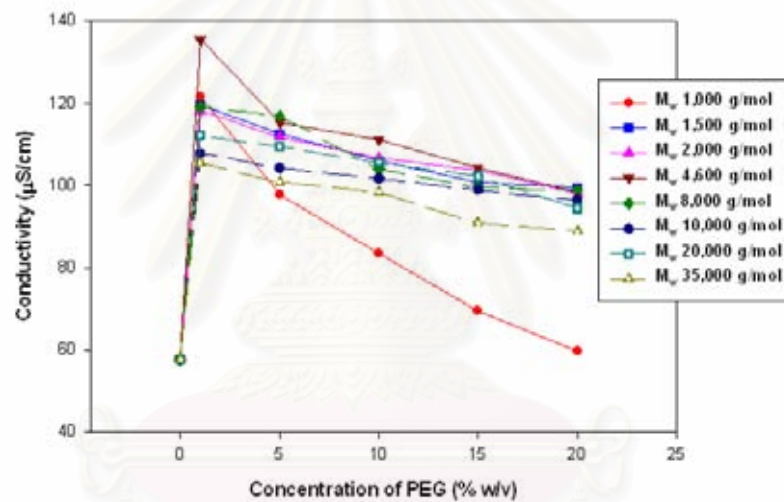
Figure 4.4 shows the properties of as-prepared solutions. The viscosity values for solutions of low molecular weight PEG (M_w 1,000-4,600 g/mol) were found to range between about 1420 and 1830 cp, the viscosity values for solutions of high molecular weight PEG (M_w 8,000-35,000 g/mol) were found to increase with increasing PEG concentration.



(a)



(b)



(c)

Figure 4.4 (a) viscosity, (b) surface tension and (c) conductivity as a function of PEG concentrations for solution of PEO blended with PEGs.

The surface tension values were found to slightly decrease with increasing PEG concentration all the molecular weight of PEG. The surface tension decreased because of the PEG have properties a nonionic surfactant.

The conductivity for solution of all molecular weight PEGs were found to slightly decrease the surface tension and a decrease in the conductivity of the resulting solution. The significant increase in the viscosity of the solutions with increasing PEG concentration is obviously due to the increased molecular entanglements.

Figure 4.4 shows scanning electron micrographs in order to illustrate the effect of the concentration of PEG solutions on the morphological appearance of the obtained as-spun materials. At low concentration all molecular weights, a large number of beaded fibers were present. At such low viscosities, the viscoelastic force (a result of the low degree of chain entanglement) in a given jet segment was not large enough to counter the higher coulombic force, resulting in the break-up of the charged jet into smaller jets. The beaded fibers occurred when the PEG concentrations of low molecular weight (M_w 1,000-4,600 g/mol) were increased, the fibers were fused together, which occurred the film. The film could be a result of in aqueous solutions, there is inter-chain bonding between the polar hydroxyl groups in the PEG molecules. In addition, hydrogen bonding between the PEG chains and the water molecules is also established after dissolution. But the high PEG concentration of the high molecular weight (M_w 8,000-35,000 g/mol), the charged jet did not break-up into small droplets, a direct result of the increased chain entanglements and hence an increase in the viscoelastic force which were sufficient to prevent the break-up of the charged jet and to allow the coulombic stress to further elongate the charged jet during its flight to the grounded target, which ultimately thinned down the diameter of the charged jet.

Figure 4.5 illustrates the average diameter of as-spun PEO blended with PEG fibers. The average fiber diameter of molecular weight PEG 8,000-35,000 g/mol were found to monotonically increase when increasing both the concentration and the viscosity of the solutions. With increasing concentration enabled the charged jet to withstand a large stretching force from the coulombic repulsion, resulting in the observed larger diameter of the charged jet. In addition, the observed larger diameter had an adverse effect on the extent of the bending instability which determined the total path length of a jet segment during its flight to the grounded target.

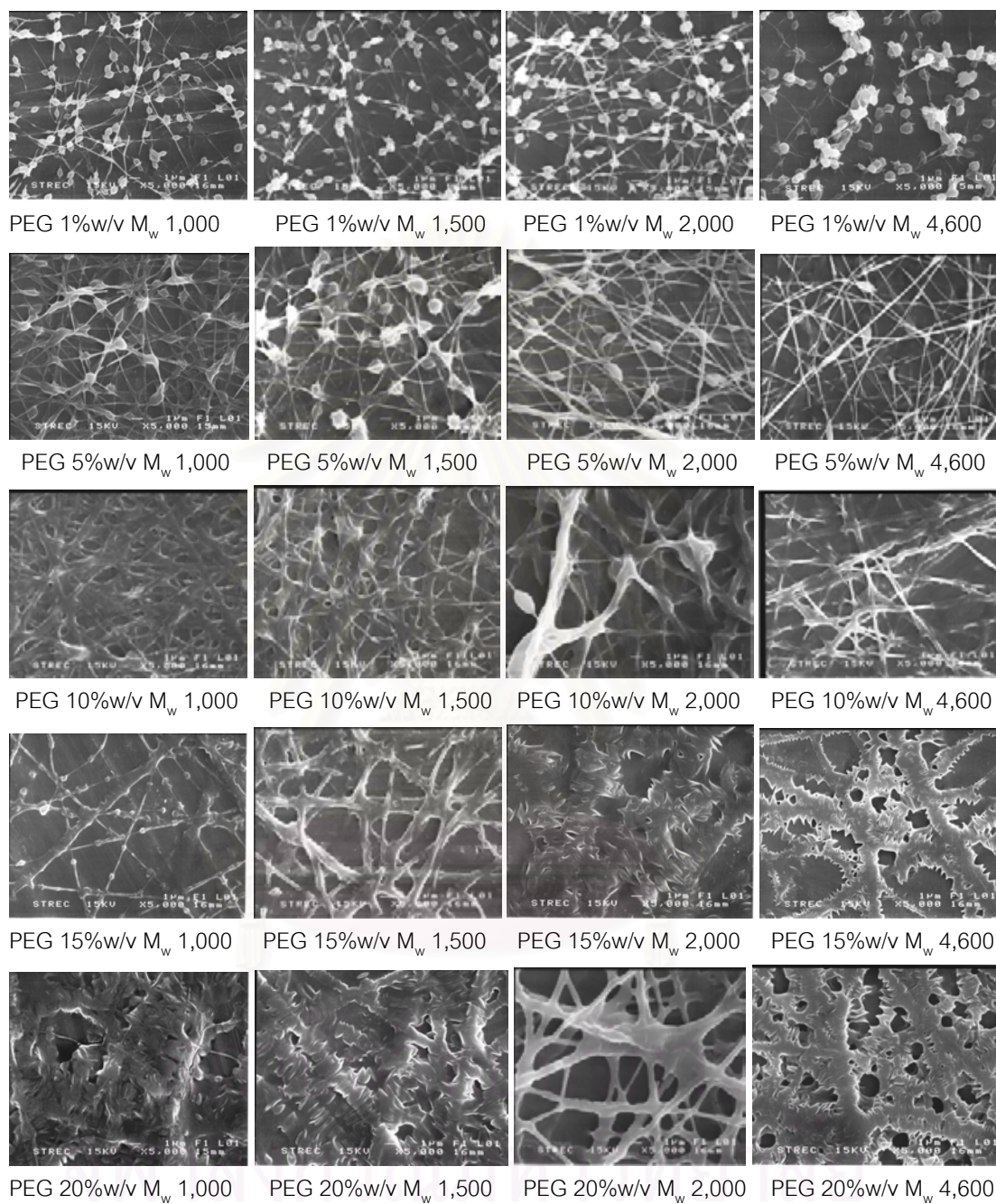


Figure 4.5 Scanning electron micrographs of electrospun fibers obtained from solutions of PEO blended with PEG in various concentration and various molecular weight

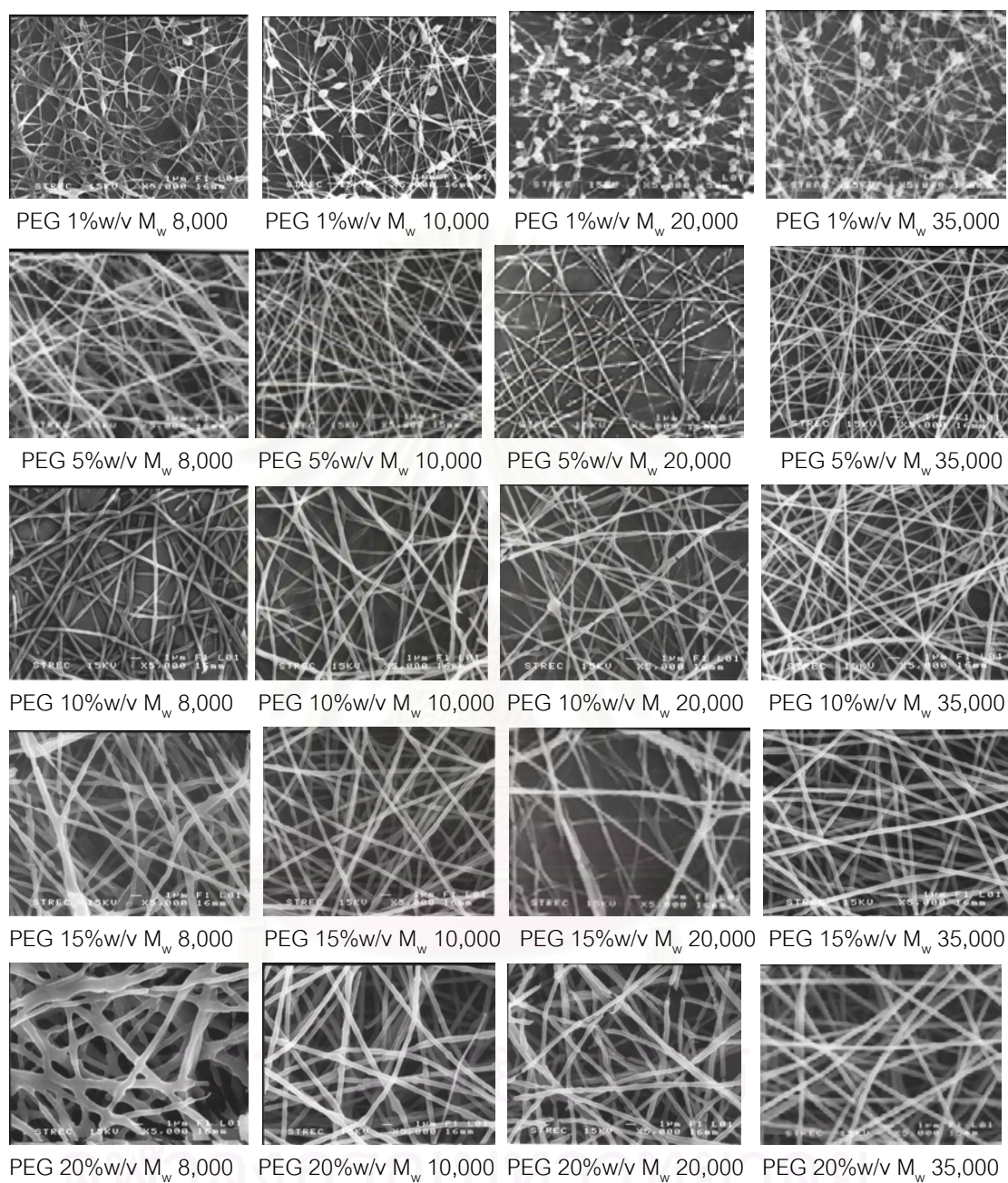


Figure 4.5 Scanning electron micrographs of electrospun fibers obtained from solutions of PEO blended with PEG in various concentration and various molecular weight. (continuous)

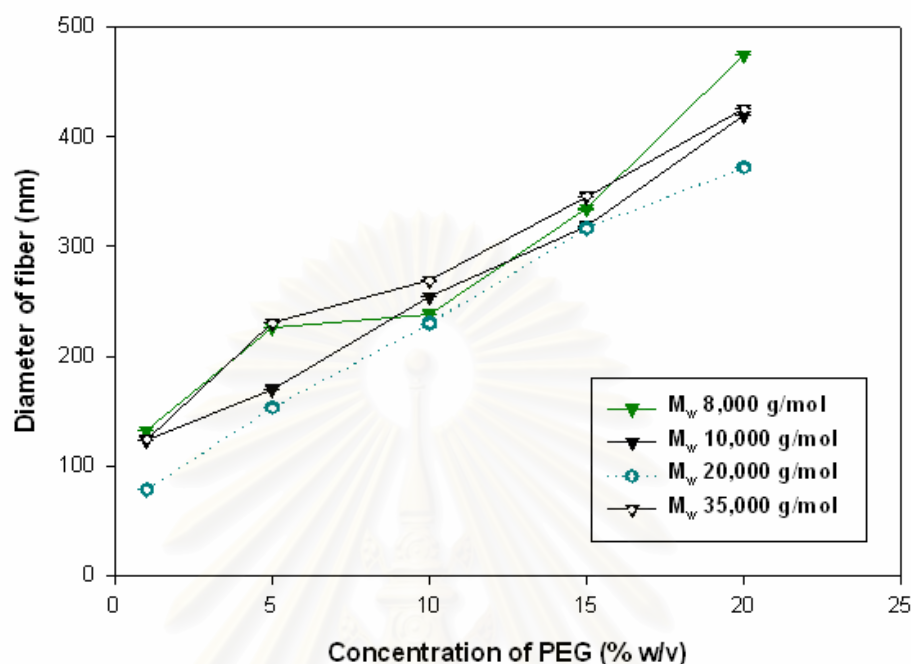


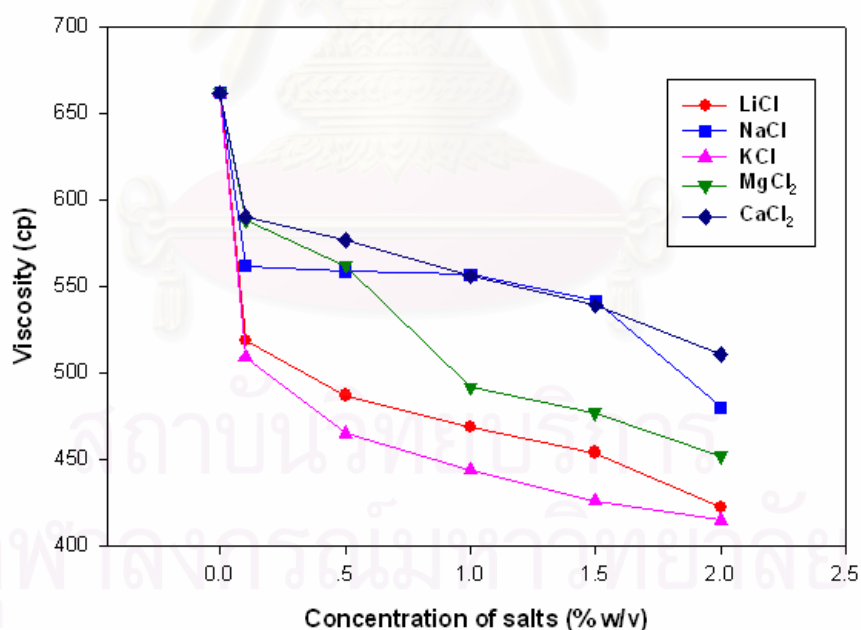
Figure 4.6 Average diameter of as-spun PEO blended with PEG fibers plotted as a function of the PEG concentration.

4.3 Effect of salts

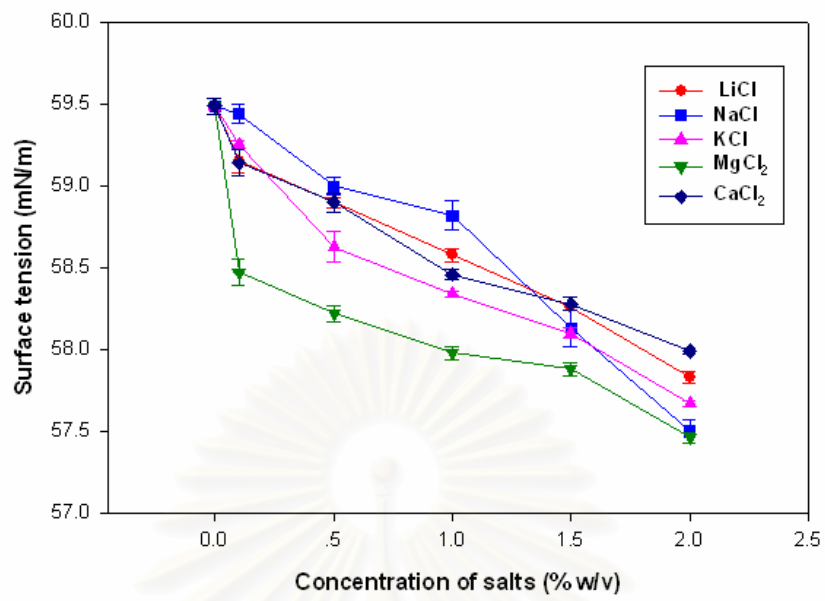
As described above, the presence of PEO in distilled water at concentration 4% w/v favors the formation of beaded fibers and fibers. It was also found, that addition of proper additives, e.g. some organic or inorganic salts, in the PEO solutions could inhibit the formation of “beaded” fibers. A common feature in these systems was that electrical conductivity of these solutions increased after addition of the additives.

In order to investigate the effect of salt addition on the morphological appearance of the obtained electrospun fibers, various types of inorganic salts (LiCl, NaCl, KCl, MgCl₂, and CaCl₂) in the amount ranging between 0.1 and 2.0% w/v were added to 4% w/v PEO solution (the condition at which both beads and beaded fibers were observed).

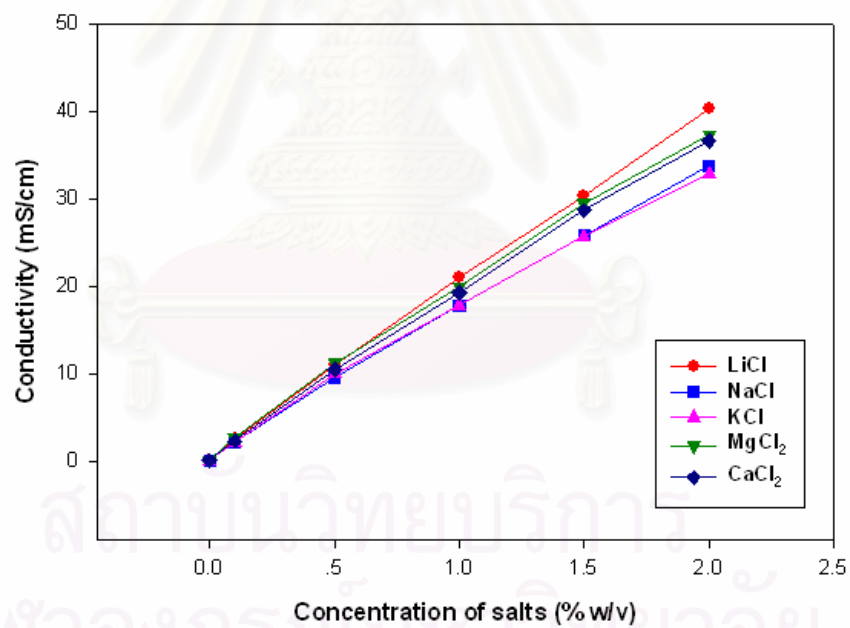
Figure 4.6 shows the viscosity, surface tension, and conductivity values of salt added PEO solutions as a function of salt concentrations. Figure 4.6 (a) shows viscosity as a function of salt concentration for the five type of salts. The values was found to decrease with increasing salt concentration. The presence of inorganic salts in the PEO solutions can also reduce the hydrodynamic volume of the polymer, with attendant reduction in intrinsic viscosity. Figure 4.6 (b) shows the surface tension as a function of salt concentration. The surface tension values were found to decrease with increasing the salt concentration. Figure 4.6 (c) illustrates the conductivity as a function of salt concentration. The conductivity values of the solutions were found to increase monotonically with an increase in the salt content.



(a)



(b)



(c)

Figure 4.7 (a) viscosity, (b) surface tension and (c) conductivity as a function of salt concentrations for solution of PEO mixed salts.

Figure 4.7 shows selected scanning electron micrographs of the products from the PEO solution with added salts. At low salt concentrations, the samples containing LiCl, NaCl, KCl, MgCl₂, and CaCl₂ salts resulted in the formation of beaded fibers. When the salt addition increased, instead of obtaining fibers, PEO films with occasional presence of salts were obtained. Only the PEO solutions containing NaCl resulted in the formation of beaded and smooth fibers. With increasing NaCl content, the morphology of the fibers changed from beaded fibers with occasional beads into smooth fibers.

Figure 4.8 shows scanning electron micrographs of the as-spun fiber of NaCl in the PEO solution. The SEM images clearly show that the formation of bead defects was prohibited by an increase in NaCl concentration. Without NaCl, the fibers electrospun from a 4% w/v PEO solution exhibited beaded fibers with occasional beads. An increase in the NaCl content resulted in a vast reduction in the number of beads. At 0.5% w/v of NaCl, PEO fibers without any beads at all were obtained.

Figure 4.9 shows the average fiber diameter of the as-spun PEO fibers as a function of NaCl concentration. The increase in the fiber diameters with increasing amount of salt could be a result of the net charge density. Experimental results show that the addition of NaCl to the PEO solution increases the net charge density carried by the moving jet. The decrease in the resistivity of the solution is not enough for simple ionic conductivity to account for the increase in transported charge. The observed decrease in resistivity on addition of salt is due to the increased net charge that flows into the jet as it passes through the tip of the needle. This higher net charge then increases the force exerted on the jet. The average fiber diameter increased from about 73.47 nm for 0.1% w/v NaCl in 4% w/v PEO solution to 205.11 nm for 2.0% w/v NaCl in 4% w/v PEO solution. The increase in fiber diameter could be a result of the increase in the viscoelastic force and increase in the mass flow due to the increase in the electrostatic force acting on the jet segment.

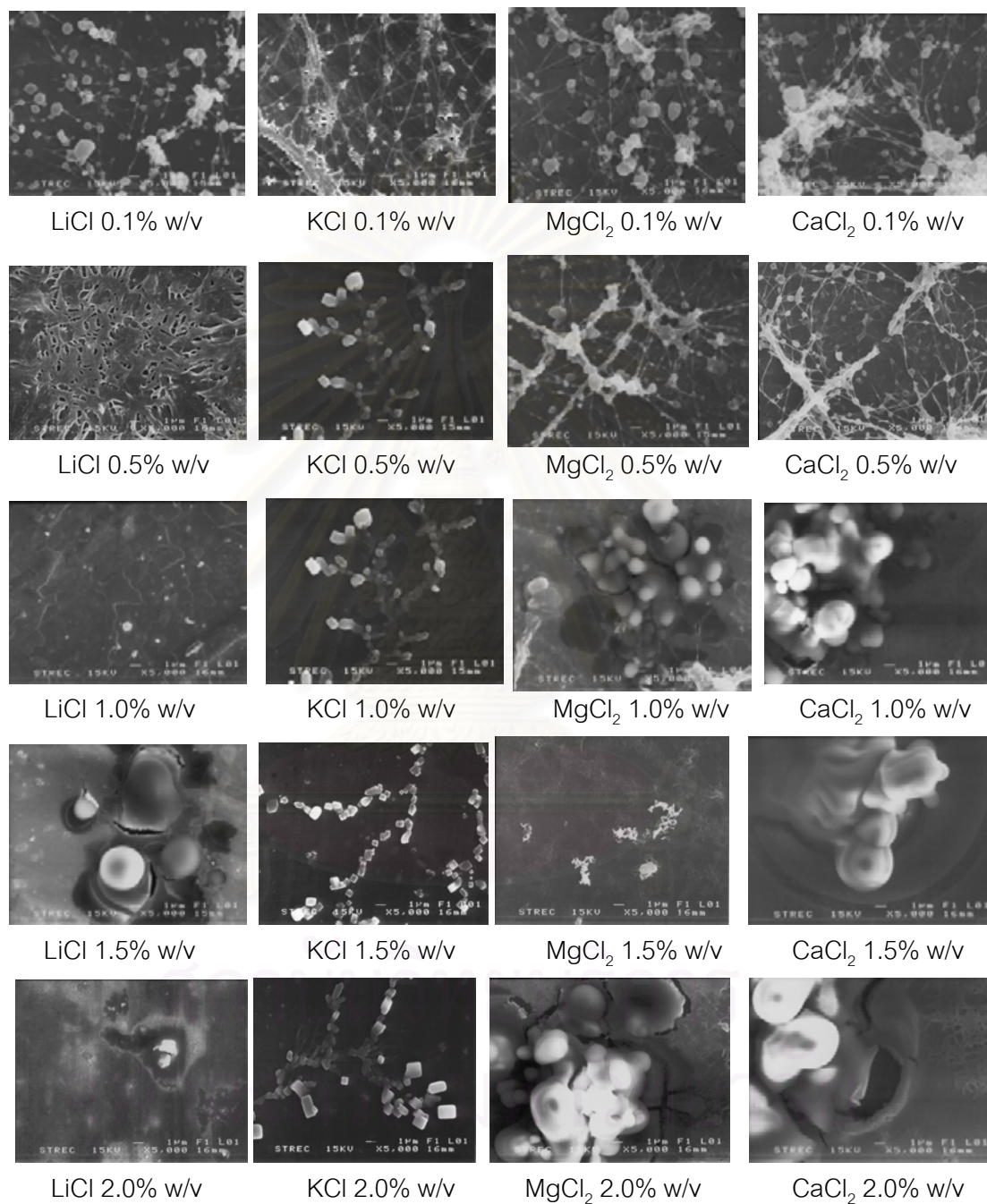


Figure 4.8 Scanning electron micrographs of electrospun fibers obtained from solutions of 4% w/v PEO concentration were added LiCl, KCl, MgCl₂, and CaCl₂ in various concentration 0.1, 0.5, 1.0, 1.5, and 2.0% w/v, respectively.

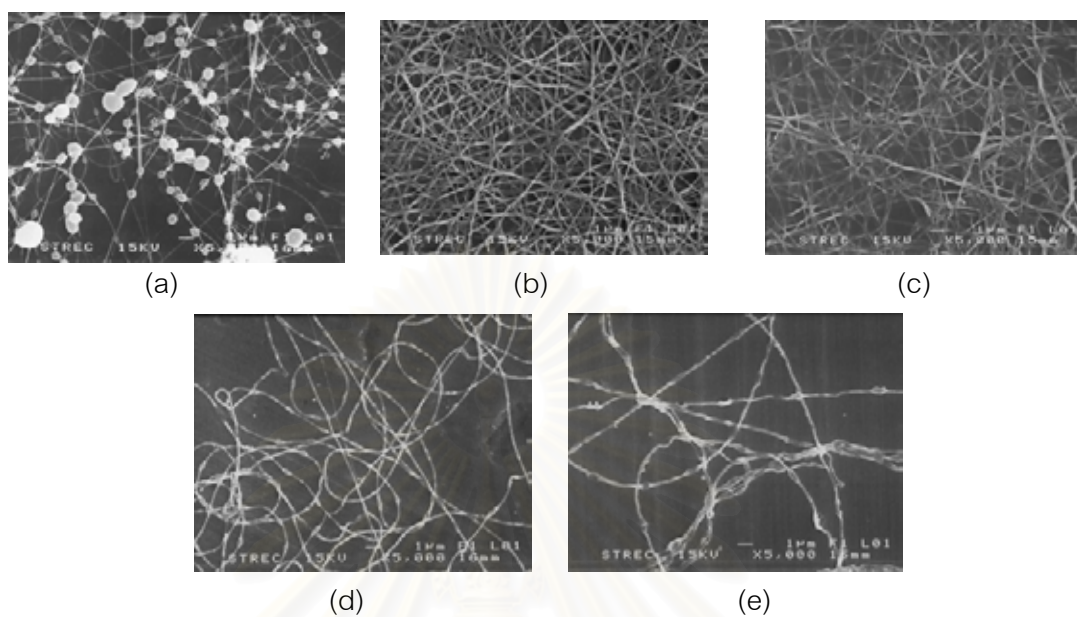


Figure 4.9 Scanning electron micrographs of electrospun fibers obtained from solutions of 4% w/v PEO concentration were added NaCl in various concentration (a) 0.1% w/v, (b) 0.5% w/v, (c) 1.0% w/v, (d) 1.5% w/v, and (e) 2.0% w/v, respectively.

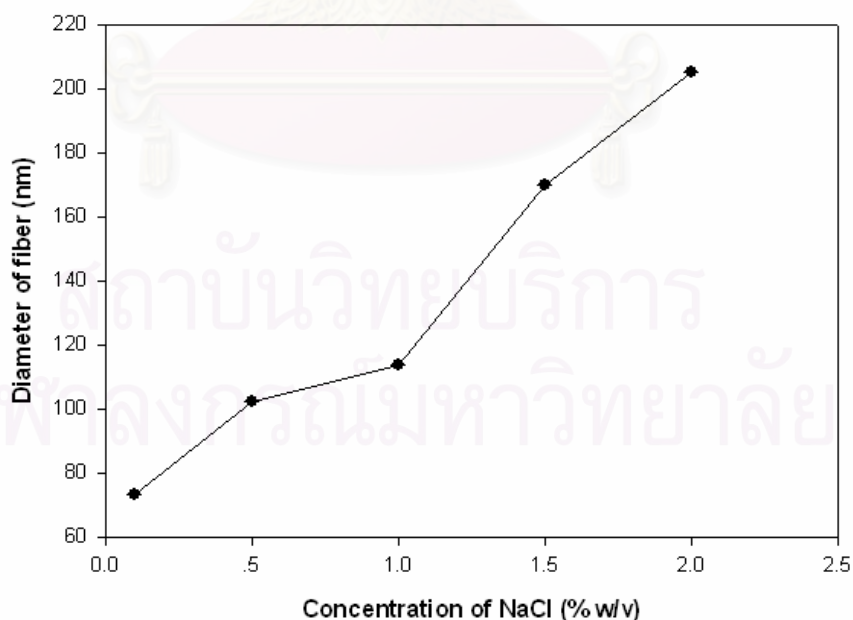


Figure 4.10 Average diameter of as-spun PEO/NaCl fibers plotted as a function of the NaCl concentration.

4.4 Effect of anionic surfactant

The objective of the first experiment was to investigate the effects of polymer concentration on morphological appearance of electrospun PEO fibers. The optimal condition for achieving beaded fibers of uniform shape and size was when the concentration of the solution was 4% w/v. SDS was added in the 4% w/v PEO solution, to investigate the effect of surfactant on morphological appearance of the as-spun fibers. SDS concentration was varied between 0.5 and 7.0% w/v.

Table 4.4 summarize some characterization data of PEO solutions with SDS addition. The viscosity value of the solutions was found to decrease with increasing SDS concentration. Specifically, the property value decrease from about 476 cp at the SDS concentration of 0.5% w/v to about 338 cp at the SDS concentration of 7.0% w/v.

The surface tension of the solutions was found to be lower than that of the neat PEO solution. With further increase in the amount of SDS, the property value was found to decrease slightly from about 38.45 mN/m at the SDS concentration of 0.5% w/v to about 35.5 mN/m at the SDS concentration of 7.0% w/v. The surface tension decreased because of SDS is an anionic surfactant. The alignment of the SDS molecules at the water/air interface caused the reduction in the surface tension of the solutions.

The conductivity of PEO solutions with addition of SDS was greater than that of the 4% w/v PEO solution. With increasing SDS content, the property value was found to increase significantly from about 0.926 mS/cm at the SDS concentration of 0.5% w/v to about 7.84 mS/cm at the SDS concentration of 7.0% w/v. When SDS dissolved in the PEO solution, both the number of positive (i.e. Na^+) and negative ions (i.e. $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OSO}_3^-$) in the solution increased appreciably.

Table 4.4 Viscosity, surface tension, and conductivity of PEO 4% w/v solutions were added SDS in various concentration.

Sample	Surface tension (mN/m)	Viscosity (cp)	Conductivity (mS/cm)
PEO 4% w/v	59.49 ± 0.05	662	0.05
PEO 4% w/v+SDS 0.5% w/v	38.45 ± 0.04	476	0.93
PEO 4% w/v+SDS 1.0% w/v	38.27 ± 0.06	469	1.54
PEO 4% w/v+SDS 2.0% w/v	37.34 ± 0.02	458	2.74
PEO 4% w/v+SDS 3.0% w/v	36.46 ± 0.03	407	3.98
PEO 4% w/v+SDS 4.0% w/v	36.18 ± 0.05	390	5.23
PEO 4% w/v+SDS 5.0% w/v	36.00 ± 0.04	366	6.47
PEO 4% w/v+SDS 6.0% w/v	35.86 ± 0.08	358	7.71
PEO 4% w/v+SDS 7.0% w/v	35.50 ± 0.07	338	7.84

Figure 4.10 shows the scanning electron micrographs of PEO fibers electrospun from 4% w/v PEO solution in water with addition of an anionic surfactant, sodium dodecyl sulfate (SDS). It was found that beaded fibers and smaller fibers were obtained at lower SDS concentration (i.e. 0.5% w/v and 1.0% w/v; Figure 4.10 a-b), whereas, at higher SDS concentration, only smooth fibers without beads were observed (i.e. from 2.0 to 7.0% w/v SDS, Figure 4.10 c-h). The beaded fibers changed to smooth fibers with addition of SDS. The likely explanation could be from the fact that the surface tension of the solution was found to decrease, while the conductivity was found to increase with increasing SDS content.

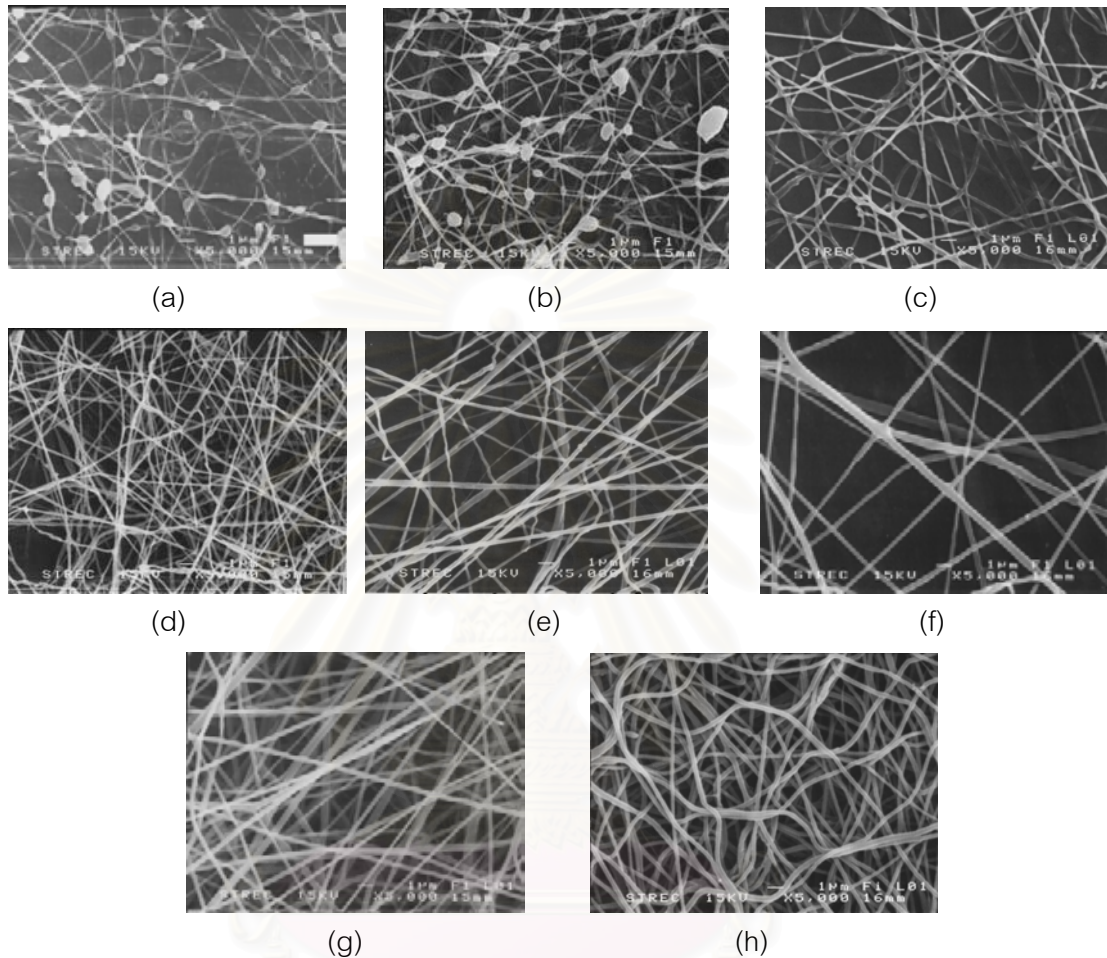


Figure 4.11 Scanning electron micrographs of electrospun material obtained from solution of PEO were added SDS concentration (a) 0.5, (b) 1.0, (c) 2.0, (d) 3.0, (e) 4.0, (f) 5.0, (g) 6.0, and (h) 7.0% w/v .

Figure 4.11 shows the average diameter of PEO fibers electrospun from PEO solutions at various contents of SDS. Obviously, the average diameter of the resulting PEO fibers was found to increase monotonically with increasing SDS concentration. Specifically, the average fiber diameter was found to increase from about 106.65 nm at the SDS concentration of 0.5% w/v to about 260.23 nm at the SDS concentration of 7.0% w/v. The SDS was anionic surfactant, it reduce surface tension.

The mostly likely explanation for such a an observation is the much greater decrease in the surface tension which prevent the surface of the charged jet from stretching. The surface tension tends to decrease the surface area per unit by changing the jets into spheres and was thought to play a very important role on the formation of “bead” fibers. The addition of SDS disrupted the components of the solution, thus lowered the surface tension and enhanced the bending instability. So the average diameter of fiber increased.

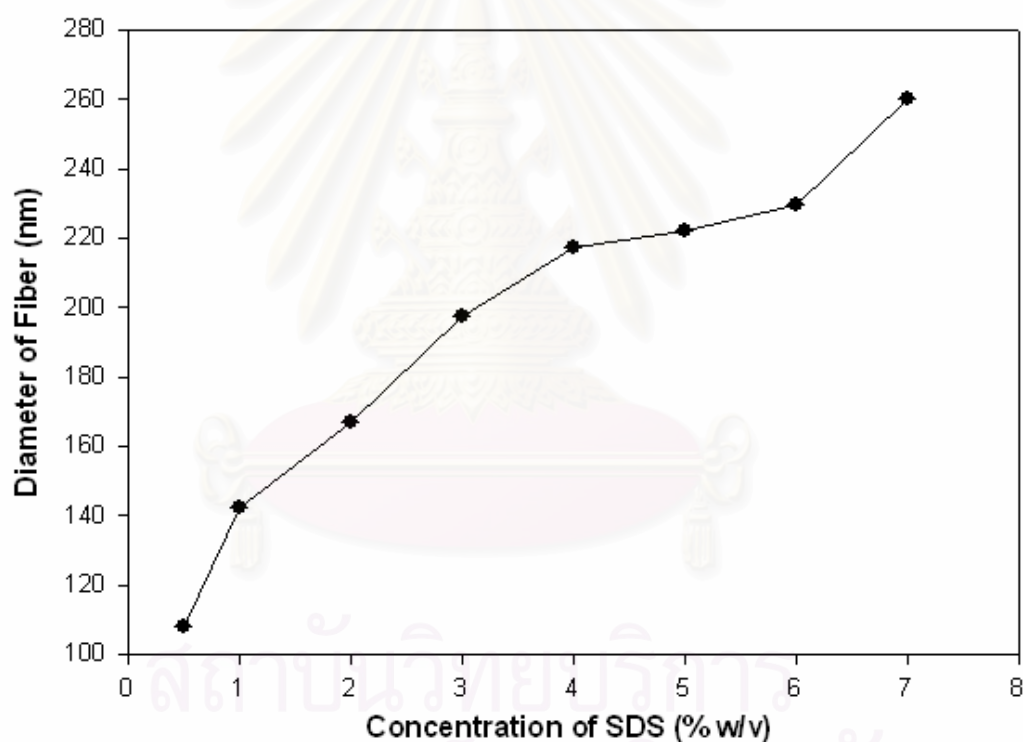


Figure 4.12 Average diameter of as-spun PEO blended with SDS fibers plotted as a function of the SDS concentration.

4.5 Effect of solvent system

Based on the previous results, 4% w/v PEO solution was chosen, based mainly on the observed beaded fibers, to investigate the effect of mixed solvent on the morphological appearance of the as-spun PEO fibers. The co-solvents used methanol, ethanol, and isopropanol. The mixed solvents were prepared in the following volumetric ratios: 90:10, 80:20, and 70:30, prior to electrospinning.

Table 4.5 Viscosity, surface tension, and conductivity of 4% w/v PEO concentration in mixed solvent distilled water and methanol, ethanol, and isopropanol in various composition.

Sample	Surface tension (mN/m)	Viscosity (cp)	Conductivity (μ S/cm)
PEO 4% w/v	59.49 \pm 0.05	662	50.05
Methanol			
water : methanol 90:10	55.81 \pm 0.04	647	97.4
water : methanol 80:20	52.01 \pm 0.02	692	70.7
water : methanol 70:30	48.19 \pm 0.03	892	58.9
Ethanol			
water : ethanol 90:10	51.37 \pm 0.03	729	74.1
water : ethanol 80:20	43.39 \pm 0.07	1089	52.4
water : ethanol 70:30	39.76 \pm 0.04	1550	37.7
Isopropanol			
water : isopropanol 90:10	39.92 \pm 0.01	828	62.3
water : isopropanol 80:20	32.69 \pm 0.04	1331	37
water : isopropanol 70:30	30.31 \pm 0.02	2179	29

Table 4.5 shows the viscosity, surface tension, and conductivity values of PEO solutions in the as-prepared mixed solvent. The viscosity value of the solutions was found to increase with increasing alcohol, with the values for PEO solutions in mixed solvent of distilled water and isopropanol being the greatest, followed by those for the solutions in mixed solvent of distilled water and ethanol and distilled water and methanol, respectively. Specifically, the property value of the PEO solutions in mixed solvent of distilled water and methanol was found to increase slightly from about 647 cp at ratio 90:10 v/v to about 892 cp at ratio 70:30 v/v. The viscosity value of the PEO solutions in mixed solvent of distilled water and ethanol was found to increase from about 729 cp at ratio 90:10 v/v to about 1550 cp at ratio 70:30 v/v, while that of the PEO solutions in mixed solvent of distilled water and isopropanol was found to monotonically increase from about 828 cp at ratio 90:10 v/v to about 2179 cp at ratio 70:30 v/v.

The surface tension value of the solution was found to monotonically decrease with increasing volumetric ratio of alcohol. The surface tension value of PEO solutions in distilled water/isopropanol was found to range between 39.92 and 30.31 mN/m, which was lower than that of the neat PEO solution, while that of the PEO solution in distilled water/methanol was found to slightly decrease from about 55.81 mN/m at ratio 90:10 v/v to about 48.19 mN/m at ratio 70:30 v/v and that of PEO solution in distilled water/ethanol was found to monotonically decrease from about 51.37 mN/m at ratio 90:10 v/v to about 39.76 mN/m at ratio 70:30 v/v. The surface tension of the PEO solutions in mixed solvents was found to decrease with increasing the ratio of the co-solvent, because of the surface tension of alcohol was lower than that of distilled water (i.e. the surface tension of methanol, ethanol, and isopropanol was measured to be about 22.1, 23.1, and 21.32 mN/m, respectively).

The conductivity value of the PEO solutions was found to monotonically decrease with increasing alcohol content. Specifically, the conductivity values of PEO solutions in distilled water/methanol, distilled water/ethanol, and distilled water/isopropanol were found to range between 97 and 58, 74 and 37, and 62 and 29

$\mu\text{S/cm}$, respectively. For a given volumetric ratio, the conductivity value of PEO solutions in distilled water/methanol was the greatest.

Figure 4.12 shows scanning electron micrographs of electrospun products obtained from PEO solutions in the mixed solvents of varying composition (i.e. 90:10, 80:20, and 70:30 v/v). Obviously, when methanol, ethanol, and isopropanol were used as the co-solvent, electrospinning of the resulting PEO solutions resulted in the formation of beaded fibers. Interestingly, for a fixed applied potential of 11.25 kV, both the diameter of beads and the diameter of the as-spun fibers were found to increase with increasing volumetric ratio of alcohol to distilled water. The increase in the diameter of beads and the diameter of fibers with increasing alcohol content could be due to the increase in both the solution viscosity and the decrease in the solution conductivity with increasing alcohol content. This simply means that, at high alcohol contents, the coulombic stretching force decreased, while the viscoelastic force increased, resulting an increase in the diameter of the as-spun fibers.

Figure 4.13 and 4.14 shows plots of the average diameter of beads and the average diameter of as-spun fibers as a function of the volumetric ratio of the mixed solvents. For distilled water/methanol system, the average diameter of the as-spun fibers was found to increase slightly from about 89 nm at ratio 90:10 v/v to about 99 nm at ratio 70:30 v/v and the average diameter of beads was found to increase monotonically from about 836 nm at ratio 90:10 v/v to about 885 nm at ratio 70:30 v/v. For distilled water/ethanol system, the average diameter of the as-spun fibers have been increase slightly from about 85 nm at ratio 90:10 v/v to about 91.91 nm at ratio 70:30 v/v and the average diameter of beads was found to increase monotonically from about 756 nm at ratio 90:10 v/v to about 827 nm at ratio 70:30 v/v. For distilled water/isopropanol system, the average diameter of the as-spun fibers was found to increase from about 77 nm at ratio 90:10 v/v to about 91 nm at ratio 70:30 v/v and the average diameter of beads was found to increase from about 875 nm at ratio 90:10 v/v to about 1250 nm at ratio 70:30 v/v. Possible explanations for the observed increase in the average fiber diameters of

the resulting PEO fibers with increasing alcohol content could be the observed increase in the viscosity of the resulting solutions or the decrease in the boiling of the resulting PEO solutions in mixed solvents.

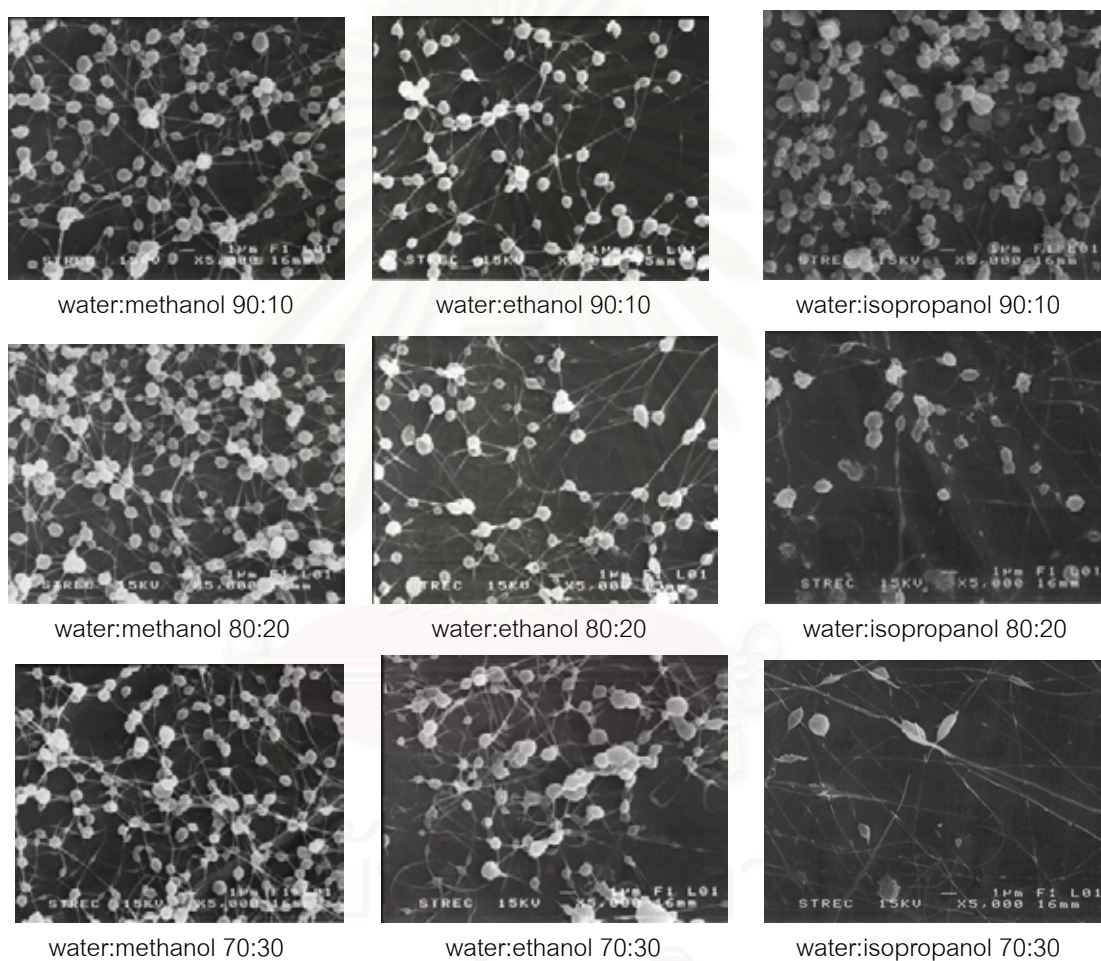


Figure 4.13 Scanning electron micrographs of electrospun fibers obtained from solution of PEO at a concentration of 4% w/v in the mixed solvent of distilled water with methanol, ethanol, and isopropanol in various compositional ratios of 90:10, 80:20, and 70:30 v/v, respectively.

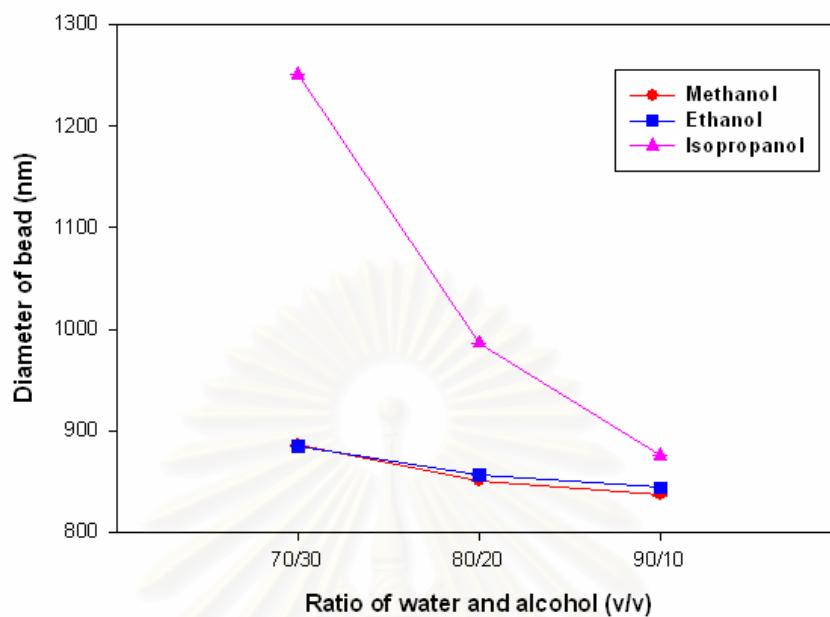


Figure 4.14 Average diameter of PEO beaded fibers plotted as a function of the ratio of water and methanol, ethanol, and isopropanol.

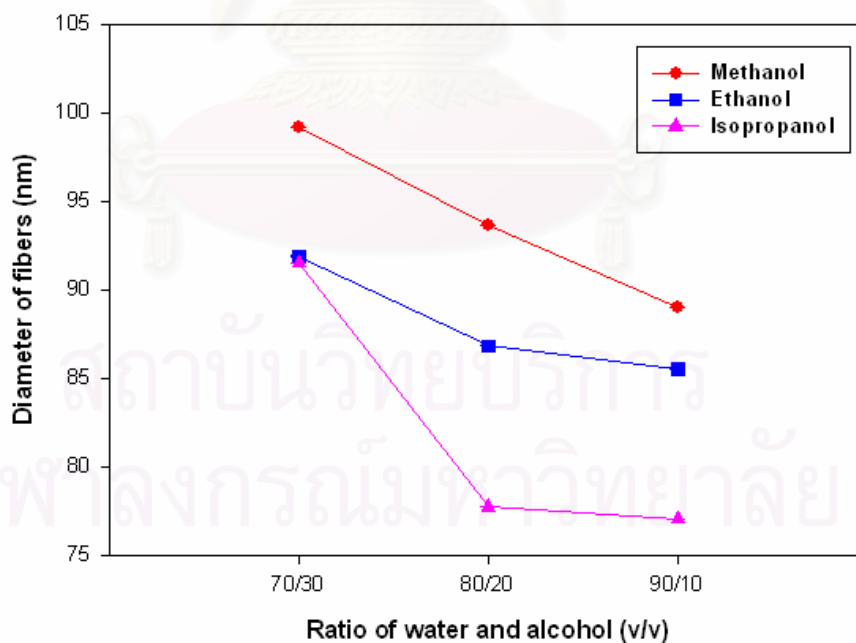


Figure 4.15 Average diameter of as-spun PEO fibers plotted as a function of the ratio of water and methanol, ethanol, and isopropanol.

The formation of beads along the as-spun fibers could be a result of a number of different phenomena. For example, it could be a result of the viscoelastic relaxation and the work of the surface tension upon the reduction of the coulombic force once the fibers are in contact with the grounded target that drives the formation of the beads. This phenomenon would only occur when the charged jet was not “dry” enough, contraction can no longer occur any longer, thus leaving only beaded fibers on the target. The “dryness” of the charged jet is controlled mainly by the amount of solvent that can evaporate during the flight of the charged jet to the target. The amount evaporating solvent is determined by a number of factors: the boiling point of the solvent, the initial concentration of the solution, the solution and the ambient temperatures, the diameter of the charged jet which continuously decrease during its flight to the target and the total path length that the charged jet travels from the needle to the target which significantly depends on the extent of the bending instability that occurs.



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CHAPTER V

CONCLUSION

1. In the first part, at low concentration (3-4% w/v) the beaded PEO fibers were formed, however at high concentration (5-7% w/v) the fibers were formed without beads. It was seen that at high viscosity polymer solution (concentration > 8% w/v) can not form the fibers since the electrostatic force can not overcome the surface tension and viscoelastic force.

2. In the second part, various molecular weight and concentration of PEG were added into 5% w/v solution. For low molecular weight of PEG (M_w 1,000-4,600 g/mol), the beaded fibers were formed at low concentration of PEG, whereas at high concentration of PEG the film were formed. For high molecular weight of PEG (M_w 8,000-35,000 g/mol), similar to low molecular weight, the beaded fiber were formed at low concentration of PEG, however at high concentration of PEG the smooth fiber were formed.

3. The effects of salt solution were studied at 4% w/v PEO concentration. Various types of salts, i.e., LiCl, NaCl, KCl, $MgCl_2$, and $CaCl_2$ and their concentrations varied from 0.1 to 2.0% w/v were investigated. At 1% w/v of salt concentration, the morphological appearance was beaded fibers. However, upon increasing salt concentration, the PEO film was formed, instead of fiber or beaded fiber, with the deposition of crystalline of salts on the surface of the film. This is because salts can not dissolve completely in the PEO solution so after the solvent evaporated completely, the salts were found as a crystalline form. Nevertheless, with the addition of NaCl solution, the fibers were formed when the concentration of salt was higher than 1% w/v. This is due to the fact that NaCl can be completely dissolved in the PEO solution.

4. Various concentration of SDS ranging from 0.5 to 7.0% w/v was added into a 4% w/v PEO solution to study the effect of anionic surfactant on the bead formation of PEO nanofiber. When the concentration of SDS was increased, the morphological of as-spun fibers were formed fibers without bead. It was seen that the

SDS decreased in the surface tension of the PEO solution which prevented the surface of the charged jet from stretching and enhanced the bending instability.

5. The effects of mixed solvents, i.e., methanol and distilled water, ethanol and distilled water, and isopropanol and distilled water were studied by dissolving the 4% w/v PEO concentration. Using these mixed solvents, the bead formation was formed because the mixed solvent reduce surface tension and boiling point of the solution. It could be a result of the viscoelastic relaxation and the reduction of the coulombic force once the fibers are in contact with the grounded target that drives the formation of the beads.

From this experiment it can be concluded that the bead formation was due to the relaxation of low molecular weight of polymer chain. When the coulombic force decreased so the polymer chains were relaxed when the charged jet moved from the tip of needle to the collecting plate. Characterization of the formation of electrospun beaded nanofibers shows that the solution viscosity, net charge density carried by the electrospinning jet, and surface tension of the solution are the main factors. The beaded fiber can be reduced by using high concentration of solution and addition of NaCl and SDS since these three parameters can increase the solution, increase net charge density, and reduce surface tension of solution, respectively.

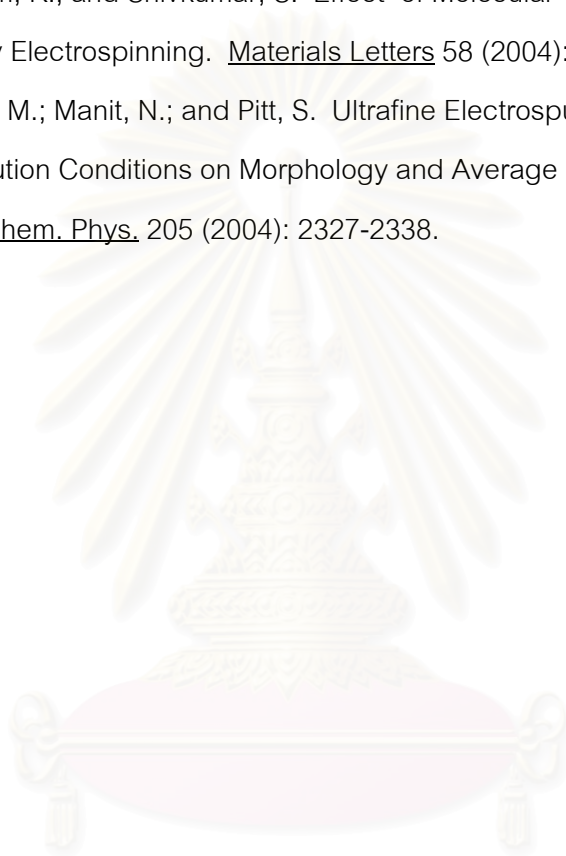
REFERENCES

1. Raleigh, L. London, Edinburgh and Dublin Philosophical Magazin 14 (1882):184-186.
2. Formhals, A. Process and Apparatus for Preparing Artificial Threads. US Patent (1934) 1,975,504.
3. Taylor, G. I. Electrically Driven Jets. Royal Society of London A 313 (1969): 453-475.
4. Baumgarten, P. K. Electrostatic Spinning of Acrylic Microfibers. Journal of Colloid and Interface Science 36(1) (1971): 71-79.
5. Larrondo, L. Electrostatic Fiber Spinning from Polymelt I. Experimental Observations on Fiber Formation and Properties. J. Polymer Sci.: Polymer Phys. Edn. 19 (1981): 909-920.
6. Larrondo, L. Electrostatic Fiber Spinning from Polymelt II . Examination of the Flow Field in an Electrically Driven Jet. J. Polymer Sci.: Polymer Phys. Edn. 19 (1981): 921-932.
7. Larrondo, L. Electrostatic Fiber Spinning from Polymelt III. Electrostatic Deformation of a Pendant Drop of Polymer Melt. J. Polymer Sci.: Polymer Phys. Edn. 19 (1981): 933-940.
8. Yarin, A. L.; Koombhongse, S.; and Reneker, D. H. Bending Instability in Electrospinning of Nanofibers J. Appl. Phys. 89(5) (2001): 3018-3026.
9. Deitzel, J. M.; Kleinmeyer, J.; and Harris, D. The Effect of Processing Variables on the Morphology of Electrospun Nanofibers and Textile. Polymer 42(1) (2001): 261-272.
10. Norris, I. D.; et a. Electrostatic Fabrication of Ultrafine Conducting Fibers: Polyaniline/ Polyethylene oxide Blends. Synth. Met. 114(2) (2000): 109-114.
11. Wang, Y.; and Serrano, S. Conductivity Measurement of Electrospun PAN-based Carbon Nanofiber. Journal of materials science letters 21 (2002): 1055.
12. Huang, L.; et al. Engineered Collagen-PEO Nanofibers and Fabrics. J. Biomater. Sci.-Polym. Ed. 12(9) (2002): 979993.

13. Huang, L.; et al. Generation of Synthetic Elastin-Mimetic Small Diameter Fibers and Fiber Networks. Macromolecules 33(8) (2000): 2989-2997.
14. Gibson, P.; and Rivin, D. Transport Properties of Porous Membranes Based on Electrospun Nanofibers. Colloids and Surfaces A : Physicochemical and Engineering Aspects 187-188 (2001): 469-481.
15. Jacobsen, M. Nonwoven Industry (1991).
16. Kim, J. S.; Reneker, D. H. Mechanical Properties of Composites Using Ultrafine Electrospun Fibers. Polymer Composites 20(1) (1991):124131.
17. Wang, X.; et al. Electrospinning Technology: A Novel Approach to Sensor Application. J. Macromol. Sci.-Pure Appl. Chem. 38(10) (2001): 1251-1258.
18. Kenawy, E. R.; et al. Release of Tetracylic Hydrochloride from Electrospun Poly(ethylene-co-vinyl acetate), Poly(lactic acid), and a Blend. Journal of Controlled Release 81(1-2) (2001): 57.
19. Schreuder-Gibson, H.; et al. Protective Textile Materials Based on Electrospun Nanofibers J. Adv. Mater. 34(3) (2002): 44.
20. Hou, H.; et al. Poly(*p*-xylene) Nanotubes by Coating and Removal of Ultrathin Polymer Template Fiber. Macromolecule 35(7) (2002): 2429-2431.
21. Reneker, D. H.; et al. Bending Instability of Electrically Charged Liquid Jets of Polymer Solution in Electrospinning. Journal of Applied Physics 89(9) (2000): 4531-4547.
22. Yarin, A. L. Free Liquid Jets and Films: Hydrodynamics and Rheology. New York: Harlow and Wiely, 1993.
23. Fong, H., and Reneker, D. H. Structure Formation in Polymeric Fibers. Germany: Hanser Gardner Publications, 2000.
24. Pual, M. 1,2 Epoxide polymers. Encyclopedia of Polymer Science and Engineering 6 (1985): 225-250.
25. Dwain, M. W. Ethylene oxide polymer. Encyclopedia of Chemical Technology 19 (1996): 701-717.

26. Kamienski, C. W.; McDonald, D. P. Lithium and Lithium Compounds. Encyclopedia of Chemical Technology 15 (1996): 434-458.
27. Bertram, B. M. Sodium Halides. Encyclopedia of Chemical Technology 22 (1996): 354-374.
28. Frillich, M. B.; and Petersen, R. L. Potassium Compounds. Encyclopedia of Chemical Technology 19 (1996): 1061-1075.
29. Reid, K. I.; Kust R. Calcium Chloride. Encyclopedia of Chemical Technology 4 (1996): 801-810.
30. Jackson, L. C.; et al. Magnesium Compounds. Encyclopedia of Chemical Tehnology 15 (1996) 684-688.
31. Lynn, J. L.; Bory, B. H. Surfactants. Encyclopedia of Chemical Technology 23 (1996): 500-505.
32. Rovner, J.; Brown, J.; and Davies, S. Methanol. Encyclopedia of Chemical Technology 16 (1996): 537-555.
33. Logsdon, J. E. Ethanol. Encyclopedia of Chemical Technology 9 (1996): 812-849.
34. Logsdon, J. E.; and Loke, R. A. Isopropanol. Encyclopedia of Chemical Technology 20 (1996); 216-236.
35. Fong, H.; Chun, I.; and Reneker, D. H. Beaded Nanofibers Formed During Electrospinning. Polymer 40 (1999): 4585-4592.
36. Deitzel, J. M.; Kleinmeyer, J.; Harris, D.; and Beck Tan, N. C. The Effect of Processing Variables on the Morphology of Electrospun Nanofibers and Textile. Polymer 42 (2001): 261-272.
37. Lee, K. H.; et al. The Change of Bead Morphology Formed on Electrospun Polystyrene Fibers. Polymer 44 (2003): 4029-4034.
38. Jing, Z.; et al. Biodegradable Electrospun Fibers for Drug Delivery. Journal of Controlled Release 92 (2003): 227-231.

39. Won, Z.; et al. The Effect of Solution Properties and Polyelectrolyte on Electrospinning of Ultrafine Poly(ethylene oxide) Fibers. Polymer 45 (2004): 2959-2966.
40. Koski, A.; Yim, K.; and Shivkumar, S. Effect of Molecular Weight on Fibrous PVA Produced by Electrospinning. Materials Letters 58 (2004): 493-497.
41. Chidchanok, M.; Manit, N.; and Pitt, S. Ultrafine Electrospun Polyamide-6 Fibers: Effect of Solution Conditions on Morphology and Average Fiber Diameter. Macromol. Chem. Phys. 205 (2004): 2327-2338.



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APPENDICES

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Appendix A Properties of PEO solution

Table A1. The characterization of the PEO 4% w/v blended with Salts

Concentration of Salt (% w/v)	Surface tension (mN/m)	Viscosity (cp)	Conductivity (mS/cm)
PEO 4% w/v	59.49± 0.05	662	0.05
PEO 4%w/v+LiCl			
LiCl 0.1% w/v	59.15 ± 0.07	519	2.64
LiCl 0.5% w/v	58.90 ± 0.03	487	10.98
LiCl 1.0% w/v	58.58 ± 0.04	469	21
LiCl 1.5% w/v	58.26 ± 0.02	454	30.3
LiCl 2.0% w/v	57.83 ± 0.04	422	40.4
PEO 4%w/v+NaCl			
NaCl 0.1% w/v	59.44 ± 0.06	562	2.16
NaCl 0.5% w/v	59.00 ± 0.05	559	9.57
NaCl 1.0% w/v	58.82 ± 0.09	557	17.84
NaCl 1.5% w/v	58.13 ± 0.11	542	25.8
NaCl 2.0% w/v	57.50 ± 0.07	480	33.8
PEO 4%w/v+KCl			
KCl 0.1% w/v	59.25 ± 0.03	509	2.18
KCl 0.5% w/v	58.63 ± 0.09	465	10.02
KCl 1.0% w/v	58.34 ± 0.02	444	17.84
KCl 1.5% w/v	58.10 ± 0.03	426	25.7
KCl 2.0% w/v	57.67 ± 0.02	415	32.9
PEO 4%w/v+CaCl ₂			
CaCl ₂ 0.1% w/v	59.14 ± 0.08	590	2.32
CaCl ₂ 0.5% w/v	58.90 ± 0.06	577	10.51
CaCl ₂ 1.0% w/v	58.46 ± 0.03	556	19.25
CaCl ₂ 1.5% w/v	58.28 ± 0.04	539	28.7
CaCl ₂ 2.0% w/v	57.99 ± 0.02	511	36.7
PEO 4%w/v+MgCl ₂			
MgCl ₂ 0.1% w/v	58.47 ± 0.08	588	2.7
MgCl ₂ 0.5% w/v	58.22 ± 0.05	562	11.24
MgCl ₂ 1.0% w/v	57.98 ± 0.04	492	20
MgCl ₂ 1.5% w/v	57.88 ± 0.04	477	29.5
MgCl ₂ 2.0% w/v	57.46 ± 0.03	452	37.3

Table A2. The characterization of the PEO 5% w/v blended with PEG

Concentration of PEG (% w/v)	Viscosity (cp)	Conductivity ($\mu\text{S/cm}$)	Surface tension (mN/m)
PEO 5% w/v	1639	57.6	58.42 \pm 0.02
M_w 1,000 g/mol			
1% w/v	1560	121.5	57.34 \pm 0.06
5% w/v	1616	97.8	56.71 \pm 0.02
10% w/v	1617	83.4	56.01 \pm 0.03
15% w/v	1537	69.4	55.75 \pm 0.04
20% w/v	1567	59.7	55.03 \pm 0.02
M_w 1,500 g/mol			
1% w/v	1549	119.6	57.90 \pm 0.05
5% w/v	1687	112.6	57.59 \pm 0.02
10% w/v	1655	106	57.20 \pm 0.04
15% w/v	1528	100.8	56.63 \pm 0.02
20% w/v	1591	99.4	55.29 \pm 0.03
M_w 2,000 g/mol			
1% w/v	1536	118.2	57.92 \pm 0.07
5% w/v	1563	111.8	57.05 \pm 0.08
10% w/v	1514	106.7	56.57 \pm 0.03
15% w/v	1429	103.6	56.08 \pm 0.04
20% w/v	1437	98.1	55.82 \pm 0.04
M_w 4,600 g/mol			
1% w/v	1542	135.5	57.67 \pm 0.07
5% w/v	1823	115.2	56.99 \pm 0.04
10% w/v	1748	111	56.53 \pm 0.06
15% w/v	1816	104.2	56.16 \pm 0.02
20% w/v	1515	98.2	55.74 \pm 0.09

Table A2. The characterization of the PEO 5% w/v blended with PEG (continue)

Concentration of PEG (% w/v)	Viscosity (cp)	Conductivity ($\mu\text{S/cm}$)	Surface tension (mN/m)
M_w 8,000 g/mol			
1% w/v	1681	119.2	58.08±0.07
5% w/v	1639	116.9	57.30±0.08
10% w/v	1611	103.9	56.57±0.05
15% w/v	2546	99.6	55.06±0.04
20% w/v	2659	98.8	54.53±0.04
M_w 10,000 g/mol			
1% w/v	1672	107.9	57.77 ± 0.04
5% w/v	1923	104.2	57.14± 0.01
10% w/v	2270	101.7	56.87 ± 0.01
15% w/v	2498	98.9	56.07 ± 0.03
20% w/v	2907	96.4	55.41 ± 0.03
M_w 20,000 g/mol			
1% w/v	1906	112.1	58.08 ± 0.06
5% w/v	2367	109.5	57.34 ± 0.08
10% w/v	2938	105.6	56.55 ± 0.02
15% w/v	3557	102.2	56.00 ± 0.05
20% w/v	4364	94.5	55.59 ± 0.01
M_w 35,000 g/mol			
1% w/v	1929	105.5	58.47 ± 0.02
5% w/v	2791	100.8	57.14 ± 0.04
10% w/v	3898	98.4	56.22 ± 0.03
15% w/v	4364	90.9	55.33 ± 0.05
20% w/v	4645	88.8	54.67 ± 0.03

Appendix B Average diameter of as-spun PEO fibers.

Table B1. Average diameter of as-spun PEO fibers as a function of the concentration

Concentration of PEO (% w/v)	Fiber size in nm (Mean)	Standard Deviation
3 % w/v	80.61	17.08
4% w/v	75.80	22.13
5% w/v	242.05	35.45
6% w/v	136.75	28.00
7% w/v	137.17	21.37

Table B2. Average diameter of as-spun PEO/NaCl fibers as a function of the NaCl concentration.

Concentration of NaCl (% w/v)	Fiber size in nm (Mean)	Standard Deviation
0.1% w/v	73.47	20.01
0.5% w/v	102.27	21.71
1.0% w/v	113.85	24.48
1.5% w/v	169.81	23.12
2.0% w/v	205.11	38.39

Table B3. Average diameter of as-spun PEO blended with SDS fibers as a function of the SDS concentration.

Concentration of SDS (% w/v)	Fiber size in nm (Mean)	Standard Deviation
0.5% w/v	106.65	33.79
1.0% w/v	142.26	43.73
2.0% w/v	167.21	20.87
3.0% w/v	195.30	26.80
4.0% w/v	217.55	47.27
5.0% w/v	222.33	31.11
6.0% w/v	229.55	32.61
7.0% w/v	260.23	38.27

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TableB4. Average diameter of PEO beaded fibers as a function of the ratio of distilled water and methanol, ethanol, and isopropanol, respectively.

Ratio of distilled water and alcohols	Bead size in nm (Mean)	Standard Deviation
Distilled water : Methanol		
90:10	885.71	221.86
80:20	851.22	160.43
70:30	836. 52	139.89
Distilled water : Ethanol		
90:10	884.73	207.66
80:20	856.57	196.44
70:30	844.09	158.80
Distilled water : Isopropanol		
90:10	1250.63	155.84
80:20	986.20	179.09
70:30	875.53	182.46

Table B5. Average diameter of as-spun PEO fibers as a function of the ratio of distilled water and methanol, ethanol, and isopropanol, respectively.

Ratio of distilled water and alcohols	Fibers size in nm (Mean)	Standard Deviation
Distilled water : Methanol		
90:10	89.04	15.24
80:20	93.68	15.46
70:30	99.19	17.46
Distilled water : Ethanol		
90:10	85.53	14.53
80:20	86.85	14.63
70:30	91.91	11.61
Distilled water : Isopropanol		
90:10	77.04	18.30
80:20	77.75	17.40
70:30	91.54	24.38

Table B6. Average diameter of as-spun PEO blended with PEG fibers as a function of the PEG concentration.

Concentration of PEG (% w/v)	Fibers size in mm (Mean)	Standard Deviation
M_w 8,000 g/mol		
1% w/v	131.95	58.84
5% w/v	226.62	73.72
10% w/v	238.46	36.78
15% w/v	334.17	58.84
20% w/v	474.74	93.64
M_w 10,000 g/mol		
1% w/v	122.87	51.34
5% w/v	169.77	35.32
10% w/v	254.12	38.77
15% w/v	318.93	47.82
20% w/v	419.64	69.70
M_w 20,000 g/mol		
1% w/v	78.47	24.11
5% w/v	153.12	38.09
10% w/v	229.88	50.55
15% w/v	316.65	45.35
20% w/v	372.01	46.52
M_w 35,000 g/mol		
1% w/v	123.94	41.41
5% w/v	230.64	52.94
10% w/v	268.73	53.87
15% w/v	345.57	44.22
20% w/v	425.24	38.32

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Publications and Presentations and Presentations:

1. Arayanarakul, K., Supaphol, P., Aht-Ong, D., (2005). "Effects of Processing Agents on Bead Formation of Electrospun Poly(ethylene oxide) Nanofiber" Abstract Book of The International Conference on Smart Materials 2004, Chiang- Mai, Thailand.
2. Arayanarakul, K., Aht-Ong, D., and Supaphol, P.(2004). " On the Bead Formation of Electrospun Poly(ethylene oxide) fibers: A Preliminary". Abstract Book of The International Conference on Smart Materials 2004, Chiang Mai, Thailand.

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1. The Third Prize Poster Presentation in Applied Science and Technology of The 13th Academic Conference at Faculty of science, Chulalongkorn University, Bangkok, Thailand.