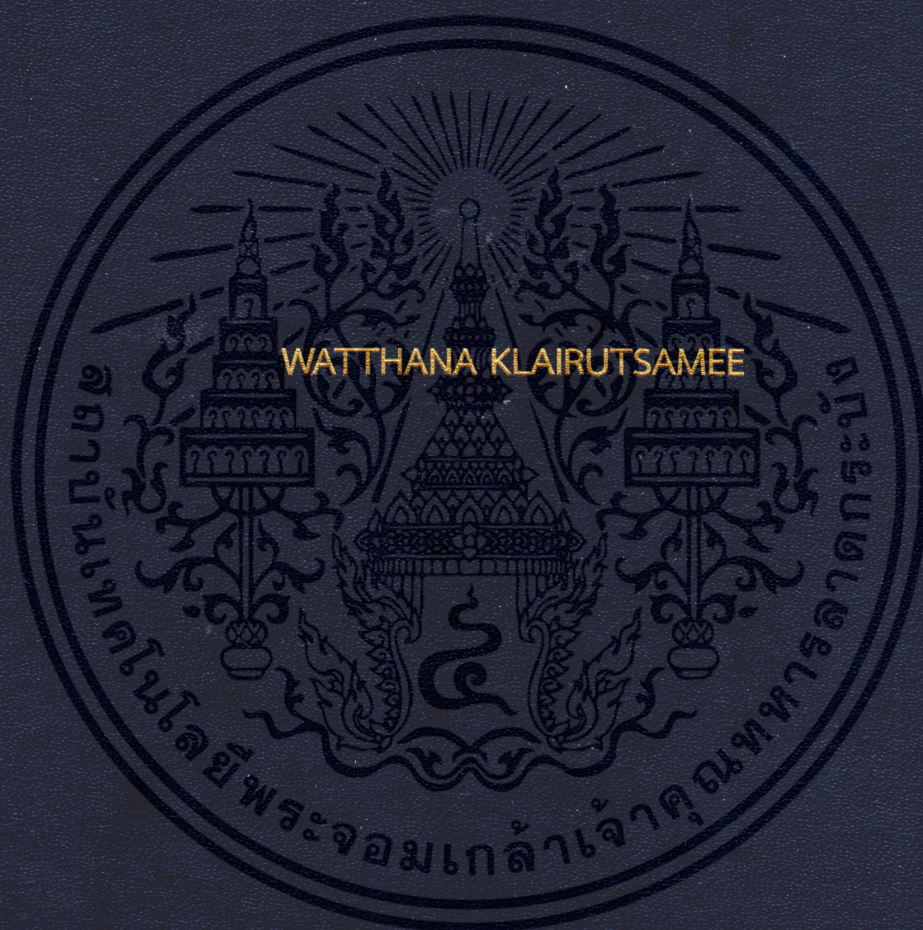


EFFECTS OF SOLVENT SYSTEMS AND ORGANIC SALTS
ON ELECTROSPINNABILITY OF ULTRAFINE
POLY (BUTYLENE SUCCINATE) FIBERS



A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY PROGRAM IN APPLIED CHEMISTRY
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ผลของระบบตัวทำละลายและเกลืออินทรีย์ที่มีต่อความสามารถในการปั่น
แบบไฟฟ้าสถิตของเส้นใยพอลิบิวทิลีนซัคซิเนตขนาดเล็กมาก

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ผลของระบบตัวทำละลายและเกลืออินทรีย์ที่มีต่อ
ความสามารถในการปั่นแบบไฟฟ้าสถิตของเส้นใยพอลิ
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บทคัดย่อ

เส้นใยที่มีขนาดเล็กมากสามารถเตรียมได้ง่ายด้วยเทคนิคการปั่นแบบไฟฟ้าสถิต อย่างไรก็ตามการเกิดเม็ดบีดอาจพบได้ถ้าระบบของสารละลายที่ใช้ไม่เหมาะสม งานวิจัยนี้มุ่งเน้นไปที่การศึกษาอิทธิพลของตัวทำละลายและเกลืออินทรีย์ต่างๆ ที่มีต่อความสามารถในการปั่นแบบไฟฟ้าสถิตของสารละลายพอลิบิวทิลีนซัคซิเนต (พีบีเอส) สารละลายพีบีเอสที่ใช้ในงานนี้ถูกเตรียมขึ้นจากตัวทำละลายเดี่ยว: คลอโรฟอร์มและไดคลอโรมีเทน ทั้งแบบใช้กับและไม่ใช้เกลืออินทรีย์ และจากตัวทำละลายผสมชนิดต่างๆ ได้แก่ คลอโรฟอร์ม:ไดคลอโรมีเทน ไดคลอโรมีเทน:คลอโรเบนซีน คลอโรฟอร์ม:เอ็นเอ็น ไดเมทิลฟอร์มาไมด์ และคลอโรฟอร์ม:เมทานอล ส่วนเกลืออินทรีย์ 4 ชนิดที่ถูกนำมาศึกษา ได้แก่ เบนซิลไตรเมทิลแอมโมเนียมคลอไรด์ (บีทีเอ็มซี) เบนซิลไตรเอทิลแอมโมเนียมคลอไรด์ (บีทีอีซี) เบนซิลไตรบิวทิลแอมโมเนียมคลอไรด์ (บีทีบีซี) และอัลคิลแอมโมเนียมเอทิลซัลเฟต (เอเออีเอส) อิทธิพลความเข้มข้นของสารละลายพีบีเอส ความเข้มข้นของเกลือและระบบของตัวทำละลายที่มีต่อลักษณะและขนาดของเส้นใย โดยเส้นใยพีบีเอสที่ถูกปั่นด้วยเทคนิคการปั่นแบบไฟฟ้าสถิตจากตัวทำละลายเดี่ยวประเภทต่างๆ คือ ระบบที่ใช้คลอโรฟอร์มและไดคลอโรมีเทนที่มีความเข้มข้นต่างๆ (8-30 เปอร์เซ็นต์โดยน้ำหนักต่อปริมาตร) เกิดเม็ดบีดที่ไม่ต่อเนื่องและเส้นใยที่มีบีดยังคงตรวจพบที่ทุกความเข้มข้น ในการศึกษาพบว่าความสามารถในการปั่นแบบไฟฟ้าสถิตของสารละลายพีบีเอสถูกปรับปรุงให้ดีขึ้นด้วยการเติมตัวทำละลายที่มีค่าคงที่ของไดอิเล็กทริกที่สูงหรือการเติมเกลืออินทรีย์ กรณีของตัวทำละลายผสมความสามารถในการปั่นแบบไฟฟ้าสถิตของสารละลายพีบีเอสในคลอโรฟอร์มถูกปรับปรุงให้ดีขึ้นด้วยการเติมเมทานอลเป็นตัวทำละลายร่วม โดยเส้นใยที่ได้เป็นเส้นใยที่เรียบปราศจากเม็ดบีด ส่วนความเข้มข้นของสารละลายพีบีเอสมีผลต่อขนาดเส้นผ่านศูนย์กลางของเส้นใยในตัวทำละลายผสมระหว่างคลอโรฟอร์ม:เมทานอลที่ถูกนำมาศึกษา พบว่าเส้นผ่านศูนย์กลางของเส้นใยพีบีเอสเพิ่มขึ้นเมื่อเพิ่มความเข้มข้นของสารละลายพีบีเอส ในการศึกษาผลของความเข้มข้นและชนิดของเกลืออินทรีย์ที่มีต่อสัณฐานวิทยาและค่าเฉลี่ยของเส้นผ่านศูนย์กลางของเส้นใยพบว่า เส้นผ่านศูนย์กลางของเส้นใยมีค่าลดลงเมื่อให้ความเข้มข้นของเกลืออินทรีย์เพิ่มขึ้น โดยพบว่าสัณฐานวิทยาและค่าเฉลี่ยเส้นผ่านศูนย์กลางของเส้นใยพีบีเอสที่ปั่นด้วยเทคนิคการปั่นแบบไฟฟ้าสถิต มีความแตกต่างอย่างมีนัยสำคัญระหว่างเกลือชนิดต่างๆ โดยเส้นใยมีขนาดเล็กลงเมื่อความเข้มข้นของเกลือชนิดต่างๆ เพิ่มขึ้น ดังนั้นเส้นใยพีบีเอสที่มีความ

เอกสารนี้เป็นเอกสารที่สงวนลิขสิทธิ์เพื่อการศึกษาเท่านั้น ไม่อนุญาตให้เผยแพร่โดยไม่ได้รับอนุญาต
ไม่ว่ากรณีใดๆ ทั้งสิ้น อีกทั้งห้ามมิให้ดัดแปลงเนื้อหา และต้องอ้างอิงถึงเจ้าของเอกสารทุกครั้งที่มีการนำไปใช้

ละเอียดสูงปราศจากเม็ดบีดสามารถเตรียมได้โดยการเติมตัวทำละลายที่มีค่าคงที่ของไดอิเล็กทริกที่สูงหรือการเติมเกลืออินทรีย์ชนิดต่างๆ ส่วนสมบัติทางความร้อน ลักษณะหมู่ฟังก์ชันและสมบัติเชิงกลของเส้นใยพียูเอสที่ปั่นด้วยเทคนิคการปั่นแบบไฟฟ้าสถิตจากสารละลายแบบใช้และไม่ใช้เกลืออินทรีย์ถูกนำมาตรวจสอบด้วยเทคนิคดีฟเฟอเรนเชียล สแกนนิ่งแคลอริมิเตอร์ (ดีเอสซี) พูรีเยร์ ทรานฟอร์มอินฟราเรด สเปกโทรสโกปี (เอฟทีไออาร์) และเครื่องทดสอบเบรกประสงค์ (ยูทีเอ็ม) จากผลการวิเคราะห์ทางความร้อนพบว่า การเติม 30 เปอร์เซ็นต์โดยปริมาตรต่อปริมาตรของเมทานอลในตัวทำละลายผสมหรือการเติมเกลืออินทรีย์ชนิดต่างๆ สามารถทำให้ความเป็นผลึกของเส้นใยพียูเอสมีค่าเพิ่มขึ้นเมื่อเปรียบเทียบกับการใช้ตัวละลายเดี่ยวที่ปราศจากเกลือ ลักษณะหมู่ฟังก์ชันเส้นใยพียูเอสที่ปั่นด้วยเทคนิคการปั่นแบบไฟฟ้าสถิตถูกนำมาวิเคราะห์ด้วยเทคนิค (เอฟทีไออาร์) สเปกโทรสโกปีได้บ่งบอกว่ามีเกลืออินทรีย์ถูกผนึกอยู่ในเส้นใย สมบัติเชิงกลของผืนผ้าเส้นใยพียูเอสที่ปั่นด้วยเทคนิคการปั่นแบบไฟฟ้าสถิตที่ถูกนำมาศึกษา พบว่าความแข็งแรงดึงและค่า Young's modulus ของเส้นใยที่เป็นแบบผ้าผืนจากสารละลายที่ใช้เกลือชนิดต่างๆ มีค่าสูงกว่าเส้นใยที่ได้จากสารละลายไม่ใช้เกลือ ส่วนเส้นใยพียูเอสที่ปั่นด้วยกระบวนการแบบไฟฟ้าสถิตจากสารละลายผสม 70:30 โดยปริมาตรต่อปริมาตรของคลอโรฟอร์มและเมทานอล ถูกนำมาใช้เป็นวัสดุภาคคงที่สำหรับทึนเลเยอร์โครมาโตกราฟี (ทีแอลซี) โดยประสิทธิภาพในการแยกของผสมระหว่างคอลเลสเตอรอลและกรดโอเลอิกบนเพลทของเส้นใยพียูเอสขึ้นอยู่กับความหนาของผืนเส้นใยและปริมาตรของสารวิเคราะห์ที่ถูกนำมาศึกษา สุดท้ายศึกษาการออกฤทธิ์ต้านจุลชีพของแผ่นเส้นใยพียูเอส พบว่าการออกฤทธิ์ของเส้นใยที่ปั่นจากสารละลายที่ใช้เกลือบีทีเอ็มซี บีทีอีซีและบีทีบีซีให้ประสิทธิภาพในการยับยั้งเชื้อ *Escherichia coli* ได้ดีกว่าเส้นใยพียูเอสที่ปราศจากสารละลายที่ไม่ใช้เกลือและเส้นใยปั่นจากสารละลายที่ใช้เกลือเออีเอส อย่างไรก็ตามจากการทดลองพบว่าที่เส้นใยดังกล่าวไม่มีฤทธิ์ในการยับยั้งเชื้อ *Staphylococcus aureus*

คำสำคัญ : การปั่นเส้นใยแบบไฟฟ้าสถิต เกลืออินทรีย์ พียูเอส เส้นใยพอลิบิวทิลีนซัคซินเนต ขนาดเล็กมาก

Thesis Title	Effects of Solvent Systems and Organic Salts on Electrospinnability of Ultrafine Poly(butylene succinate) Fibers
Student Name	Mr. Watthana Klairutsamee
Student ID	52650302
Degree	Doctor of Philosophy (Applied Chemistry)
Department	Chemistry
Year	2016
Thesis Advisor	Assoc. Prof. Dr. Ittipol Jangchud

Abstract

Ultrafine fibers can easily be prepared by electrospinning techniques. However, bead formation may observe if inappropriate solution systems are used. In this work, it was focused on studying effects of solvents and organic salts on electrospinnability of poly (butylene succinate) (PBS). PBS solutions were prepared in single solvent systems: chloroform (CF) and dichloromethane (DCM)) with and without organic salt, and mixed solvent systems, i.e., CF:DCM, CF:chlorobenzene (CB), CF:N,N-dimethylformamide (DMF) and CF:methanol (MeOH). Four organic salts were studied, i.e., benzyl trimethylammonium chloride (BTMAC), benzyl triethylammonium chloride (BTEAC), benzyl tributylammonium chloride (BTBAC) and alkyl ammonium ethyl sulfate (AAES). Effects of PBS concentrations, salts concentrations and solvent systems on the appearance and diameter of PBS fibers were studied. For electrospun PBS fibers were obtained from single solvent systems, that is, systems with chloroform (CF) or dichloromethane (DCM), at various concentrations (8–30% w/v). Discrete beads and beaded fibers were found at every studied concentrations. It was found that the electrospinnability of PBS solutions were improved by the addition of high dielectric constant solvents or organic salts. In case of mixed solvent systems, the electrospinnability of the PBS solutions in CF were improved by the addition of methanol (MeOH) as a cosolvent. The obtained fibers were smooth without any beads. Fiber diameters were affected by the amount of MeOH and the PBS concentration. It was found that the diameters of the PBS fibers increased with increasing PBS concentrations. Effects of salt concentrations and types on morphology and fiber diameter were investigated. It was found that morphology and average diameter of electrospun PBS fibers were significantly different between the salt types. The diameters of the electrospun PBS fibers decreased with increasing salt concentrations. Thermal properties, characteristic functionalities and mechanical

properties of the electrospun fibers that obtained from solutions with and without salts were investigated by using Differential Scanning Calorimetry (DSC), Fourier Transform Infrared Spectroscopy (FTIR) and Universal Tester Machine (UTM), respectively. From thermal analysis, it was found that the presence of MeOH (30 % vol) or salts could increase the crystallinity of the PBS fibers as compared with PBS single solvents without salts. FT-IR spectra indicated that salts were trapped in the electrospun PBS fibrous non-woven mats. It can be observed that the tensile strength and Young's modulus of electrospun PBS non-woven mats obtained from solutions with salts were higher than those of solutions without salts. Electrospun fibers prepared from 70:30 (v/v) CF:MeOH were used as stationary phase for Thin Layer Chromatography (TLC). Efficiency separations of the mixtures between cholesterol and oleic acid have depended the mat thickness, and analyte volumes. Finally, antimicrobial activity of PBS fibers was studied. It was found that the fiber mats spun from the PBS solution with BTMAC, BTEAC and BTBAC were able to inhibit the growth of *Escherichia coli* than fibrous mats obtained from the solution without salts and AAES. However, fibrous mats had no significant influence against *Staphylococcus aureus*.

Keywords : Electrospinning, Organic salt, PBS, Ultrafine poly (butylene succinate) fibers

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Mr. Watthana Klairutsamee

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Abbreviations

PBS	Poly (butylene succinate)
Chloroform	CF
Dichloromethane	DCM
Chlorobenzene	CB
N,N-dimethylformamide	DMF
Methanol	MeOH
Benzyl trimethylammonium chloride	BTMAC
Benzyl triethylammonium chloride	BTEAC
Benzyl tributylammonium chloride	BTBAC
Alkyl ammonium ethyl sulfate	AAES
Benzyl trialkylammonium chloride	BTAAC
Differential scanning calorimetry	DSC
Fourier transform infrared spectroscopy	FT-IR
Universal testing machine	UTM

Chapter 1

Introduction

1.1 Rationale

Electrospinning technique has been proven to be useful for producing ultrafine fibers with average diameters in a range of micrometers to nanometers. Unique fiber properties, i.e., very large surface to volume ratios, flexibility in surface functionalities, and good mechanical performance can be obtained. These characteristics are essential for various applications [1-3], including membrane [4], tissue scaffold and biomedical applications [5-8], reinforcement in composites [9], nanoelectronic [10] and analytical chemistry [11]. Morphology and fiber diameter are depended on various parameters such as solution properties (e.g., viscosity, solvent volatility and solution conductivity) and process parameters (e.g., applied voltage, polymer flow rate and capillary-collector distance). By adjusting these parameters, fibers with desirable morphology can be obtained [2-3, 12-15]. One critical requirement of ultrafine fibers with high surface area is uniform small fibers without defects, such as ‘beads’ and ribbon shaped fibers. However, electrospun polymer fibers often have beads as by products [2, 15-16]. Difference of beaded fibers and smooth fibers is shown in Figure 1.1. The viscoelasticity of solution, charge density carried by the jet and the surface tension of the solution are ones of the key factors that influence on the formation of beaded fibers [2, 16].

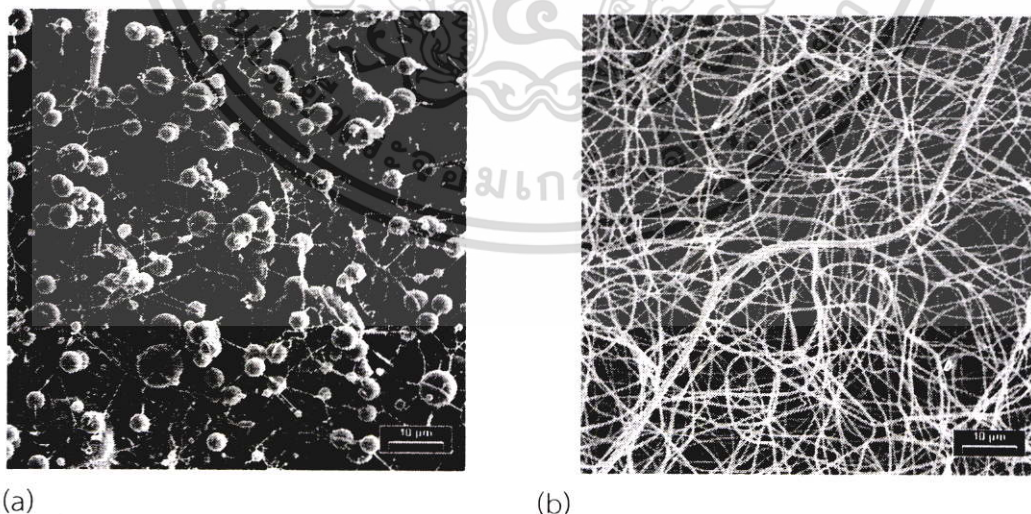


Figure 1.1 SEM micrographs showed different morphologies of (a) beaded fibers and (b) smooth fibers obtained from electrospinning process [2]

High conductivity of polymer solution can be contributed to increasing charge density carried by the polymer jet [2-3, 16]. The solvent is one of the main contributors toward the solution properties (e.g., conductivity, surface tension and boiling point). Solvents with high dielectric constant (ϵ) can interact differently with electrostatic field in electrospinning process [2-3, 16-17]. Wannatong *et al.* [17] reported that productivity of the as-spun PS fibers increased with increasing dielectric constant and dipole moment of the solvents. Moreover, additives, i.e. surfactants, hyper branched polymers, inorganic and organic salts can also be used to improve the electrospinnability and fiber morphology [18-25]. Organic salts such as fugitive salts and benzyl triethylammoniumchloride (BTEAC) [19, 21] and inorganic salts [18, 22, 24] could be used to enhance the charge strength and thus affecting final structures of electrospun fibers. Beaded fibers could be changed into uniform fibers with narrow distribution diameters. Therefore, polymer-salt-solvent interactions are important in the properties of the electrospinning [18-25].

Poly(butylene succinate) (PBS) and its copolymers are commercially available aliphatic polyesters with interesting properties, including biodegradability, melt processability, and good mechanical and thermal properties [26-27]. Because of their unique properties, they can be applied to a number of applications, such as packaging films, bags, flushable hygiene products, mulch films biomedical materials, and nonwoven electrospun PBS fibers. PBS is a biodegradable synthetic polymer with good biocompatibility as compared to poly(l-lactic acid) or poly(glycolic acid) [28]. Because of their great properties, electrospun PBS fibers can be extended further to medical treatments, textiles, biomedical applications, and more. The electrospinning of PBS solutions has been widely studied [26-27, 29-32]. In the electrospinning of the polymer solution, PBS is able to be dissolved in various solvents, such as dichloromethane (DCM), chloroform (CF), HFIP, and o-chlorobenzene. However, bead-free uniform electrospun PBS fibers have been reported when various solvent systems were tested. Jeong *et al.* [31] reported that ultrafine PBS fibers were successfully prepared by the electrospinning PBS solution in several mixed-solvent systems. Tserki *et al.* [32] studied the morphology and thermal properties of PBS fibrous mats electrospun from mixed solvent systems. Microbeads and ultrafine fibers were observed from electrospinning PBS solutions in dichloromethane (DCM)/N,N dimethylformamide (DMF) mixtures. It depended on ratios of the two solvents [32].

Thin Layer Chromatography (TLC) has been widely used in many areas of science including on-site environmental studies, organic chemistry, food industry, clinical analyses as well as in pharmaceutical industry [33]. In addition to conventional TLC,

High Performance Thin Layer Chromatography (HPTLC) and Ultrathin Layer

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ไม่ว่ากรณีใดๆ ทั้งสิ้น อีกทั้งห้ามมิให้ดัดแปลงเนื้อหา และต้องอ้างอิงถึงเจ้าของเอกสารทุกครั้งที่มีการนำไปใช้

Chromatography (UTLC) are also available [33-34]. Recently, several researcher groups [35-38] attempted to prepare stationary phase for TLC by using electrospinning technique. Polyacrylonitrile (PAN), Poly (vinyl alcohol) (PVA) and glassy carbon were successfully used as stationary phases for UTLC using electrospinning method. It showed greatly improved efficiency compared to traditional TLC plates and other UTLC plates. Advantages of electrospun UTLC are simple, fast, and inexpensive. Electrospun UTLC separations are also fast and require minimal mobile phase solvents [35-38].

Fabrication of ultrafine materials with biocide property from electrospinning process have recently gained much attention, due to high surface ratio to volume of electrospun fibers. Two basic approaches, i.e., originally antimicrobial polymers and incorporation of exogenous biocide in electrospun fibers were prepared with antimicrobial activity [39]. In recent years, there has been an increasing interest in exploiting the incorporation of quaternary alkylammonium chloride into the electrospun fibers [40-42]. Antimicrobial activity of electrospun fibers from the PC solution with BTEAC exhibited better excellent antimicrobial activity than those prepared without BTEAC [41]. Moreover, 3-(trimethoxysilyl) propyldimethyl octadecyl ammonium chloride (AEM) was treated on cellulose electrospun nanofiber mats against *S. aureus*. The *S. aureus* bacteria growth was inhibited with 2-7% w/w AEM treated cellulose electrospun mats [42].

Although electrospun PBS bead-free fibers can be prepared when various solvent systems were investigated, beaded fibers could be observed depending on solvent systems. The solvents used in those works were expensive and affect cost of electrospinning process.

Weak molecular interactions might be one of the most important factors contributing to zero shear viscosity of the solution lower than critical values. It was difficult to gain electrospin smooth fibers without bead defects. To solve this problem, several methods can be adopted. Chain extension by using chain-extending agents can be used to improve electrospinnability of PBS fibers. No report has been conducted to illustrate effects of organic salts and dielectric constant of solvents on solution properties and morphology of PBS fibers. Main objectives of this work were to produce the electrospun PBS ultrafine fibers without bead defects using organic salts and high dielectric constant solvent systems. Two instabilities (e.g., Rayleigh instability and whipping instability) and six forces would be used to explain effects on morphology and diameters of PBS ultrafine fibers. Moreover, feasibility study preparing stationary phase with biodegradable property for TLC from the electrospun PBS fibrous mats was carried out. The last part involved a

study of antimicrobial activity of electrospun PBS fiber obtained from solution with and without salts.

1.2 Objectives

- 1) To study electrospinnability of PBS fibers obtained from single and mixed solvent systems,
- 2) To study effects of 4 organic salts on PBS solution properties, morphology and fiber diameters, thermal properties, characteristic functionality of electrospun PBS fibers,
- 3) To study the feasibility of using electrospun PBS fibers as a stationary phase of TLC,
- 4) To study the antimicrobial activity of electrospun PBS fiber with organic salts.

1.3 Scopes of study

- 1) Effects of solvent systems and PBS concentrations on electrospinnability of PBS fibers (i.e., morphology and fiber diameter) and PBS solution properties (i.e., viscosity, conductivity and surface tension of solution) were studied.
- 2) Effects of PBS concentrations and applied electrical field strength on electrospinnability of PBS fiber obtained from the optimum ratios of mixed solvent system were studied.
- 3) Effects of organic salts, salt concentrations and PBS concentrations on electrospinnability of PBS fibers (i.e., morphology and fiber diameter) and PBS solution properties (i.e., viscosity, conductivity and surface tension) were studied.
- 4) Thermal properties, characteristic functionalities and mechanical properties of the electrospun fibers obtained from PBS solutions with and without the organic salts 1% (w/v) were investigated by using Differential Scanning Calorimetry (DSC), Fourier Transform Infrared Spectroscopy (FTIR) and Universal Tester Machine (UTM), respectively.
- 5) Feasibility study for applications of electrospun PBS fibers to be used as stationary phase in Thin Layer Chromatography (TLC) was carried out. Parameters used to study in this part included:
 - Thickness of electrospun PBS ultrafine fibrous mats obtained at various spinning times,
 - Comparatively study of mobile phase velocities on stationary phase between conventional TLC and electrospun PBS fiber mats,
 - Effects of thickness of electrospun PBS mats on separation efficiency of cholesterol and oleic acid samples and

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-Effects of various volumes of cholesterol and oleic acid samples on separation efficiency of electrospun PBS fibrous mats.

6) Antimicrobial activity of PBS fibrous mats electrospun from solutions with and without 1% (w/v) organic salts was studied. Testing antimicrobial activity of the electrospun PBS fibers was carried out against Gram positive *Staphylococcus aureus* (*S. aureus* ATCC 25923) and Gram negative (*E.coli* ATCC25922) by the non-woven fabric attachment method.

1.4 Expected results

1) Results obtained from this work could be provided better understanding on the mechanisms to enhance the electrospinnability of PBS fibers without the formation of beads,

2) Effects of organic salts on the morphological appearance and fiber diameters, including properties of electrospun PBS fibers can be elucidated.

3) Effects of balanced forces during the electrospinning process, i.e., viscoelastic, coulombic, electrostatic forces, and surface tension, can be explained in this work.

4) Electrospun PBS fibers mat can be prepared to use as a stationary of TLC.

5) Electrospun PBS fibers obtained from solution with salts can be used as a fibrous mat with inherent ability to inhibit the growth of microorganisms.

Chapter 2

Theories and Literature Reviews

2.1 Electrospinning

In recently years, a large number of works have reported on the preparation of electrospun nanofibers from a wide range of polymer materials [1-11]. Electrospinning is a direct process producing ultrafine fibers with average diameters in a range of micrometers to nanometers. Electrospun nanofibers have distinctive properties such as high surface area to volume ratios, high porosity, and enhanced specific mechanical performance [1-3, 43]. Diameters of nanofibers produced by electrospinning, can be controlled by varying certain parameters such as solution properties (e.g., viscosity, conductivity and surface tension), process conditions (hydrostatic pressure, needle-to-collector distance, needle size and electric potential) and spinning conditions (e.g., temperature and humidity). Smaller sizes of individual fibers result in high surface to volume ratios yielding special physiochemical characteristics. They are of potential values to any fields that require high surface area of materials, for example, filtration [44], catalysis and aerosol barrier, [45], composite reinforcements [9, 46], drug-delivery vehicles [47], and scaffolds for tissue cultures [29], etc.

2.2 Historical background

Both of electrospinning and electrospraying techniques are related to electrostatic force, when liquid drops are placed in an electric field. In the late 1500s, William Gilbert [48-49] found the phenomenon that a water drop on a dry surface was drawn into a cone, when an electrical charge applied on it. This was the first recorded observation of electrospraying. It was also the beginning of the era of electrospinning. In 1800s, Lord Raleigh [48-49] investigated the condition of instability occurring in electrically charged liquid droplets. He showed that when the electrostatic force overcame the surface tension force, the charged liquid sphere became unstable and generated fibers. The resulting information from this study was used to fabricate the electrospun fiber cellulose acetate from acetone. The first description of an electrospinning process, it was patented by J. F. Cooley [48-49]. In this patent, it showed the generated fibers rather than droplets. Conditions were (i) fluid must be sufficiently viscous, (ii) solvent volatile enough to evaporate to allow regeneration of the solid polymer, and (iii) electric field strength must be within a certain range. The crucial patent in electrospinning of polymeric materials, it was first

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ไม่ว่ากรณีใดๆ ทั้งสิ้น อีกทั้งห้ามมิให้ดัดแปลงเนื้อหา และต้องอ้างอิงถึงเจ้าของเอกสารทุกครั้งที่มีการนำไปใช้

patented by Anton Formhals in 1934 [50-53]. He improved and described different designs for setting up of experiments, the electrospinning process, the collection methods, and the applications. By 1944, He had filed several other patents [50-53] on improved process and techniques for fabricating nanofiber mats, later as well to produce continuous fine fibers for use on standard textile machinery. Despite these early discoveries, the procedure did not utilize commercially. In 1970s, Sim *et al.* patented the production of fibers with diameters of less than 1 μm [54]. However, electrospun fibers were first commercialized for filter applications, as part of nonwovens industry. Since 1990, techniques on the electrospinning process are interested and studied from both academic and industry [55]. In 1994, Reneker and Doshi contributed reviews on the electrospinning technique [54]. The number of publications related to electrospinning process are reflected by the skyrocketing numbers of scientific publications and patents as shown in Figure 2.1.

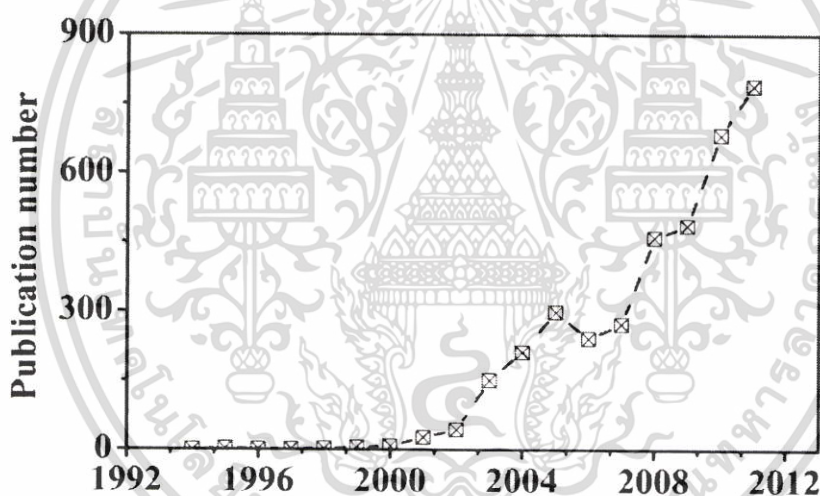


Figure 2.1 Number of scientific publications titled with the key words “electrospinning” and “electrospun” from 1994 to 2012 [55]

2.3 Electrospinning process

Electrospinning is a simple technique used to produce non-woven fibers or nanofibers from a wide range of materials by using an electrical force. Electrospinning polymer melts and solutions have been studied in the various fields [1-3, 55]. Figure 2.2 shows a typical electrospinning process that can be easily setup in a laboratory. The major components are: (1) a polymer reservoir attached to a small capillary tube (e.g. metallic capillary needle), (2) a high voltage power supply and (3) a screen collector [2-3].

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ไม่ว่ากรณีใดๆ ทั้งสิ้น อีกทั้งห้ามมิให้ดัดแปลงเนื้อหา และต้องอ้างอิงถึงเจ้าของเอกสารทุกครั้งที่มีการนำไปใช้

Polymer solution is contained in a syringe. The narrow end of the syringe has connected to blunt ended stainless steel capillary or metallic capillary needle. The alignment of the syringe is usually horizontal although vertical setups have also been described [2-3]. If the capillary is arranged in a vertical position, the solution can flow from the capillary solely due to gravitational forces and a syringe pump may then not be needed. However, this setup allows for much less control than the use of a syringe pump, and consequently the horizontal setup or an arrangement including a syringe pump is preferred. The metallic capillary needle is connected to a high voltage DC supply and collector wrapped with a foil.

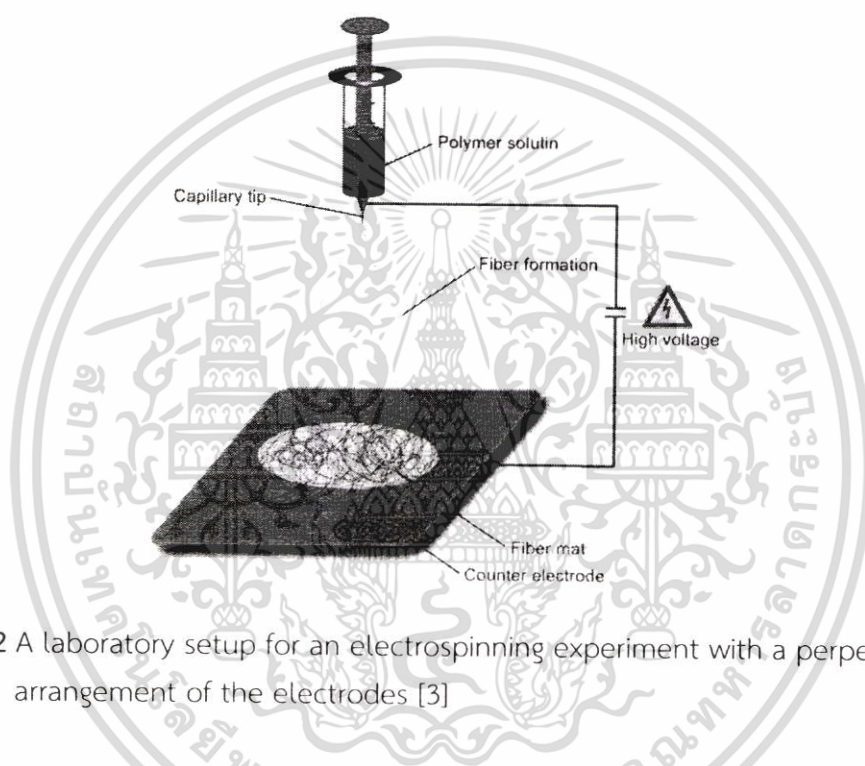


Figure 2.2 A laboratory setup for an electrospinning experiment with a perpendicular arrangement of the electrodes [3]

A high electrical field of 10-50 kV is applied. The distance between of nozzles as an electrode and a counter electrode for collect electrospun fiber is 10-25 cm in laboratory systems. The high electrical voltage, as high as several kV/cm^2 is applied. The droplet of polymer liquid at the end of nozzle is stretched into structure called a "Taylor cone", when electrical field strength is about to overcome the surface tension of polymer liquid at a critical voltage. Such of cone angle is about 30° at the end of capillary of electrospinning process. Rayleigh [2-3] who calculated the maximum amount of charge (A critical voltage) to be held on a drop of liquid, before the electric field overcomes the surface tension of the drop. Taylor [2-3] found that the cone with a semi vertical angle of 49.3° from the capillary outlet formed under an electric field is stable. An electrically charged polymer fiber jet is an attractive force from the tip of the Taylor cone and moves toward a grounded metallic target

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or collector. In electrospinning process, there are six major forces [2, 17] acting on an infinitesimal segment of polymer jet, i.e.,

1) Body or gravimetric force, this force is influenced on density of the polymer solution if electrospinning process arranged to vertical process.

2) Electrostatic force, which is used to extend the charged jet from the nozzle toward the collecting target. This force is determined by the applied electric field

3) Columbic repulsion force, which occurs on the surface of the polymer jet. The magnitude of this force is dependent on the characteristic of the polymer and solvent. It is responsible for the thinning or the stretching of the charged jet during its flight to the target. This force is related to charged density of polymer and conductivity of polymer solution.

4) Viscoelastic force, this force performs against the elongation of the jet subjected in the electric field. This force depends on the polymer molecular weight, solvent, and type of polymer.

5) Surface tension force, this force works against the stretching of the surface of the charged jet.

6) Drag force, which performs between the surface of the polymer jet and the surrounding air.

Combination of these forces, the electrical charged jet travels in a straight trajectory for only a short distance (around several millimeters) before undergoing bending instabilities. After bending instability occurs, the three dimensional bending coil goes downstream and increases in diameter to form a spiral path. The shape that is occupied by the spiral path. It is called an envelope cone. As the diameter of the jet decreases, the path of the jet becomes unstable again and a new smaller diameter electrical bending instability develops. Sometimes a third or much smaller diameter bending instabilities can be observed as well before the jet solidified. Solvent can be evaporated during the electrospinning process, and a solid fiber is left on the collector. The fiber might be elongated by large factors (10,000 times) from the initial length of the fluid segment. Under many circumstances, as the solvent evaporates and the ionic conductivity of the jet decreases, secondary and tertiary bending instabilities can be observed as well (the green and blue part in Figure 2.3).

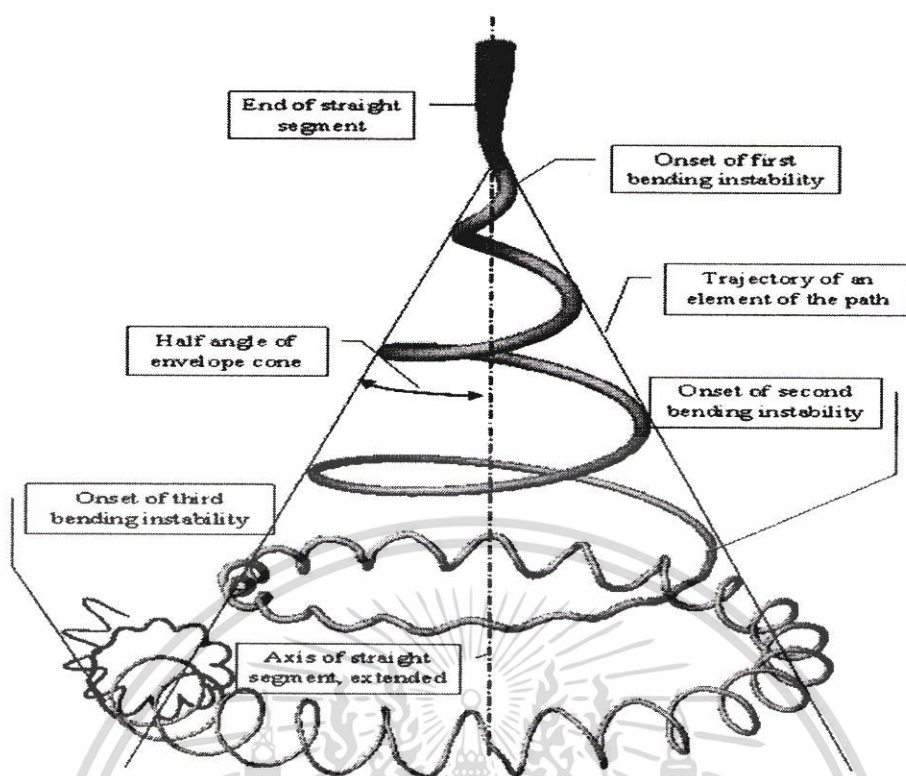


Figure 2.3 Typical electrospinning jet path, The straight segment is shown in red, the first bending coil in orange, the secondary bending coil in green, and the third bending coil in blue [57]

The charge concentration increased through on the fibers surface along with thermally induced phase separation [2, 52], occurring due to evaporative cooling, induces a bending, or whipping in the polymer jet. This referred to the whipping, or bending, instability. The occurrence of bending instability is due to the competition between the viscous stress along the jet and the electrostatic force working on the jet. Therefore, the polymer fiber continues to elongate and thin along a chaotic path extending from the capillary tip to collector plane with the whipping or bending instability. The fiber diameters are reduced continuously due to solvent evaporation. Eventually, the fiber diameters are reduced to constant diameters as they are dried and deposited upon the grounded metallic target.

Although electrospinning is a simple process that can produce continuous ultrafine fibers. Parameters influenced on the electrospinning technique can be divided into two major categories, i.e., system and process parameters. Ultrafine fibers or nanofibers with desired morphology can be obtained by appropriately adjusting all or some above parameters.

2.4 Parameters influenced on electrospun fibers

Qualities of ultrafine fibers have obtained depending on the number of parameters. In principal, these parameters can be divided into two major categories, namely process parameters and solution parameters. Fibers properties can be obtained, when system and process parameters were controlled by appropriate adjustment of these parameters [2-3, 12, 54].

2.4.1 Process parameters

Process parameters are important factors affecting on morphological appearance and structure of ultrafine fibers. The most important parameters can be divided into 3 items, i.e., applied voltage, polymer flow rate and capillary-collector distance. All these parameters can be used to produce and control electrospinnability.

- Applied voltages

It has been known that the high voltage can induce the necessary charges on the polymer solutions in electrospinning process. It initiates to electrospin fibers when electrostatic force in the polymer solution overcomes the surface tension of solution. The optimized high voltages often lead to the greater stretching of polymer jet when under the high electrical field. The high strength of electrical field can control the formation of fibers with diameters from nanometers to a few micrometers. However, non-optimal field strength can led to bead defects in the electrospun fibers. Reviewed literatures showed that there was an optimal range of electric field for a certain polymer solvent system. Either too weak or too strong a field will lead to the formation of beaded fibers. In addition, it was found that such results varied strongly with the polymer systems. A high electrical field of 10-50 kV was mostly used to study effects of parameters on the appearance of ultrafine fibers [2-4, 58].

- Flow rates

Polymer flow rate has influenced on the fiber size and geometry. When the flow rate is increased, possibility of an increase in the fiber diameter, including amount of beaded defects might be increased. Because of high flow rate, it leads to inadequate drying of the solvent from polymer jet prior to reaching the surface of collector. It could be caused by the collapsing fibers leading to the formation of bead defects or ribbon-like fibers. Therefore, a lower feed rate is more desirable as the solvent must has more time to evaporate. Moreover, some research groups tilted the capillary at defined angles to control spinning rate [2-3]. Introduction of the programmable syringe pump ensuring a very specific controlled spinning rate can be achieved [54].

- Capillary to collector distances

Distance between capillary tip and collector has influenced on both of flight time of electrospun jet and strength of electrical field. The flight time of electrospun jet is the time available for evaporation of the polymer solution before the ultrafine fibers reach the collector surface. An optimal distance between of capillary and collector is required to give an optimal field strength and sufficient time to dry the electrospun polymer jet. Moreover, the fiber diameters are decreased as the Taylor's cone to collector is increased. Decreasing the gap distance will affect both fiber surface morphology and the average diameters. Very small gap distance can lead to fuse of fibers and result in beaded defect which can be attributed to inadequate drying of the polymer fiber prior to reaching the collector. As the electrical field strength between the needle and collector was increased. It caused faster acceleration of the jet to the collector [55, 57, 58-60].

All conditions of process parameters have strong influence on morphological appearance and structure of ultrafine fibers. They can be summarized and shown in Figure 2.4.

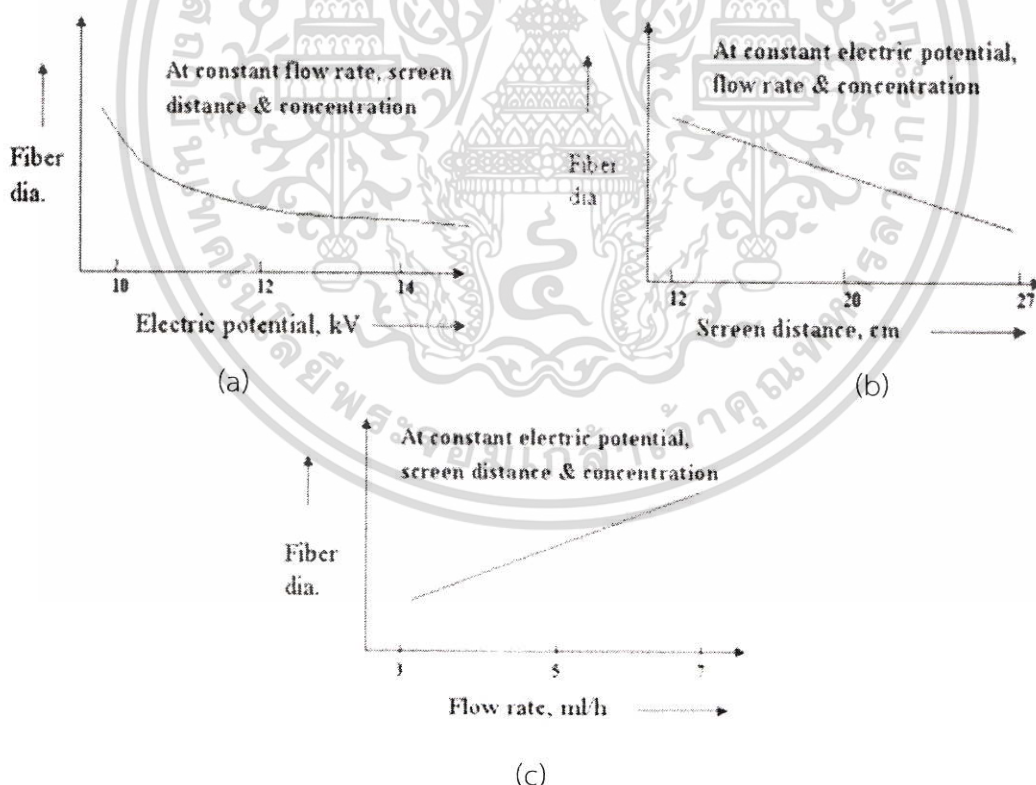


Figure 2.4 Summary of process parameters affecting on the fiber diameters;
(a) electric potential, (b) screen distance and (c) flow rate [1]

2.4.2 Solution parameters

Besides the process parameters, solution parameters have also played important roles to control the fiber formation and the morphological appearance of fibers. These parameters include polymer concentration, surface tension, solution conductivity and dielectric effect, etc. These solution parameters can be discussed in details in the next topic.

- Polymer concentration

The concentration of polymer solution has a dominant effect on both fiber diameter and morphology. This parameter also relates to viscosity and chain entanglement of polymers. At a lower critical concentration (C^*), the density of chain entanglement in a given solution is appreciably less than a critical value. Polymer jet cannot be withstood electrical forces. It breaks up into droplets or discrete [2]. Beyond this point, optimal entangled polymer molecules are formed. The continuous uniform fibers can be electrospun when the concentration is higher than the critical value. As the increased concentration, the morphology is of the obtained fibers were changed from beads to beaded fibers and bead-free continuous fibers, respectively [4, 61-63]. Figure 2.5 shows morphological appearance of electrospun nanofibers from different viscosities of polymer solutions. Effects of concentration on the qualities of electrospun PLGA fibers were shown in Figure 2.6.



Figure 2.5 SEM micrographs of electrospun nanofibers from different polymer solution viscosities [1]

However, high concentrations of polymer solution can lead to practical difficulties in electrospinning process. Moreover, high concentrations of polymer generally tend to yield large average diameters of nanofibers. Nevertheless, different morphologies and diameter sizes of nanofibers could also be observed depending on polymer and solvent systems [2-3, 62].

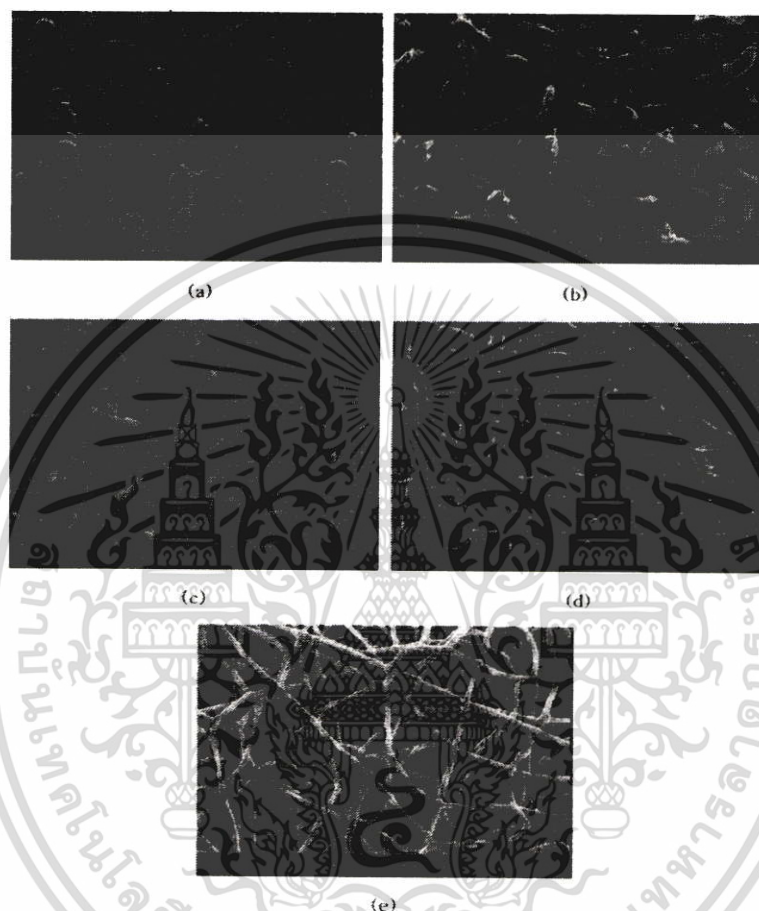


Figure 2.6 SEM micrographs of electrospun PLGA fibers at different concentrations in chloroform: (a) 9%, (b) 11%, (c) 13%, (d) 15%, and (e) 17% [63]

- Solution conductivity

Sufficiently conductivity of the solution is required to provide high charged density of polymer jet in the electrospinning. If solution has a zero conductivity, it cannot be used in electrospinning process [2, 30]. A minimal electrical conductivity in the solution is therefore essential for electrospinning. Solutions with high conductivities have been generated to have high charged density on surface of polymer jet. Small size of electrospun nanofibers, then can be obtained. For polymer solution, solubility parameter, boiling point of solvent and dielectric constant are parameters that should be also considered. Higher the dielectric constant of solvent is able to increase polymer solution conductivity.

Therefore, the fiber jet might be produced from solution by using solvent with high

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dielectric constant. It has tendency to generate smaller uniform fibers without beads. 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) is a sample solvent with high dielectric constant. It can be used to increase solution conductivity to produce continuous uniform fibers without bead defects [63-64]. Moreover, an organic or inorganic salt, or a surfactant can be also used to improve the polymer solution conductivity [3, 59, 2]. For example, NaCl and trialkylbenzyl ammonium chloride, may be used at very low concentrations to improve conductivity of polymer solutions. Adding ionic species or organic salts to the polymer solutions is able to generate a relative higher surface charge density to be maintained on the jet [2, 62]. Figure 2.7 shows SEM micrographs revealing effects of organosoluble salt on the appearance electrospun PHBV fibers.

From above mentions, solutions with high conductivities have greater charge-carrying capacities than solutions with lower conductivities. Therefore, the fiber jets produced from solutions with high conductivities. They are subjected to greater tensile forces in an electric field than fiber jets from solutions with low conductivities. In the presence of a strong electric field, on the other hand, high conductive solutions are extremely unstable. Therefore, dramatic bending instabilities and border diameter distribution of fiber could be obtained.

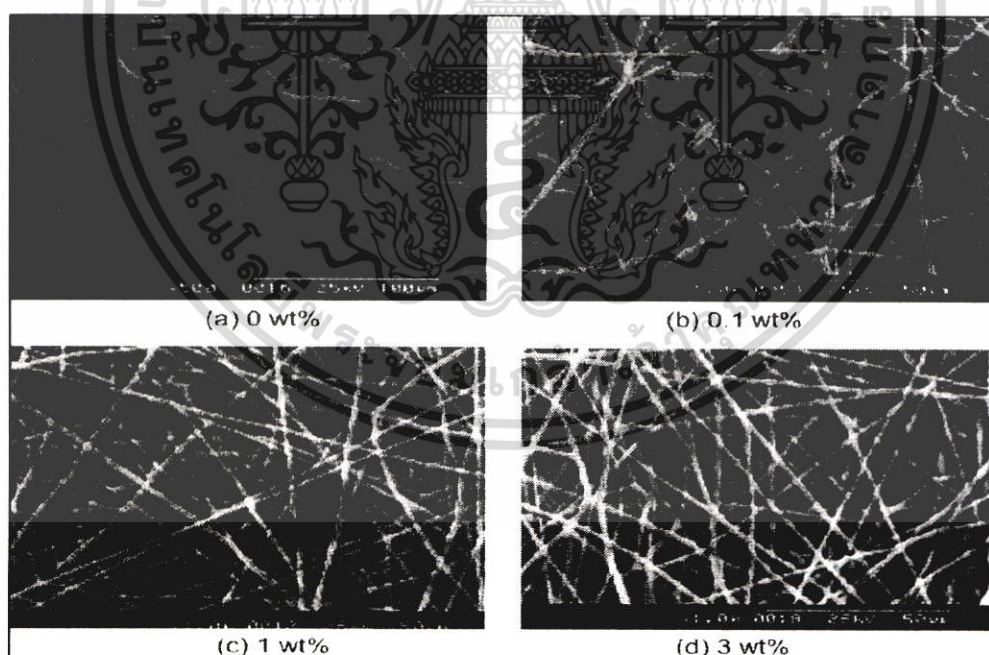


Figure 2.7 SEM images of ultrafine PHBV fibers electrospun from 20 g/mL of PHBV solution with different amounts of BTEAC: (a) 0 wt.%, (b) 0.1 wt.%, (c) 0.5 wt.%, and, (d) 3.0 wt.% [65]

- Surface tensions

Surface tension of the solution is one of dominant effects of bead generation along the electrospun nanofibers on the collector. The surface tension is the primary force opposing columbic repulsion. Its role in determining electrospinnability cannot be overstated. In the instability region of the polymer jet that obtained fiber extension, electrostatic forces are countered primarily by surface tension forces. It is this balance between surface tension, cohesive force and surface electrostatic repulsion, i.e. $Vq/\gamma R^2$. They determine the curvature in bending of the jet during whipping instability. Then, bead formation in electrospinning can be induced by changing surface tension of solution. At the critical voltage, it can initiate polymer jet formation. A critical voltage (V_c) is proportional to $\gamma^{1/2}$, suggesting that the electrospinning can initiate fiber when surface tension of solution is reduced. Surface tension of polymer solution can be controlled by judicious selection of the solvent. However, polymer concentrations and chemical nature of polymers can also affect the surface tension. In general, increasing polymer concentration will decrease the surface tension of solution as illustrated in Figure 2.8.

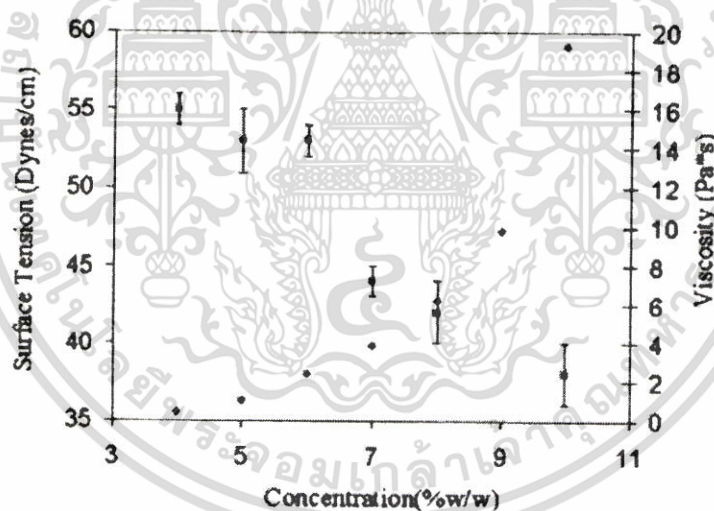


Figure 2.8 Dependence of solution surface tension (squares) and solution viscosity (diamonds) as a function of concentration for PEO/water solutions [4]

- Dielectric constant of solvents

Generally, the polymer solution with a high dielectric constant (ϵ) of solvent can produce ultrafine fibers without beaded defects. The surface charge density on the jet tends more evenly dispersed when that of solvent was added. A high dielectric constant of solvent can improve charged density on surface of polymer jet. N,N-dimethylformamide (DMF), HFIP and tetrahydrofuran (THF) are solvents with a high dielectric constant which can increase conductivity of polymer solution. Therefore, a solution with greater dielectric property can reduce the bead

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formation, as well as diameter of electrospun fibers. All above parameters that influenced on the electrospun fibers were summarized in Table 2.1.

Table 2.1 Summarized effects of electrospinning parameters on fiber formation

Parameters	Conditions	Effects of parameter
Process parameters	Applied voltage	It must be higher than the critical voltage. Inappropriate conditions are either too weak or too strong, and bead can be observed.
	Flow rate	A lower feed rate is more desirable to obtain small fiber. High feed rate can cause a bead or a flat ribbon fiber formation because of inappropriate drying time.
	Spinning distance	An optimal distance is required to give an optimal field strength and sufficient time to dry before the fibers reach the collector.
Solution parameters	Solution concentration	Fibers with more uniform diameter can be obtained when it results in the critical entanglement concentration. However, large fiber diameter mostly obtained from high polymer concentration
	Solvent volatility	It has influenced on the fiber morphology and electrospinnability. Polymer with high volatile solvent may clog on the needle. Slow evaporation solvent can be caused the flat ribbon fiber.
	Solution conductivity	High conductivity polymer solution can improve electrospinnability and fiber quality. Small fiber without out bead can be obtained from the high conductivity of the solution.
	Molecular weight	Low a molecular weight solution tends to form beads rather than fibers and a high molecular weight solution gives fibers with larger average diameters.

2.5 How to control quality of electrospun fibers

Bead formation in electrospinning process is one of the most common defects encountered in electrospun fibers. Electrospun beaded fibers are related to two instabilities of the jet of polymer solution, i.e., axis-symmetric and nonaxis-symmetric instabilities (Figure 2.9). These instabilities depend on the factors related to solution properties and operating conditions: solution viscosity, conductivity, surface tension, and the strength of the applied electrostatic field. In the former instability (Rayleigh instability), the centerline of the jet is the axis, which is not deflected, but the radius of the jet changes in a symmetric and wavelike manner. This instability is dominated by surface tension and produces drops rather than fibers [2, 19, 66-67]. Nonaxis-symmetric instabilities (Whipping instability) is generated by the electrostatic field, which causes bending and stretching of the jet through a spiraling motion. The latter instability dominated along with viscosity and conductivity of polymer solution [2, 19, 66-67].

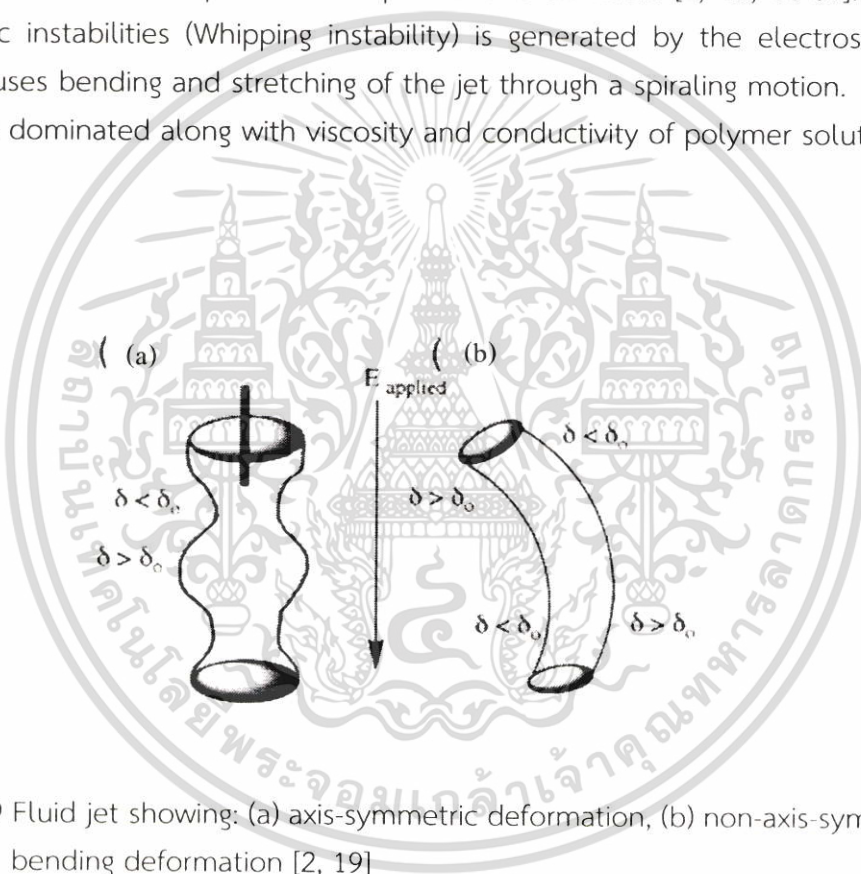


Figure 2.9 Fluid jet showing: (a) axis-symmetric deformation, (b) non-axis-symmetric bending deformation [2, 19]

The axis-symmetric instability is likely to occur when repulsive forces are high. It is governed by fluctuations in the dipolar component of the charge distribution on the surface jet. This results in “varicose” features in the solution jet, but fiber integrity is retained and resulting beaded fibers. This is more commonly observed in fluids that are spun at lower voltage, but is suppressed at higher field strength or charge density. The non-axis-symmetric conducting instability is responsible for bending the fluid jet and leading to “whipping”. This mode is responsible for the finer fibers [2, 19, 68]. From above information, the formation of beaded fibers can be obtained from electrospinning process. The solution viscosity, net charge density carried by the

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electrospinning jet and surface tension of the solutions are the main factors for controlling the bead formation. High viscosity of solution favors formation of fibers without beads. While higher net charge density favors formation of fibers not only without beads, but also thin fibers. In practices of electrospinning process, several approaches are available to control bead formation in electrospinning of polymer nanofibers.

2.5.1 Polymer concentration

Rayleigh instability occurs when the viscosity of solution is below the critical value concentration. This low concentration results in a low viscoelastic force because the chain entanglement in a given solution is appreciably less than a critical value. This might not have been enough to form a stable polymer jet. Therefore, it is not sufficient to counter the stretching forces from both the electrostatic and coulombic repulsion forces. Meanwhile, the polymer concentration has increased beyond the critical values. It leads to increasing chain entanglement density. It has resulted in more chain entanglement yielding an increase in the viscosity of the polymer solution. The Rayleigh instability can be suppressed when these concentrations are used [3, 19, 62].

2.5.2 Applied voltages

The applied voltage is one of important parameters that influenced on the electrospinning process. Fiber formation occurs when the voltage attains the critical value. Increasing the applied voltage is able to enhance the surface charges of the jet [2-3]. As a result, it is able to promote stretching of polymer jet leading to ultrafine fiber. Rayleigh instability occurs either when strength of electrical field is low or polymer solution viscosity is below the critical values [2 and 19]. However, the highest voltage is applied. It may enhance mass flow of polymer jet that travel to the collector. It can lead to increase bead formation due to inadequate time for evaporation solvent of the polymer jet. Moreover, research groups [2] reported that beaded free fibers are not depended on only voltage condition, but also polymer solution concentration and electrical field strength. The beaded fibers can be suppressed by balancing these parameters [2, 58, 62].

2.5.3 Using additives to increase surface charge density on polymer jet

Additives have been proven to be useful in improving electrospinnability and controlling fiber morphology through the modification of solution properties, i.e., conductivity, surface tension and viscosity. Additives such as inorganic salts, cationic surfactants, and organic salts have been used to increase the conductivity of polymer

solutions [2, 18-21]. Lin *et al.* [20] reported that organic salts, such as, dodecyl trimethyl ammonium bromide (DTAB) and tetrabutyl ammonium chloride (TBAC) were added in PS solution in mixed solvent (DMF:THF; 1:1). Beads in electrospun PS fibers were efficiently suppressed. Qin *et al.* [18] reported that inorganic salts i.e. LiCl, NaNO₃, NaCl and CaCl₂ were able to change properties of polyacrylonitrile (PAN) solutions. The conductivity trend was LiCl > NaNO₃ > CaCl₂ > NaCl. However, the viscosity and surface tension of the electrospinning solutions were slightly affected.

2.5.4 Using additives to decrease surface tension of polymer solutions

Some additives are able to reduce surface tension of polymer solutions yielding a reduce in bead formation. Yao *et al.* [2] reported that adding a surfactant such as Triton X-100 or sodium dodecyl sulfonate (SDS) suppressed beads in electrospun PVA or PEO fibers. Lin *et al.* [20] studied effects of a non-ionic surfactant, Triton X-405, on the electrospun fibers were also studied. The addition of Triton X-405 did not eliminate the fiber beads, but reduce the bead numbers and changed the morphology. Effects of electrospinning process and properties of polymer solutions, especially conductivity of solution should be considered.

2.6 Applications of electrospinning

Due to the ease of manufacturing, versatility, high surface area, and high porosity of the products and many other benefits, electrospinning has been applied in various applications. In this section, these applications shall be discussed in more details.

2.6.1 Drug deliveries

Electrospinning provides great flexibility in selecting matrix materials for drug delivery. Both degradable and non-degradable polymers can be electrospun into nanofibers and loaded with drugs. Accordingly, due to the diverse material selection, variety of drugs can be encapsulated including antibiotics, anticancer drugs, proteins and DNA. The formation of drug delivery system can be changed also, for example, into a monolithic system by electrospinning a mixture of drug and polymer solution and reservoir system by co-axial electrospinning. These techniques can be used to control the drug release kinetics [69].

Kenawy *et al.* [70] successfully electrospun poly(ethylene-co-vinylacetate), poly (lactic acid) and blends together with tetracycline hydrochloride. In addition to, it was reported that more than 50 different electrospun drug delivery systems were studied [2-3, 70]. Most of them were just performed *in vitro*. Currently, the major opportunity for this area has been in real *in vivo* applications. The drug loaded fibrous mats can be used as transdermal drug delivery, wound dressing, and direct

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local attachments. So far, the better understanding of drug/polymer/tissue interaction is also critical [70-71]. Further, drug diffusion into body circulation is another significant issue. With more *in vivo* tests, the electrospinning process can be designed to obtain the desired drug release profiles.

2.6.2 Tissues engineering

Structural mimics of extracellular matrix, electrospun nanofibers were used to prepare as scaffold for cell growth in the area of tissue engineering and tissue regeneration [72-75]. A great number of polymers, including biodegradable polymers (e.g., polylactide), non-degradable polymers (e.g., polyurethane) and natural polymers (e.g., collagen), have been electrospun into porous non-woven mats to support cell proliferation. Most of the research focused on skin, blood vessel, bone, nerve and cartilage tissue engineering. Attempts to replicate complicated nature of native ECM have led to electrospinning of a wide range of fiber formations and compositions, as well as tailored biological, chemical and mechanical properties of the nanofibers. Qiu and coworkers [76] synthesized and electrospun copolymers of caprolactone and lactide nanofibers as scaffolds for vascular tissue engineering. Ma *et al.* [77] also studied surface modified electrospun PET fibers intended for blood vessel engineering. A rotating frame cylindrical collector was used by Zhu *et al.* [78]. It was used to produce highly porous nanofiber mats for skin tissue engineering. Chen *et al.* [79] proved that electrospun collagen/chitosan nanofibers had both biocompatibility and activity for wound healing. Prabhakaran *et al.* [80] prepared PCL/collagen nanofibers by electrospinning in aim of nerve tissue engineering. Pure hydroxyapatite (HA) nanofibers were made by electrospinning and further removal of polymers. The resulting HA fibers were highly crystallized and capable to guide bone regeneration [81]. Researchers also immobilized growth factors on electrospun poly(lactic-co-glycolic acid) (PLGA) as tendon and cartilage tissue scaffolds [82]. Thus, the capability to generate porous structures with large surface area and versatility to modify bulk and surface properties makes electrospun nanofibers great candidates for tissue engineering applications.

2.6.3 Antibacterial materials

Electrospun nanofibers containing antibacterial agents can be also prepared easily. Jin *et al.* [83] directly incorporated silver nanoparticles in polymer solution, and then conducted electrospinning to make nanofibrous mats with excellent biocidal activity. Silver nitrate was also incorporated in polymer nanofibers by electrospinning, and further reduced its size into Ag nanoparticles [84]. Silver-imidazole complexes also enhanced their antibacterial performance by being loaded

in electrospun fibers [84-85]. The fiber mats slowly released nanosilver, and as a result, showing sustained bacteria killing behavior. Ren *et al.* [86] loaded N-halamine onto polyacrylonitrile nanofibers with “rechargeable” antibacterial activity. This research showed that electrospun fiber mats could be fascinating carriers for biomedical materials.

2.6.4 Filters and membranes

With controllable porous structures and fiber surface morphology, electrospun nonwoven mats are one of promising materials for filtration applications, even ultrafiltration. Polysulfone [87], poly(vinyl alcohol) [88], poly(acrylonitrile) [89], and other polymers have been applied in order to separate particles or solvent from bulk. Among them, the most efficient and realizable technique is the multi-layers setup [90-91]. The support layer provides mechanical strength. Electrospun layer exhibited the ability of separating water and oil can be developed by using some techniques, such as, particle decoration [92] and/or co-axial electrospinning [93]. Then, the electrospun membranes with superhydrophobic property might be fabricated. These membranes could be potentially useful not only in ultrafiltration, but also in self-cleaning textiles and construction materials. Electrospun proton exchange polymers are also good candidates for fuel cells membranes [92]. Furthermore, TiO_2 nanofibrous membranes were prepared via electrospinning with removable polymer template, intended for photovoltaic applications [93] and solar cells [94]. Potential useful applications include ultrafiltration, self-cleaning textiles and construction materials. Electrospun proton exchange polymers are also good candidates for fuel cell membranes [92]. Furthermore, TiO_2 nanofibrous membranes were prepared via electrospinning with removable polymer template, intended for photovoltaic applications and solar cells [92].

2.6.5 Sensors

Electrospun nanofibers have been investigated as a variety of sensors, including chemical sensors, optical sensors, and biological sensors. There are two major approaches, i.e., direct electrospinning of active polymers and loading/conjugating active compounds, including reactive small molecules, fluorescent dyes or dots, and enzymes, on electrospun fibers. Aligned electrospun fibers showed even higher sensitivity and selectivity. Yoon *et al* [89] successfully electrospun polydiacetylene-embedded nanofibers used as a colorimetric assay for organic solvents.

2.6.6 Catalysts

Similar to sensor applications, electrospun nanofibers with reactive compounds can be used as catalysts or catalyst supports. It has been well known that catalysts are more active with increasing the surface area of the catalyst per unit volume. As mentioned above, one of the important advantages of nanofibers is their high surface areas, which make them tremendously applicable in modern catalysis. Zhang et al, [95] prepared Fe-TiO₂/SnO₂ hybrid nanofibers by electrospinning as a photocatalyst for environmental remediation. Electrospun nanofibers can also play a protective role in maintaining the activity of the nano-catalyst. Not only organic and inorganic catalysts can be loaded on electrospun fibrous mats, but also enzymes and other bio-catalysts. For example, Sakai *et al.* [95] successfully immobilized lipase on polystyrene nanofibrous mats with enhanced performance application.

2.6.7 Analytical chemistry

Nanomaterials have emerged as having excellent properties for analytical chemistry applications due to their large surface area to volume ratios, and availability of a wide variety of chemical and morphological modification methods. In analytical chemistry, electrospun nanofibers were studied as a platform for low resolution separation or as a chromatographic sorbent. Moreover, many researchers have also studied the electrospun fibers for using in detection systems as colorimetric probes [96].

2.7 Bioplastics

Most of commodity plastics used in today are based on fossil fuels. Mat plastics are non-biodegradable and persist to environment over a long time. The bioplastics obtained from renewable resources have high potentials to support a green economy. Bioplastics can be broadly classified based on raw material sources. Normally, these plastics are classified into three major types, i.e.,

- a) Renewable resource based bioplastics
- b) Petroleum based biodegradable plastics
- c) Plastics from mixed sources (renewable and petroleum)

Classification of bioplastics can be depicted in Figure 2.10 based on the current state of feed stock. It is expected that some of polymers may change from one classification to another on the basis of the raw material sources.

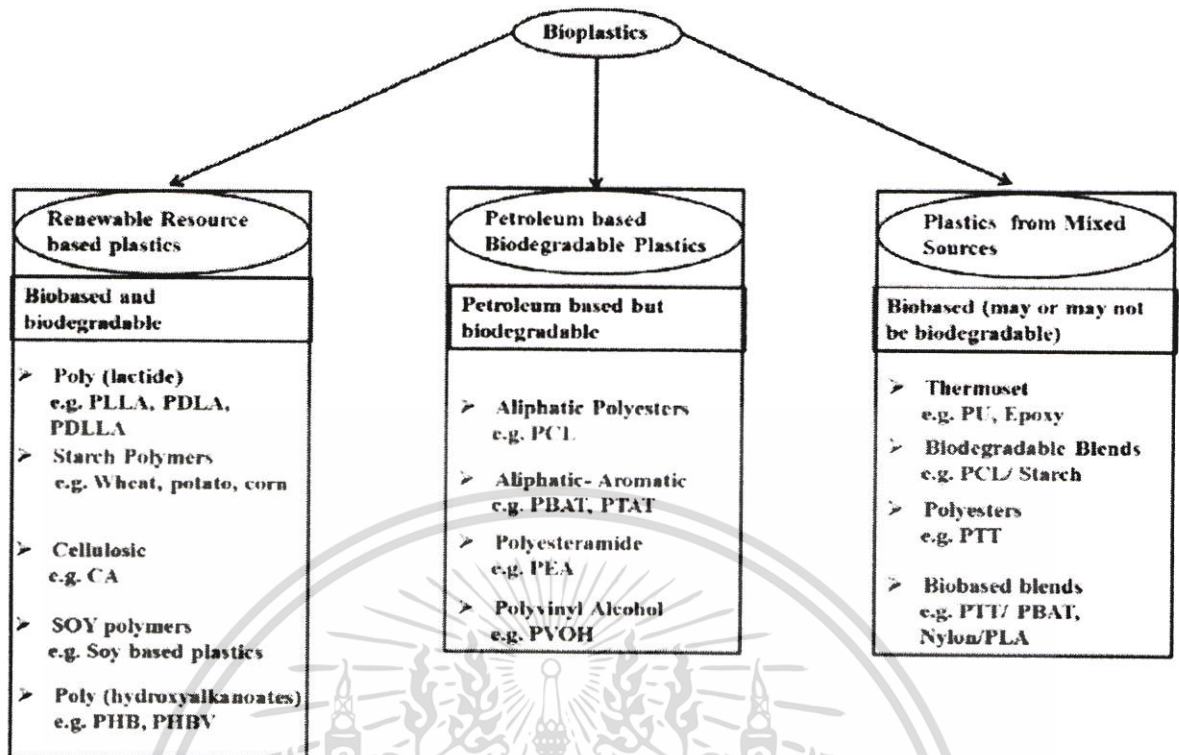


Figure 2.10 Classification of bioplastics based on feedstock [97]

2.7.1 Renewable resource based plastics

Renewable resource based plastics have either their origins from plants or biological resources. Bioplastics related in this class include poly (lactic acid) (PLA), starch, and cellulosic materials [26, 97].

2.7.2 Petroleum based biodegradable polymers

These polymeric materials do not occur in the nature. They are synthesized by means of chemical reactions called polymerization. Polymerization is performed on the monomers that are derived from the fossil fuels. Most of the commercial polymers belong to the category of synthetic polymers. Synthetic polymers can be reclassified based upon their thermal behaviors, monomer sequences, types of monomer, types of reaction, types of process, nature of application and types of structure. Most widespread petroleum based biodegradable polymers are aliphatic polyesters, and polyesteramides [97].

2.7.3 Polymers from mixed sources (renewable and petroleum)

2.7.3.1 Polyesters

Poly (trimethylene terephthalate), PTT (Figure 2.11) is a condensation polyester of 1,3-propanediol and terephthalic acid. 1,3-propanediol monomer can be renewable resource based while terephthalic acid monomer can be based on fossil fuel. Resources of monomers from renewable resources increases the bio-based content of PTT. The renewable resource content of PTT is 37% by weight. This polyester has many desirable properties like heat resistance, strength, stiffness, and toughness. It also has low melt temperatures, and faster cycle time with excellent dimensional stability and chemical resistance [97].

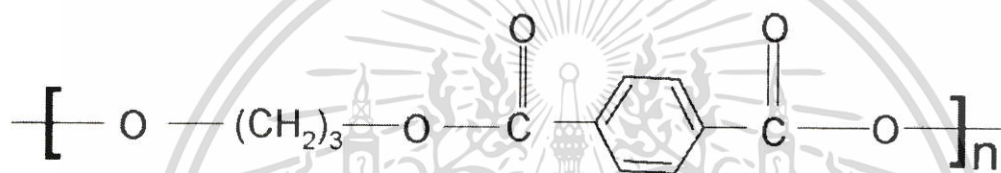


Figure 2.11 Structure of poly (trimethylene teraphthalate), PTT [97]

2.7.3.2 Thermosets

This happens due to crosslink reaction during the formation of thermoset. Examples of thermosets are unsaturated polyester resins, epoxy resins, and urethane resins. Bio-based thermoset is a terminology for a thermoset in which certain portion is produced from renewable resources. Polyester resins are made of a glycol and an unsaturated acid. An unsaturated polyester resin being blended with derivatized vegetable oil has been used as a matrix material for composite for applications in the housing structures. Polyurethanes (PU) are a class of thermosets that are made by the reaction of an isocyanate and a polyol. The isocyanate component is always derived from the petroleum resources but the polyol component has a potential to be derived from bioresources. Bio-based epoxy is another class of thermoset that is gaining popularity in the recent times. Blending epoxidized vegetable oil with petro-based epoxy resin can result in bio-based epoxy resin [97].

2.8. Poly (butylene succinate) (PBS)

Poly (butylene succinate) (PBS) and its copolymers are commercially available aliphatic polyesters with interesting properties, including biodegradability, melt

processability, and good mechanical and thermal properties. It is a highly crystalline polyester. Figure 2.12 shows a typical structure of PBS. The tensile yield strength of injection molded specimen has been reported in range of 30–35 MPa [97]. It has high elongation at break with very low modulus (~450 MPa). The lack of appropriate stiffness-toughness value makes PBS unsuitable for many applications. Various properties of PBS can be tailored by random copolymerization with various chemical reagents in presence of the suitable catalysts [27, 97-98]. Titanium compounds display the highest catalytic activity for polyester from poly condensation reactions [27, 97].

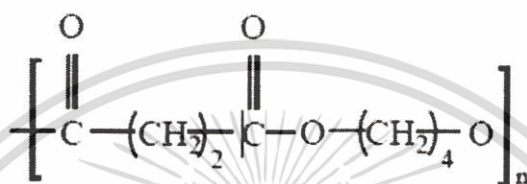


Figure 2.12 A typical structure of poly (butylene succinate) (PBS) [26-27]

The word-wide interest bio-based monomers have become accelerated developments in the fermentation technology. One of the top twelve bio-based chemicals that are produced from sugars and have potential market value is succinic acid (SA) [26-27, 97-99]. Succinic acid is used as a monomer for the production of poly(butylene succinate), (PBS). Reduction of succinic acid (SA) further gives 1,4-butanediol (BDO). BDO is another monomer that is used in synthesis of PBS. It can be fully bio-based plastics. It has been reported that polyolefins can be substituted by PBS in some applications [26-27, 97].

Recently, a copolymer, poly (butylene succinate-co-adipate) (PBSA) has been developed which has better thermal stability. Copolymerization with adipic acid gives a particularly useful copolymer: poly (butylene succinate-co-adipate), PBSA. PBSA has unique properties depending on the amount of adipic acid monomer in the chains. Figure 2.13 shows a general structure of the copolymer. The values of 'x' and 'y' in the structure shown in the Figure 2.13 can be varied to give aliphatic polyesters of various structures and properties. Table 2.2 shows various types of polyesters that are possible with the variation of 'x' and 'y'.

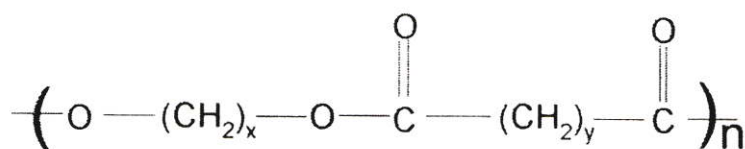


Figure 2.13 General structure of aliphatic copolyesters [97]

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ไม่ว่ากรณีใดๆ ทั้งสิ้น อีกทั้งห้ามมิให้ดัดแปลงเนื้อหา และต้องอ้างอิงถึงเจ้าของเอกสารทุกครั้งที่มีการนำไปใช้

Table 2.2 Values of ‘x’ and ‘y’ for aliphatic polyester [97]

x	y	Name of the aliphatic polyesters
2	2	Poly (ethylene succinate)
3	2	Poly (butylene succinate)
4	2,4	Poly (butylene succinate-co-butylene adipate)

Table 2.3 shows various thermal properties of PBS and its copolymers. Melting point (T_m) and glass transition temperature (T_g) of PBSA are closely related to the copolymer contents. PBSA with 20% adipic acid has shown a decrease in melting point (Table 2.3). PBS under trade name “Bionolle[®]” was first commercially manufactured by Showa High Polymer Company, Japan [26-27, 97-99]. Bionolle[®] is aliphatic polyester. Its process ability is similar to the conventional resins like polyethylene. It is one of the most suitable materials for processing into films which can be used to make agricultural films, shopping bags, compost bags, and so on.

Table 2.3 Thermal properties of PBSA [27]

PBS/PBSA-x	T_g (°C)	T_m (°C)	% Crystallinity
PBS/PBSA-0	-18	112	61.1
PBSA-5	-21	108	87.0
PBSA-10	-23	103	65.7
PBSA-15	-27	99	72.3
PBSA-20	-34	92	53.9

Note: Degree of crystallinity calculated from DSC considering melting enthalpy of completely crystalline material as 110.0 J/g. PBSA, where x is a amount of adipic acids (%) [27]

2.9 Thin layer chromatography

Thin layer chromatography (TLC) is a simple and important technique commonly used in analytical fields, such as, synthetic chemistry, environmental analysis, food, clinical and pharmaceutical industries. TLCs were originally developed in the 1950s, also called planar chromatography [100-101, 103]. Stationary phases of TLC can be made from a variety of materials such as alumina, cellulose and silica gel. These materials were coated on solid supports so called TLC plate. The analysis in TLC is carried out by spotting mixtures well above the edge of the device, placing that edge into a chamber in contact with the mobile phase, and allowing the solvent to move the analytes through the media by capillary action. As the mobile phase rises up the TLC plate by capillary action, the components from analytes dissolve in the solvent and move up along the TLC plate. Individual components move up at different

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ไม่ว่ากรณีใดๆ ทั้งสิ้น อีกทั้งห้ามมิให้ดัดแปลงเนื้อหา และต้องอ้างอิงถึงเจ้าของเอกสารทุกครั้งที่มีการนำไปใช้

rates, depending on intermolecular forces between the component, the stationary phase and the mobile phase [37-38]. The movement of the mobile phase through the stationary phase is referred to as the development step. The record of the detector response plotted against the separation distance is called a densitogram. Figure 2.14 shows example of development step and densitogram of separation of six dyes [33]. Differential migration is results of varying degree of affinity of the mixture component between of stationary phase and mobile phase. Various separation mechanisms are involved predominant adsorption and absorption.

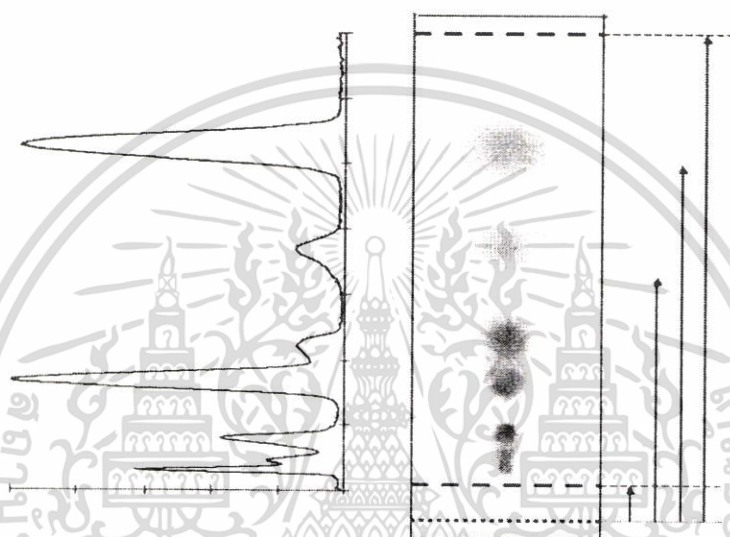


Figure 2.14 Separation of six dyes (CAMAG III mix, no. 032.8003), with the relevant densitogram, on a SiO_2 plate, developed with toluene. With increasing R_f values: Ciba F-II (violet), indophenol (Indigo blue), Ariabel red (red), Sudan blue II (blue), Sudan IV (Scarlet red) and N,N-dimethylaminobenzene (yellow) [33]

Thin layer chromatography (TLC) is a broad categorization that also encompasses other techniques like high-performance TLC (HPTLC) and ultrathin layer chromatography (UTLC). HPTLC first developed in the 1970s [98-99] and takes advantage of stationary phases with smaller dimensions, as well as instrumental methods for spotting the sample and analyzing the resulting chromatogram. The advent of HPTLC allows for thin layer chromatography to be used for quantitative analysis as well as qualitative analysis. Ultrathin layer chromatography (UTLC) was developed in 2001 to further improve sensitivity and reduce analysis time and amount of consumable required for conventional TLC. Generally, TLC plates are composed of a sorbent layer with a thickness that ranges from 100-400 μm . In contrast to new UTLC plates with nanostructure are created by using a monolithic silica gel with a thickness of about 10 μm . UTLC devices have been reported to have

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ไม่ว่ากรณีใดๆ ทั้งสิ้น อีกทั้งห้ามมิให้ดัดแปลงเนื้อหา และต้องอ้างอิงถึงเจ้าของเอกสารทุกครั้งที่มีการนำไปใช้

lower limits of detection and faster analysis times but lower resolution when compared to HPTLC. A comparison information and performance separation of three planar modes have been shown in Tables 2.4-2.5. Table 2.6 shows the retention behavior, efficiency, migration times, detection limits, and solvent consumption of UTLC plates compared with the corresponding data of HP-TLC and TLC silica gel 60 precoated layers by the separation of caffeine and paracetamol [33, 104-105].

Table 2.4 Comparisons of characteristic information of three planar chromatography modes [33]

Modes of planar chromatography	TLC	HPTLC	UTLC
Plate size (cm)	20×20	10×10	6×3.6
Separation time (min)	30-200	3-20	1-5
Development distance (cm)	7-15	3-7	1-3
Layer thickness (µm)	100-250	100-200	10-35
Application volume (µl)	1-5	0.1-0.5	0.01-0.1
UV-Vis detection limit (ng)	1-5	0.1-0.5	0.01-0.1

Table 2.5 Comparisons of detection limits, migration times and solvent consumption in TLC, HP-TLC and UTLC [33]

Type of layers	Detection limit for caffeine (ng)	Migration time (s)	Solvent consumption (ml)
TLC	25	935	100
HP-TLC	10	385	40
UTLC	1	105	3

Table 2.6 Comparisons of hR_f and plate height in TLC, HP-TLC and UTLC [33]

Type of layers	hR_f		Plate height (µm)		Resolution
	Caffeine	Paracetamol	Caffeine	Paracetamol	
TLC	10.7	32.4	172	52	4.1
HP-TLC	13.3	36.7	50	50	4.6
UTLC	15.0	45.0	104	80	2.1

2.9.1 Measurement of chromatographic system efficiency

- Model of theoretical plates

The model of theoretical plates begins from the theory distillation model. It was also adapted for chromatographic processes by Martin and Synge [33]. This model has been recognized to be useful in the highly sophisticated column techniques e.g. gas chromatography (GC) and high liquid performance chromatography (HPLC). The demand for the concept of theoretical plates in TLC seemed less in the portion to the comparatively lower separation efficiency of this method. In view of the recent and successful attempts to enhance efficiency in the field also, the idea of theatrical plates applied to TLC for the first time became actually and fully relevant. Broadening of chromatographic spot can be simply explained in terms of the numbers of theoretical plates given the chromatographic system [33].

$$N = 16 \left(\frac{lZ}{W} \right)^2 \quad (2.1)$$

where l and Z are the migration lengths of the mobile and solute, respectively. W is the width of chromatographic spot that is on the direction of mobile phase (see Figure 2.15).

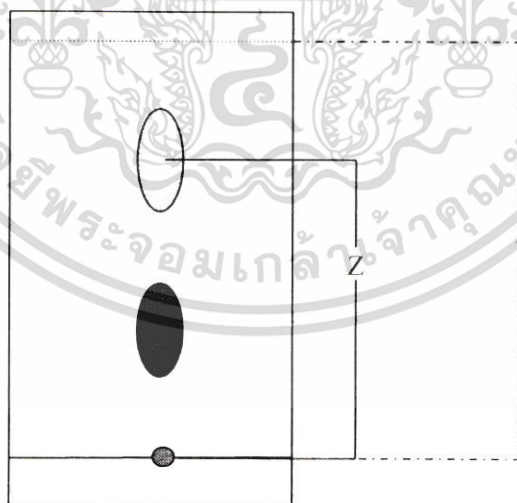


Figure 2.15 Thin layer chromatographic parameters used in the calculation of the theoretical plate number: Adapted from[33]

Although the value of N attained for different solutes on the same chromatographic plate proved to coincide fairly well, they usually differ significantly from the analogous values characteristic of the another plate type, For this reson, เอกสารนี้เป็นเอกสารที่สงวนไว้สำหรับการใช้งานเพื่อการศึกษาเท่านั้น ไม่อนุญาตให้นำไปใช้ประโยชน์ด้านการค้า ไม่ว่ากรณีใดๆ ทั้งสิ้น อีกทั้งห้ามมิให้ดัดแปลงเนื้อหา และต้องอ้างอิงถึงเจ้าของเอกสารทุกครั้งที่มีการนำไปใช้

the quantity N can be regarded as an approximate measure of the separating efficiency of the chromatographic plates. It is proportional to the migration length of the mobile phase l , so that, the Z/w ratio being constant. A increase in l results in an increase of N and better separation. This proportionality of N and l is given by the relationship is given by the relationship:

$$N = \left(\frac{l}{H} \right) \quad (2.2)$$

where H is the so-called HETP value (High equivalent of a theoretical plate). The quantity H or simply the plate height, measures the efficiency of a given chromatographic system per unit length of the migration distance l of the mobile phase. Small H values mean more efficient chromatographic systems and large N values. The main goal of efforts to enhance performance of thin layer is the attainment of small H values and maximum N values. As in the other chromatographic techniques, the efficiency of a given TLC system is better, i.e. H is smaller for:

- smaller particles of the stationary phase or supports
- lower mobile-phase flow rates
- less viscous mobile phase
- small solute molecules.

- Van Deemter equation

The simplest measure of spot broadening was introduced in the form of quantity H , the plate height. The Van Deemter equation attempts to estimate the relative contributions of Eddy and molecular diffusion, and the effects of mass transfer, on H . It is an empirical, originally established for column chromatographic techniques but valid also for thin-layer chromatography. The Van Deemter relationship can be written in the complete version [33].

$$H = A + \frac{B}{u} + Cu + D \quad (2.3)$$

where u is the flow rate of the mobile phase and A , B , C and D are the equation constants, measuring contribution of the different spot-broadening process to the quantity H . The effects of Eddy diffusion and mass transfer on the following mobile phase are described jointly by A . The molecular diffusion is reflected in B , while C and D correspond to the effects of mass transfer in the stagnant mobile and stationary phase, respectively. The constants A , B , C and D depend mostly on the parameters of the microporous solid, but they are also influenced by the nature of

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the solute and the mobile phase and by the working temperature of the chromatographic system.

- **The Retardation Factor (R_f) [33]**

The R_f factor is used for the qualitative evaluation of a TLC separation. It is the quotient of the distance of the substance zone from the sample origin to the front of the mobile phase (Z_f). Historically, Goppelsroder was the first person to use this R_f value (relation to front expression) to characterize planar separations:

$$R_f = \left(\frac{Z_s}{Z_f - Z_0} \right) \quad (2.4)$$

where

Z_s = distance of the substance zone from the sample origin (mm)

Z_f = solvent front migration distance (mm)

Z_0 = distance between immersion line and sample origin (mm)

By definition, the R_f value cannot exceed 1. To avoid the decimal point, the R_f value is sometimes multiplied by 100 and then described as the hR_f value. The value of the retardation factor in a given separation system at constant temperature depends entirely on the characteristic properties of the separated substances. It is important for identification purposes that R_f values are accurate and reproducible, but this is difficult to achieve, since it is almost impossible to adequately control all the experimental conditions that influence the separation process (Figure 2.16). This problem is avoided by defining a retardation factor for a standard substance (R_{st}) that has been already separated in the system.

$$R_{st} = \left(\frac{Z_s}{Z_{st}} \right) \quad (2.5)$$

where

Z_s = distance of the substance zone from the sample origin (mm)

Z_{st} = distance of the standard substance zone from the sample origin (mm)

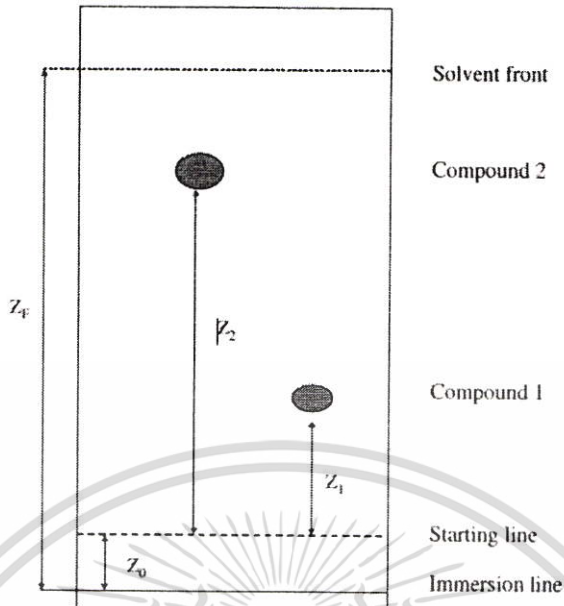


Figure 2.16 Calculation of R_f values [33]

- The Thermodynamic R_f' Factor

While an empirical R_f' value can be provided from a densitogram, the thermodynamic R_f' value (also known as the true R_f' value) correctly represents the behavior of the substance in the separation system. The thermodynamic R_f' value is defined as the fraction of time the analyte is dissolved in the mobile phase (t_m) in relation to the total development time (t_{ms}) [33, 104-105].

$$R_f' = \left(\frac{t_m}{t_m + t_s} \right) \tag{2.6}$$

where
 t_m :time analyte is dissolved in the mobile phase
 t_s :time analyte is associated with the stationary phase

The relationship between the mass of the substance in the mobile and stationary phases is independent of time. By assuming a constant distribution between phases, the mass distribution for an analyte is described by:

$$R_f' = \left(\frac{m_m}{m_m + m_s} \right) \quad (2.7)$$

where

m_m = sample mass in the mobile phase

m_s = sample mass in the stationary phase

The empirically measured R_f values are only identical with the thermodynamic R_f' values if one of the following conditions can be applied:

- If the phase ratio remains constant for the whole layer.
- If the mobile phase composition does not change during development.
- If the stationary phase is free of solvent prior to development.
- If the solvent front velocity is the same as the mobile phase velocity at the spot position.

Since these conditions are never fulfilled in the real world, the observed R_f value will always be smaller than the “true” or thermodynamic R_f' value. R_f values ranging from 62 to 100% of the thermodynamic R_f' values are quoted in the relevant literature [33, 104-105]. A reasonable approximation for the thermodynamic R_f' value is obtained by multiplying the observed R_f value by 1.1. Moreover, here the R_f value is used without differentiating between the “measured” or “thermodynamic” values. If not mentioned further, the abbreviation R_f is taken to mean a correctly measured R_f value identical with the thermodynamic value.

2.9.2 Development of electrospun fibers for thin layer chromatography

Materials, i.e. silica gel, cellulose and mixed cellulose, alumina, polyamides, ion exchange resins, and even intricate nanostructures have been developed and studied for use as a stationary of TLC [35-36, 102, 106]. Recently, electrospun fibers are ones of materials which have proven to be ideal for using in that application [35-36, 106-108]. Clark *et al.* [36] showed a technique for fabricating stationary phase of TLC obtained from electrospun PAN nanofiber. They described that this stationary allowed for a decrease in analysis time as well as a decrease in the volume of solvent needed to perform analyses, also while increasing the efficiency of the separations. Figure 2.17 shows a comparison in the mobile phase velocities of two commercial silica TLC plates and the electrospun PAN UTLC device. Moreover, they [37] showed development and application of electrospun glassy carbon nanofibers for UTLC. This stationary showed very high plate numbers (10,000–100,000 s) and differing selectivity for the analysis of a set of 6 laser dyes as well as complete

Beilke *et al.* [107] demonstrated the applicability of aligned electrospun nanofibers to UTLC analysis. These devices represent a further enhancement in separation efficiency relative to electrosospun UTLC stationary phases while decreasing time of analysis by over 50%. Su-utha [108] prepared the thin layer chromatographic plates that obtained from cellulose acetate (CA) by using electrospinning process. They found that electrospun plates could be successfully applied for the steroid separation with the high resolution when 40:60 (v/v) water-methanol was used as a mobile phase.

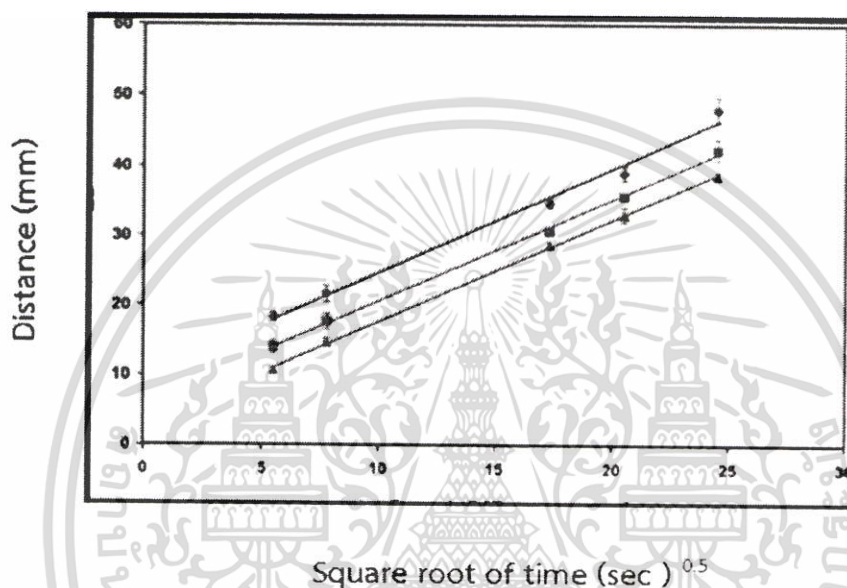


Figure 2.17 Comparison of mobile phase migration distances using varying TLC devices: ▲, commercial silica phase; ■, cyano phase; and; ◆, 400 nm electrospun PAN UTLC phase [37]

2.10 Antimicrobial materials obtained by electrospinning methods

Fabrication of nanofibrous materials with biocide property from electrospinning process has recently gained much attentions [30, 41-42, 84-85]. With basic approaches, i.e., originally antimicrobial polymer and incorporation of exogenous biocide in the fibers with antimicrobial activity can be currently experienced in electrospinning process [39]. The antimicrobial polymeric materials are a class of polymer materials with the inherent ability to inhibit the growth of microorganisms such as bacteria, fungi or protozonans [39]. They can be divided into two main groups, i.e., natural polymers or biopolymers and engineered polymers. Polysaccharide and protein are a classes of biopolymers that can display inherent bioactivity properties. Chitosan is a nontoxic biocompatible and biodegradable polysaccharide that is well known to have antimicrobial activity [39] because it has a

cationic nature in their structures. Antimicrobial activity was associated with the presence of protonated glucosamine fraction in chitosan structure.

On the other hand, engineered antimicrobial polymers are artificial materials generally produced by attaching, inserting or incorporating an active antimicrobial agents into polymer fibers [39]. This is straightforward strategy to get nanofibers with improved protection against bacteria. As a second route is a method that incorporate biocide substance into nanofibers habitually involves solubilizing the substance into the polymer solution prior to electrospinning [39].

2.10.1 Quaternary ammonium chlorides (QACs)

Quaternary ammonium chlorides (QACs) are recognized unique agents in the world of antimicrobial compounds [40]. QACs have molecular structures containing a positively charged nitrogen atom covalently bonded to four carbon atoms. This quaternary ammonium group is responsible for the name of these antimicrobial compounds and also plays a dominant role in determining their chemical behaviors.

-Chemical diversity of Quaternary ammonium chlorides

Quaternary ammonium chloride (QAC) has a quaternary nitrogen atom in their structures. It can be used to kill or inhibit the growth of bacteria. QACs are actually ammonium salts. Like acid salts, these quaternary ammonium salts are colorless, odorless, crystalline solids that have high melting points. Quaternary nitrogen atoms are found in the chemical structures of many naturally occurring substances in living cells, such as choline and others. These substances are generally not toxic to microorganisms [40].

The first antimicrobial quaternary amines synthesized were rather simple, with three methyl groups and one linear, saturated alkyl groups attached to a single, positively charged nitrogen atom (alkyltrimethylammonium chloride) in Figure 2.18. The nonpolar “tail” and polar “head” regions make them similar to soap molecules. However, since soap molecules contain anionic head groups, these cationic molecules were dubbed “invert soaps”. This second type of QAC, namely alkyldimethyl- benzylammonium chlorides (ADBACs), they were the first class of QAC to find acceptance and utilization as disinfectants in medical applications. Recently, chemists added an ethyl group to the aromatic ring, further increasing detergency action and antimicrobial activity [40]. A third class of QAC emerged 30 years later in 1965, when new synthetic techniques were developed to allow the economically feasible formation of twin chain or dialkyldimethylquaternary ammonium chlorides

(DDACs). These QACs exhibit even higher biocidal efficiency than their predecessors [39-40].

In 1938, a creative departure from the relatively simple alkyl groups substituted on the quaternary nitrogen resulted in an entirely different quaternary amine, benzethonium chloride (BEC). The distinguishing feature of this rather complex group is best described by BEC's IUPAC name, N,N-dimethyl-N-[2-[2-[4-(1,1,3,3-tetramethylbutyl)phenoxy]ethoxy]ethyl]benzenemethanaminium chloride. As seen in Figure 2.19, this complex nitrogen substituent contains branched hydrocarbons, phenoxy, and ethoxy components. Ethoxylation increases detergency, and the complex nature of this group enhances the spectrum of activity when compared to more traditional QACs. The unique chemical character of BEC establishes it as a very different fourth class of QACs [40].

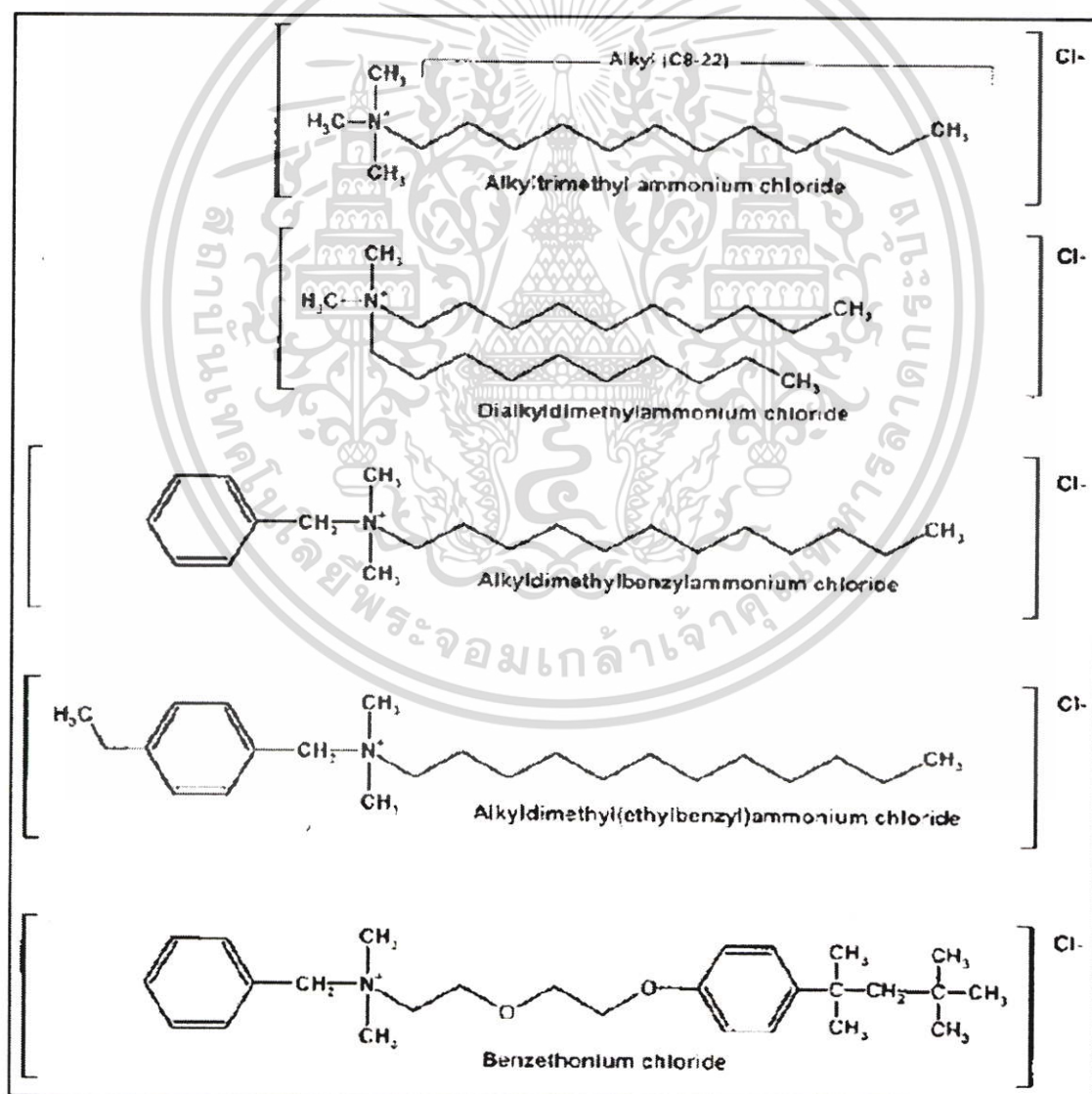


Figure 2.18 Generalized chemical structures of quaternary ammonium chloride compounds with antimicrobial activity [40]

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ไม่ว่ากรณีใดๆ ทั้งสิ้น อีกทั้งห้ามมิให้ดัดแปลงเนื้อหา และต้องอ้างอิงถึงเจ้าของเอกสารทุกครั้งที่มีการนำไปใช้

Benzalkonium chloride, (BAK) is one of the most well known QACs. It is actually a mixture of alkybenzyltrimethylammonium chlorides, differing only in the length of their alkyl groups. While chain length of the various analogs includes C8 to C18, the actual distribution is clearly defined: not less than 40% C12 and 20% C14, with the sum of these two not to be less than 70% of the total [35]. Benzalkonium chloride is most often commercially available dissolved in water or alcohol or mixtures of at either 50% or 80% active concentrations. Benzethonium chloride (BEC) is supplied as a white crystalline, odorless material. Early in BEC's history, a methylated derivative, methylbenzethonium chloride, was also available, but it has all but disappeared from use in the last two decades. Both compounds are soluble in polar solvents such as water, low molecular weight alcohols, glycols and also in nonpolar solvents such as carbon tetrachloride, tetrachloroethane, and benzene. Aqueous solutions of benzethonium chloride are stable within a pH range of 4–7. BEC offers better detergency action than BAK and exhibits different antimicrobial activity.

2.10.2 Chemical structure and mechanism of QAC antimicrobial activity

Antimicrobial activity of QACs extends across a broad spectrum of microbes, including bacteria, yeasts, molds, and viruses. This varies between organisms and efficacy for each organism also depends upon the chemical nature of each QAC. Many investigators have offered explanations for QAC mechanisms of antimicrobial action [40]. Most theories center on the interactions between QACs and the membranes of their target cells [39]. The surfactant natures of these agents suggest that they act as other membrane-active agents, perturbing homeostasis. However, the manner in which they interact with the membrane itself is not always clear. Disruption of membrane integrity has been observed by monitoring the release of intercellular materials following treatment by QACs [40]. Following exposure to one QAC, gram-positive cells released cellular components more rapidly than gram-negative bacteria. Potassium ions were released first, followed by phosphates, then by larger molecular weight molecules. The exact target of attack at the membrane surface is still contested. The negatively charged phospholipids offer a natural target, due to electrostatic attraction. However, the detergent action of QACs works extremely well on nonpolar oils and lipids as well as anionic lipids. QACs also have a strong affinity for proteins. Subsequent denaturation of proteins or inhibition of important transport proteins may be a primary or complementary mechanism of biocidal activity. Further experiments with bacteria revealed the dependence of activity on chain lengths of alkyldimethyl benzylammonium chlorides [40]. Table 2.7 summarizes these results, showing that activity increases as chain length increases

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from C8 to C14. However, as chain length increases beyond this point, activity decreases [40].

Table 2.7 Effects of chain lengths of alkyl dimethyl benzyl ammonium chloride on the minimal inhibition concentration [40]

Alkyl chain length (Carbon)	Minimal inhibitory concentration (ppm)		
	<i>Staphylococcus aureus</i>	<i>Salmonella typhosa</i>	<i>Pseudomonas aeruginosa</i>
8	3000	4500	60000
9	800	1400	2500
10	450	300	1200
11	160	130	400
12	45	40	120
13	25	20	50
14	15	12	40
15	25	20	70
16	30	25	200
17	170	15	360
18	450	60	1000
19	330	90	1300

Mechanism of antimicrobial agent, therefore, can be briefly summarized which is accomplished through a series of steps, as shown in Figure 2.19. First, the polymer with inherent bioactivity agent must adsorb onto the bacterial cell wall. Most bacterial surfaces are negatively charged, therefore the adsorption of polymeric with cationic structure has proved to be more effective than adsorption of polymeric anions. The antimicrobial agent must then diffuse through the cell wall and adsorb onto the cytoplasmic membrane. Small molecule antimicrobial agents excel at the diffusion step due to their low molecular weight. Meanwhile adsorption is better achieved by antimicrobial polymers. Cytoplasmic membrane and subsequent leakage of cytoplasmic constituents are disrupted leading to the death of the cell [109].

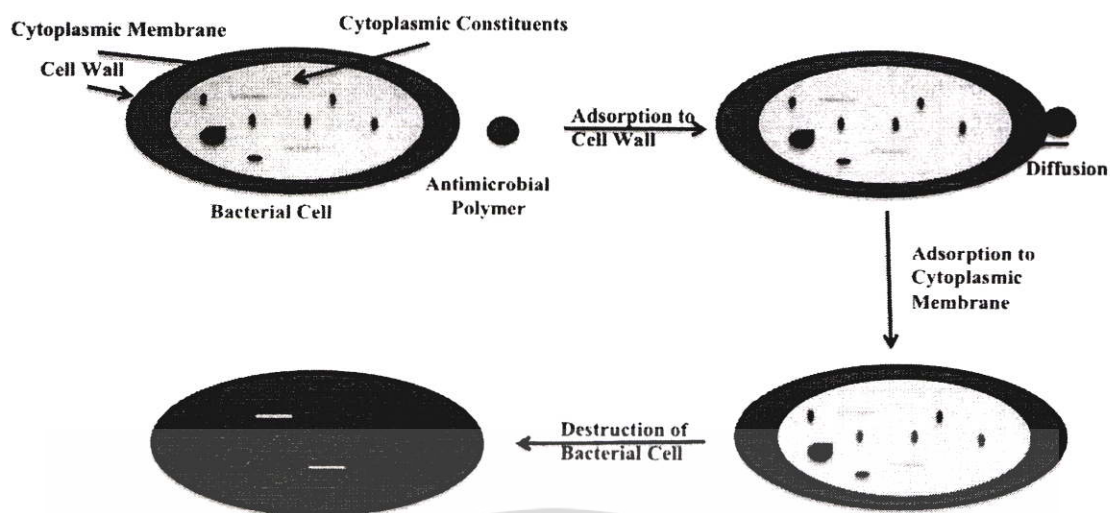


Figure 2.19 A schematic of how an antimicrobial polymer kills a bacterial cell [109]

2.11 Literature reviews

Lin T. *et al* [20] studied charge effects of cationic surfactants on the elimination of fiber beads in the electrospinning of polystyrene (PS). Cationic surfactants, i.e., dodecyltrimethyl ammonium bromide (DTAB) and tetrabutylammonium chloride (TBAC) were added in PS solution. Figure 2.20 shows that the addition small amount of cationic surfactants TBAC has effectively stopped the formation of beaded fibers during the electrospinning. However, the presented non-ionic surfactant DTAB was not able to stop the bead fibers formation, but the bead numbers were reduced. Moreover, they described that concentration of the cationic surfactant increased leading to the thin fiber. Surfactants were also found to improve the solution conductivity, but had no effect on the viscosity. Meanwhile, the effect of the surfactants on the surface tension of solutions was studied. They reported that DTAB led to a slight decrease in the surface tension whereas TBAC did not show influence on the surface tension as increased concentration of surfactants.

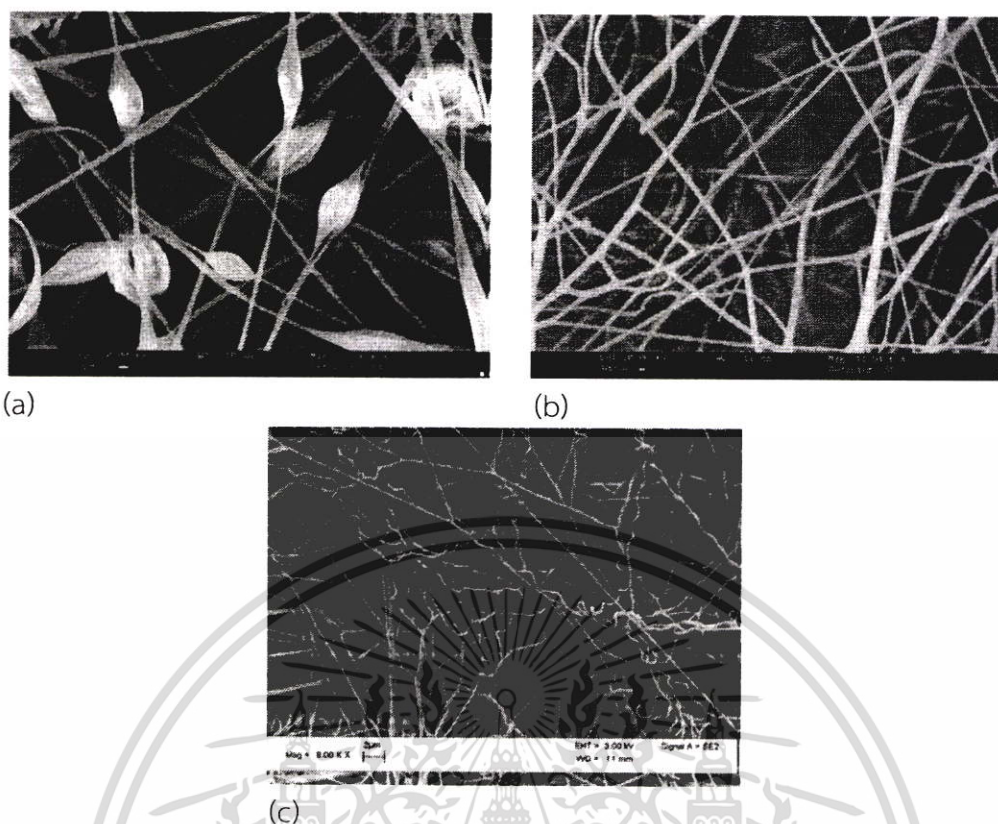


Figure 2.20 Morphology of polystyrene nanofibers electrospun from solution in DMF/THF 1:1 w/v with and without the cationic surfactants (a) 10% PS solution without surfactant, (b) and (c) PS solution with 10% mmol/L TBAC and DTAB, respectively [20]

Choi J. S. *et al.* [65] investigated effects of organosoluble salts on the nanofibrous fibers of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) electrospun from PHBV solution in chloroform with and without organic salts. Ultrafine PHBV fibers were obtained by electrospinning of 20 % (w/v) PHBV solution in chloroform without salts and the resulting fiber diameters were in the range of 1.0–4.0 μm . Small amounts of benzyl triethylammonium chloride (BTEAC) were added to the PHBV solution. It was able to reduce the average diameters of fibers at around 1.0 μm . Meanwhile, straighter shape and smaller diameters of the electrospun fibers were observed. Moreover, the addition of BTEAC to PHBV solutions caused significant increase in conductivity of PHBV solutions with increasing amounts of BTEAC up to 3 wt.% (Figure 2.21). Continuous fibers were obtained from the electrospinning of 15% PHBV solution with 2 wt.% BTEAC. Moreover, it was found that the concentration of the PHBV solution was a major parameter affecting the morphology and diameter of the electrospun PHBV fibers as shown in Figure 2.22.

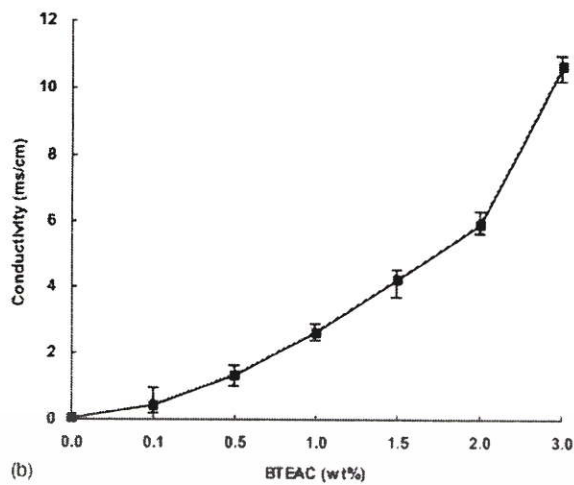


Figure 2.21 Variations of conductivity of the PHBV solution in chloroforms according to the content of BTEAC [65]

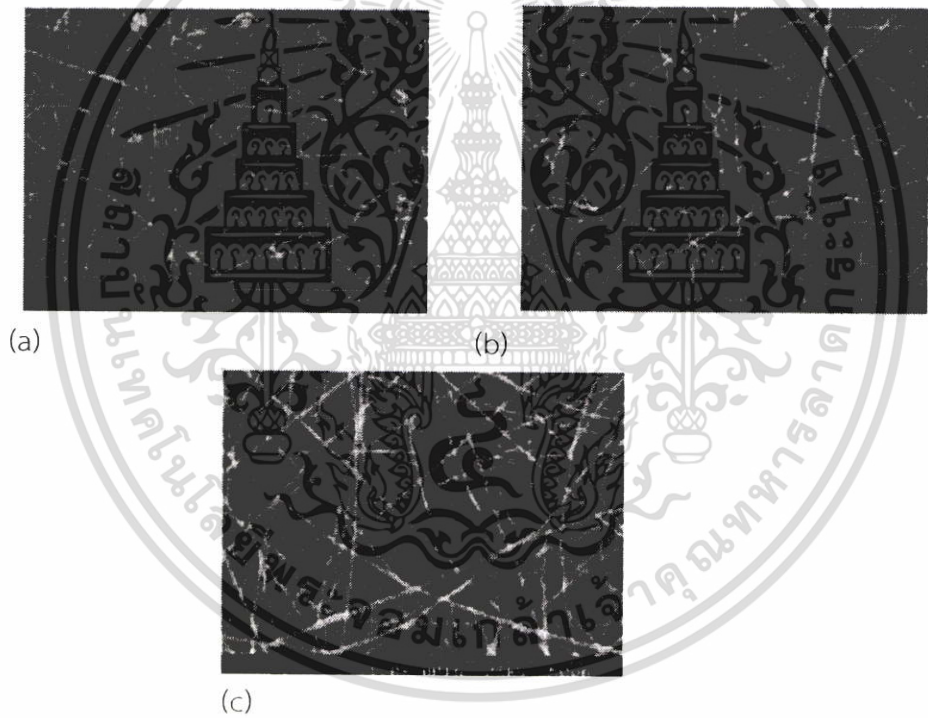


Figure 2.22 SEM micrographs of PHBV fibers electrospun at different PHBV concentrations with 2 wt.% BTEAC: (a) 10%; (b) 15%, and; (c) 20% (w/v) [65]

Qin X-H. *et al.* [18] investigated effects of different salts on electrospinning of polyacrlonitrile (PAN) solution. The various inorganic salts used in this work included LiCl, NaNO₃, NaCl, and CaCl₂. The results showed that when the salts were added into different concentrations of PAN solution, the order of conductance was LiCl > NaNO₃ > CaCl₂ > NaCl > no salt added. Viscosity and shearing strength of

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electrospinning solutions were slightly affected by the addition of salts (Figure 2.23) and mainly affected by the changes in concentration of PAN solutions. The diameter of nanofibers electrospun by solutions with different salts size down as follows: LiCl > NaNO₃ > CaCl₂ > NaCl. The fibers diameter of those fibers are summarized in Table 2.8.

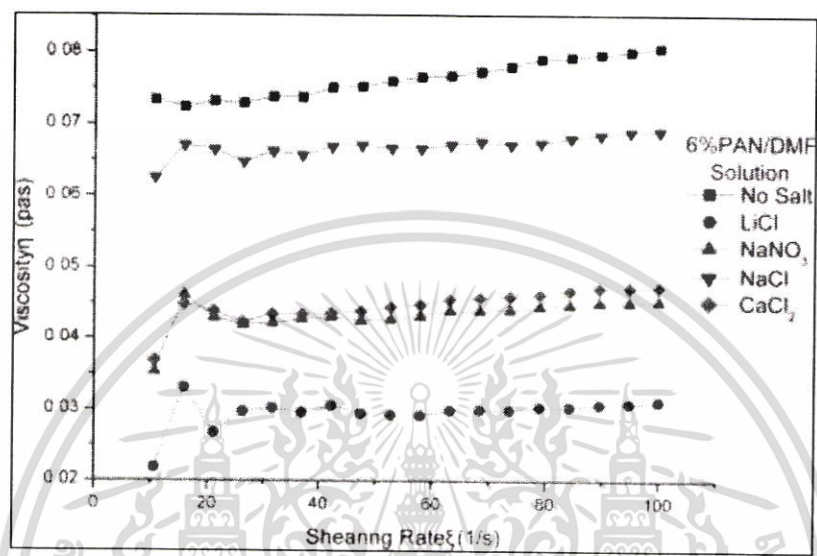


Figure 2.23 Comparisons of viscosity influence of 6 wt % PAN/DMF electrospinning solutions with different salts [18]

Table 2.8 Mean values of PAN fibers diameters electrospun from solutions with different salts [18]

Type of inorganic salts	Mean diameter of electrospun fibers
LiCl	473
NaNO ₃	462
CaCl ₂	444
NaCl	410

Seo J. M. *et al.* [110] reported the effects of adding small amounts of a room-temperature ionic liquid (RTIL), hexamethylimidazolium chloride (HMIMCl), on the electrospinning process of poly(L-lactic acid) (PLLA) in chloroform, and effects of quaternary ammonium salt, triethylbenzylammonium chloride (TEBAC). Effects of adding HMIMCl, an RTIL with delocalized charges, and TEBAC, a quaternary ammonium salt, were evaluated on the solution properties, electrospinning process, and fiber diameter and morphology of PLLA. The key morphology could be observed from increasing the solution conductivity by adding salts in this work. The fiber aggregation process was possibility observed due to the increased conductivity of solution. These results could be led to occur back building and the fiber fusion. It

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began to occur closer to the needle and before all the solvent has evaporated. It can produce larger, rather than smaller diameter fibers. These results dominated by solution conductivity. The greatest difference in the performance of the two salts was a difference in the extent of fiber fusion. The electrospun PLA fiber obtained solution containing HMIMCl was more fusion of fibers as compared with those of PLA solution with TEBAC. The two salts gave different but inconsistent effects on viscosity and surface tension, so even though these properties could affect the fusion process. However, main reason of difference in the extent of fiber fusion may be due more to a difference in the phase of the added salt. State of HMIMCl is a liquid solution. It could facilitate fiber fusion after solvent evaporation. In contrast to TEBAC is a high-melting solid during the spinning process may solidifies. Then, the ability of fibers to aggregate and/or fuse were reduced.

Cheng W. *et al.* [111] studied effects of different ionic liquids on the electrospinning of a polyacrylonitrile polymer solutions. Effects of adding small amounts of four different types of ionic liquids, i.e., 1-butyl-3-methylimidazolium chloride (C_4MIMCl), 1-dodecyl-3-methylimidazolium chloride ($C_{12}MIMCl$), 1-ethyl-3-methylimidazolium bromide (C_2MIMBr), and 1-ethyl-3-methylimidazolium phosphate ($(C_2MIM)_3PO_4$) on the solution properties, electrospinning process, and characteristics of polyacrylonitrile (PAN) were investigated. Ionic liquids can be used to control the diameter and morphology of electrospun PAN nanofibers. The addition of different ionic liquids, including C_4MIMCl , $C_{12}MIMCl$, C_2MIMBr , and $(C_2MIM)_3PO_4$, with concentrations ranging between 0.1 and 1.0 wt %, did not much affect the viscosity and surface tension of the PAN polymer solutions. However, the conductivity significantly increased compared to the original PAN/DMF solution, and the conductivity decreased in the following order: $(C_2MIM)_3PO_4$, C_2MIMBr , C_4MIMCl , $C_{12}MIMCl$. However, these values were higher than that of the solution without ionic liquids. Ionic liquids added to the spinning solution formed visible crystals and made the fiber surfaces rough, and some fiber segments underwent partial aggregation. Figure 2.24 shows the relationships between the electrospun PAN/ ionic liquid fiber diameter and the ionic liquid content. The diameters of the PAN/ionic liquid fibers first decreased and then increased in a vibration manner as the content of ionic liquid increased. There existed a regularity between the minimum mean diameter of the PAN/ionic liquid fibers and the structure of the ionic liquid. The PAN/DMF/ $(C_2MIM)_3PO_4$ solution had a relatively high conductivity, and the minimum mean diameter of the PAN/ $(C_2MIM)_3PO_4$ fibers appeared at a relatively low ionic liquid concentration of 0.25 wt %. However, the PAN/ DMF/ $C_{12}MIMCl$ solution had a relatively low conductivity. Minimum mean diameter of the PAN/ $C_{12}MIMCl$ fibers

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appeared at a relatively high ionic liquid concentration of 0.8 wt %. Although the conductivity of the PAN/DMF/C₂MIMBr solution was higher than that of the PAN/DMF/C₄MIMCl solution, the minimum mean diameters of the PAN/C₂MIMBr fibers and PAN/C₄MIMCl fibers appeared at the same ionic liquid concentration of 0.5 wt % because of the similar ionic activities of C₂MIMBr and C₄MIMCl [111].

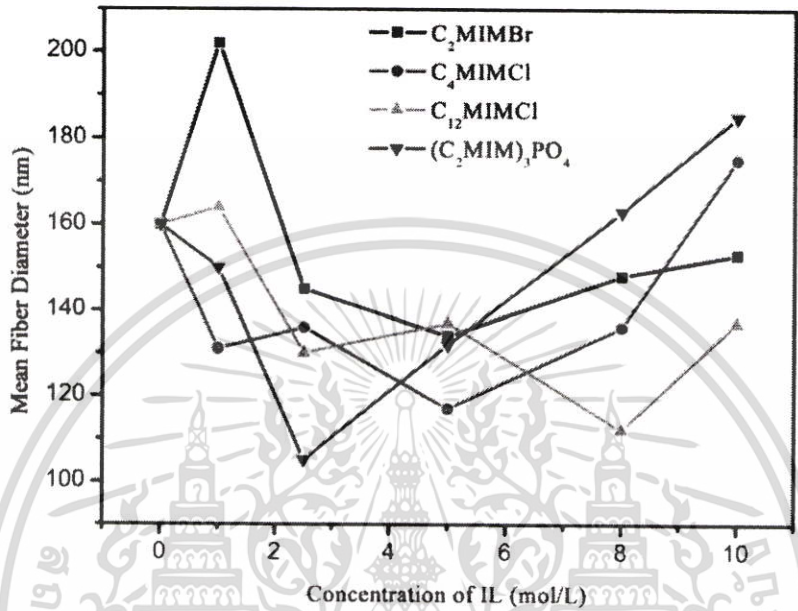


Figure 2.24 Relationship of the mean diameter of the electrospun PAN/ionic liquid fibers and concentration of the ionic liquid [111]

Beilke, M. C *et al.* [107] demonstrated the applicability of aligned electrospun polyacrylonitrile (PAN) nanofibers to ultrathin layer chromatography (UTLC). They hypnotized that UTLC with aligned the electrospun nanofibers. It was able to enhance in chromatographic performance as compared with non-aligned electrospun UTLC plates. Effects rotational speed of drum device used to control the aligned electrospun PAN fiber were decribed in this work. This experiment performed at rotational speeds of 500, 750, 1000, 1250, and 1500 rpm in triplicate. This experiment showed that the aligning the electrospun nanofibers with a rotating drum collector was increased not only the directional orientation of the nanofibers but also the straightness of the individual nanofibers. The electrospun plates that obtained from collected from 750 to 1250 rpm yielded good alignment. However, the 1250 rpm was chosen to prepare AE-UTLC plates because slightly smaller standard deviation of the average fiber alignment between mats were observed. The studying performance chromatography of the aligned electrospun ultrathin layer chromatography (AE-UTLC) was used to compare the electrsospun non-aligned electrospun polyacrylonitrile (E-UTLC) and commercial thin layer chromatography.

The AE-UTLC devices were used to separate a mixture of β -blockers and steroidal

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compounds to illustrate the properties of AE-UTLC. This experimental shown the AE-UTLC devices represented a further enhancement in separation efficiency as compared with E-UTLC phases and commercial TLC. They found that time of analysis of the former nanofibers phase decreased over 50%. Those results were compared with E-UTLC, the former devices provided a more rapid and consistent time of analysis while also showed an increase in efficiency and reproducibility.

Lu T. *et al.* [112] fabricated the polyvinyl alcohol (PVA) ultrathin layer chromatographic (PVA-UTLC) plates by using in-situ crosslinking electrospinning technique. They found that morphology of PVA-UTLC was crosslinked. It was well maintained after soaked in water and the mobile phase used in this study as compared with PVA nanofibers without crosslinking. Meanwhile, the chromatographic efficiency of the UTLC was evaluated by using the fluorescent labeled amino acids (FITLC). These results were compared with commercial silica gel high-performance thin layer chromatography (HPTLC) plate. The selectivity of FITC-labeled amino acids studied on PVA UTLC was different from that on Si-Gel HPTLC except for methionine (met) and glutamine (gln) met/gln. Efficiency development depending on the mat thickness, capillary size, analyte concentration, and analyte volume was studied and optimized. For the three layered thick electrospun ULTC plates, smaller capillary tube and smaller analyte volume applied showed higher efficiency. Analyte concentrations below or equal to 7 mM showed similar efficiency, but 14 mM analyte showed much lower efficiency. The measured efficiency on the PVA ULTC plate was much higher than the efficiency on Si-Gel plate. The separation of unlabeled amino acids showed higher selectivity and four amino acids were baseline separated using a simple and nontoxic ternary mobile phase. Hydrolysis products, aspartic acid (asp) and phenylalanine (phe), of aspartame in diet coke were successfully separated and identified using PVA-UTLC plate. This preliminary study of amino acid analysis also indicated potential use of PVA plate in separations of other biomolecules.

Kim S. J. *et al.* [41] prepared and characterized antimicrobial nanofibrous membrane from poly (carbonate) (PC). They found that addition of small amount of BTEAC to the PC solution caused a significant decrease in the average fiber diameters from 8.1 to 1.0 μm and continuous fiber formation with uniformity without blockage of spinning tip. It was also found that the conductivity of the PC solution was a major parameter affecting the morphology and diameter of the electrospun PC fibers. The PC nanofibrous membrane with BTEAC had an excellent antimicrobial activity and filtration performance. Non-woven membranes of PC ultrafine fibers would be further studied as an antimicrobial filter.

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Chapter 3

Experimental Details

3.1 Chemicals

1. Polybutylene succinate (PBS) Bionolle[®] (Grade 3001G, Showa Highpolymer Co., Ltd.) Some properties of PBS are shown in Table 3.1.
2. Dichloromethane (AR grade, Fisher Scientific Co., Ltd.)
3. Chloroform (AR grade, Carlo Erba Co., Ltd)
4. Methanol (AR grade, Fisher Scientific Co., Ltd.)
5. N,N-Dimethylformamide (AR grade, Carlo Erba Co., Ltd.)
6. Chlorobenzene (AR grade, Carlo Erba Co., Ltd.)
7. Benzyl trimethylammonium chloride (BTMAC) (AR grade, Sigma Aldrich Co., Ltd.)
8. Benzyl triethylammonium chloride (BTEAC) (AR grade, Merck Co., Ltd.)
9. Benzyl tributylammonium chloride (BTBAC) (AR grade, Merck Co., Ltd.)
10. Alkyl ammonium ethyl sulfate (AAES) (Effka[®] 6782) (Commercial grade; BASF Co., Ltd.)
11. Ethyl acetate (AR grade; Lab Scan Co., Ltd.)
12. Hexane (AR grade; Lab Scan Co., Ltd.)
13. Iodine pellets (AR grade; Merck Co., Ltd.)
14. Oleic acid (AR grade, Sigma Aldrich Co., Ltd.)
15. Cholesterol (AR grade, Sigma Aldrich Co., Ltd.)

Table 3.1 Some physical properties of PBS used in this work

Properties	Units	PBS
Density	g/cm ³	1.23-1.26
Degree of crystallinity	%	20 - 35
Melting temperature (T _m)	°C	93 - 95
Glass transition temperature (T _g)	°C	-45
Crystallization temperature (T _c)	°C	50
Melt flow rate (MFR) (190 °C, 2.16 kg)	g/10 min	1.4

Note: Data from the manufacturer

3.2 Equipments

1. High voltage DC power supply (Model UC5-30P, Gamma High Voltage Research, USA).
2. 20-gauge blunt-ended stainless steel needle (outer diameter 0.91 mm)
3. Rotating drum collector
4. Beakers
5. Cylinders
6. Mohr Pipets
7. Aluminium foil
8. Erlenmeyer flask
9. Glass syringe
10. Stirrer
11. Hot air oven (Model UM 400, Memert Co., Ltd.)
12. Scanning electron microscope (SEM; JEOL JSM-6400, JEOL Co., Ltd.)
13. Universal testing machine (UTM; Model LR 100N, Lloyd Instrument Co., Ltd.)
14. Differential scanning calorimeter (DSC; Model DSC1, Mettler Toledo Co., Ltd.)
15. Fourier transform infrared spectrometer (FTIR; Model FTIR Spectrum GX, PerkinElmer Co., Ltd.)
16. Brookfield programmable viscometer (Model TVB-10MW, TOKI SANGO Co., Ltd.)
17. Tensiometer (Model JZYW-200A, Laryee Co., Ltd.)
18. Conductivity meter (Model Jenway 4130, Scientific Co., Ltd.)
19. Compact coating thickness gauges (Model MP0R, Fisher Co., Ltd.)
20. Micropipettes (Model Boeco SA, (Model BOE 9610002 (Measurement range 0.25-2.5 μ L) Boeco (Germany) Co., Ltd.)
21. Thin layer chromatography (TLC) plates silica gel 60GF₂₅₄ (Merck Co., Ltd)
22. High performance optical microscope (Model BX 51M, Olympus Co., Ltd.)

3.3 Procedures

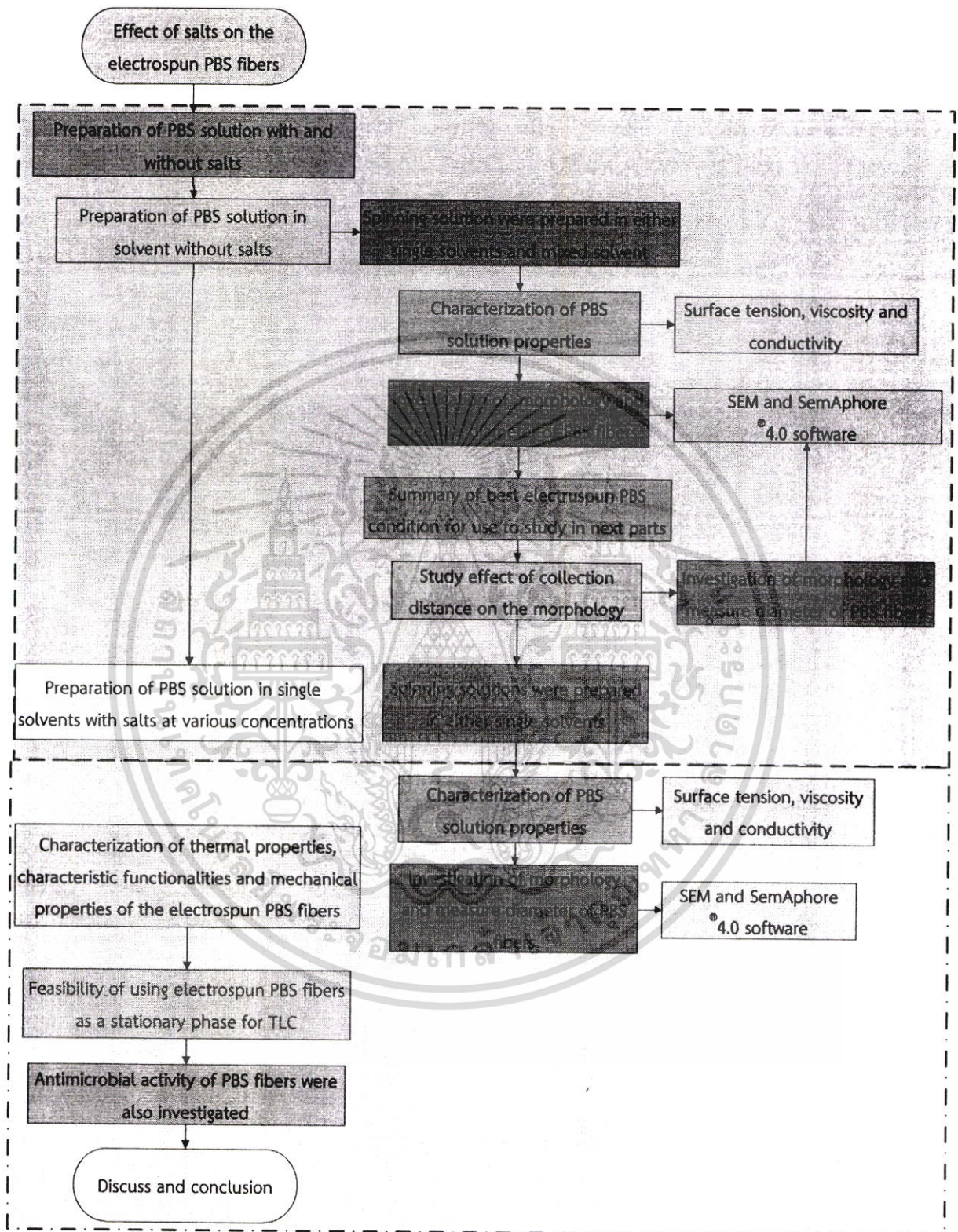


Figure 3.1 Flowchart of thesis research work

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3.3.1 Preparation of PBS solution with and without organic salts

3.3.1.1 Preparation of PBS solution in single and mixed solvent systems.

1) In case of single solvent systems, 8%, 12%, 16%, 20% and 30% (w/v) of PBS solutions were prepared by dissolving 4, 6, 8, 10 and 15 g of PBS pellets in 50 ml of chloroform (CF) and dichloromethane (DCM), respectively.

2) In mixed solvent systems, 12% (w/v) of PBS solution in mixed solvent systems were prepared by dissolving 6 g of PBS in 50 ml of various mixed solvent systems. Ratios of mixed solvents used in this work are summarized and shown in Table 3.2.

3) All PBS solutions were stirred at room temperature for 2 hours by using magnetic stirrer. These solutions were measured for solution properties, i.e., viscosity, surface tension and conductivity. Average solution properties were measured from 3 times. All measured properties of PBS solutions were then used to fabricate ultrafine fiber by electrospinning process, respectively.

Table 3.2 Ratios of mixed solvent systems at 12 % (w/v) PBS concentrations

Mixed solvent systems	Ratios of solvents(v/v)
Chloroform:dichloromethane (CF:DCM)	50:50
Dichloromethane:chlorobezene (DCM:CB)	50:50, 70:30 and 90:10
Chloroform-N.N.-dimelthformamide (CF:DFM)	
Chloroform-methanol (CF:MeOH)	

3.3.1.2 Preparation of PBS solution with organic salts

- Preparation of 12% (w/v) PBS solutions with various amounts of AAES salts

To investigate the effects of alkyl ammonium ethyl sulfate (AAES) on the PBS solution and morphology of electrospun PBS fibers, PBS solutions with the salt were prepared and characterized. Chemical structure of AAES is shown in Figure 3.2.

12% (w/v) PBS in chloroform (CF) and dichloromethane (DCM) with addition of AAES at different concentrations (0.25, 0.5, 1, 2 and 4 % (w/v)) were investigated. 0.125, 0.25, 0.5, 1 and 2 g of AAES salt were dissolved in 50 ml of CF and DCM, respectively.

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ไม่ว่ากรณีใดๆ ทั้งสิ้น อีกทั้งห้ามมิให้ดัดแปลงเนื้อหา และต้องอ้างอิงถึงเจ้าของเอกสารทุกครั้งที่มีการนำไปใช้

All solutions with the salt were stirred at room temperature for 10 minutes. Afterward, 6 g of PBS pellets was dissolved in those solvents and stirred at room temperature using magnetic stirrer for 2 hours.

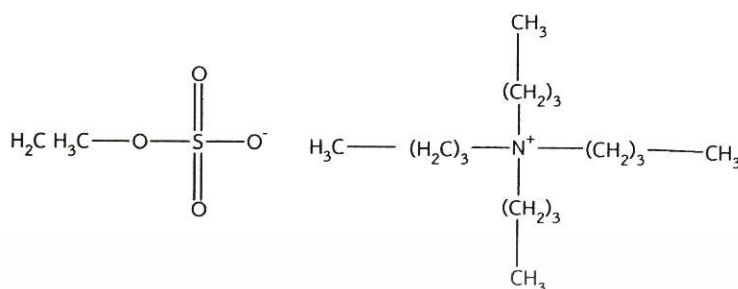


Figure 3.2 A typical structure of alkyl ammonium ethyl sulfate, AAES

- Preparation of PBS solution at various concentrations of PBS in solutions with 1% (w/v) AAES

To investigate the effects of PBS concentrations on the morphology of electrospun PBS fibers obtained from PBS solution with AAES 1% (w/v) AAES, PBS concentrations at 8, 12, 16 and 20% (w/v) were used to study.

First, 0.5 g of AAES was dissolved in 50 ml of in CF in order to get 1% (w/v) of AAES solutions. Afterward, 4, 6, 8, 10 g of PBS pellets were dissolved in those of solutions, and stirred at room temperature for 2 hours. 8, 12, 16 and 20% (w/v) of PBS in solutions with AAES 1 % (w/v).

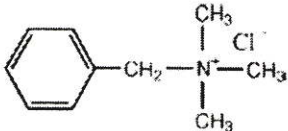
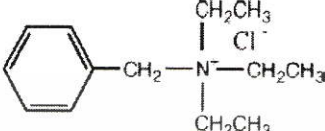
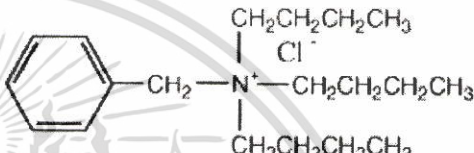
- Preparation of PBS solutions with benzyltrialkylammonium chlorides

To investigate the effects of organic salts, i.e. benzyltrimethylammonium chloride (BTMAC), benzyltriethylammonium chloride (BTEAC) and benzyl tributylammonium chloride (BTBAC), solutions of 12% (w/v) PBS in CF were prepared with addition of different concentrations (i.e., 0.25, 0.5, 1, and 2% (w/v)) of benzyl trialkylammonium chlorides. Chemical structures of benzyl trialkylammonium chlorides used in this work are shown in Table 3.3.

0.125, 0.25, 0.5 and 1 g of various benzyl trialkylammonium chlorides were dissolved in 50 ml of CF. These solutions were stirred at room temperature for 10 minutes.

6 g of PBS was dissolved in those of solutions. Then, they were stirred using magnetic stirrer for 2 hours before measuring solution properties and electrospinning.

Table 3.3 Chemical structures of quaternary ammonium salts [65]

Quaternary ammonium salts name	Chemical structures
Benzyl trimethylammonium chloride (BTMAC)	
Benzyl triethylammonium chloride (BTEAC)	
Benzyl tributylammonium chloride (BTBAC)	

3.3.2 Electrospinning process setup

1) Electrospinning of as-prepared solutions was carried out by connecting the emitting electrode of positive polarity from a high voltage DC power supply to the solutions contained in a standard 50 ml glass syringe. The open end of the syringe was attached with a blunt gauge-20 stainless steel needle (outer diameter =0.91), used as the nozzle, and the grounding electrode to a rotating drum collector.

2) All solutions in items 3.3.1.1-3.3.1.2 were used in this electrospinning. 30 ml of PBS solutions was contained in 50 ml of glass in syringe with steel needle. Electrospinning of the as-prepared solutions was carried out by connecting the emitting electrode of positive polarity from a high-voltage DC power supply to the solution contained in syringe. The open end of the syringe was attached to a blunt guage-20 stainless needle (outer diameter = 90 mm) used as the nozzel, and the grounding electrode to the collector. The applied potential used in this work was 20 kV across a fixed collection distance of 18 cm between the tip of the nozzle and outer surface of the collector. Both the needle and the syringe were tilted about 45° from a horizontal baseline to maintain constant presence of a droplet at the tip of the needle. The collection time was fixed at 1 hour. The experimental setup for the needle electrospinning is shown in Figure 3.3.

3) All morphologies and fiber diameters of electrospun PBS fibers were investigated by a scanning electron microscope (SEM).

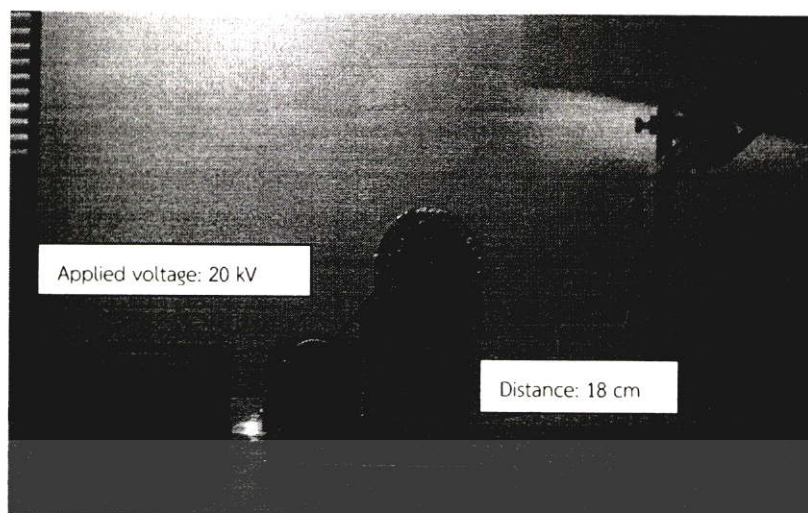


Figure 3.3 Photo of experimental setup for electrospinning in this work

3.3.3 Part I Effects of organic salts on electrospinnability of PBS solution

3.3.3.1 Characterization of PBS solution properties with and without organics salts

To investigate the effects of organic salts on the PBS solution properties with and without salt were investigated, i.e.,

- Surface tension

50 ml of PBS solutions was poured in glass beaker. The surface tension of solutions with and without salts was measured using digital tensometer.

- Conductivity

20 ml of PBS solutions was poured in glass beaker. The conductivity of solutions with and without salts was measured using conductivity meter.

- Viscosity

Viscosity of PBS solutions **was** measured using a digital brookfield viscometer (Brookfield Model TVB-10). Spindle no. and speed rotor used in this work are M1 and 60 rpm, respectively.

3.3.3.2 Morphology characterization

The morphology of the as-spun PBS fibers from solutions with and without salts was observed by using a scanning electron microscope (SEM). Each of the electrospun fiber mats was mounted on the metal stubs using double-side adhesives tape and vacuum-coated with a thin layer of gold. Those samples were coated with a thin layer of gold by using an Ion sputtering machine (Jeol JFC-1100E) with 15 mA for 3 minutes prior to SEM observation. The average diameters of electrospun fibers or beaded fibers were performed from >50 ($n \geq 50$) measurement

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randomly selected fibers for each sample using the SEM images analysis software (SemAphore[®] 4.0 software) at magnification of 5000X. For average diameters of beaded fibers, only sections of the fibers between beads were measured.

3.3.4 Part II Effects of collection distances on morphology and fiber diameters

3.3.4.1 Electrospinning process setup

1) To investigate effect of collection distances on the morphology and fiber diameter of electrospun PBS fibers, PBS pellets were dissolved in 70:30 (v/v) CF-MeOH. PBS concentrations were fixed at 12% (w/v). The applied potential conditions (20kV/15cm, 20kV/18cm and 20kV/25cm) were used in this part. The collection time was fixed at 1 hour.

2) Electrospinning of as-prepared solutions were carried out by connecting the emitting electrode of positive polarity from a high voltage DC power supply to the solutions contained in a standard 50 ml glass syringe, the open end of which was attached to a blunt gauge-20 stainless steel needle (outer diameter =0.91), used as the nozzle, and the grounding electrode to a rotating drum collector. The applied electrostatic field strength was varied (i.e., 20kV/15cm, 20kV/18cm and 20kV/25cm, respectively.). Both the needle and the syringe were tilted about 45° from a horizontal baseline to maintain constant presence of a droplet at the tip of the needle. The collection time was fixed at 1 hour. The experimental setup for the needle electrospinning is shown in Figure 3.4.

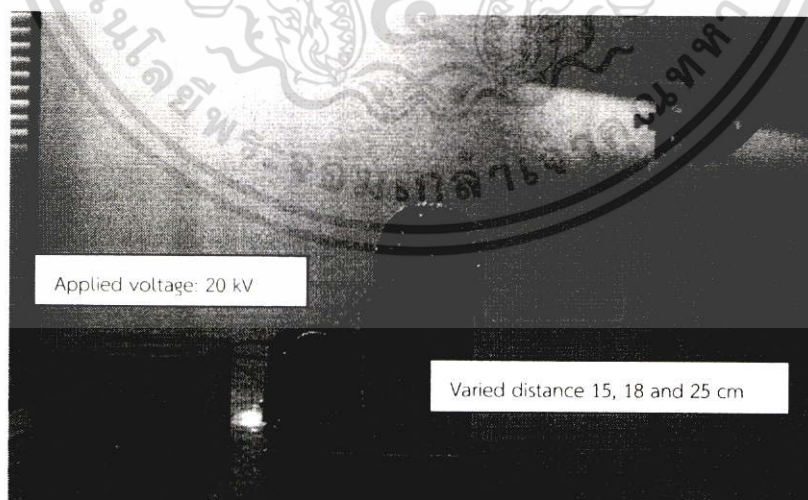


Figure 3.4 Photo of electrospinning experimental setup to study effects of collection distances

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3) Morphologies of the as-spun PBS fibers were observed by using scanning electron microscope (SEM). Each of the electrospun fiber mats was mounted on the metal stubs using double-side adhesive tape and vacuum-coated with a thin layer of gold prior to SEM observation. Those samples were coated with a thin layer of gold by an ion sputtering (Jeol JFC-1100E) with 15 mA for 3 minutes prior to SEM observation. The average diameters of electrospun fibers or beaded fibers were performed from >50 ($n \geq 50$) measurement randomly selected fibers for each sample using the SEM image analysis software (SemAphore[®] 4.0 software) at magnification of 5000X. For average diameters of beaded fibers, only the sections between beads were measured.

3.3.5 Part III Characterization for thermal and mechanical properties, and characteristic functionalities.

3.3.5.1 Thermal properties

This part divided into 3 parts; (1) effects of different concentrations of AAES salt on thermal properties of electrospun fibers obtained from 12 % (w/v) PBS solutions in single solvents of CF and DCM, (2) effects of different PBS concentrations on the thermal properties of electrospun fibers obtained from PBS solutions in chloroform with 1% (w/v) AAES and (3) effects of different organic salts on the thermal properties of electrospun fibers obtained from 12 % (w/v) PBS solutions in chloroform with 1% (w/v) organic salts, respectively. All electrospun fibers were characterized by conducting differential scanning calorimeter (DSC) (Model DSC1; Mettler Toledo Co., Ltd.). The furnace was heated from 25 to 120 °C at heating rate of 10°C/min. The equation used to analyze the degree of crystallinity is shown by Equation 3.1

$$X_c(\%) = \frac{\Delta H_m}{\Delta H_m^0} \times 100 \quad (3.1)$$

where $X_c(\%)$ is percentage of crystallinity

ΔH_m is the melting enthalpy

ΔH_m^0 is melting enthalpy of 100% crystalline PBS (210 J/g) [26]

In the first part, effects of amounts of AAES on electrospun nonwoven PBS fiber obtained from solution in CF and DCM were investigated. In this part, เอกสารนี้เป็นเอกสารที่สงวนไว้สำหรับการใช้งานเพื่อการศึกษาเท่านั้น ไม่อนุญาตให้นำไปใช้ประโยชน์ทางการค้า ไม่ว่ากรณีใดๆ ทั้งสิ้น อีกทั้งห้ามมิให้ดัดแปลงเนื้อหา และต้องอ้างอิงถึงเจ้าของเอกสารทุกครั้งที่มีการนำไปใช้

effects of PBS concentrations on thermal properties of nonwoven PBS fiber electrospun from solution in CF with 1% (w/v) AAES were studied. Finally, thermal properties of electrospun PBS fibers obtained from the solutions in CF with salts and the fiber electrospun from solution in 70:30 (v/v) CF-MeOH were studied comparatively.

3.3.5.2 Characterization of characteristic functionalities of electrospun PBS fibers mats

Electrospun fiber mats obtained from PBS solution with and without salts were analyzed for absorbance by Attenuated Total Reflection Fourier Transform Infrared Spectrometer (ATR-FTIR: Perkin Elmer Model FTIR Spectrum GX). Samples were measured in the range of $4000\text{--}500\text{ cm}^{-1}$ with scanning cycle of 10 times.

3.3.5.3 Mechanical properties of electrospun PBS fibers mats

Mechanical properties in terms of tensile strength, Young's modulus and % Elongation at yield of the electrospun fiber mats were investigated using Lloyd LRX universal testing machine (UTM) with a load cell of 100N, crosshead speed of 10 mm min^{-1} . For comparison effect of organic salts on mechanical properties, electrospun fiber mats were prepared from 12% (w/v) PBS in 70:30 (v/v) CF and MeOH and PBS solution in CF with 1% (w/v) salts. Prior to testing, all of electrospun samples were prepared as following method adapted from a literature [113].

- 1) A paper cardboard sheet was cut as shown in Figure 3.5. Double slide adhesive tapes were adhered onto the top and bottom areas of the sheet as a template.
- 2) The template was then glued using latex adhesive onto both sides template.
- 3) The template was cut into rectangular frame between gauge length of specimen (35 mm) along the vertical line.
- 4) The electrospun fiber mats were cut into rectangular pieces, and take placed to adhere on the along the vertical line.
- 5) The resulting specimen had a planar rectangular shape (width 15 mm x length 55 mm). Gauge length was 35 mm.
- 6) The basic parameters were used to evaluate mechanical properties of electrospun fibers mats, i.e., tensile strength (3.2), Young's modulus (3.3) and %elongation at yield (3.4), respectively.

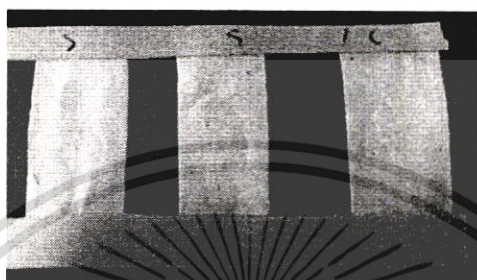
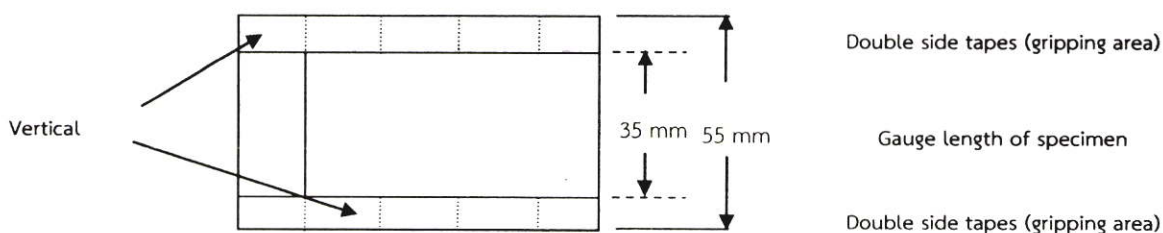


Figure 3.5 A cardboard template used to prepare tensile specimen of the electro-spun non-woven mat

where

$$\text{Tensile strength at yield} = \frac{\text{Force (N)}}{A \text{ (mm}^2\text{)}} \quad (3.2)$$

when F = Load recorded at yield (N)

A = Cross section area (mm²)

$$\text{Young's modulus} = \frac{\text{Difference in stress (MPa)}}{\text{Difference in corresponding strain}} \quad (3.3)$$

$$\% \text{ Elongation at yield} = \frac{\text{Increased length at yield point}}{\text{Initial gauge length}} \times 100 \quad (3.4)$$

Note Young's modulus calculated from the initial slope at 2 and 3% of elongation

3.3.6 Part IV Preparation of TLC plates from electrospun PBS fiber plates

1) Electrospun PBS fiber plates were prepared as follows. First, 12% (w/v) PBS solution in 70:30 % (v/v) chloroform: methanol was filled in a 50 ml glass syringe, the open with a blunt ended gauge-20 stainless steel needle (out diameter=0.91) used as the nozzle, and the grounding electrode to a rotating collection drum. The PBS solution was electrospun at a positive voltage of 20kV from a high voltage power supply onto aluminium plate on the drum which acted as

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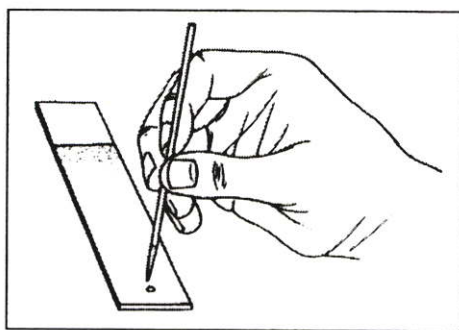
a ground collector. The studied times for electrospun PBS fibers deposited on a rotating collection plates were 1, 3, 6 and 12 hours. To evaluate efficiency of TLC plate application, thickness of the stationary phases was investigated. For these studies, the PBS fibrous mat for TLC plate was cut into a small piece (1 cm x 1 cm). The cut mat was placed on an ABS stage for measurement thickness by using High performance optical microscope. Each electrospinning experiment typically resulted in three plates.

2) Ultrafine fibrous PBS plates were electrospun onto the aluminium for used as a stationary phase of TLC. They were cut into rectangular plates (3 cm x 7 cm). During the cutting of the plates to ensure that the stationary phase was not damaged or pulled away from the aluminium foil substrate. Each electrospinning experiment typically resulted in three plates.

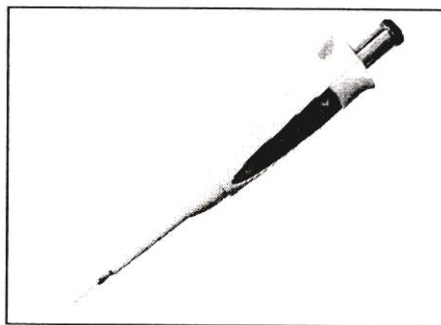
3) To evaluate the chromatographic performance of electrospun PBS fibrous mats, the mobile phase system was also investigated. In order to optimize the mobile phase of compositions to separate the mixture between cholesterol and oleic acid, retardation behavior of each component was evaluated under various ratios of ethyl acetate and hexane.

4) Electrospun PBS fiber plates (3 cm x 7 cm rectangular plates) were used to study possibility for stationary phase of TLC. Two analytes, i.e., cholesterol and oleic acid were used for testing separation performance. The concentration of analytes was 1 µg/µL.

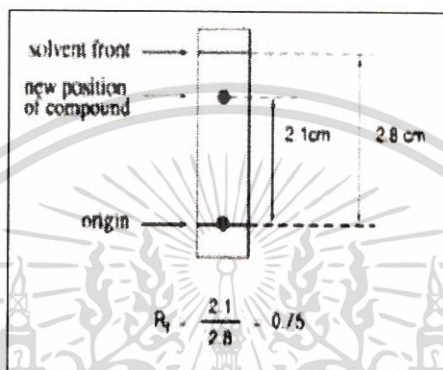
5) These plates were spotted with different volumes of analytes, i.e. 0.5, 1 and 2 µl by micropipette. Figure 3.6 shows example of spotting method of solution on plate of TLC. All plates were developed using 5 ml of mobile phases in a sealed chamber. The development chamber was a cylindrical glass with volume of 250 ml. Mixture of 30:70 (v/v) ethyl acetate and hexane was the optimized mobile phase for using to separate analytes. The resulting spots were stained using iodine vapor in chamber for 5 min. After that, each spot was observed visually and measured by a high performance microscope. The parameters including retardation factor, efficiency, resolution and developing time were investigated and calculated.



(a)



(b)



(c)

Figure 3.6 Spotting method used to spot sample on surface of TLC and example of micropipette used in this work: (a) spotting solution method, (b) micropipette used to spot sample and (c) calculation method of R_f [114]

The basic parameters were used to determine developing of analytes on the electrosun PBS plates are the retarding factor (R_f) where

$$R_f = \left(\frac{\text{Distance moved by solutes}}{\text{Distance moved by mobile phase}} \right) \quad (3.5)$$

The efficiency of a TLC plates separation is described in equation (3.6), where Z_s is the distance travelled by solvent front and w is the width of the developed sample spot.

$$\text{where } N = 16 \left(\frac{Z_s}{w} \right)^2 \quad (3.6)$$

This equation predicts that efficiency is increased with the square of the ratio Z_s/w .

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The mathematical description of resolution is R . The resolution of two adjacent chromatographic lower and upper spots is defined as being equal to the distance between the two spot centers ($Z_2 - Z_1$) divided by the mean spot widths (equation (3.7))

$$\text{where } R = \left(\frac{Z_2 - Z_1}{w_1 + w_2} \right) \quad (3.7)$$

3.3.7 Part V Preparation and characterization of antimicrobial PBS nanofibrous mats

In this part, the nonwoven fibrous mats electrospun from 12% (w/v) PBS in chloroform with and without 1% (w/v) salts was studied antimicrobial activity. Criteria used to judgment in this part is an inhibition zone of antimicrobial test by using ATCC method.

- Antimicrobial test (Inhibition zone)

Antimicrobial activities of the electrospun PBS fibers with and without 1% (w/v) salts were tested against Gram positive *Staphylococcus aureus* (*S. aureus* ATCC 25923) and Gram negative (*E.coli* ATCC25922) by the nonwoven fabric attachment method. The agar plates containing the test sample and control (blank) were incubated at 37 °C for 24 hours. The zone of inhibition was observed after 24 hours of incubation and the diameter of the zone was measured. This test was performed in triplicate. The antimicrobial efficiency results were investigated by measuring inhibition zone. Figure 3.7 shows example of inhibition zone in antimicrobial test.

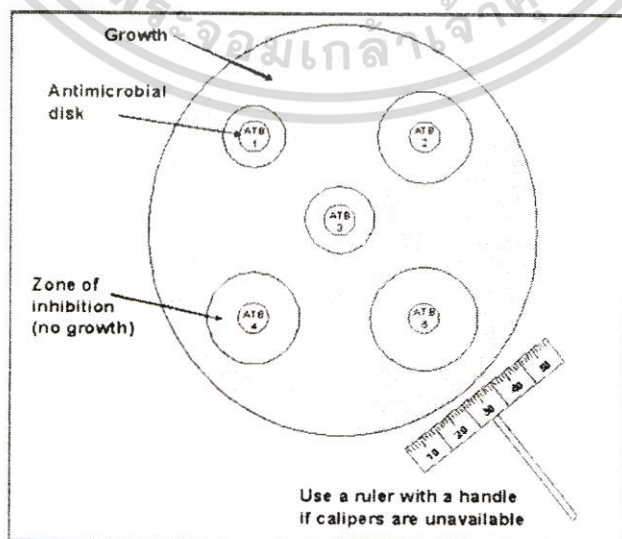


Figure 3.7 Example of inhibition zone in antimicrobial test [115]

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Chapter 4

RESULTS AND DISCUSSION

In electrospinning process, properties of polymer solution, i.e., concentration, conductivity and surface tension have dramatically influenced on morphology and diameter of electrospun fibers. Ultrafine fibers without beads can be prepared by optimizing the polymer solution properties. Solvent is one of the main contributors towards solution properties, e.g. conductivity, surface tension, solubility and boiling point. The conductivity of solution shows an important role influencing the fiber morphology and diameters [2-3, 16]. Polymer solution with high conductivity contributes higher net charge density of electrospun polymer jet yielding bead-free ultrafine fibers. Solution conductivity can be tailored by adding high dielectric constant solvents (cosolvents) or salts. The objective of this work was to enhance the electrospinnability of PBS fibers in order to produce bead-free ultrafine fibers. Factors affecting properties of electrospinning PBS solution, i.e., solvent systems, polymer concentrations and type of organic salts on the electrospinnability, morphological appearance and properties of electrospun fibers were studied. This work can be roughly divided into five parts. First, effects of solvent systems on electrospinnability of PBS solution were studied. Next, effects of salts on properties of electrospun fibrous mats were then investigated. In the third part, thermal properties, characteristic functionalities and mechanical properties of the electrospun fibers obtained from PBS solutions with and without organic salts were investigated. Next, feasibility study for applications of obtained electrospun PBS fibers as a stationary phase for thin layer chromatography (TLC) was evaluated. Finally, antimicrobial activities of benzyl trialkylammonium chloride (BTAC) and alkyl ammonium ethyl sulfate (AAES) incorporated into the electrospun PBS fiber mats against bacteria were investigated.

4.1 Effects of single and mixed solvent systems

In the first part, effects of solvent systems, i.e., single solvent and mixed solvent systems on morphology of ultrafine PBS fibers were investigated. Chloroform (CF) and dichloromethane (DCM) were chosen as a single solvent for preparing PBS solutions. Effects of polymer concentrations and dielectric constants of solvents were studied. To investigate the effects of dielectric constant, high dielectric constant solvents, i.e., N,N-dimethyl formamide (DMF), Chlorobenzene (CB) and methanol (MeOH) were chosen to improve the electrospun PBS fibers in order to eliminate bead defects. In this part, PBS concentration in mixed solvent systems was

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fixed at 12% (w/v). Some properties of these solvents (i.e. boiling point, dipole moment, dielectric constant, surface tension, viscosity, and solubility parameter) are summarized Table 4.1.

Table 4.1 Properties of solvents used in this work [116-118]

Solvent	Boiling point (°C)	Dipole moment (Debye)	Dielectric constant (ϵ)	Surface tension (mN/m ²)	Viscosity (mPa. s)	Hansen solubility parameter (MPa) ^{1/2}
Chloroform (CF)	61.2	1.01	4.8	26.6	0.54	19.0
Dichloromethane (DCM)	39.8	1.60	8.9	27.2	0.79	20.0
Chlorobenzene (CB)	131.7	2.27	9.8	32.3	0.69	19.3
N,N-dimethyl formamide (DMF)	153.0	3.82	37.0	34.3	0.79	24.0
Methanol (MeOH)	64.7	1.69	32.6	22.1	0.54	29.6

Note: Hansen solubility parameter of poly (butylene succinate) is 19.0 (MPa)^{1/2} [119].

4.1.1 Single solvent systems

In electrospinning process of polymer solutions, it has been known that viscosity and concentration of polymer solution are one of the most crucial parameters determining diameter and morphology of fibers. It has been reported that number of chain entanglement related to the viscosity and polymer concentration. The bead-free nanofibers could be presented when the concentration of polymer solution is higher than chain entanglement concentration (C_e) [2-3, 16, 120]. However, bead formation can occur if the used polymer concentration is below than C_e . On further increasing the polymer concentration, the frequency of bead formation decreases. However at high concentrations, polymer solution cannot produce fiber due to the high solution viscosity [2, 120]. In this part, CF and DCM were chosen as single solvent systems for preparing PBS solutions. Hansen solubility parameters of CF and DCM are close to that of PBS as shown in Table 4.1. CF and DCM were able to dissolve PBS pellets to form a clear solution within two hours. Effects of PBS concentrations on the PBS solution properties and morphology of electrospun fibers were investigated. Table 4.2 summarizes the viscosity, conductivity and surface tension of the as-prepared PBS solutions. As expected, viscosities of PBS solutions in both solvents increased with increasing PBS concentrations. However, surface tension and conductivity of PBS solution slightly changed as the PBS concentration increased in both solvents. The

increase in viscosity of the PBS solution with increasing concentrations of the solutions was obviously a result of the increase in the chain entanglement.

Table 4.2 Viscosity, conductivity and surface tension of as-prepared PBS solutions in CF and DCM

Solvent	PBS concentration (%w/v)	Viscosity (mPa. s)	Conductivity (μS/cm)	Surface tension (mN/m ²)
CF	0	0.54	0.03	26.6
	8	94.3	0.03	34.0
	12	115.0	0.04	34.2
	16	158.0	0.05	34.5
	20	191.0	0.04	35.2
	30	281.0	0.03	35.4
DCM	0	0.79	0.15	28.5
	8	96.0	0.15	34.5
	12	118.4	0.14	35.2
	16	160.0	0.15	35.5
	20	195.0	0.15	35.4
	30	285.0	0.14	35.6

Table 4.3 shows SEM images of electrospun fibers obtained from the PBS solutions in single solvent systems at various concentrations. As seen in Table 4.3, sprayed droplets obtained from electrospinning process were found when PBS concentration in CF was less than 12% (w/v) (inserted image a) in Table 4.3, whereas, beaded fibers obtained from PBS solution in DCM was found at 8 % (w/v) (inserted image (f) in Table 4.3). When PBS solution concentration was increased (12-30% (w/v)), morphology was changed into beaded fibers. Bead sizes of electrospun PBS fibers had a trend to reduce as PBS concentration was increased . Small beaded fibers were still found in all concentrations of CF and DCM solutions. This result was similar to report of Tian *et al.* [30]. They reported that PBS/chloroform solution was unsuccessfully electrospun due to large beaded fibers.

In theory, electrospinning mechanism is governed under two instabilities, i.e., axis-symmetric varicose instability (Rayleigh instability) and non-axis-symmetric whipping instability [19, 110]. These instabilities are determined by factors related to solution properties and operating condition, i.e., solution viscosity, conductivity, surface tension, and the strength of the applied electric field [2, 19, 110]. Two instabilities can be clearly explained by six forces [2, 16, 121] i.e.,

1) Gravitation force (F_G), towards the collector plate in vertically arranged apparatus. This force depends on density of polymer solution.

2) Electrostatic force (F_E), which is used to extend the jet polymer and propel it towards the grounded collector. This force is determined by the applied electric field

3) Coulombic force (F_C), which occurs on the surface of the polymer jet. The magnitude of this force is dependent on the characteristic of the polymer and solvent. It is responsible for the thinning or the stretching of the charged jet during its flight to the target. This force is related to charged density of polymer and conductivity of polymer solution.

4) Viscoelastic force, which works against elongation of the jet in the electric field. This force depends on polymer molecular weight, solvent and type of polymer.

5) Surface tension force, which works against the stretching surface of the charge jet.

6) Friction or drag force, which acts between the surface of the polymer jet and the surrounding air.

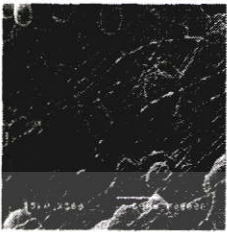
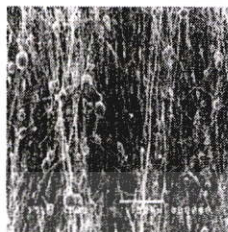
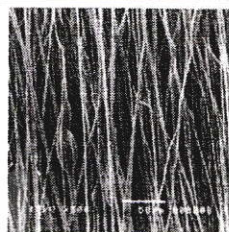
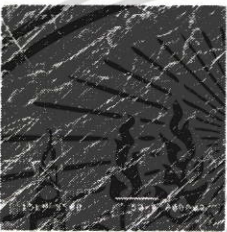
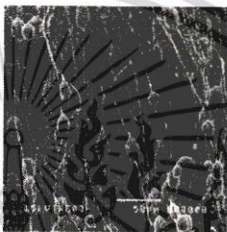
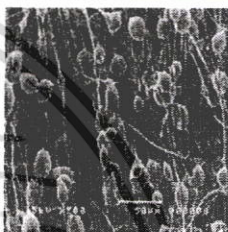
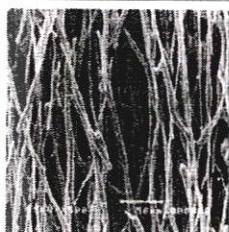
Among these forces, only the coulombic, the viscoelastic, and the surface tension forces dominate the formation of beads as well as thinning of the charged jet during its flight to the grounded target. Axis-symmetric varicose (Rayleigh instability) results from the surface tension of the solution [2, 19, 110] and produces drops rather than fibers. It can occur when the strength of electrical field is lower or the viscosity of the solution is below a critical value. Non-axis-symmetric instability (whipping instability) is presented by the electrostatic field and charge density of polymer jet. It results in bending and stretching of the jet through a rapidly spiraling motion. Polymer solution factors, i.e., viscosity and conductivity of solution, can be used to suppress the Rayleigh instability. Solution viscosity is dominated by the solution concentration or polymer molecular weight. This factor is related to the extent of polymer chain entanglement. The latter is governed by conductivity of polymer solution.

In these work, as seen as sprayed droplets obtained from 8 % (w/v) PBS solution in CF, poor chain entanglement density in the PBS solution was expected. Insufficient resistance to the electrical field resulted in polymer jet break up into PBS droplets. Low entanglement of polymer chains might not be enough to form a stable polymer jet. This phenomenon can be called “electrostatic atomization” [2]. Meanwhile, the beaded fibers were obtained from PBS solution in DCM as compared to the same PBS concentration (8% (w/v)) rather than sprayed droplets. It might be due to fast evaporation of DCM (boiling point 39.8 °C) compared to CF (boiling point

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ไม่ว่ากรณีใดๆ ทั้งสิ้น อีกทั้งห้ามมิให้ดัดแปลงเนื้อหา และต้องอ้างอิงถึงเจ้าของเอกสารทุกครั้งที่มีการนำไปใช้

61.2 °C). The polymer jet formed beaded fibers before they reached the grounded collector. Moreover, subsequent evaporation of the DCM from inside the polymer jet resulted in the increasing viscoelastic force. Therefore, it was able to counter the stretching forces from both electrostatic and coulombic repulsion forces. Therefore, the sprayed droplets were not observed in this condition. However, in this part, uniform PBS fibers could not be obtained from the single solvent system even though PBS concentrations were increased up to 30% (w/v). This reason was considered to have derived from low conductivity of CF and DCM, since CF and DCM have low dielectric constants (dielectric constant (ϵ) CF is 4.8 and dielectric constant (ϵ) DCM is 8.), as shown in Table 4.1. Then, the PBS solution in both of CF and DCM can be expected to have low conductivity since the polymer does not contain the site to rapidly adsorb charges. Therefore, the low conductivity of PBS solutions in CF and DCM were unable to suppress the Rayleigh instability. It promoted beaded fibers rather than uniform fibers. Effects of solvent dielectric constants on fiber morphology were reported by several research groups [17, 22, 121]. Even though, solution concentration is one of key factors that can suppress the Rayleigh instability. Nevertheless, non-uniform PBS fibers were still observed at high concentrations due to the low conductivities of PBS solution in both single solvents. Therefore, attempts to increase solution conductivity were carried out by adding other solvents with high dielectric constants (mixed solvent systems) or organic salts in order to improve electrospinnability of PBS solutions. Although, DCM could dissolve PBS solution to form a clear solution, resulting PBS solutions were difficult to use in electrospinning processes because the solutions often clogged the tip of nozzle due to low boiling point (39.8 °C) and rapid evaporation of DCM.

Table 4.3 SEM images (500x) of electrospun PBS obtained from 8, 12, 16, 20 and 30% (w/v) PBS solutions in single solvent systems

Solvent	Concentration of PBS solution (%w/v)				
	8	12	16	20	30
	(a)	(b)	(c)	(d)	(e)
CF					
	(f)	(g)	(h)	(i)	(j)
					
DCM					

4.1.2 Mixed solvent systems

As shown in previous results, PBS solutions in single solvent system possessed poor electrospinnability. Beaded PBS fibers during electropinning process were still presented due to low conductivity of solutions. A number of research groups reported that the use of high dielectric constant solvents results in increased uniformity and reduced number of beads in the electrospun fibers [1, 17, 117, 120-122]. Additives, i.e. organic/inorganic salts and surfactants are also demonstrated as the same effect [18-22, 65]. In this work, electrospinnability and morphology of PBS fibers can be improved by an addition of a co-solvent with high dielectric constant and/or organic salt. High dielectric constant solvents, i.e., chlorobenzene (CB), N,N-dimethyl formamide (DMF) and methanol (MeOH) were chosen to improve the electrospinnability of PBS fibers. Effects of organic salts on electrospinnability of PBS solutions were discussed in the next part. In this part, PBS concentration in mixed solvent systems was fixed at 12% (w/v). The applied electrostatic field strength was fixed at 20 kV. The distance between needle tip and collector was kept constant at 18 cm. Ratios of mixed solvents used in this work are summarized and shown in Table 4.4.

Table 4.4 Ratios of mixed solvent systems at 12 % (w/v) PBS solution

Mixed solvent system	Ratio of solvent (v/v)
Chloroform:Dichloromethane (CF:DCM)	50:50
Dichloromethane:Chlorobezene (DCM:CB)	50:50, 70:30 and 90:10
Chloroform-N.N.-dimethyl formamide (CF:DMF)	
Chloroform-Methanol (CF:MeOH)	

- Chloroform-Dichloromethane(CF:DCM)

In this part, 12 % (w/v) of PBS solution was prepared in 50:50 (v/v) CF:DCM. Some of solution properties, i.e., viscosity, conductivity and surface tension of the PBS solution are summarized in Table 4.5.

Table 4.5 Viscosity, conductivity and surface tension of as-prepared PBS solutions in mixed solvent systems as a function ratio of the solvents

Solvent system	Ratio of mixed solvents (v/v)	Viscosity (m Pas)	Surface tension (mN/m ²)	Conductivity (μS/cm)
CF:DCM	50:50	113.8	34.5	0.08
DCM:CB	90:10	110	34.0	2.2
CF:DMF	90:10	120	37.9	2.0
CF:MeOH	70:30	118	33.1	2.8
	90:10	113	34.0	1.9

Table 4.6 shows SEM images and diameters of electrospun PBS fibers obtained from 12% (w/v) PBS solution in the CF:DCM (inserted image 4.6 (a) in Table 4.6). Bead-on-string morphology of PBS fibers was still observed. This might be derived from the low conductivity of solution. Average diameters of PBS fibers obtained from this solvent system were in range of 286±49 nm (Table 4.6). Small fiber diameters were obtained by measuring on the fiber section between the beads.

Dielectric constant relates to the ability of polymer solution to conduct the electric charge in the electrospinning process. Insufficient dielectric constant can result in low conductivity of the solution. The low PBS solution conductivity resulted in the low charge densities of polymer jet. Rayleigh instability cannot be suppressed leading to beaded finer fibers. Moreover the clogging of the tip due to the fast evaporation of the electrospun products due to low boiling point of DCM.

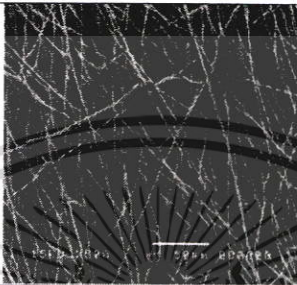
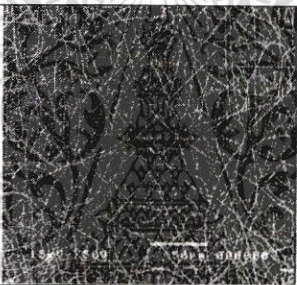
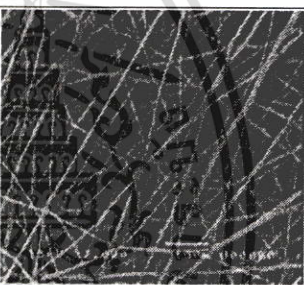
เอกสารนี้เป็นเอกสารที่สงวนไว้สำหรับการใช้งานเพื่อการศึกษาเท่านั้น ไม่อนุญาตให้นำไปใช้ประโยชน์ด้านการค้า ไม่ว่ากรณีใดๆ ทั้งสิ้น อีกทั้งห้ามมิให้ดัดแปลงเนื้อหา และต้องอ้างอิงถึงเจ้าของเอกสารทุกครั้งที่มีการนำไปใช้

- Dichloromethane-Chlorobenzene (DCM:CB)

Dielectric constant and boiling point of CB are higher than those of DCM. Solubility tests of PBS in mixed solvent systems were performed in different various mixing ratios of DCM:CB. It was found that PBS could not be dissolved in DCM:CB within 2 hours if CB loading was higher than 10% (v/v). Therefore, this ratio was chosen to study in this part. Effects of CB addition on the PBS solution properties and morphology of electrospun PBS were shown in Tables 4.5 and 4.6, respectively. Conductivity of PBS solution in DCM was increased after addition of CB into PBS solution. Viscosity and surface tension of PBS solution were decreased slightly as compared with those of PBS solutions in pure DCM. The increased conductivity of PBS solution was derived from the dielectric constant of the CB ($\epsilon = 9.8$) which was higher than that of the DCM ($\epsilon = 8.9$). It resulted in increasing ion species in the mixed solvent and the conductivity of PBS solution.

Morphology and average fiber diameter of electrospun fiber prepared with 12% (w/v) PBS solution in the mixed solvent system are shown in Table 4. 6 (inserted images 4.6 (b)). Morphological appearance of electrospun PBS fiber can be improved after addition of CB into PBS solution in DCM. It might be due to an increase in conductivity of the PBS solution due to greater dielectric constant of CB. The increased conductivity of PBS solution in this mixed solvent led to the increased surface jet charges. Under a given electric field, the increased conductivity results in stronger elongation forces imposed to the jet. It caused self-repulsion of the excess charges on the surface. This effect suppressed the Rayleigh instability yielding enhanced whipping action and minimized defects. However, few beaded fibers were still presented (inserted value in Table 4.6). The clogging of the spinneret at the tip due to the fast evaporation of the hanging droplets can be found. Low boiling point of DCM was a main reason for clogging.

Table 4.6. SEM images and diameters of electrospun PBS fibers produced from 12% (w/v) PBS solution in variety of mixed solvent systems, i.e., 50:50 (v/v) CF:DCM, 90:10 (CB:DCM), and 90:10 (v/v) CF:DFM, respectively

Solvent system	Ratio of mixed solvent (v/v)	Magnification		Average fiber diameter (nm)
		500x	5000x	
4.6 (a)				
CF:DCM	50:50			286±49
4.6 (b)				
DCM:CB	90:10			212±70
4.6 (c)				
CF:DMF	90:10			744± 55

- Chloroform-N,N dimethyl formamide (CF:DMF)

Previously, the PBS solutions in CF were quite easy to use in electrospinning processes because the solutions did not clog at the tip of nozzle. In this part, CF was used as a main solvent for dissolving PBS pellets. DMF is one of solvents with high boiling point and dielectric constant [1, 121]. Lee *et al.* [123] reported that smooth nanofibers of PCL could be electrospun by adding DMF in PCL solution in DCM. DMF decreased viscosity and increased the electrical conductivity of the PCL solution. In this work, DMF can be used to increase conductivity of PBS solution in CF. Solubility tests of PBS in mixed solvent system were first performed

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in different mixing ratios of CF:DMF. It was found that PBS could not be dissolved in CF:DMF within 2 hours if DMF loading was higher than 10% (v/v). Therefore, this ratio was chosen to study in this work. Effects of DMF addition on the PBS solution properties and morphology of electrospun PBS are shown in Tables 4.5 and 4.6, respectively. As expected, conductivity of PBS solution in CF was increased after addition of DMF into PBS solution. This result was agreed with results of Lee *et al.* [123]. They reported that nanofibers could be collected because DMF decreased the viscosity and increased the electrical conductivity of the PCL solution. Viscosity and surface tension of PBS solution were slightly increased as compared with those of PBS solutions in pure CF.

Morphology and average fiber diameters of PBS fibers prepared with 12% (w/v) PBS solution in the mixed solvent system are shown in Table 4.6. Adding DMF into the electrosinning PBS solution was shown to improve PBS fibers morphology as seen in inserted images 4.6 (c) in Table 4.6. Electrospinnability of the mixed-solvent system could be improved because of high dielectric constant DMF. The increased conductivity of PBS solution in mixed solvent led to the increased surface jet charges. Under a given electric field, the increased conductivity results in stronger elongational forces imposed to the jet. It causes self-repulsion of the excess charges on the surface. This effect suppresses the Rayleigh instability yielding enhanced whipping action and minimized bead defects. However, few beads and large PBS fibers were found in this solvent system. It could be attributed to high boiling point DMF.

- Chloroform-Methanol

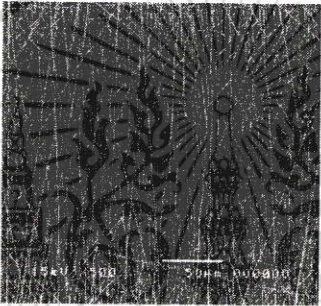
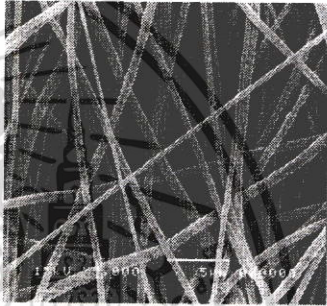
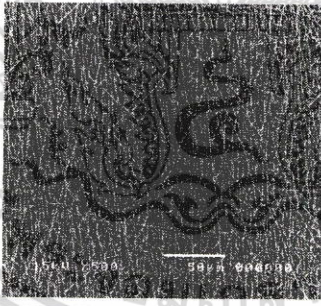
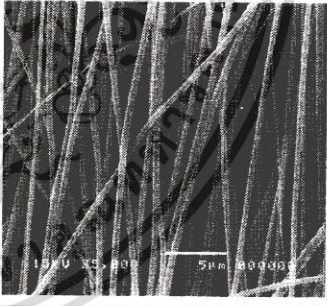
MeOH is one of solvents with high dielectric constant as seen in Table 4.1. It was found that PBS could not be dissolved in CF:MeOH within 2 hours if MeOH loading was higher than 30% (v/v). 12% (w/v) PBS solution in these mixed solvent systems were studied in this part. Some properties, i.e., viscosity, surface tension and conductivity of PBS solution are summarized in Table 4.5. As expected, the conductivity of PBS solutions increased with adding MeOH content into mixed solvent system as compared to PBS solution in CF. It can be explained that dipole moment and dielectric constant of MeOH are higher than those of CF. It resulted in increasing ion species in the mixed solvent.

Table 4.7 shows that amount of MeOH added to the PBS solution has significant effects on structures of electrospun PBS fibers. As the MeOH loading was increased from 0 to 30%, morphologies of electrospun PBS fibers were changed from beaded fibers to smooth fibers. Moreover, average diameters of PBS fibers were decreased from 575 nm (inserted image 4.7 (a)) to 480 nm (inserted image 4.7(b))

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with increasing MeOH contents as shown in Table 4.7. This was likely a result of the increased dielectric constant of the MeOH (ϵ of MeOH is 32.6 and ϵ of CF is 4.8). The results were similar to Lee *et al.* [123], Nitanan *et al.* [124] and Wannatong *et al.* [17].

Table 4.7. SEM images of fibers and diameters of electrospun PBS fibers produced from 12% (w/v) PBS solution in variety of mixed solvent systems 90:10 and 70:30 (v/v) CF:MeOH

Solvent system	Ratio of mixed solvent (v/v)	Magnification		Average fiber diameter (nm)
		500x	5000x	
CF:MeOH	90:10			575±84
	70:30			480± 70

By adding a high dielectric constant solvent into polymer solution, it leads to an increase in conductivity of the solution. Surface charges of spinning jet obtained from electrospinning were increased. It caused the coulombic stretching forces to increase. As a result, increasing elongation forces imposed to the jet caused by the self-repulsion of the excess charges on the surface. Increasing charge density was able to promote the whipping or bending instability because high surface charges simultaneously suppressed the axisymmetric modes. These phenomena might result in a higher degree of elongation of the jet. This process occurred during the transition of solution jet to the collector. Smooth defect-free ultrafine PBS fibers with smaller diameters could be obtained by using these systems. It was clearly

seen that continuous ultrafine fibers can be obtained dramatically depending from types of solvents and optimal ratios of mixed solvent system.

4.1.3 Effects of PBS concentrations in chloroform and methanol

In this part, in order to investigate effects of solution concentrations on the morphology and size of electrospun PBS fibers, PBS solutions of different concentrations (8, 12, 16 and 20 % (w/v)) were prepared. 70:30 (v/v) CF:MeOH was chosen for preparing ultrafine fibers from electrospinning process. Solution properties, i.e., viscosity, surface tension, conductivity are presented in Table 4.8. As expected, viscosities of the solutions largely were increased with increasing solution concentrations. Insignificant changes were observed in the conductivities and surface tensions of PBS solutions.

Table 4.8 Viscosity, conductivity and surface tension of 8, 12, 16 and 20 (%w/v) PBS solutions in the mixed solvent of 70:30 (v/v) CF:MeOH

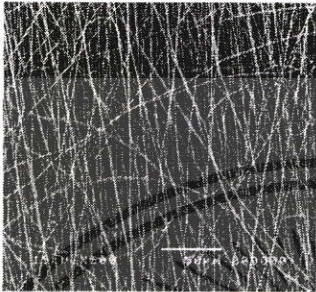
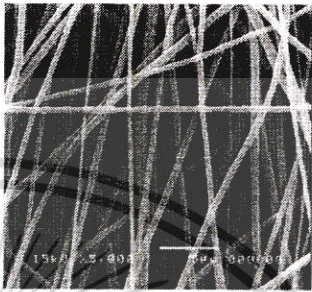
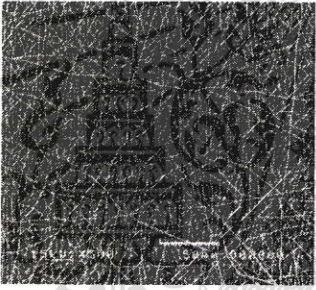
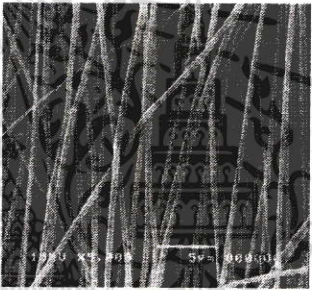
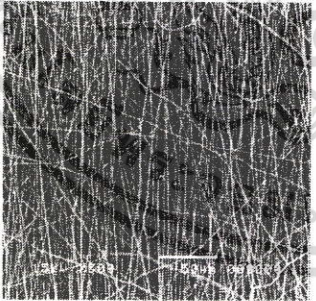
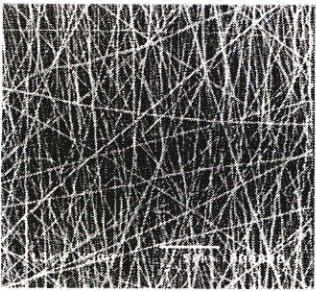
Concentration %(w/v)	Shear viscosity (m Pas)	Surface tension (mN/m)	Conductivity (μ S/cm)
8	98	32.8	2.83
12	118	33.1	2.81
16	184	33.4	2.83
20	202	33.3	2.85

Table 4.9 shows SEM images of the fibers and average diameters. At 8% (w/v) of PBS solution (inserted 4.9 (a)), few beaded fibers were obtained. This low concentration resulted in low viscoelastic force because chain entanglement in a given solution was appreciably less than a critical value. It might not be enough to form a stable polymer jet. Therefore, it was not sufficient to counter the stretching forces from both electrostatic and coulombic repulsion forces. Overstretching of the charged jet resulted in partial break up of the jet. Surface tension of solution tended to minimize the surface areas by forming individual droplets. Beaded fibers, therefore, were formed on some fibers [15-18] by this PBS concentration. However, continuous and smooth fibers were obtained by spinning 12-20 % (w/v) (inserted 4.9 (b) to 4.9 (d)) PBS solutions. Increasing PBS concentrations clearly resulted in increasing viscosity of PBS solutions. This led to an increase in the viscoelastic force. Changing morphology of electrospun fibers from beaded fibers to smooth fibers by increasing concentration can be attributed to competition between the surface tension and viscosity. At these high concentrations, high viscoelastic force could be enough

against the electrostatic stretching force. These high PBS concentrations resulted in more chain entanglement yielding an increase in viscosity of polymer solution. The Rayleigh instability resulted in this elongated Taylor cone to break into droplets was suppressed when these concentrations were used. Moreover, increasing concentration yielded an increase in the viscoelastic force. It was able to counterbalance the coulombic stretching force and therefore resulting in smooth PBS fibers and suppress the jet break-up. This result was similar to the Son *et al.* [125] and Moghe *et al.* [19] reported that the polymer concentration was less than a critical value. The jet formed breaks up into droplets, due to the set in off Rayleigh instability, leading to beaded fibers. Bead-free fibers were only formed after a critical chain entanglement density was achieved. In this region, the high resistance offered by the chain overlap to the jet break up suppressed the Rayleigh instability [19].



Table 4.9. SEM images of electrospun PBS fibers and diameters of electrospun PBS fibers produced from 8, 12, 16 and 20 % (w/v) PBS in the mixed solvent of 70:30 (v/v) CF:MeOH

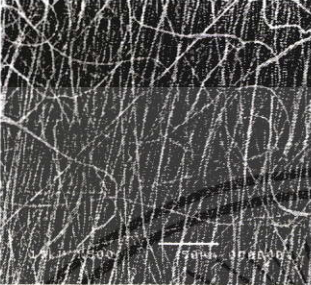
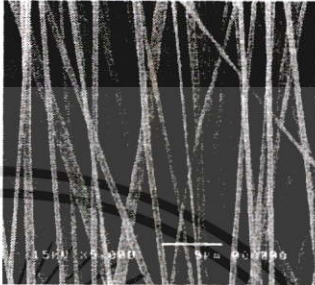
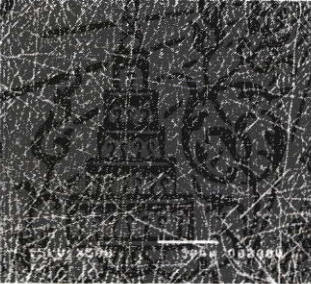
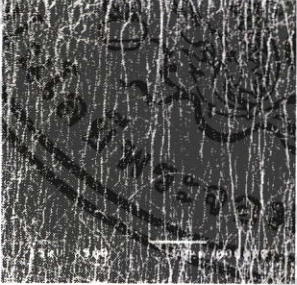
Concentration % (w/v)	Magnification		Average fiber diameter (nm)
	500x	5000x	
8	4.9 (a)		404 ±55
			
12	4.9 (b)		480± 70
			
16	4.9 (c)		664± 50
			
20	4.9 (d)		874 ±86
			

เอกสารนี้เป็นเอกสารที่สงวนไว้สำหรับการใช้งานเพื่อการศึกษาเท่านั้น ไม่อนุญาตให้นำไปใช้ประโยชน์ด้านการค้า ไม่ว่ากรณีใดๆ ทั้งสิ้น อีกทั้งห้ามมิให้ดัดแปลงเนื้อหา และต้องอ้างอิงถึงเจ้าของเอกสารทุกครั้งที่มีการนำไปใช้

4.14 Effects of capillary-collector distance

Distance between capillary tip and collector is one of the most important parameters affecting fiber size and morphological appearance. Electrical strength as well as the time available for evaporation of solvent before the fibers reach the collector surface depend on the distance [56]. Diameters of electrospun fibers are decreased as a result of increased distance of Taylor cone at end of capillary tip to the collector [53]. Table 4.10 shows the effects of capillary-collector distance on diameter size and morphological appearance of the electrospun PBS fiber from 12% (w/v) solution in 70:30 (v/v) CF:MeOH. As seen in SEM in Table 4.10, at 15 cm capillary-collector distances (inserted 4.10 (a)), few beaded fibers were observed. It might be due to high boiling point MeOH used as a co-solvent in mixed solvent. Flying time that of polymer jet might not has enough for evaporating solvent from the surface of ultrafine PBS fibers. However, continuous and smooth fibers were obtained by using 18 and 25 cm distance (inserted 4.10 (b) to 4.10 (c)). Average diameters of fibers decreased from 534.7 to 425.2 nm when the distance was increased. This result agreed with Manee *et al.* [126]. They reported that PS fibers spun from solutions in different solvents with collection distance at 7, 10 and 15 cm. They found that diameter fibers decreased with increasing in collector distance. Moreover, Zhang *et al.* [127] and Ki *et al.* [128] reported that an optimal distance was required to give an optimal field strength and sufficient time to dry fibers before they reached collector. If suboptimal distances were either too close or too far, beads were observed with electrospinning of PVA and gelatin. It was reported that flat fibers could produce at closer distances, but with increasing in the distance, rounder fibers were observed. However, Li *et al.* mentioned the influence of capillary – collector distance on the fiber diameters was complex. It depended on the competition and the electric field intensity and the flying time [129].

Table 4.10 SEM images of electrospun fibers from 12% (w/v) PBS solution of CF:MeOH (70:30 (v/v)) at different collection distances, i.e., (a) 15 cm, (b) 18 cm, and (c) 25 cm

Collection distance (cm)	Magnification		Average fiber diameter (nm)
	500x	5000x	
15	4.10 (a)		534.7±41
			
18	4.10 (b)		480± 70
			
25	4.10 (c)		425± 60
			

4.2 Effects of organic salts on electrospun PBS fibers

As mentioned above, conductivity of the PBS solution is one of key factors for determining morphological appearance, such as, fiber diameter, size distribution and bead formation. From literature surveys [2, 17, 19, 126, 130-131], conductivity of polymer solution in electrospinning process can be improved by adding high dielectric solvents or salt. Some researchers reported the use of additives, i.e., inorganic salts, organic salts and surfactants for altering morphological appearance of

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ไม่ว่ากรณีใดๆ ทั้งสิ้น อีกทั้งห้ามมิให้ดัดแปลงเนื้อหา และต้องอ้างอิงถึงเจ้าของเอกสารทุกครั้งที่มีการนำไปใช้

electrospun fibers [2, 18-22, 65]. Salts have been manifested to be useful in improving electrospinnability and controlling fiber morphology through the modification of solution properties. In order to study effects of salts on electrospinnability of PBS solution, four organic salts were chosen to study, i.e., alkyl ammonium ethyl sulfate (AAES), benzyl trimethylammonium chloride (BTMAC), benzyl triethylammonium chloride (BTEAC), and benzyl tributylammonium chloride (BTBAC). Chemical structures of these salts are shown in Table 4.11, respectively. From literature surveys, no study has been conducted to demonstrate the effects of the salts on the PBS solution properties and the morphology of PBS fibers. Therefore, the aim of this work was to investigate those effects of the salts. First, effects of adding AAES on the electrospinnability of PBS solution were investigated. Effects of PBS concentrations and solvents systems, on the PBS solution properties, appearances and diameters of PBS fibers were also studied. Next, comparative study of AAES and benzyl alkyl ammonium chlorides (BTMAC, BTEAC and BTBAC) on the electrospinnability of PBS solution was carried out. Effects of the salts on thermal and mechanical properties of electrospun non-woven mats were studied as well.

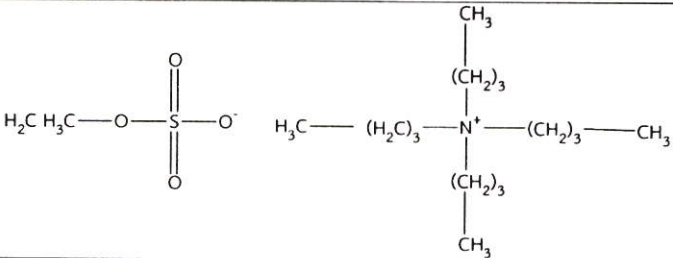
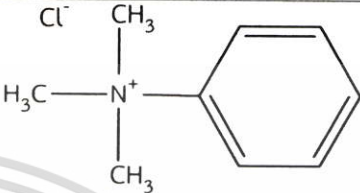
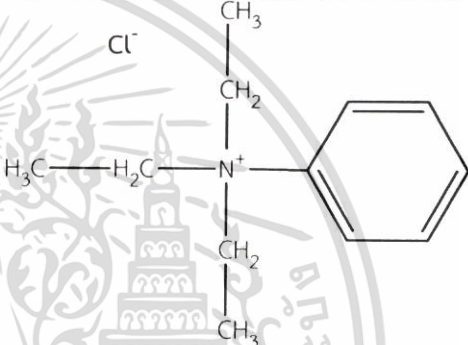
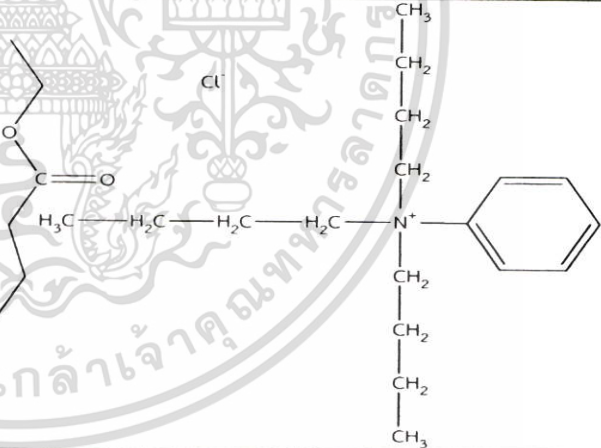
4.2.1 Effects of alkyl ammonium ethyl sulfate (AAES)

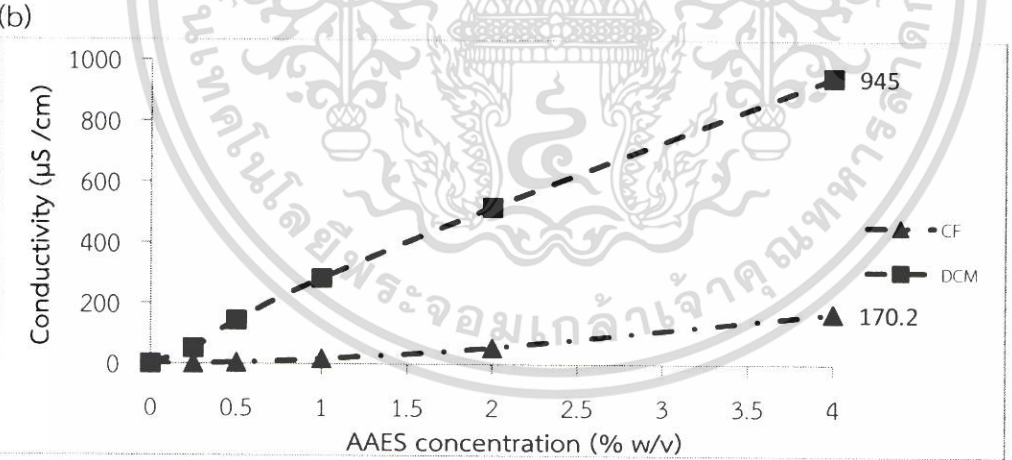
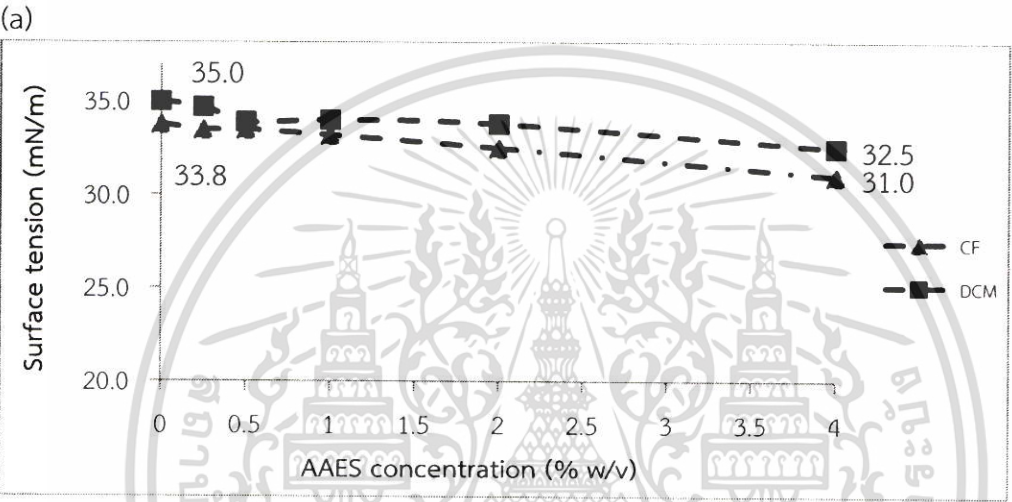
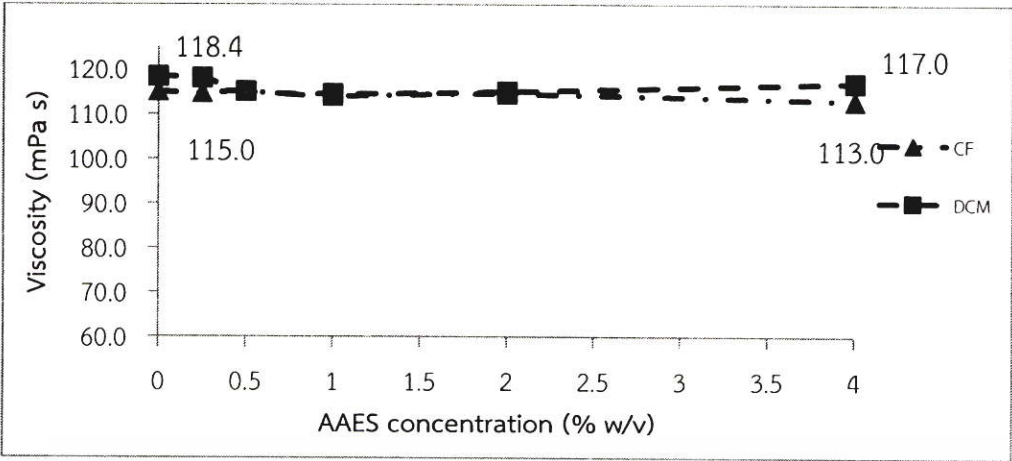
AAES was chosen as the salt for increasing the PBS solution conductivity because it consisted of organic cations and inorganic anions. The changes in the fiber diameters and morphology by adding salts were investigated in terms of solution viscosity, surface tension, and conductivity.

- Effects of AAES amounts on PBS solutions

In this part, different AAES concentrations, i.e., 0.25%, 0.5%, 1.0%, 2.0% and 4% (w/v) was prepared in the 12% (w/v) PBS solution in CF and DCM. Figure 4.1 shows PBS solution properties, that is, viscosity, surface tension, and conductivity, before and after the addition of AAES. It was found that the salt addition showed a little effect on the viscosity and surface tension of the solutions. Viscosity and surface tension of PBS solution in CF and DCM with various AAES concentrations slightly decreased as small amounts of AAES were added. It was found that the surface tension of the PBS solution in CF decreased from 33.8 to 31.0 mN/m. Meanwhile, the surface tension of PBS solution in DCM decreased from 35.0 to 32.5 mN/m as compared to PBS solution in the pure solvent, whereas, conductivity of PBS solution was dramatically increased with increasing salt loading in PBS solutions. Moreover, the conductivity of PBS solution in DCM with various salt concentrations was increased.

Table 4.11 Chemical structures of quaternary ammonium salts [65]

Quaternary ammonium salt names	Chemical structures
Alkyl ammonium ethyl sulfate, (AAES)	
Benzyl trimethylammonium chloride (BTMAC)	
Benzyl triethylammonium chloride (BTEAC)	
Benzyl tributylammonium chloride (BTBAC)	



(c)

Figure 4.1 Properties of 12% (w/v) PBS solution in CF and DCM with different AAES loadings; (a) viscosity, (b) surface tension and (c) conductivity

Tables 4.12-4.13 show morphology of PBS fiber electrospun from 12% (w/v) PBS solution in single solvent (CF and DCM) with and without AAES. Figure 4.2 shows the average fiber diameters electrospun from 12% (w/v) PBS solution in CF and DCM with different concentrations of AAES. Small beaded fibers were still found

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when 0.25% (w/v) AAES was added in PBS solution in CF (inserted images 4.12 (a) and 4.13 (a) in Tables 4.12 and 4.13). In contrast, bead-free ultrafine PBS fibers were found when 0.5% (w/v) AAES was added in 12% (w/v) PBS solution in CF. On the other hand, 0.25% (w/v) AAES was added in PBS solution in DCM, electrospinning of solution resulted in smooth fibers without beads.

Regarding effects of AAES concentration on PBS solution properties, it was clearly seen that the addition of AAES in the PBS solution in DCM, the solution conductivity was higher than PBS solution in CF. Since dielectric constant DCM of (ε 8.9) was higher than that of CF (ε 4.8). It might be a contributor for serving quaternary ammonium and sulfate anions of AAES. It was easier to dissociate to free ions in DCM as compared with PBS solution in CF at the same AAES concentration. It might contribute to an increase of surface charges of polymer jet. Stronger elongation forces are imposed to the jet, leading to bead-free PBS fibers. Therefore, smooth fibers without beads were presented from PBS solution in DCM with 0.25% (w/v) AAES

Formation of beaded fibers in electrospinning process were controlled by the key solution properties, i.e., viscoelasticity of the solution, charge density carried by the jet, and the surface tension of the solution [2, 16, 20]. Higher viscosity solution favors formation of fibers without beads, higher net charge density. It favors not only formation of fibers without beads, but also thinner fibers. Surface tension drives towards the formation of beads, hence reduced surface tension favors the formation of fibers without beads. These factors related to physical instabilities axis-symmetric varicose instability (Rayleigh instability) and non-axis-symmetric whipping instability [2, 19, 21, 110]. Rayleigh instability presents when the strength of electric field, charge density or the viscosity of the solution is below the optimum value. Use of very low viscosity solutions causes jet break-up and leads to the bead-on-fiber morphology. It is dominated by surface tension and produces drops rather than fibers. Rayleigh instability is suppressed at high electric fields (charge densities) or when using higher concentration of polymer in the solution [16, 20]. Meanwhile, non-axis-symmetric conducting instability is responsible for bending the fluid jet leading to “whipping” instability. This mode is governed by electrical field strength and conductivity of solution. Addition of the AAES in PBS solution increased the charge density in ejected jet. It yielded a stronger elongation force of the polymer jet due to the self-repulsion of the excess charges under the electrical field resulting in substantially straighter shape and smaller diameters of electrospun fibers. This suppressed the Rayleigh instability, enhanced whipping and reduced defects. Uniform fiber morphology with a narrow diameter distribution was obtained due to the charged density of polymer jet increased by adding the organic salt (AAES).

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ไม่ว่ากรณีใดๆ ทั้งสิ้น อีกทั้งห้ามมิให้ดัดแปลงเนื้อหา และต้องอ้างอิงถึงเจ้าของเอกสารทุกครั้งที่มีการนำไปใช้

Figure 4.3 shows average diameters of the resulting electrospun PBS fibers as a function of the amount of AAES. As expected, average diameters of electrospun fibers obtained from solution in CF and DCM with AAES were decreased with increasing AAES concentrations as seen in Figure 4.3. It could be caused by the fact that the addition of salt can increase the charge density in ejected jet from the Taylor cone at the end of tip syringe. Under a given electric field, it yields an increase in the elongation force on the jet. It could be caused by the self-repulsion of the excess charges on the surface of polymer jet. This inhibited the Rayleigh instability, enhanced whipping and led to bead-free ultrafine fibers. It was clearly seen that continuous ultrafine fibers can be obtained greatly depending on conductivity of PBS solutions. However, it was found that the fiber diameters slightly increased when 2% and 4% (w/v) AAES were added in the PBS solutions. By increasing charge densities of polymer jet by adding AAES in the solutions, it could occur 2 factors influenced on fiber morphology. These factors are competitive and varied depending on the conductivity of solution, i.e., (1) increasing charge densities of polymer jet resulted in the strong repulsive forces, led to increase a high degree of elongation forces of the polymer jet. Finally, it could be resulted in a reduction of fiber diameters. (2) Nevertheless, the increased charges density of polymer jet was over than optimal value. It caused the jet to travel closer to collector, before undergoing the bending instability, resulting in the reducing time of flying time of polymer jet. Large fiber diameter could be obtained. Therefore, the increased fiber diameters when 2% and 4% (w/v) AAES were added in the PBS solutions. This results can be explained by latter reason. Moreover, it was found that 2% and 4% (w/v) of AAES added in PBS solution both of CF and DCM were difficult to electrospin because the PBS solution was clogged at the end of tip during the electrospinning process. This could be caused by an excessive high conductivity of PBS solution. It was similar to the work done by Nitanan *et al.* [124] which revealed the clogging of PS solution with tetrabutylammonium bromide (TBAB) at capillary tip during the electrospinning process because of excessively high PBS solution conductivity. A possible mechanism clogging is described in Figure 4.3.

Table 4.12 SEM images of electrospun PBS fibers produced from 12% (w/v) PBS in single solvents (CF and DCM) at various AAES concentrations.
(Scale bar = 50 μm and magnification of 500x)

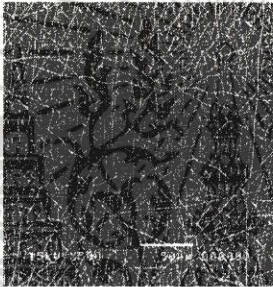
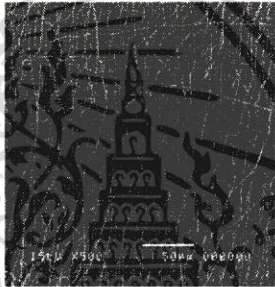
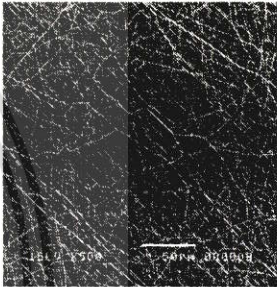
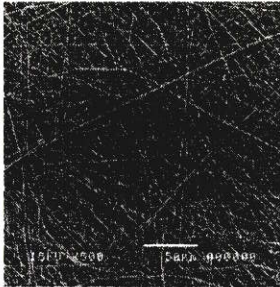
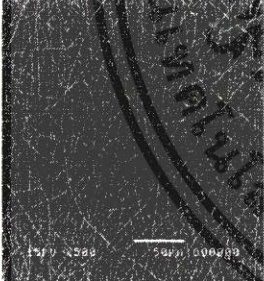
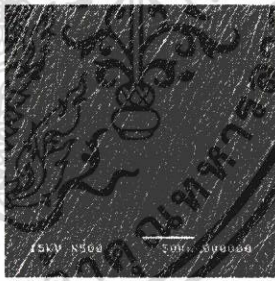
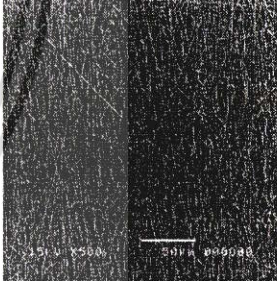
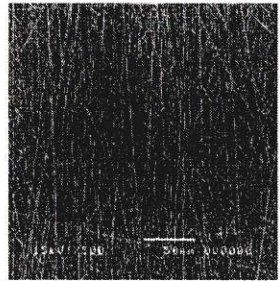
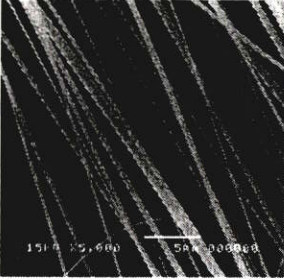
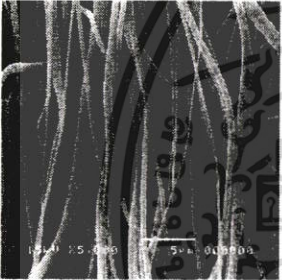
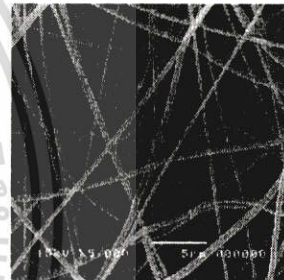
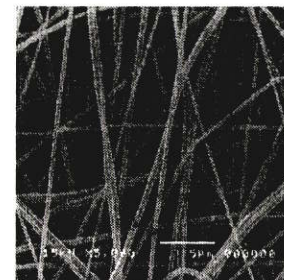
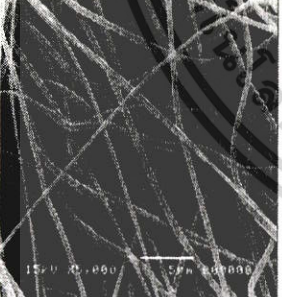
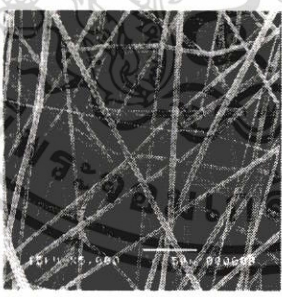
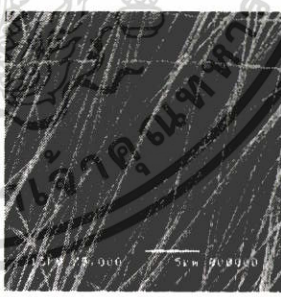
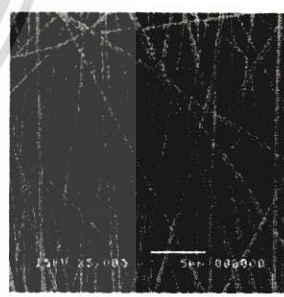
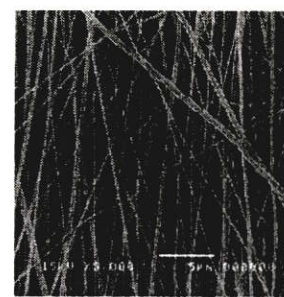
Solvents	AAES concentrations (%w/v)					
	0	0.25	0.5	1	2	4
CF	(a)	(b)	(c)	(d)	(e)	(f)
						
	(g)	(h)	(i)	(j)	(k)	(l)
						

Table 4.13 SEM images of electrospun PBS fibers produced from 12% (w/v) PBS in single solvents (CF and DCM) at various AAES concentrations (Scale bar = 5 μ m and magnification of 5000x)

Solvents	AAES concentrations (%w/v)					
	0	0.25	0.5	1	2	4
CF	(a)	(b)	(c)	(d)	(e)	(f)
						
	(g)	(h)	(i)	(j)	(k)	(l)
						

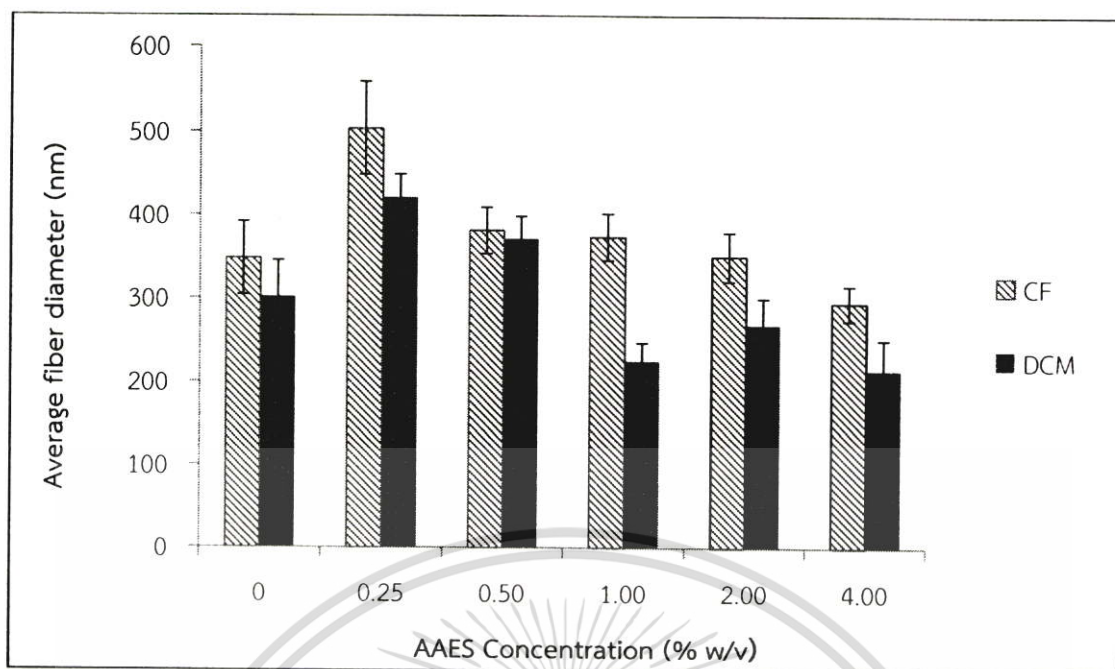


Figure 4.2 Effects of the salt concentrations on the diameters of electrospun fibers obtained from 12% (w/v) PBS solutions in CF and DCM with various AAES concentrations

A possible mechanism of clogged polymer solution at the end of the tip may involve fiber aggregation as shown in Figure 4.3. In the electrospinning process of the PBS solution without conductive additives, the positively charged fibers moved in a normal way to the grounded collector and repelled one another, as shown in Figure 4.3 (a), because of the repulsion theory of similar charges. Figures 4.3 (b) and (c) show a possible mechanism to account for the fiber attraction, which leads to fiber aggregation. The conductive organic salts offered excess charges to the solution jet. Negative charges were drawn back through the positively charged jet, so these fiber segments contained excess negative charges. If those segments still present closer to the needle with excess positive charges, it can draw by the negatively charged fiber segments before hitting the collector, yielding the aggregate fibers. The back building of charges and fiber aggregation climbed nearly to the needle. This effect involving fibers closer to the needle is represented in Figure 4.3 (c) [21, 110-111].

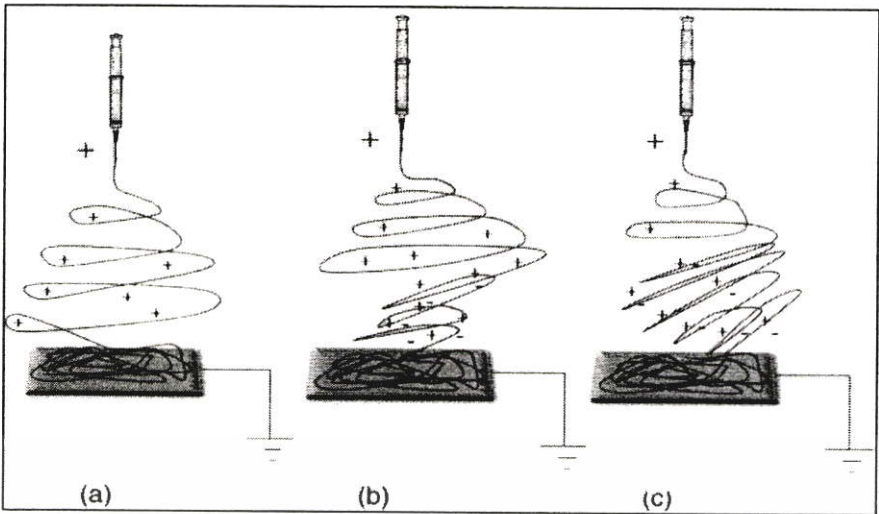


Figure 4.3 Mechanisms of fiber aggregation in electrospinning process, (a) polymer solution electrospun with no conductive additives, (b) polymer solution electrospun with conductive additive and (c) polymer solution electrospun with increased conductive additive [21, 110-111]

In this part, we considered the electrospinnability of PBS fibers by proposing preliminary force-balanced model that could be predicted the PBS fiber formation. Viscoelastic, coulombic, electrostatic forces and surface tension could be affected on the fiber morphology. Those forces were attempted to explain this model (equation 4.1) which adapted from [132]

$$\Gamma = \frac{1}{\rho_s} \left[\frac{d_s}{\eta_s \gamma_s} \right] \tag{4.1}$$

where

- ρ = Solution density
- η = Solution viscosity
- γ = Surface tension
- d = Dipole moment (It related to dielectric constant or conductivity)
- Γ = Fiber diameter
- Subscript S is PBS solution

From this model, electrical force was fixed. Meanwhile, fibers without beads could be spun when the electrostatic force are higher than the forces from viscosity and surface tension. Therefore, to produce electrospun nanofibers from a viscous solution with low dipole moments, the electrostatic force can be adjusted by increasing the conductivity of PBS solution. However, the viscosity should be high enough to work against the coulombic forces of the charges. If viscosity of the used solution is too low, the electrospun PBS fibers may break apart and continuous fiber

cannot be produced from the polymer solutions with high charges density. Moreover, Hohman [133], and Fridrikh *et al.* (Fridrikh, unpublished) [134] .proposed equation for the lateral growth of the jet excursions arising from the whipping. It could be used to explain the fiber formation. This equation contains terms due to acceleration of the charged jet (Related conductivity of PBS solution) under the influence of the applied electric field normal stresses due to surface tension and bending of electric field lines, and charge-charge repulsion [133-134]. The competition between surface tension and charge repulsion can be used to define a “stability parameter” S as shown in equation 4.2.

$$\frac{1}{S} = \left(\frac{\pi(2\ln\chi - 3)}{2\gamma\bar{\epsilon}} \right)^{\frac{1}{2}} \left(\frac{I}{Q} \right)^{\frac{2}{3}} h \quad (4.2)$$

where

γ = Surface tension

Q = Solution flow rate

I = Electrical current

$\bar{\epsilon}$ = Dielectric constant (Related to conductivity of solution)

χ = Wavelength of the whipping instability,

h = Jet diameter

χ was described as a “dimensionless of the whipping instability. While $I/Q = \Sigma$ describes as the volume density of charge.

It takes on values of $S < 1$ initially, indicative of instability with respect to the whipping mode, but rapidly increases to 1 as h is reduced under the action of the growing lateral perturbations. When $S = 1$, the destabilizing effect of charge repulsion is exactly balanced by the stabilizing effect of surface tension, leading to the cessation of stretching and definition of a limiting “terminal jet” diameter. A family of such instabilities exists and can be analyzed for different conditions of the symmetry (axisymmetric or non-axisymmetric) of the growing perturbations of the jet, using linear instability analysis. Figure 4.4 illustrates the perturbations associated with several of the lowest-order instabilities [134]. Therefore some of the key results from these studies could be summarized as follows:

- 1) axis-symmetric instabilities are controlled by surface tension (non-conducting) or electrostatic forces (conducting) and resulted in droplets or varicose
- 2) non-axis-symmetric whipping instabilities (conducting) are dependent on electrostatic forces, resulted in the jet thinning. It could be controlled by high charge density related fluid with characteristic conductivity.

เอกสารนี้เป็นเอกสารที่สงวนไว้สำหรับการใช้งานเพื่อการศึกษาเท่านั้น ไม่อนุญาตให้นำไปใช้ประโยชน์ด้านการค้า ไม่ว่ากรณีใดๆ ทั้งสิ้น อีกทั้งห้ามมิให้ดัดแปลงเนื้อหา และต้องอ้างอิงถึงเจ้าของเอกสารทุกครั้งที่มีการนำไปใช้

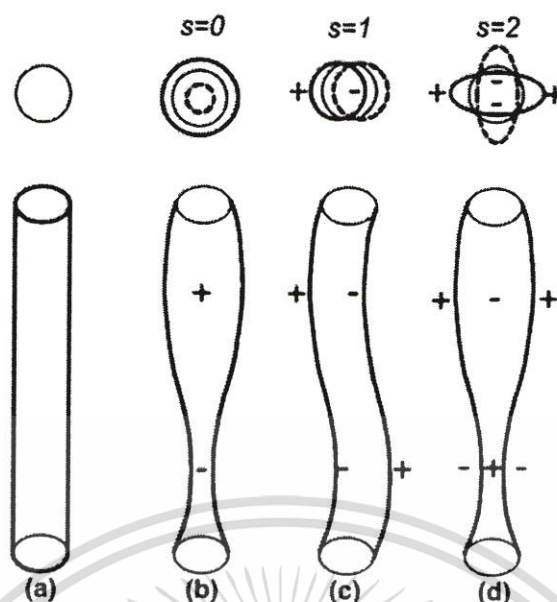


Figure 4.4 Schematic illustration of perturbations associated with several of the lowest order instabilities, distinguished by their azimuthal wavenumber, S . Top views illustrate cross-sections of the jet at maximum amplitudes of (oscillatory) perturbation, with bold and dashed contours representing different positions along the jet length. Bottom views illustrate changes in shape and centerline down the length of the jet. $+/ -$ are used to indicate regions of positive or negative deviation from the unperturbed jet shape. Perturbations are exaggerated beyond the linear instability regime. (a) unperturbed cylindrical fluid element; (b) varicose ($s=0$) instability; (c) whipping ($s=1$) instability (also called “bending” or “kink” instability in the literature); (d) splitting ($s=2$) instability. Growth of the varicose instability leads to equal sized droplets; growth of the splitting instability leads to two equal sized sub-jets. Higher order ($s>2$) instabilities are also conceivable [134]

In order to have a better understanding in effects of balanced forces during electrospinning process, possible mechanisms of electrospun fiber formation can be summarized in Figure 4.5. Viscoelastic, coulombic, electrostatic forces and surface tension are important interactions that influence the fiber formation [2, 16, 19, 110]. Two instabilities of polymer jet related to these forces are involved in this mechanism. These forces can be adjusted in a balance condition in order to prevent bead formation. Increased charges density of polymer jet by adding high dielectric constant solvents or organic salts shall affect fiber diameter and morphology of electrospun fibers. In this work, the sprayed droplets of PBS were obtained from electrospinning of PBS solutions in both single solvents. This behavior can be explained by Figure 4.5 (a).

เอกสารนี้เป็นเอกสารที่สงวนไว้สำหรับใช้ภายในเพื่อการศึกษาเท่านั้น ไม่สามารถนำไปใช้ประโยชน์ด้านการค้า
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Very low viscosity of PBS solutions resulted in the low chain entanglement densities in polymer jet. It was not sufficient to counter the stretching forces from both electrostatic and coulombic repulsion forces. Eventually, it caused the jet break up, leading to droplets. These defects could be suppressed by increasing the charges density of polymer jet or solution viscosity. Effects of charge density of polymer jet and solution viscosity on morphology of polymer fibers can be explained in Figure 4.5 (b). By increasing viscosity of PBS solution, the chain entanglement density of polymer molecules was increased. It was able to suppress the break-up of the polymer jet. However, low conductivity of PBS solutions led to very low charges density of PBS jet. Therefore, it was unable to suppress the Rayleigh instability. Black positive ions in Figure 4.5 (c) are obtained from the strong electrostatic field whereas red positive ions obtained from increasing the polymer solution conductivity. It could enhance charge density of polymer jet, leading to suppression of the Rayleigh instability. It promoted beaded fibers rather than uniform fibers. Figure 4.5 (c) explained results of enhancing charge density of polymer jet by increasing conductivity of PBS solutions. In this work, high dielectric constant solvents and organic salt (AAES) were added in the PBS solution for increasing charge density of polymer jet. The greatly excess density of polymer jet resulted in stronger elongation forces caused by self-repulsion of the excess charges on the surface. The Rayleigh instability could be suppressed, whereas bending and whipping instabilities were enhanced, yielding the defect reduction. Finally, the uniform fiber morphology with narrow size distribution could be obtained. Therefore, it can clearly be seen that the Rayleigh instability is one of the most important factors that can cause the bead formation.

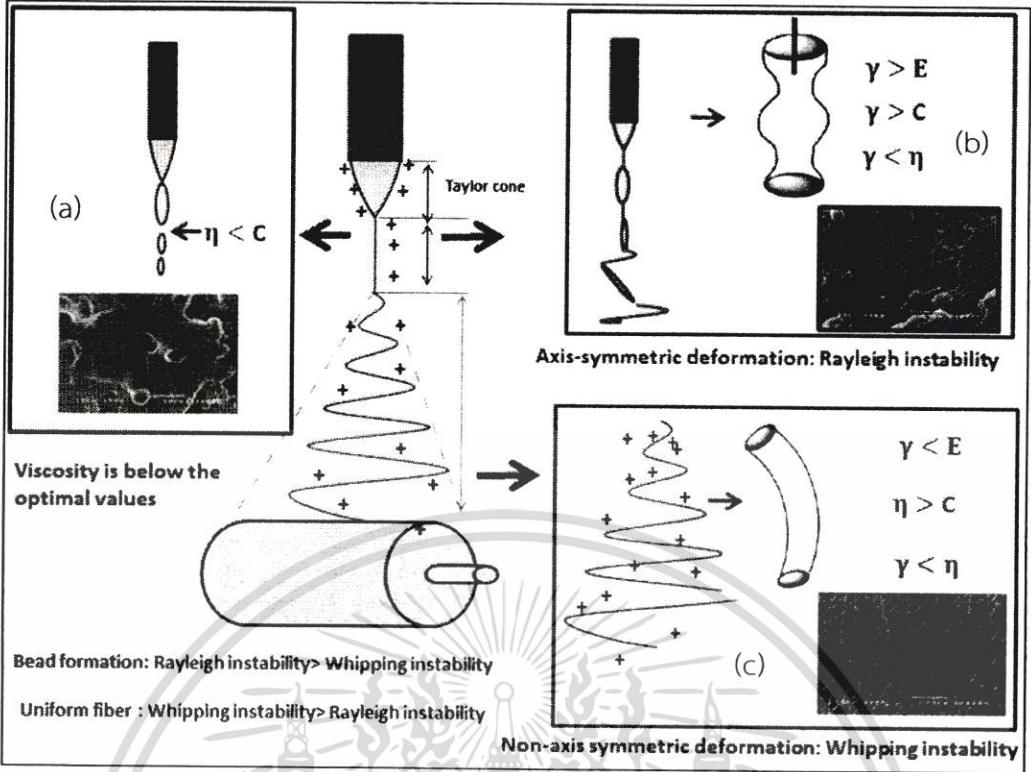


Figure 4.5 Possible mechanism of electrospun fibers proposed by using interaction of various forces caused by the viscosity (η), electrostatic force (E), surface tension (γ) and coulombic stretching force (C); (a) formation of droplet defects from electrospinning process, (b) Beaded fiber from axis-symmetric varicose instability (Rayleigh instability) and (c) non-axis-symmetric whipping instability [131]

4.2.2 Effects of PBS concentrations in solution with 1% (w/v) AAES

From the above results, 1% (w/v) AAES was an optimum amount of the salt for preparing bead-free ultrafine fibers in this work. To investigate the effects of solution concentrations on the morphology and size of the electrospun PBS fibers from solution with AAES, PBS solutions of different concentrations (8, 12, 16 and 20 % (w/v)) were prepared. Solution properties i.e. viscosity, surface tension and conductivity of PBS solutions (CF and DCM) with and without AAES were shown in Table 4.14. As expected, the viscosities PBS solution in both of the solvents with AAES increased with increasing solution concentrations. The observed increase in the viscosity of the PBS solutions might be due to enormously increase in the number of chain entanglements. However, insignificant changes were observed in those of conductivity and surface tension of PBS solution. Tables 4.15 and 4.16 show SEM images and average fiber diameters obtained from the PBS solution in CF and DCM with 1% (w/v) AAES. At 8% (w/v) of PBS solution in CF with AAES 1%, it was found that few beaded fibers were found. This effect was attributed to the poor chain

entanglement density in the PBS solution. Therefore, It was not sufficient to counter the stretching forces from both electrostatic and coulombic repulsion forces. Overstretching of the charged jet, as a result of these forces, resulted in partial break up of the jet. Surface tension of solution tended to minimize the surface areas by forming individual droplets. Beaded fibers, therefore, were found in some spinning conductions. In the case of the PBS solution in DCM, the morphology of the electrospun fibers obtained from all of the concentrations were significantly different compared with the PBS fibers obtained from solutions in CF. This effect could be caused by the conductivity of the PBS solution in DCM (16.7 $\mu\text{S}/\text{cm}$) which was higher than that of the PBS solution in CF. The dielectric value of DCM (ϵ 8.9) was higher than that of CF (ϵ 4.8). This result can be explained by similar reason to as described in Part 4.1.1.

Table 4.14 Viscosity, surface tension and conductivity of PBS solutions in CF and DCM

Solvent	PBS concentration %(w/v)	Viscosity (mPa s)	Surface tension (mN/m)	Conductivity ($\mu\text{S}/\text{cm}$)	Characteristic of electrospun fiber
CF	8	96.3	32.0	16.7	Partial beaded fibers
	12	114.0	33.2	17.8	Smooth fibers
	16	159.0	34.0	17.4	Smooth fibers
	20	191.5	34.3	17.3	Smooth fibers
DCM	8	97.5	34.5	282.5	Smooth fibers
	12	114.5	35.0	284.0	Smooth fibers
	16	162.0	35.8	283.0	Smooth fibers
	20	196.0	36.3	283.8	Smooth fibers

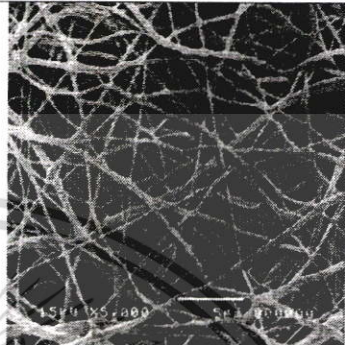
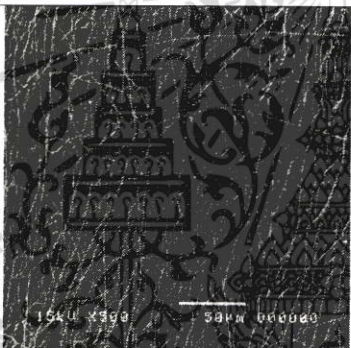
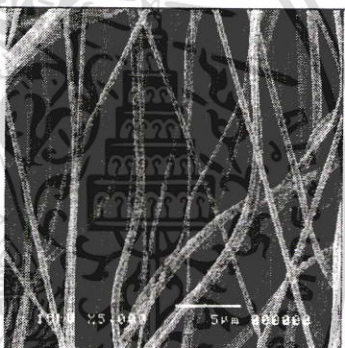
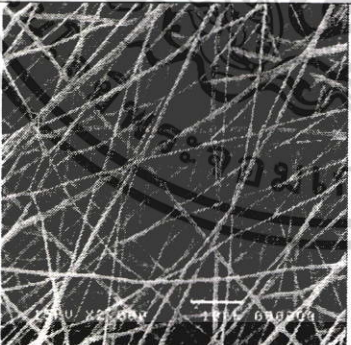
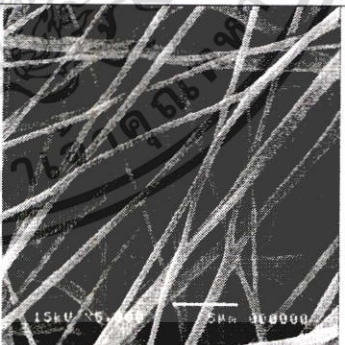
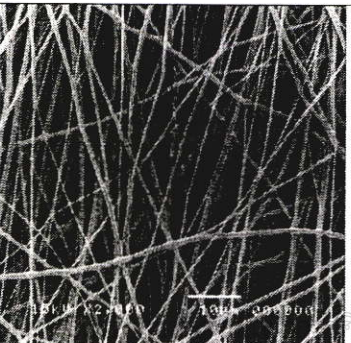
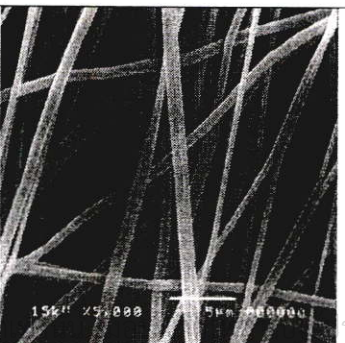
Figure 4.6 shows relationship between average diameters and PBS concentrations obtained from solution in CF and DCM with and without AAES. As expected, the diameters of electrospun fibers increased linearly with increasing polymer concentrations. The average diameter of the electrospun PBS fiber obtained from the solutions in CF increased from 199 to 540 nm when the concentrations were increased from 8% to 20 % (w/v). Meanwhile, average diameter of the electrospun PBS fiber obtained from the solutions in DCM increased from 150 nm to 456 nm when the concentrations were increased from 8% to 20 % (w/v). Considering effects of solvent type on the fiber diameter, it was clear that diameters of electrospun PBS fibers obtained from solutions in DCM were smaller than those of electrospun PBS fibers obtained from solutions in CF. It might be derived from higher dielectric constant of DCM as compared to that of CF. It resulted in increasing conductivity of

solution. Then, it could contribute to increase charge density in ejected jet yielding a stronger elongation force of the jet due to self-repulsion of the excess charges under the electrical field. Then, greater repulsion and a greater bending instability during the electrospinning process resulted in smaller fiber diameter. However, PBS solutions in DCM were difficult to use in electrospinning process, because the solutions often clogged at the tip of the nozzle. Clogging by this solution was due to low boiling point of the DCM (39.8 °C) resulting in a rapid evaporation of the solution.



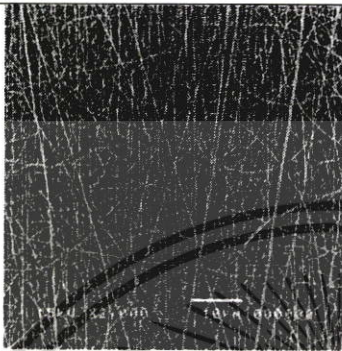
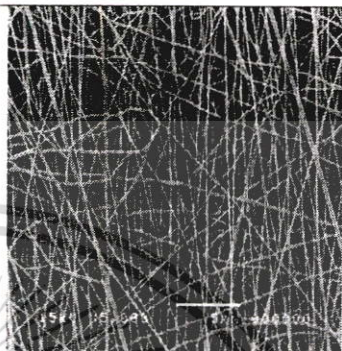
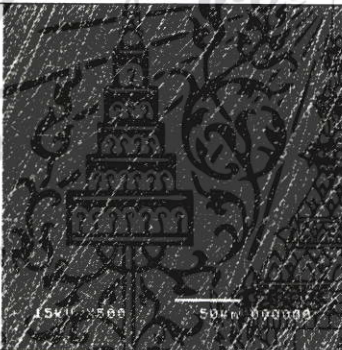
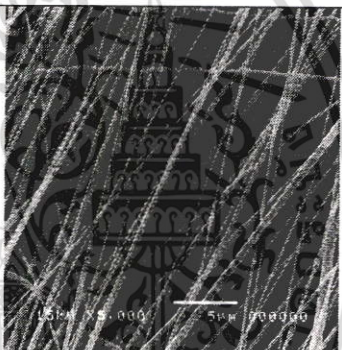
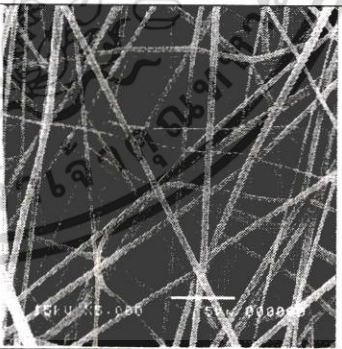
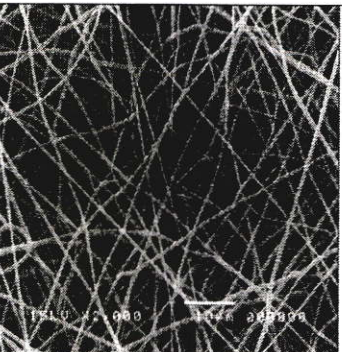
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ไม่ว่ากรณีใดๆ ทั้งสิ้น อีกทั้งห้ามมิให้ดัดแปลงเนื้อหา และต้องอ้างอิงถึงเจ้าของเอกสารทุกครั้งที่มีการนำไปใช้

Table 4.15 SEM images of electrospun PBS fibers and diameters produced from 8, 12, 16 and 20 % (w/v) PBS solutions in CF with 1% (w/v) AAES

Concentration % (w/v)	Magnification		Average fiber diameter (nm)
	2000x	5000x	
4.15(a)			
8			199±28
4.15(b)			
12			374±50
4.15(c)			
16			411±42.
4.15(d)			
20			540±44

เอกสารนี้เป็นเอกสารที่สํานักงานส่งเสริมการค้าระหว่างประเทศ กระทรวงพาณิชย์
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Table 4.16 SEM images of electrospun PBS fibers and diameters produced from 8, 12, 16 and 20 % (w/v) PBS solution in DCM with 1% (w/v) AAES

Concentration % (w/v)	Magnification		Average fiber diameter (nm)
	2000x	5000x	
4.16(a)			
8			150±20
4.16(b)			
12			255.7±21
4.16(c)			
16			365±20
4.16(d)			
20			456±25

เอกสารนี้เป็นเอกสารที่สํานักงานส่งเสริมการค้าระหว่างประเทศ กระทรวงพาณิชย์
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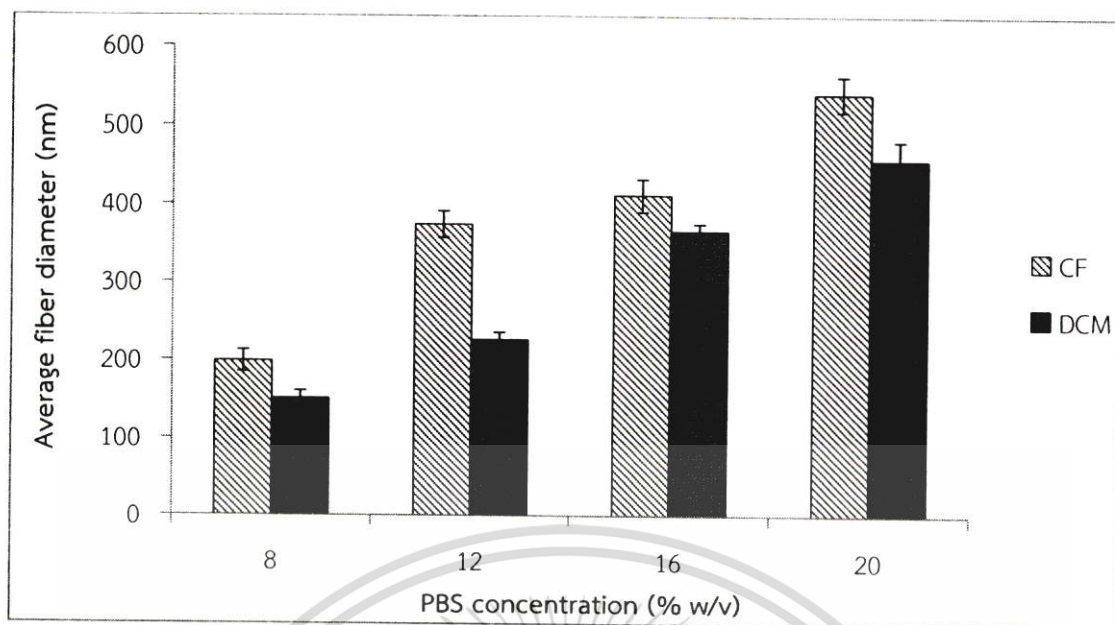


Figure 4.6 Diameters of the electrospun PBS fibers as a function of concentrations of PBS solutions in CF and DCM with 1%(w/v) AAES.

4.2.3 Effects of benzyl trialkyl ammonium chloride

To investigate the effects of benzyl trialkyl ammonium chloride (BTAAC) on electrospinnability of PBS, three organic salts, i.e. benzyl trimethylammonium chloride (BTMAC), benzyl triethylammonium chloride (BTEAC), benzyl and tributylammonium chloride (BTBAC) were investigated. The chemical structures of these salts are shown in Table 4.11. As mentioned previously, using DCM as a solvent for preparing PBS solution in this part was impractical because DCM has fairly low boiling point. Meanwhile, CF has high boiling point for electrospinning of PBS solution in single solvent. In this part, 12% (w/v) PBS solution in CF with salt was studied. The applied electrostatic field strength was fixed at 20 kV/18 cm. Physical properties of PBS solution were investigated as a function of loading organic salt (0-2% (w/v)) as shown in Figure 4.7. It was found that benzyl trialkyl ammonium chlorides slightly affected the viscosity and surface tension of PBS solution, regardless of the different structures of the salts. As expected, the conductivity of PBS solutions dramatically increased as compared with PBS solution in pure CF while organic salts were added. The conductivity of polymer solution depended on free ions in the solution. The added organic salts can increase conductivity of PBS solution since organic salt dissolved as free ions. As mention previously, amounts of organic salts were studied as a % weight/volume. The effect of amounts of the organic salts as a molar concentration on the conductivity PBS solution were further studied. The conductivity of those PBS solutions were summarized in Table 4.17

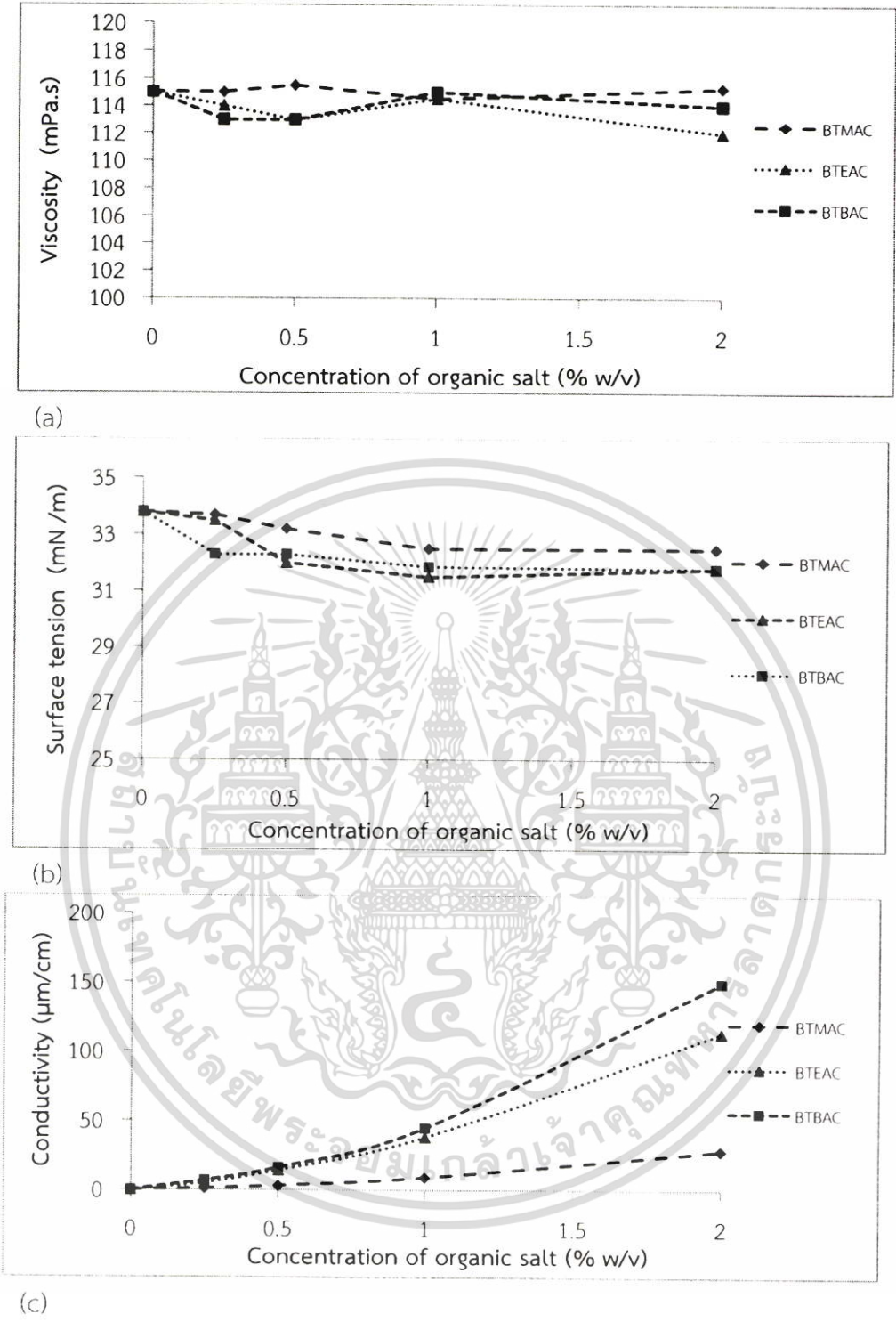


Figure 4.7 Properties of 12% (w/v) PB S solution with different organic salts in various concentrations ranging from 0 to 2.0% (w/v); (a) viscosity, (b) surface tension and (c) conductivity

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Table 4.17 Effects of amount of salts on the conductivity of PBS solutions as compared as a mole unit

Type of salt	Molecular weight (g/mol)	Concentration (M)	Conductivity ($\mu\text{S}/\text{cm}^3$)
BTMAC	185	1	30.1±0.5
BTEAC	205	1	183.9±0.5
BTBAC	277	1	243±0.5

As expected, PBS solution with BTBAC had the highest conductivity of PBS solution. These results corresponded to the PBS conductivity studied as a % weight/volume (Figure 4.7). A main reason affected on those of solutions conductivity, possible mechanisms can be summarized in Figure 4.8. From Figure 4.7, different conductivities of PBS solutions were carried out. It might be derived from dissociate ability of ionic of organic salts. Therefore, main reasons used to explain the increase in conductivity of PBS solution as a function of organic salt structures can be discussed as follows.

The reasons used to describe these results could be divided into three parts.

First, the dissociate ability of ionic of organic salts in PBS solution might depend the inductive effect of alkyl groups attached on nitrogen atom of quaternary salt. Ammonium quaternary groups had a positive charge characteristic. Meanwhile carbon atoms of alkyl groups attached on nitrogen of ammonium groups is a donating group. Then, carbon atoms were share electron toward quaternary ammonium salt by inductive effect. The inductive effect of carbon atoms in this case is said to exhibit + I inductive effect (plus effect called +I effect) [133-136]. Increasing +I effect of carbon atom on the ammonium quaternary groups derive from increasing long chain of carbon groups. Therefore, it pushed electron density toward nitrogen. It yielded an increase in negative characteristic on the quaternary ammonium group. It might be occurred to increasing repulsive force between quaternary ammonium salt and Cl^- which was counter ion. It leads the counter anion (Cl^- ion) remains dissociated rather than paired with the cation (quaternary ammonium ion). From this reason, it might be a factor contribute to dissociate BTBAC was maximum as compared to other organic salts.

Second, dissociate ability of ionic of organic salts in PBS solution might governed by steric effect. BTMAC had a small size of alkyl quaternary group. This can lead to strong interaction between of oxygen (δ^-) on carbonyl group of PBS structure and ammonium quaternary salt (δ^+). Such interaction was stronger than BTEAC and BTBAC. From this effect resulted in the quantity of free ions in the solution decreased. This yielded a low conductivity of the PBS solution. However, increasing chain of alkyl groups, resulting in reducing attract force between of oxygen (δ^-) on carbonyl group of PBS structure and ammonium quaternary salt (δ^+).

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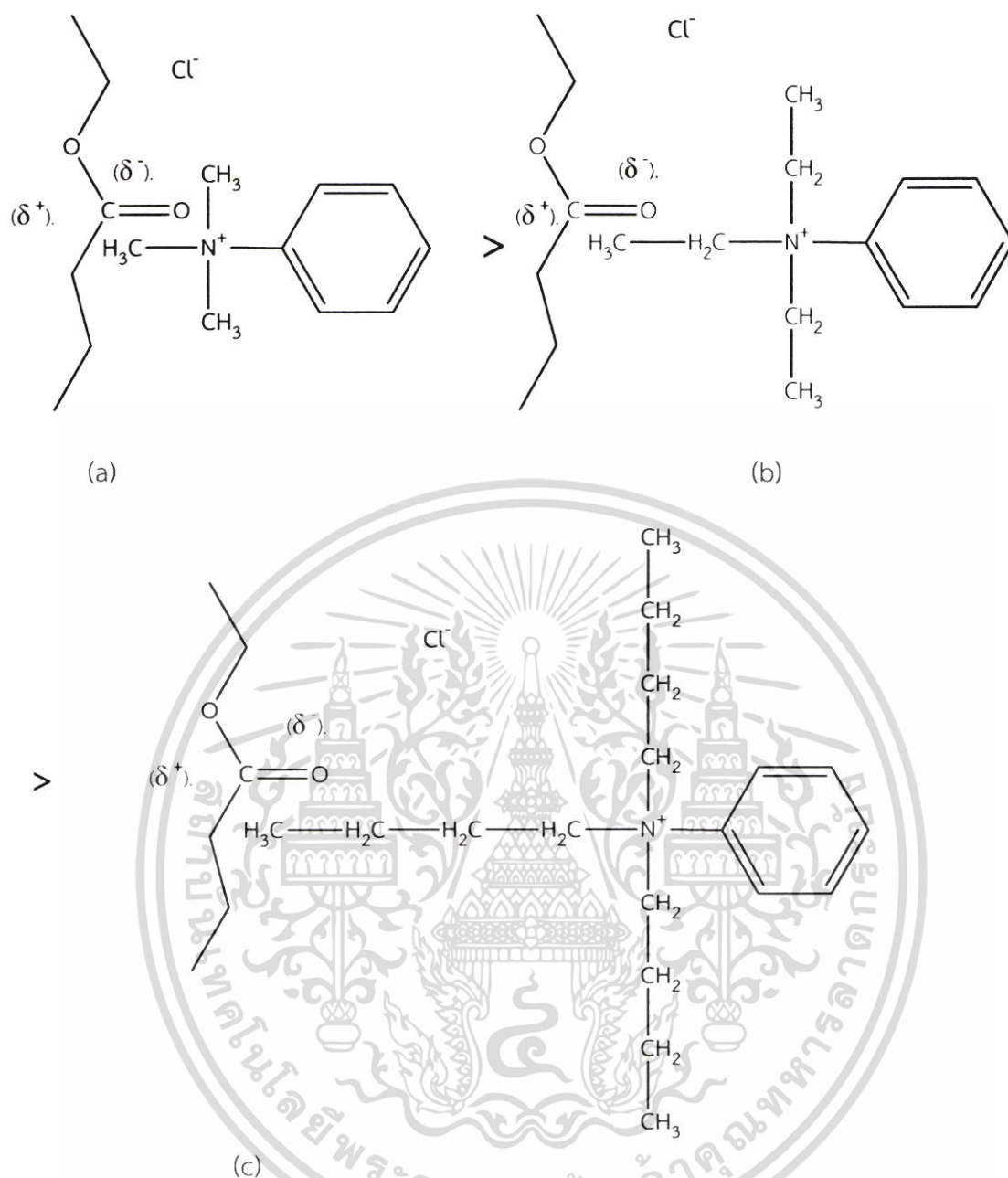


Figure 4.8 Proposed possible mechanisms of interaction between quaternary ammonium salt and carbonyl groups on PBS structure arranged from high to low interaction., (a) BTBAC>, (b) BTEAC> (c) BTMAC, respectively

This might be attributed to steric hindrance of increased carbon chains. Long chains of butyl groups were attached on ammonium quaternary ions resulting in steric hindrance effect. It leads to reducing attractive force between oxygen (δ^-) on carbonyl group of PBS structure and ammonium quaternary salt (δ^+). From this effect resulted in the quantity of free ions in the solution increased; this yielded a high conductivity of the solution. Figure 4.8 shows possible mechanism of interaction between quaternary ammonium salt of trialkyl benzyl ammonium chlorides and carbonyl groups of PBS. It was rearranged from high interaction to low interaction as follows; (a) BTMAC >, (b) BTEAC > and (c) BTBAC, respectively. These results

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corresponded to Cheng *et al.* [111], They reported that ionic sizes might affect the conductivity of PAN solutions. They found that strong polarity of PAN, the $C\equiv N$ functional groups had a strong attraction to halogen anions, resulting in the reduction of free ions in the solution. As the anion sizes i.e., Cl^- , Br^- or PO_4^- , increased the association interaction became weaker, the quantity of free ions in the solution increased. So the organic salts with small sizes of quaternary ammonium groups were possible to interact easily on the carbonyl groups of PBS. This effect was one of the most important factors contributed easily to the lowest conductivity of PBS solution with BTMAC.

Third, dissociate ability of ionic of organic salts in PBS solution might governed by “like dissolves like” rule. By referring on the polarity of systems, i.e., non-polar molecules dissolve in non-polar solvents (e.g. chloroform, dichloromethane and hexane) and polar molecules dissolve in polar solvents (e.g. water, alcohol). Polarity of organic salt molecules was decreased with increasing number of hydrocarbon atoms attached on nitrogen atom of quaternary salt. As expected, polarity of BTBAC was lower than those of BTEAC and BTBMC. The non-polarity of organic salts could be arranged from high to low polarity as BTBAC, BTEAC, and BTMAC. CF is one of non-polar solvents. It might contribute to enhance the dissociate ability of BTBAC in the PBS solution. Conductivity of PBS solution is related to the ion concentration in the solution. From this reason, it could be factor contribute to the highest conductivity of PBS solution with BTBAC as compared to other organic salts.

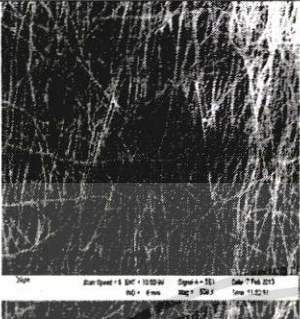
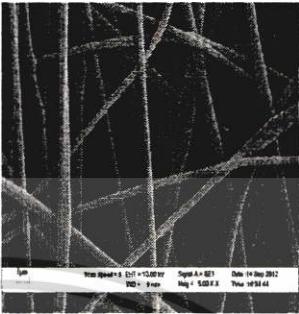
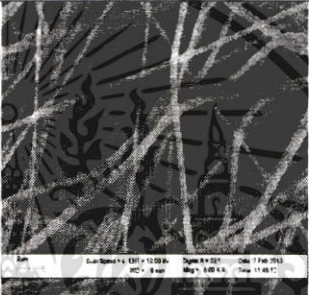
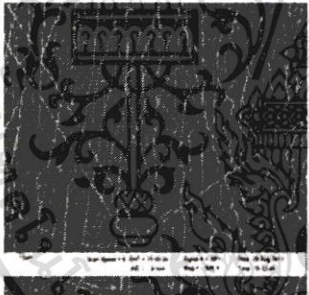
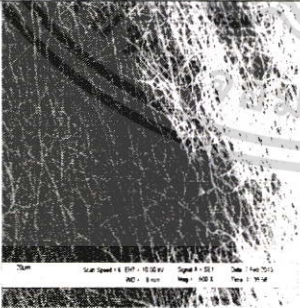
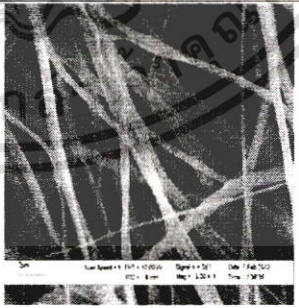
Effects of salt concentrations and types on morphology and average fiber diameter are shown in Tables 4.18-4.20. As expected, the average diameter of electrospun PBS fiber was decreased with increasing salt concentrations. Morphology and average diameters of electrospun PBS fibers were significantly different between the salt types. Regarding salt concentrations on the morphological appearance, beaded fibers were still presented at PBS solution with 0.25 % (w/v) BTMAC. Morphology of PBS fiber obtained from solution with 0.25 % (w/v) BTEAC and BTBAC appeared to smooth fibers. It might be attributed to conductivity of PBS solution with BTEAC or BTBAC was higher than that of PBS solution with BTMAC.

Table 4.18 shows SEM images of electrospun fibers obtained from solution with BTMAC. Small bead fibers were still presented at 0.25% (w/v) of BTMAC. When BTMAC concentration was increased (0.5-2% (w/v)), morphology was changed to be smooth fibers. As expected, fiber diameter was decreased with increasing BTMAC concentrations.

Tables 4.19 and 4.20 show SEM images of electrospun fibers obtained from solution with BTEAC and BTBAC, respectively. Smooth fibers were presented when 0.25% salts were added.

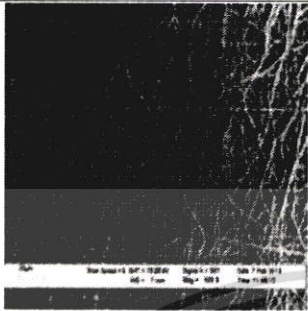
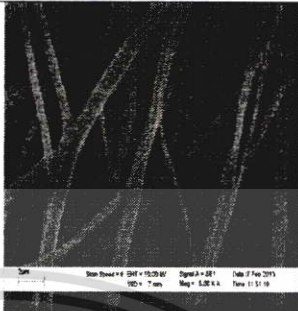
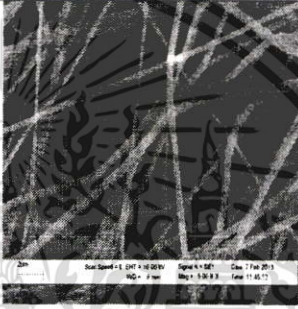
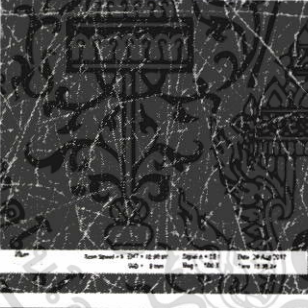
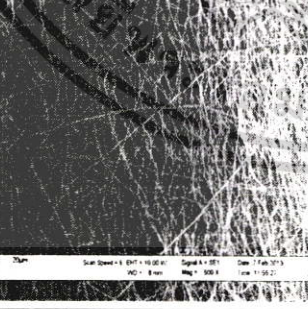
เอกสารนี้เป็นเอกสารที่สงวนไว้สำหรับการใช้งานเพื่อการศึกษาเท่านั้น ไม่อนุญาตให้นำไปใช้ประโยชน์ด้านการค้า
ไม่ว่ากรณีใดๆ ทั้งสิ้น อีกทั้งห้ามมิให้ดัดแปลงเนื้อหา และต้องอ้างอิงถึงเจ้าของเอกสารทุกครั้งที่มีการนำไปใช้

Table 4.18 SEM images of electrospun PBS fibers and diameters produced from 12 % (w/v) PBS solutions in CF with various amounts of BTMAC

Salt concentration % (w/v)	Magnification		Average fiber diameter (nm)
	500	5000	
0.25			543±32
0.5			391±36
1			376±25
2			370±24

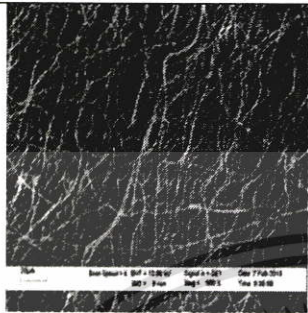
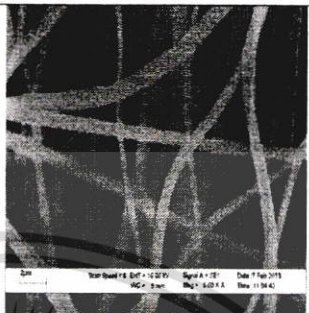
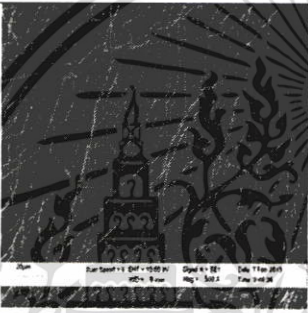
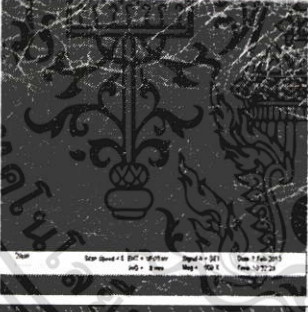
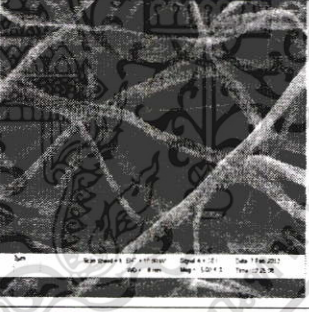
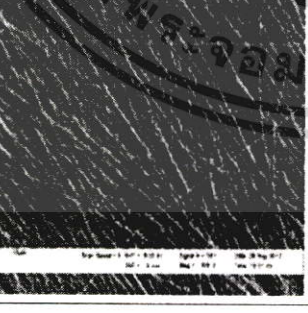
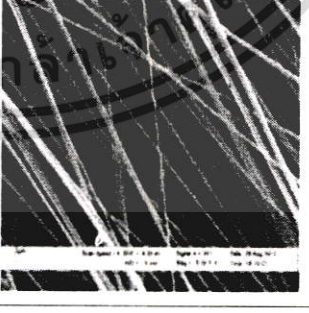
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Table 4.19 SEM images of electrospun PBS fibers and diameters produced from 12 % (w/v) PBS solutions in CF with various amounts of BTEAC

Salt concentration % (w/v)	Magnification		Average fiber diameter (nm)
	500	5000	
0.25			497±28
0.5			371±24
1			357±24
2			341±22

เอกสารนี้เป็นเอกสารที่สงวนไว้สำหรับการใช้งานเพื่อการศึกษาเท่านั้น ไม่อนุญาตให้นำไปใช้ประโยชน์ด้านการค้า ไม่ว่ากรณีใดๆ ทั้งสิ้น อีกทั้งห้ามมิให้ดัดแปลงเนื้อหา และต้องอ้างอิงถึงเจ้าของเอกสารทุกครั้งที่มีการนำไปใช้

Table 4.20 SEM images of electrospun PBS fibers and diameters produced from 12 % (w/v) PBS solutions in CF with various amounts of BTBAC

Salt concentration % (w/v)	Magnification		Average fiber diameter (nm)
	500	5000	
0.25			487±20
0.5			372±22
1			348±20
2			338±24

เอกสารนี้เป็นเอกสารที่สงวนไว้สำหรับการใช้งานเพื่อการศึกษาเท่านั้น ไม่อนุญาตให้นำไปใช้ประโยชน์ด้านการค้า ไม่ว่ากรณีใดๆ ทั้งสิ้น อีกทั้งห้ามมิให้ดัดแปลงเนื้อหา และต้องอ้างอิงถึงเจ้าของเอกสารทุกครั้งที่มีการนำไปใช้

Figure 4.9 shows average diameters of electrospun PBS fibers as a function of the salt loading. As expected, the diameters of electrospun PBS fibers decreased when amounts of the salts were increased.

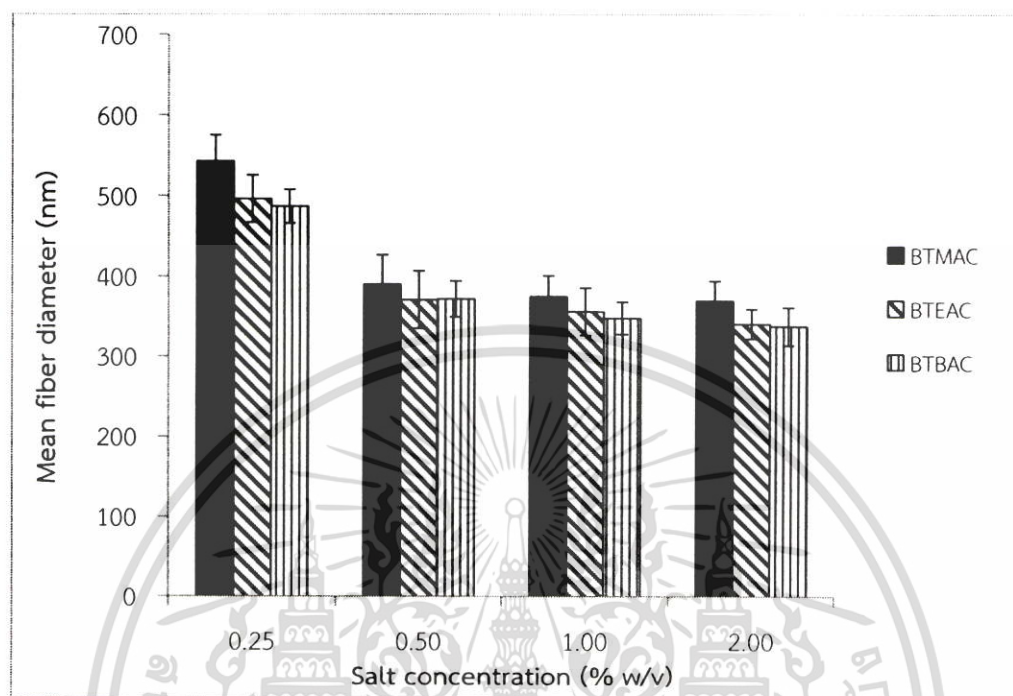


Figure 4.9 Effects of the organic salt concentrations on the average diameters of the electrospun PBS fibers

From above results, it can be concluded that the increased conductivity of PBS solutions is one of most important factors dominating the instabilities of electrospinning process. The increased conductivity of PBS solutions was able to increase charge density of polymer jet during electrospinning process. An increased charge density enhanced the whipping instability. A high surface charge simultaneously suppressed the axis-symmetric instability (i.e., Rayleigh) and enhanced whipping instability. The increased whipping instabilities generated a bending force on the jet, led to increase a high degree of elongation forces of the polymer jet. Therefore, the increased whipping could be resulted in a defect reduction. Finally, the uniform fiber morphology with a narrow size distribution was obtained. Therefore, it was clearly shown that the Rayleigh instability was one of the most important factors that caused bead formation. The Rayleigh instability was suppressed when increasing conductivity of PBS solution. The increased the polymer solution conductivity led to enhancing the charge density of the polymer jet and resulted in a suppressed Rayleigh instability.

4.2.4 Comparison of organic salts on electrospinnability of PBS fibers

It was clearly seen previously that solution conductivity was one of the most important factors influencing fiber diameters. To compare the effects of the four organic salts on PBS solution properties and fiber diameters were investigated. All solution properties, that is, viscosity, surface tension and conductivity, before and after the addition of organic salts (0.25–1% w/v) were summarized in Figure 4.10. It was clear that the addition of organic salts to the PBS solution caused a significant increase in the conductivity of the PBS solution. The conductivity of the PBS solution in CF with BTBAC was the highest. This reason was attributed to strong polarity of carbonyl groups on PBS structure whereas the quaternary ammonium salt of BTBAC had a weak attraction. It resulted in the increasing of free ions in the PBS solution. However, the viscosity and surface tension of the PBS solutions in CF decreased slightly when the salts were added.

Effects of salt concentrations and salt types on the morphology and average fiber diameter are shown in Table 4.12 and Figure 4.2 for PBS in CF with AAES and Tables 4.18-4.20 for PBS in CF with benzyl trialkyl ammonium chlorides (BTAAC). As expected, the diameter of electrospun PBS fiber was decreased with increasing salt concentrations as shown in Figure 4.11. Therefore, adding salts in PBS solution was prone to enhance conducting mode of PBS solution. The surface charges of the spinning jet obtained from electrospinning of the solutions were increased. This yielded a stronger elongation force of the polymer jet because of the self-repulsion of excess charges on the surface. It led to increase stretching of polymer jet due to the enhanced charge density, leading to a decrease in fiber diameter. However, morphologies and diameters of electrospun PBS fibers were significantly different between the salt types. Regarding salt concentrations on the fiber morphology, beaded fibers were still presented at PBS solution with 0.25 % (w/v) BTMAC and AAES concentrations whereas PBS fibers obtained from solution with 0.25 % (w/v) BTEAC and BTBAC, smooth fibers were presented. It might be derived from high conductivity of PBS solution. With dramatically increased conductivity of PBS solution by adding BTEAC and BTBAC, it was able to enhance the columbic repulsion of mutual charges presented within the jet. Under a given electric field, these results could increase the elongation force on the jet. It could be caused by self-repulsion of the excess charges on the surface of polymer jet. From this phenomena, it was able to inhibit the Rayleigh instability (axis-symmetric instability) and enhance to whipping instability (non-axis-symmetric instability). The ultrafine fibers were easily obtained when BTEAC and BTBAC were used.

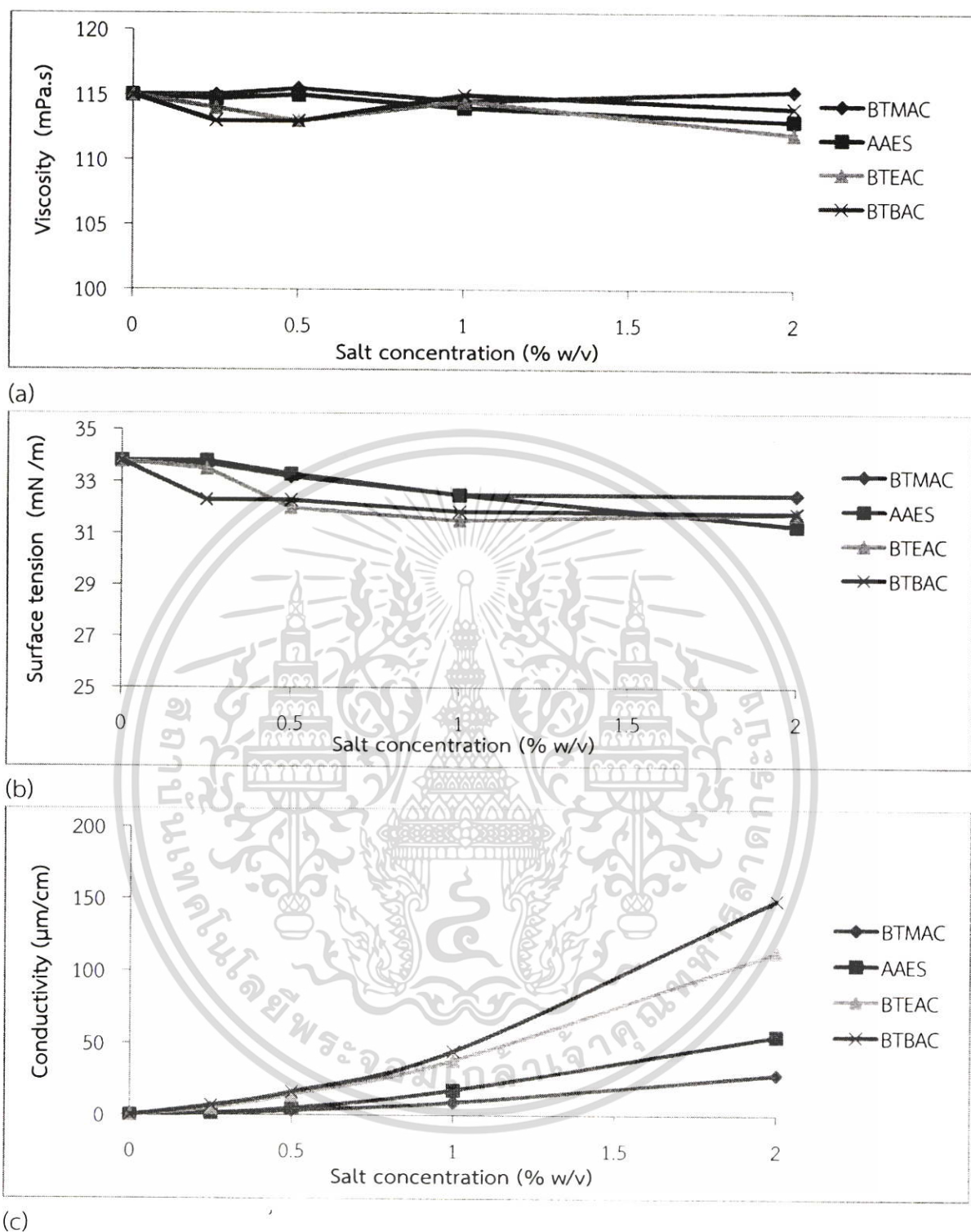


Figure 4.10 Properties of 12% (w/v) PBS solution in CF with different salts at various concentrations; (a) viscosity, (b) surface tension and (c) conductivity

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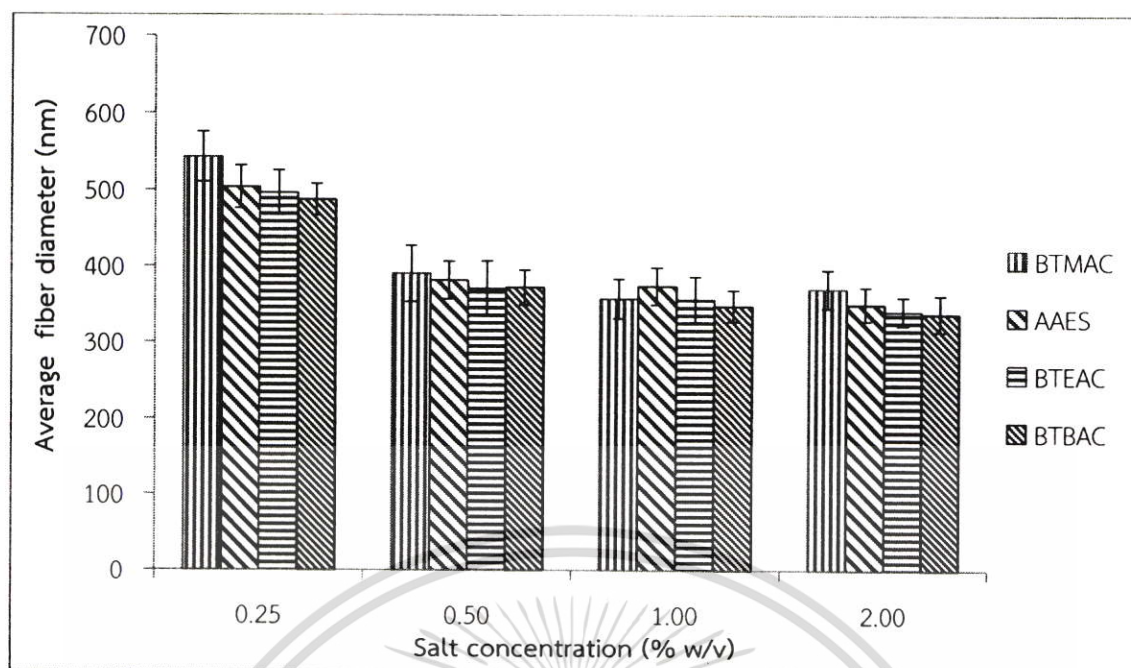


Figure 4.11 Effects of salt concentrations and types on the mean diameter of the electrospun PBS fibers

4.3 Effects of salts on thermal properties, characteristic functionalities and mechanical properties of electrospun non-woven PBS fibers

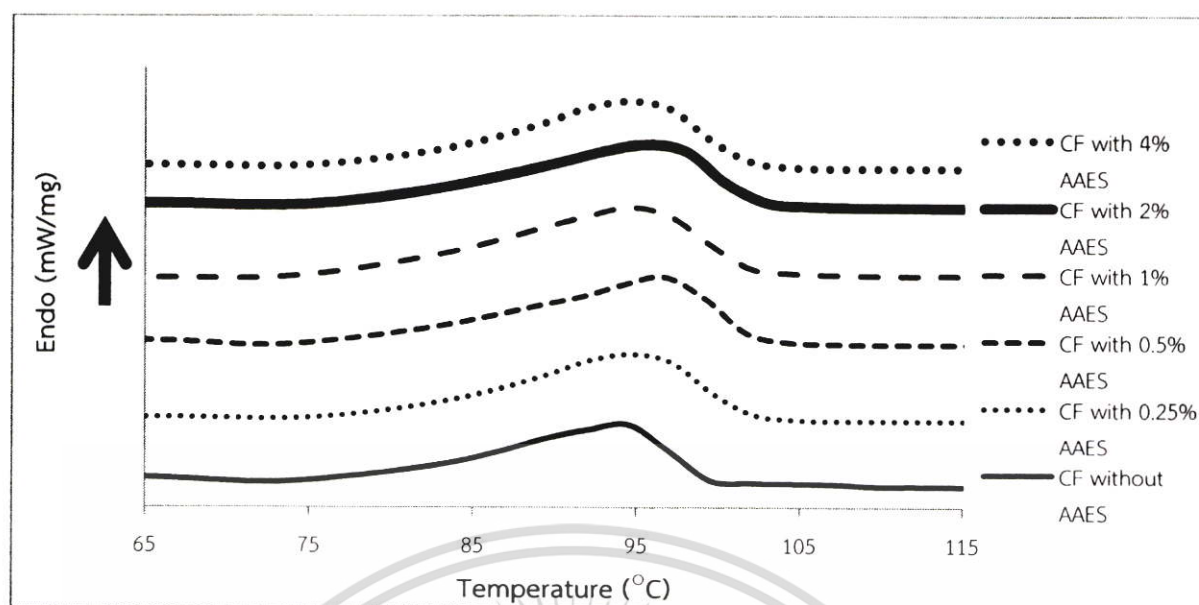
In this part, effect of organic salts on thermal properties, characteristic functionalities, and mechanical properties of the electrospun non-woven PBS fibrous mats were investigated. Differential scanning calorimetry (DSC) was used to analyze thermal properties of non-woven fibrous mats. Characteristic functionalities of these mats were characterized by FT-IR spectroscopy. Mechanical properties of non-woven fibrous mats were investigated by tensile experiments.

4.3.1 Effects of salts on thermal properties

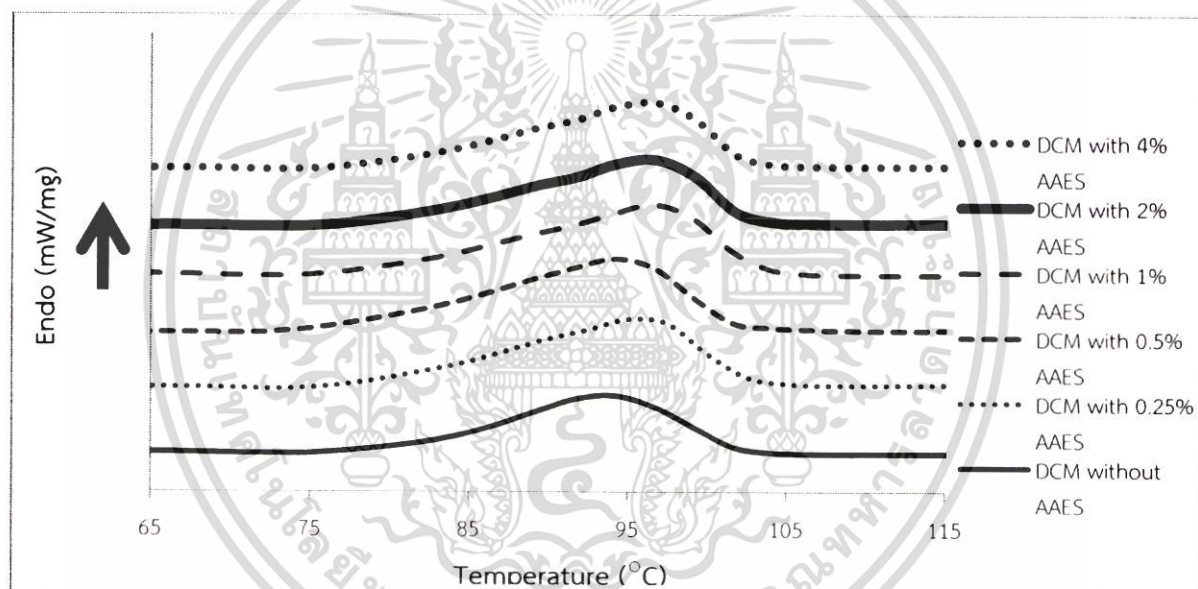
In this part, DSC was used to determine effects of organic salts on the thermal properties of electrospun PBS fiber as non-woven mats. From thermograms, melting temperature (T_m) and degree of crystallinity (X_c) of the nonwoven mats were studied. First part, effects of amounts of AAES on electrospun non-woven PBS fiber obtained from solution in CF and DCM were investigated. In the second part, effects of PBS concentrations on the thermal properties of non-woven PBS fiber electrospun from solution in CF with 1% (w/v) AAES were studied. Finally, comparison effects of alkyl ammonium ethyl sulfate and benzyl trialkyl ammonium chloride salts on the thermal properties were investigated.

4.3.1.1 Effects of AAES on thermal properties

Figure 4.12 shows DSC thermograms of electrospun PBS fibrous nonwoven mats fabricated from solution in CF (4.12 (a)) and DCM (4.12 (b)) with various amounts of AAES. The melting temperature and degree of crystallinity of each PBS fibrous mat were summarized in Table 4.21. It was found that the melting temperature (T_m) of PBS had a trend to increase when AAES was added in PBS solution. It might be derived from addition of the AAES in PBS solution resulted in increase the charge density in ejected jet. It yielded a stronger elongation force of the polymer jet due to the self-repulsion of the excess charges under the electrical field. It led to increase chain orientation aligns along the fibers better than that of electrospun fibers obtained from the solutions without salt. It could be contributed to increase degree of crystallinity and the development of a level of preferred orientation of the fibers. From this reason, T_m of ultrafine fibers were higher than beaded fibers. Moreover, the degree of crystallinity of electrospun fibers increased when increasing amounts of AAES. This suggested that the increasing conductivity of polymer solutions resulted in a high degree of elongation of the jet with better chain orientation and increasing crystallization of PBS. It could lead to increase alignment of the molecular chains along the fiber axis. Then degree of crystallinity of the PBS fiber had a trend to increase when AAES was added to PBS solution in both CF and DCM.



(a)



(b)

Figure 4.12 DSC thermograms of the electrospun ultrafine PBS fibers from solution in (a) CF and (b) DCM with and without 1% (w/v) AAES

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Table 4.21 Thermal properties of electrospun PBS fibers obtained from 12 % (w/v) PBS in CF and DCM with various AAES concentrations

Solvents	Concentration of AAES % (w/v)	T _m (°C)	ΔH _m (J/g)	Degree of Crystallinity (%)
CF	0	94.2	38.3	18.2
	0.25	94.6	41.3	19.7
	0.5	97.2	48.5	23.1
	1	94.5	52.7	25.0
	2	96.1	45.7	21.8
	4	95.2	46.7	22.2
DCM	0	92.0	38.4	18.3
	0.25	97.4	48.5	23.1
	0.5	94.1	49.5	23.6
	1	96.3	52.6	25.0
	2	96.5	42.7	20.3
	4	96.8	45.1	21.5

Note: Heat of fusion for PBS 100%=210 J/g [26]

4.3.1.2 Effects of PBS concentrations on thermal properties

This part shows the effects of PBS concentrations on the electrospun PBS non-woven mats obtained from PBS solution in CF with 1% (w/v) AAES. As expected, diameter of the fibers increased with increasing PBS concentration (Table 4.15). Figure 4.13 and Table 4.22 show DSC thermograms and thermal properties of the non-woven mats. As seen in Table 4.22, insignificant changes were observed in T_m of the electrospun PBS fibers. The lowest crystallinity of electrospun PBS fiber was found when using 8 % (w/v) PBS concentration. It could be attributed to the beads on string of PBS fibers. It might be due to the low chain entanglement of polymer jet to withstand the stretching chains under the electrical field strength. Moreover, non-irregular fibers is one of factors that reduce the chain orientation of electrospun PBS fiber. It was able to reduce the degree of crystallinity. Conversely, it was observed that the electrospun PBS fibers obtained from 12% (w/v) solution had the highest

degree of crystallinity. The degree of crystallinity was slightly decreased when increasing PBS concentration. This might be due to effect of fiber diameters. This result corresponded to the Wong *et al.* and Arinstein *et al.* They reported the effect of diameter size on the degree of crystallinity of electrospun fibers [137-140]. They found that as fiber diameter of electrospun polyester fiber was reduced, at some critical fiber diameters, the size of the skin region became comparable to the overall diameter of the fiber. As the size of the fiber was reduced; the size of the supramolecular structure containing amorphous oriented macromolecules was more significant compared to the fiber diameter. Thus, at the critical fiber diameter, the properties of the fiber were controlled by the oriented amorphous macromolecules in the supramolecular region whereas when the fiber diameter was increased, orientation of the chains at the surface of the fiber walls became less compared to the majority of the chains in the fiber core region. Those information might be used to explain the reason why the diameter of fiber increased and the degree of crystallinity of electrospun fibrous mat decreased.

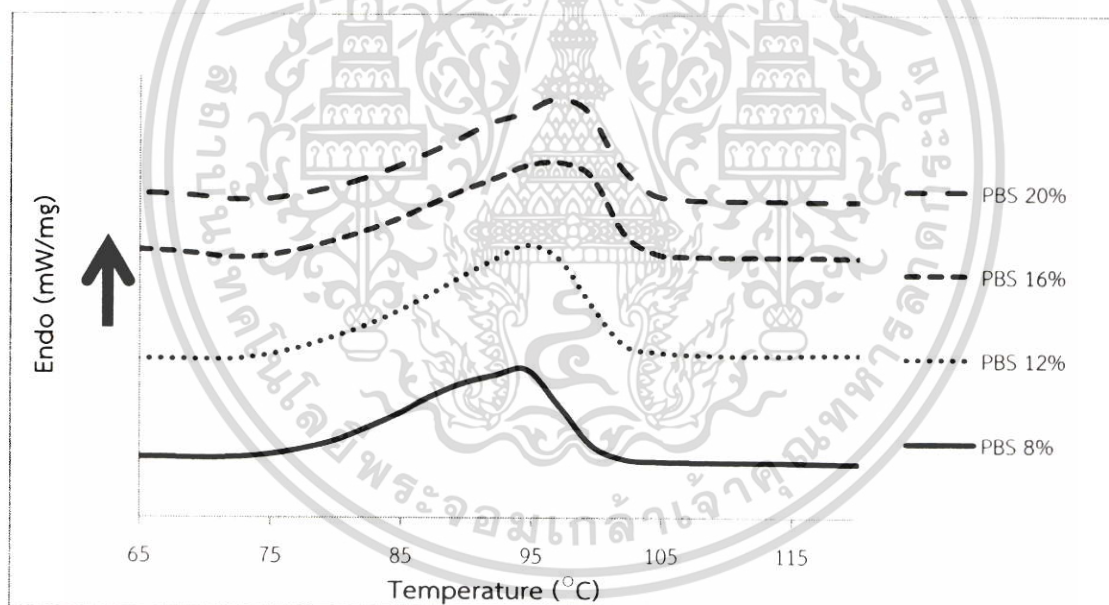


Figure 4.13 DSC thermograms of electrospun ultrafine PBS fibers obtained from solution in CF with 1% (w/v) AAES at various PBS concentrations

Table 4.22 Effects of PBS concentrations on thermal properties of ultrafine PBS fibers obtained from solution in CF with 1% (w/v) AAES

Concentrations AAES % (w/v)	T _m (°C)	ΔH _m (J/g)	Degree of crystallinity (%)
8	94.6	41.3	19.7
12	94.5	52.7	25.0
16	96.3	49.4	23.5
20	97.2	48.2	22.9

Note: Heat of fusion for PBS 100%= 210 J/g [26]

4.3.1.3 Effects of organic salts on thermal properties

In this part, effects of different salts on thermal properties of electrospun PBS fibers were studied. Thermal properties of ultrafine PBS fibers obtained from electrospun PBS solution 12 % (w/v) in single solvent with and without salt and mixed solvent of 70:30 % (v/v) CF:MeOH. Table 4.23 shows thermal properties of electrospun PBS fibrous mats, i.e., melting temperature (T_m), heat of fusion and % crystallinity of electrospun fibers obtained by DSC. Regarding thermal properties, T_m of ultrafine PBS fibers that spun from solution with and without salt was investigated. It is noticeable that the melting temperature for the electrospun PBS fibers did not change significantly. These values are very close to the reported value (~ 94 °C) from Tserki *et al* [32]. However, % crystallinities of electrospun PBS fibers obtained from solutions with salts were higher than those of electrospun fibers from solution without salt. Electrospun PBS fiber from CF without salt showed the lowest % crystallinity of ultrafine fibers. Electrospun PBS fibers from CF with BTBAC showed the highest % crystallinity of ultrafine fibers. Figure 4.14 shows DSC curves of all samples that were electrospun from PBS solution with and without salts.

Addition of salts in PBS solution was able to increase the charge density in surface of polymer jet. It could be due to a strong elongation force of jet from self-repulsion of the excess charges under the electrical field. These repulsive forces promoted instability i.e., bending and wiping instability of polymer jet more than the less charged jet. This whipping instability produced a bending force on the jet stretched polymer chains in the direction of electrostatic field, resulting in degree elongation of the jet higher than the jet electrospun from solution without salts. Such

phenomena might contribute to high alignment of polymer chains in the direction of fiber axis.

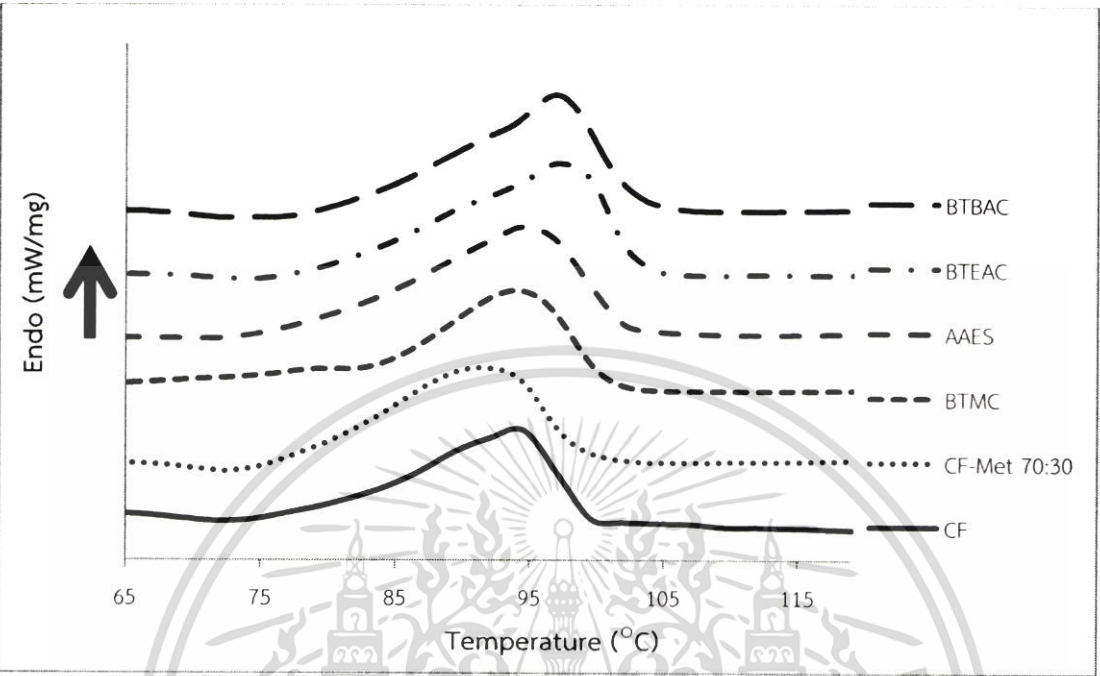


Figure 4.14 DSC thermograms of electrospun ultrafine PBS fibers obtained from solution in CF with and without 1% (w/v) salts

Table 4.23 Thermal properties of electrospun fibers obtained from 12% (w/v) PBS solution in CF with and without salts, and mixed solvent (CF:MeOH)

Types of organic salts	T_m (°C)	ΔH_m (J/g)	% Crystallinity
Without salt 1*	94.2	38.3	18.2
Without salt 2**	91.3	47.0	22.4
BTMAC	94.5	50.5	24.0
AAES	94.5	52.7	25.0
BTEAC	97.0	52.8	25.1
BTBAC	96.4	56.2	26.8

Note: 1. Heat of fusion for PBS=210 J/g.[26]

2. * Thermal properties of electrospun fibers obtained from 12% (w/v) PBS solution in CF without salt

3. ** Thermal properties of electrospun fibers obtained from 12% (w/v) PBS solution in mixed solvent of CF:MeOH (70:30 (v/v))

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4.3.2 Characterization of electrospun PBS fibers by using FT-IR spectroscopy

This part was focused on characterization of functionality of electrospun PBS fibers using FT-IR spectroscopy. Absorption bands of electrospun PBS fibers obtained from solutions with and without organic salts are shown in Figure 4.15. In case solution without salt, the absorption spectra of the electrospun PBS fibers were obtained from solution in mixed solvent of 70:30 % (v/v) CF:MeOH. In case solution with salts, the electrospun PBS fibers were obtained from PBS solution in CF with 1% (w/v) organic salts. In Figure 4.15, the spectrum of electrospun PBS fibers obtained from solutions without salt showed characteristic absorption peaks of the stretching vibration of the -COO- at ~ 1161 , ~ 1329 cm^{-1} and the stretching vibration of the C-O-C and 1720 cm^{-1} for carbonyl groups of ester linkages. These results were similar to Zhao *et.al.* and Phua *et.al.* [141-142]. Absorption spectra of electrospun fibrous non-woven mat obtained from solutions with salts yielded absorption bands at same positions as compared to that of electrospun PBS fibrous mat. In addition, overtone absorption peaks were observed at 2357 cm^{-1} . It might be attributed to the C-H stretching of alkyl groups that was found in quaternary ammonium ions of salts [143].

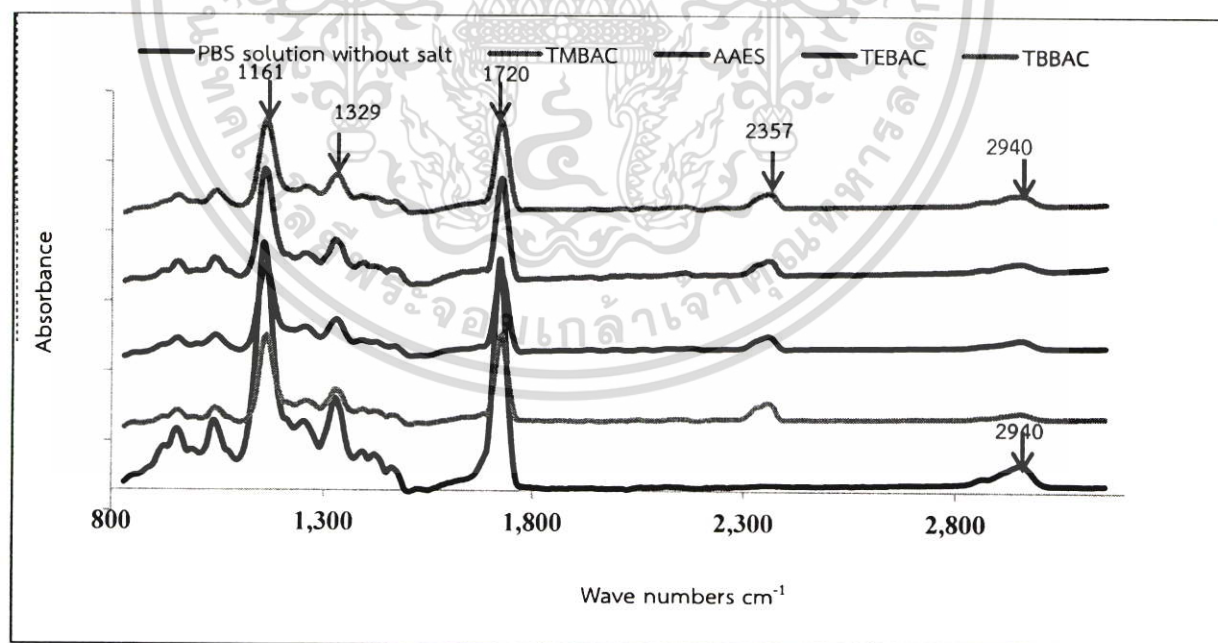


Figure 4.15 Infrared absorbance spectra of electrospun PBS fibrous non-woven mats obtained from solution with 1% (w/v) organic salts

4.3.3 Mechanical properties of electrospun PBS fibrous mats

Mechanical properties of electrospun fibrous non-woven mats are of importance in a variety of application areas, i.e., tissue engineering scaffolds, filtration fabrics, protective membranes and sensors. As mentioned previously, organic salts could dramatically affect the solution properties, fiber sizes, morphological appearance and thermal properties of electrospun PBS fibrous mat. Figure 4.16 shows mechanical properties of non-woven mats electrospun ultrafine fibrous mats obtained from solution with and without salts (PBS fibrous mats spun from solution in CF-MeOH). Meanwhile, Table 4.24 compares morphology, % Crystallinity and mechanical properties of electrospun fiber obtained from the PBS solutions with and without salts. It can be observed that tensile strength and Young's modulus of electrospun ultrafine PBS fibrous non-woven mats obtained from solution with salts were higher than those without salt (fibrous mats spun from solution in 70:30 (v/v) CF:MeOH). It could be caused by adding organic salts in the PBS solutions. It resulted in an increase in conductivity in PBS solution. It was able to increase the charge density of the polymer jet. It yielded a stronger elongation force of the polymer jet due to the self-repulsion of the excess charges under the electrical field. It led to increase chain orientation aligns along the fibers better than that of electrospun fibers obtained from the solutions without salt. It was able to enhance the tensile strength and modulus properties of the electrospun PBS fibers as compared to the PBS fiber which spun from solution in CF-MeOH. However, percentage elongation at yield of the ultrafine PBS fibrous slightly decreased as compared with PBS fibrous mats spun from solution in CF-MeOH. These results related to increased % crystallinity of the electrospun PBS fibers after the addition of organic salt to the PBS solution (As summarized in Table 4.24). As expected, tensile strength and Young's modulus of ultrafine PBS fibrous mats spun from solution with BTBAC had the highest tensile strength and the Young's modulus. The results were similar to Wong *et al.* and Li *et al.* [137, 140]. They demonstrated that the finer fibers were obtained when the polymer jet stretched to a greater extent during the electrospinning process resulting in higher orientation of macromolecular chains and higher mechanical behaviors of electrospun fibers.

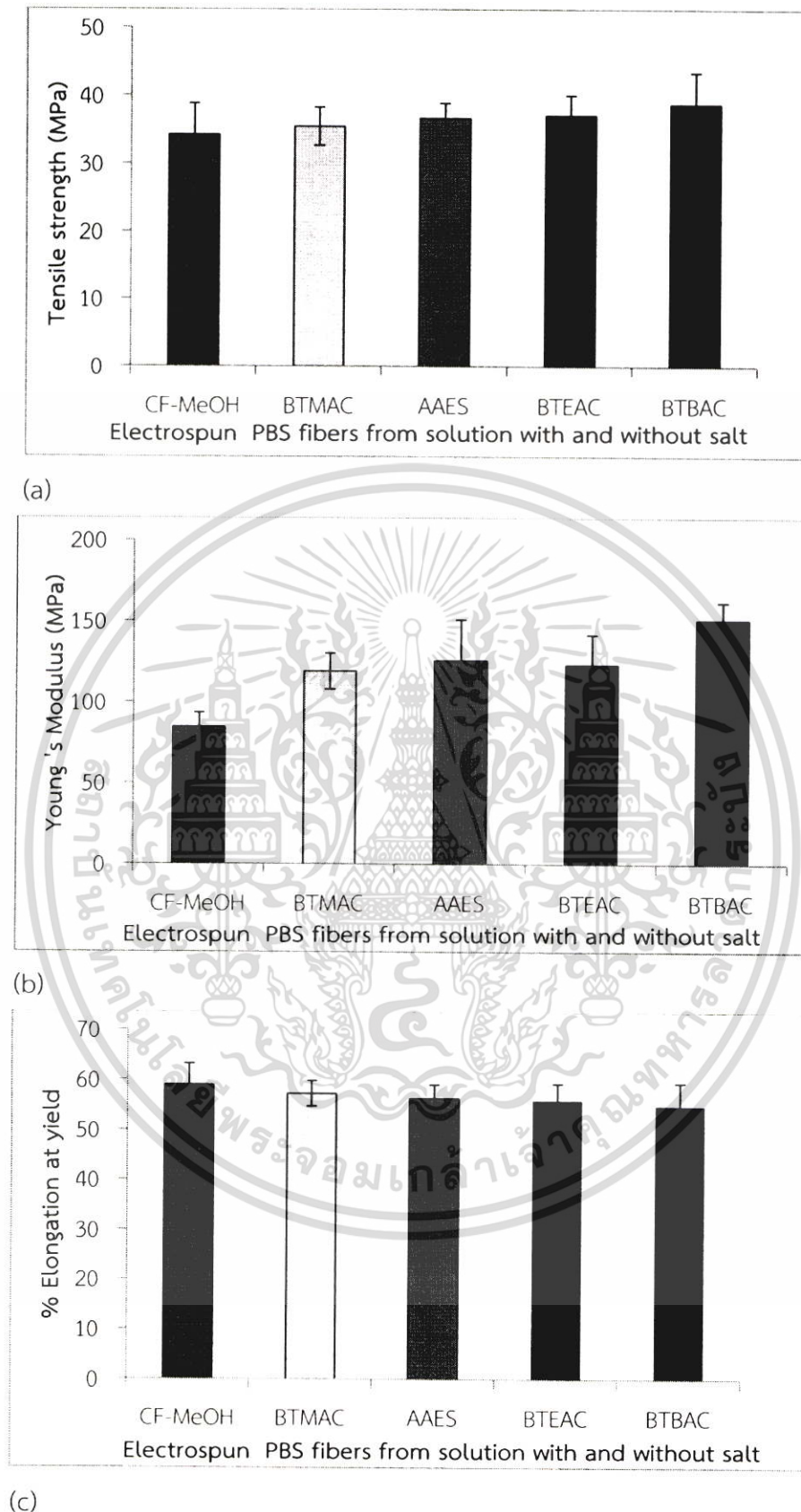
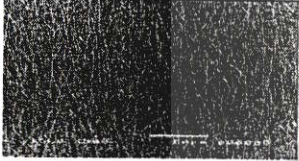
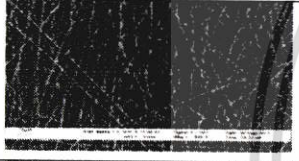
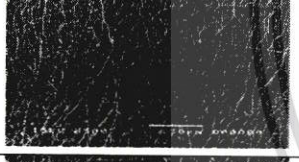
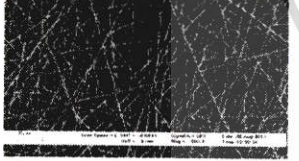
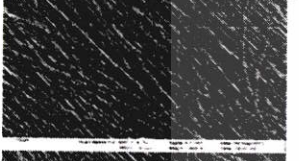


Figure 4.16 Mechanical properties of electrospun PBS fibrous mats obtained from direction of rotating drum (a) Tensile strength, (b) Young's Modulus and (c) % Elongation at yield

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Table 4.24 Morphology, % Crystallinity and mechanical properties of electrospun PBS fibers obtained from solutions with and without salts

Condition	Magnification (500X)	% Crystallinity	Mechanical properties		
			Tensile strength (MPa)	Young 's Modulus (MPa)	% Elongation at yield
(CF:MeOH) 70:30		23.5	34.3 ±4.5	84.6± 8.7	59.0 ±4
BTMAC		25.2	35.5± 2.8	119.0± 11.0	57.2 ±2.5
AAES		26.3	36.7± 2.2	125. ±9 25	56.4 ±2.7
BTEAC		26.4	37.1 ±2.8	123.1± 18.4	56 ±3.3
BTBAC		28.1	38.8± 4.6	150.8 ±10.8	55 ±4.5

4.4 Electrospun PBS fibrous mat for Thin Layer Chromatography

Thin Layer Chromatography (TLC) is one of the most uncomplicated techniques used in analytical chemical method. Separation of components in TLC is a result of differential interactions between mobile and stationary phases. Various materials, such as, silica gel, cellulose and mixed cellulose, alumina, polyamides, ion exchange resins, chemically modified silica gel and nanostructure materials have been developed as stationary phases of TLC [102]. Recently, electrospinning process has been proven to be a simple method for fabricating a stationary phase of TLC [102,106-108]. Various polymers, i.e., polyacrylonitrile (PAN), poly (vinyl alcohol), cellulose acetate, can be successfully fabricated as the stationary phases by using electrospinning process [102, 106-108]. In this part, electrospun PBS fibrous mat was studied for using as a stationary phase of TLC. In order to evaluate performance of electrospun PBS mats, cholesterol and oleic acid were used to analyze for a proof of concept. The results were compared with a commercially available silica TLC plate. Parameters, i.e., analyte volume, and mat thickness, were used to check efficiency of the separation of electrospun PBS mat compared with the conventional TLC plate.

4.4.1 Preparation thin layer chromatography (TLC)

Electrospinning is a simple method for producing ultrafine fibers with average diameters in range of micrometers to nanometers. Due to the high surface area to volume of the obtained fibers resulted in a potential candidate for using to fabricate stationary phase of TLC. One critical requirement of ultrafine fibers with high surface area is uniform small fibers without defects. However, electrospun polymer fibers often have beads as by products. Therefore, the optimal conditions for producing the electrospun ultrafine fiber without beads are required. Stationary plate prepared from electrospinning process plates are particularly attractive for a number of reasons, i.e., no binder material is required in fabrication, the solid support and mat thickness are readily variable and small dimensions of the fibers provide a support with high surface area [107]. In this work, 70:30 v/v was the best ratio of CF:MeOH for preparing ultrafine fibers without bead defects from the electrospinning process. This optimal condition was used to prepare stationary phase of TLC plates.

4.4.2 Effects of electrospinning times on the thickness of electrospun fibrous mats

Mat thickness of the electrospun TLC plate can affect the efficiency of the separation [102, 106, 108]. To evaluate efficiency of TLC plate application which prepared from electrospinning of PBS solution, thickness of the stationary phases was first investigated. In this study, different thicknesses of electrospun PBS mats were obtained from different spinning times, i.e., 1, 3, 6 and 12 hours. Mat thickness was

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ไม่ว่ากรณีใดๆ ทั้งสิ้น อีกทั้งห้ามมิให้ดัดแปลงเนื้อหา และต้องอ้างอิงถึงเจ้าของเอกสารทุกครั้งที่มีการนำไปใช้

measured by using a high performance optical microscope (HP-OM). Figure 4.17 shows optical micrographs of electrospun PBS mats obtained at various spinning times. Figure 4.18 shows the relationship between electrospinning time and the thickness of the electrospun mat. As expected, the increased mats thicknesses were directly proportional to the electrospinning times. Moreover, the resulting electrospun plates were mechanically stable. They can be handled in the same manner as commercially available TLC plates. These results were similar to Clark *et. al.* [35-36] and Lu *et. al.* [37]. Moreover, Clark *et. al.* and Lu *et. al.* mentioned the electrospun PAN UTLC plates without binder. In contrast, commercial TLC plates use a binder to ensure that the stationary phase particles remain attached to the substrate. Frequently, the presence of this binder limits the chromatography performance of the devices.

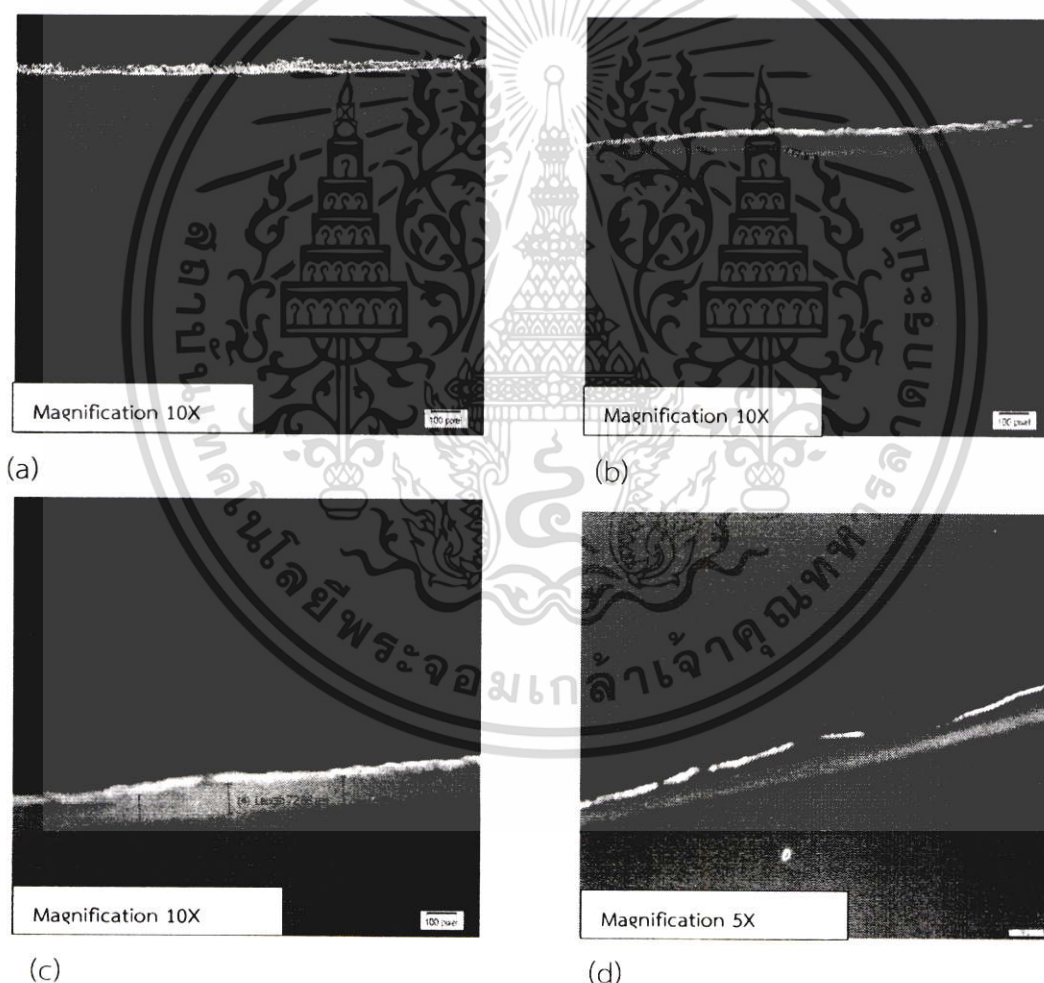


Figure 4.17 Optical micrographs of electrospun PBS mats spun for different times; (a) 1, (b) 3, (c) 6 and (d) 12 hours

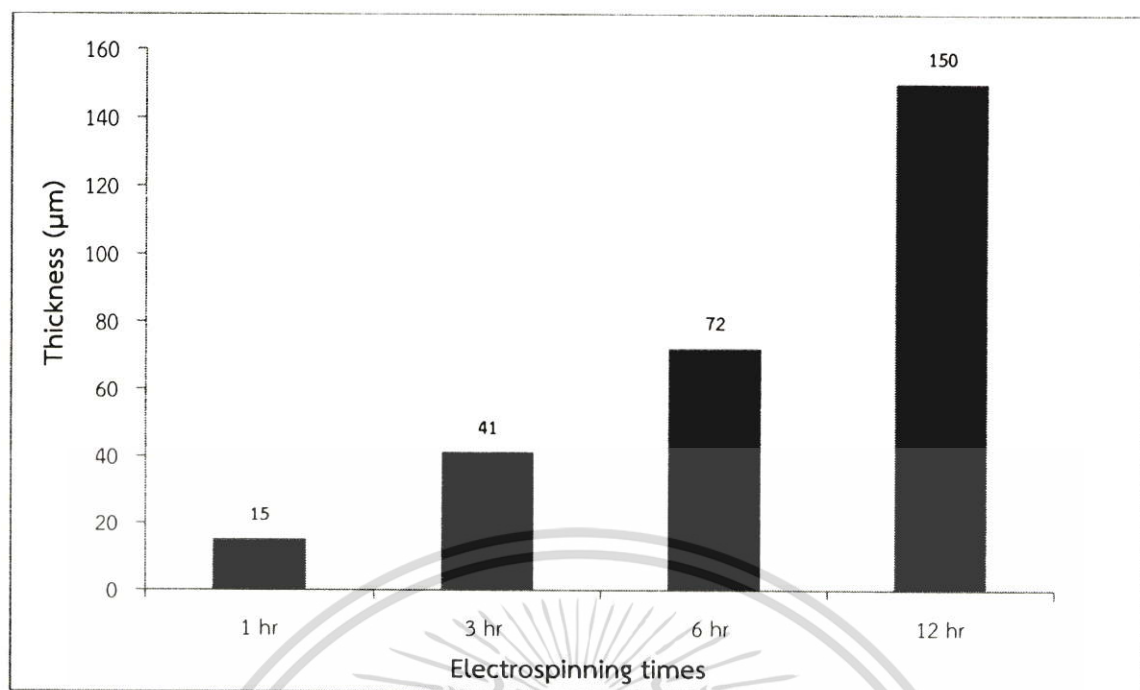


Figure 4.18 Thickness of electrospun PBS mats as a function of electrospinning times

4.4.3 Selection of mobile phases

To evaluate the chromatographic performance of electrospun PBS fibrous mats, the mobile phase system was also investigated. The aim of this study was to find out at least one usable mobile phase composition. PBS fibrous mats for stationary phase for TLC were electrospun from 12% PBS solution in 70:30 (v/v) CF:MeOH under electrical field strength of 20 kV/18 cm for 6 hours. Cholesterol and oleic acid were used to evaluate separation performance of electrospun PBS fibrous mats. Concentration of these compounds was fixed at 2.5×10^{-3} M. Ethyl acetate and hexane were used in different compositions of mobile phase for investigating the effectively separated mixture component. Cholesterol and oleic acid have a mono unsaturated chemical structure as shown in Figure 4.19 [143-144]. The staining of TLC plate with iodine vapor is one of most popular techniques used for detection of organic compound by visualization. Iodine vapor has a high affinity for the both unsaturated and aromatic compounds. Therefore, this visualization method has been used to study the developing the cholesterol and oleic acid on the surface of commercial TLC plates and electrospun PBS plates.

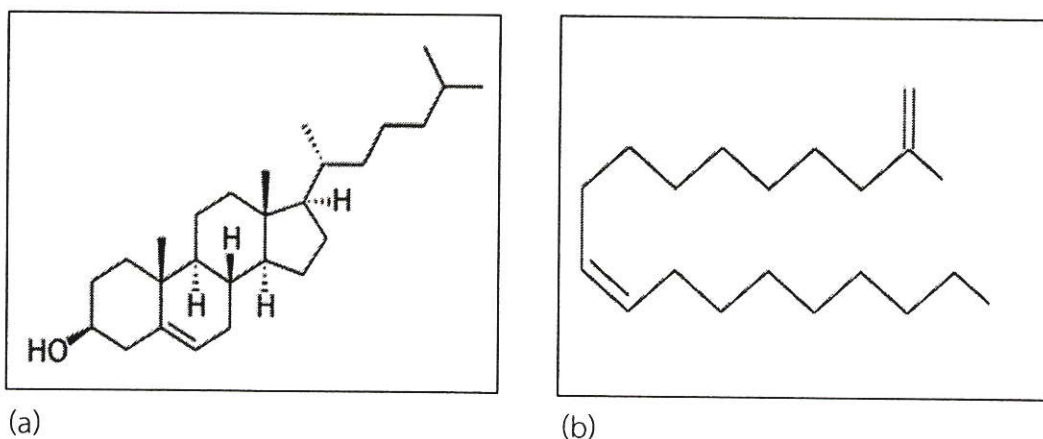
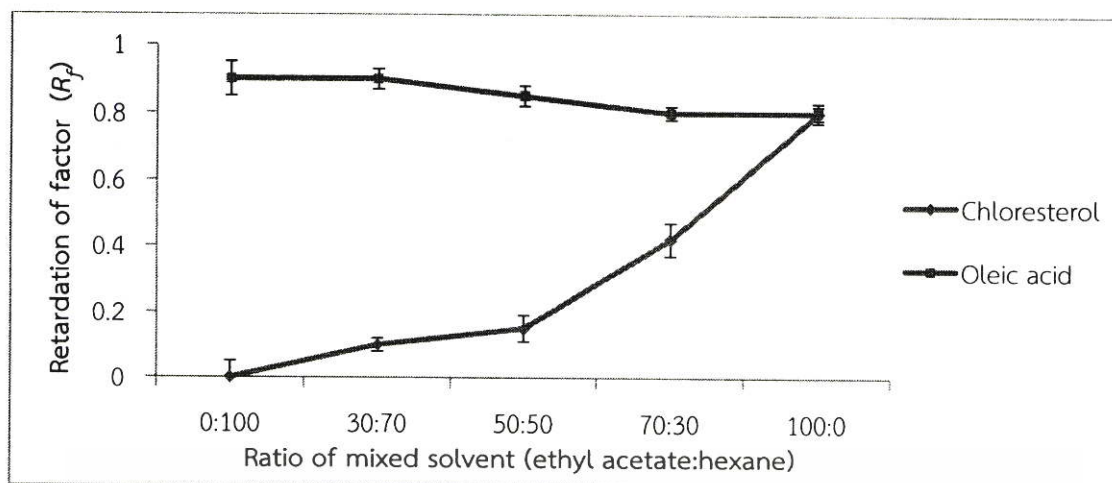


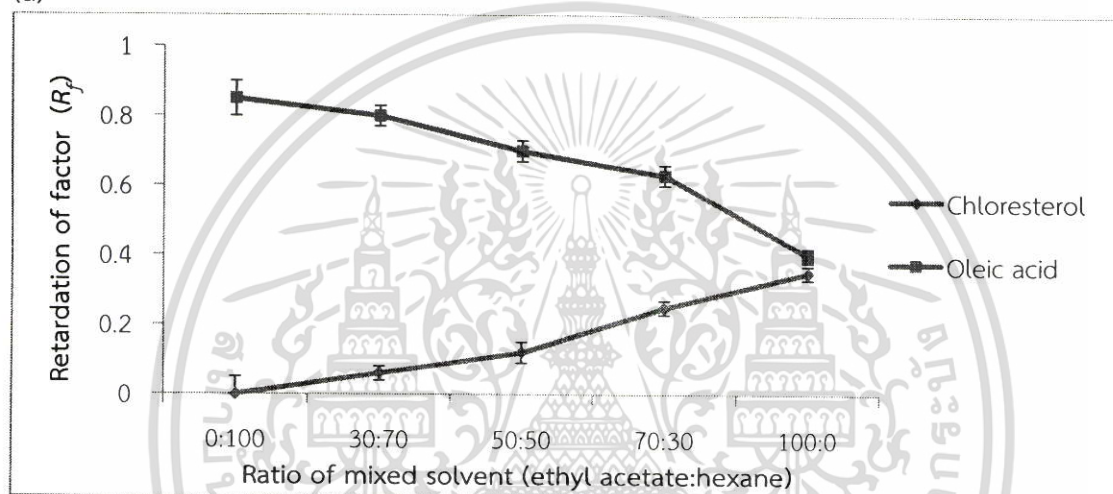
Figure 4.19 Chemical structures of substances used to study in this part; (a) cholesterol and (b) oleic acid [143-144]

In order to optimize compositions of the mobile phase to separate the mixture between cholesterol and oleic acid, retardation behavior of each component was evaluated under various ratios of ethyl acetate and hexane. Ethyl acetate and hexane seemed to be the most common solvents for cholesterol and oleic acid [97, 104]. They were chosen as a binary mobile phase for developing analytes (cholesterol and oleic acid) on surface of TLC plates. Figure 4.20 shows the different stationary phase, i.e., commercial TLC plates (silica gel) (Figure 4.20 (a)) and electrospun fiber plates (Figure 4.20 (b)), and the effects of the mobile. Thickness of the electrospun fibrous plate used in this part was 72 μm .

From Figure 4.20, it was found that the mobile phase of 30:70 (v/v) ethyl acetate and hexane showed the best separation of cholesterol and oleic acid on both electrospun PBS fibrous mat and commercial silica gel TLC plate. Thus, 30:70 (v/v) ethyl acetate and hexane were chosen as the mobile phase for the separation studies of mixture compounds in next part.



(a)



(b)

Figure 4.20 Comparison of retardation factors (R_f) of cholesterol and oleic acid by using mixed solvents of ethyl acetate and hexane in different ratios; (a) commercial silica gel TLC plate and (b) electrospun PBS plates

4.4.4 Comparison of mobile phase velocities

Developing time or speed of mobile phase is one of the most important parameters used to evaluate efficiency of TLC plate. The research obtained from Olesik [35-37, 107, 112] reported that Ultrathin Layer Chromatography (UTLC) was prepared by using electrospinning process. It is a new technique that could decrease developing time of analysis due to faster mobile phase transport. It was reported that the electrospun UTLC devices demonstrated faster mobile phase transport than commercial silica-based TLC devices. In this part, velocities of separation were measured and compared by the developing time when the mobile traveled on the electrospun PBS mats with different mat thicknesses. The developing time defines as the time that solvent or mobile phase use to migrate from the start to the end point on the plate [106, 108]. Comparison of speed of mobile phase traveled on stationary between commercial TLC plate (silica gel plate) and electrospun PBS plates were

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ไม่ว่ากรณีใดๆ ทั้งสิ้น อีกทั้งห้ามมิให้ดัดแปลงเนื้อหา และต้องอ้างอิงถึงเจ้าของเอกสารทุกครั้งที่มีการนำไปใช้

investigated. 30:70 (v/v) ethyl acetate and hexane were chosen as the mobile phase for studying in this part. Table 4.25 compares the developing times depending on the thickness of electrospun PBS fibrous mats. It was found that the electrospinning time was decreased with increasing thickness of the electrospun fibers mat. This led to decrease the developing time as shown in Table 4.25. This effect might derive from the increased thickness of stationary phase. It led to increase porosity and high surface to volume ratio of electrospun PBS fibers. It may act as a chromatographic bed to pull up the solvent along the plate, due to the increased capillary forces. This result was similar to Clark *et. al.* and Lu *et. al* [35 and 37]. They reported that the increasing thickness of electrospun fibrous mats directly resulted in the shorted developing time.

Table 4.25 Developing times of mobile phase traveled on the PBS fibrous mats (distance of 60 mm) spun at various spinning time

Thickness of electrospun PBS mats (μm)	Developing time (minutes)
15	15.0
41	13.2
72	10.5
150	9.2

Table 4.26 shows developing times on stationary phases of commercial TLC and electrospun PBS plates. This experimental results show that the electrospun PBS fibrous mat at 150 μm used developing time for 9.2 minutes, whereas commercial silica gel plate was developed around 11.5 minutes. It was shown that the electrospun PBS plates could decrease in time of analysis due to use the developed time of mobile phase on the plate less than that of commercial silica-based TLC devices. It might derive from the dimensions size of the electrospun PBS fibers (480 nm) which was smaller than that of silica particles (4–8 μm). It provided a support with high surface area and capillary force compared to the commercial TLC. The results are similar to Clark *et al.* [103], Lu *et al* [106]. and Su-ultra [108]. They showed the shorted the speed time of mobile phase moving on the plate as compared to commercial of TLC plate at the same travel distance. These plates were prepared by electrospinning process.

Table 4.26 Developing times on stationary phase between commercial TLC and electrospun PBS plate

Stationary types	Time to reach 60 mm (min)
Commercial TLC- (Siligagel GF-254) (175-250 µm)	11.5
Electrospun PBS fibers 12% (w/v) with thickness (150 µm)	9.2

4.4.5 TLC performance of PBS electrospun fibrous plates

To evaluate TLC performance, electrospun PBS fiber plates were prepared by different spinning times. Analyte volume and mats thickness were used to evaluate the chromatographing performance of PBS fibrous plates in the separation of cholesterol and oleic acid. Calculated chromatographic parameters, i.e., R_f values, plate efficiency (N) and resolution (R) as well as the tailing of spot are summarized in the Table 4.27. Various analyte volumes, i.e., 0.5, 1 and 2 µl were used for the spotting the analyte solution on the electrospun PBS fiber plates. The PBS plates spun from different times, i.e. 1, 3, 6 and 12 hours were used to evaluate performance separation. The plate thicknesses used to study the separation efficiency of the PBS plates are summarized in Table 4.27. From the results, it was found that the mat thickness of the electrospun TLC plates clearly affected the efficiency of the separation. At 15.0 and 41 µm thickness of electrospun PBS plates were found Tailing spot (band dispersion) and overloaded. It might be less thicknesses of mats for loading amounts of analyte solution. These characteristics of the thin mat could be an insufficiency separation. These results corresponded to Lu *et. al.* [37] and Su-utha [108] reported that CA and PVA fiber mats spun with a low thickness could observed the overloaded the mixture as a result of their too thin plate. However, increased electrospinning time of PBS fiber plates was able to improve the separation cholesterol and oleic acid in the mixture analytes. Cholesterol and oleic acid in mixture analytes were successfully separated with high resolution when electrospun PBS fiber plates for 6 and 12 hours were used. The mat thickness obtained from these conditions was 72 and 150 µm. This might be attributed to the increase electrospinning time. It produced the thick layer of electrospun PBS plates. It could be increased a chromatographic bed leading to increase the loading capacity of electrospun plate. It was able to increase the efficiency of the separation. These results corresponded to Lu *et. al.* [37] and Su-utha [108]. However, efficiency (N) and resolution (R) were reduced when volume of analytes were increased. The tailing of mixed analytes still presented when 2 µl substance was spotted on PBS plate with 72 and 150 µm. By comparing the commercial TLC, phenomena of overload volume

analyte and tailing of spot analyte could not be found. The commercial TLC plates were much thicker than electrospun PBS plate. Therefore, the loading capacity of TLC plate was larger than electrospun PBS plates. From Table 4.27 the minimum analyte volumes were able to apply on electrospun PBS mats at 72 and 150 μm to get the optimal efficiency. It should be not over 1 μl . The efficiency and resolution of electrospun PBS plate were higher than those of conventional TLC when mention conditions were used .



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Table 4.27 Summary of the average retardation factors (R_f), efficiency (N), and resolution of electrospun PBS fiber plates in separation of the cholesterol and oleic acid

Thickness (μm)	Volume of Analyte (μL)	TLC parameter				
		Retardation factor (R_f)		Efficiency (N)		Resolution (R)
		Cholesterol	Oleic acid	Cholesterol	Oleic acid	
18	0.50	Tailing	Tailing	-	-	-
	1	X	X	-	-	-
	2	X	X	-	-	-
41	0.50	Tailing	Tailing	-	-	-
	1	Tailing	Tailing	-	-	-
	2	Tailing	Tailing	-	-	-
72	0.50	0.25	0.60	7844	7200	2.19
	1	0.23	0.63	2095	2592	1.51
	2	Tailing	Tailing	-	-	-
150	0.5	0.25	0.61	7793	7278	2.25
	1	0.24	0.63	2178	2178	2.50
	2	Tailing	Tailing	-	-	-

4.4.6 Efficiency of Electrospun PBS stationary phase

As mentioned above, the TLC devices were obtained from the electrospun PBS fibrous mat. It revealed that the developing time of mobile phase was shorter than those of conventional silica gel TLC. This result provided a decrease in analysis time and increase in the efficiency of separation. To evaluate performance of separation mixed components of cholesterol and oleic acid were obtained using 2 types stationary phase. Plate numbers (N) can be regarded as an approximate measure of the separating efficiency of the chromatographic plates as shown in Equation 2.1. Therefore, N was used to investigate the efficiency of separation in this

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Table 4.28 Comparison of analyte broadening, plate number between commercial silica gel of TLC and electrospun PBS fibrous mat

Analyte	Type of TLC devices	
	Commercially silica gel of TLC 175-250 (μm)	Electrospun PBS fibrous mat at 150 (μm)
	Plate numbers	Plate numbers
Chloresterol	2844	7844
Oleic acid	3600	7200

The efficiency separation of the cholesterol and oleic acid are compared between the electrospun PBS plate and silica gel plate (commercial TLC plate) as shown in Table 4.28. It was found that the optimal ratio of mobile phase was 30:70 (v/v) ethyl acetate and hexane. As mentioned earlier, all TLC devices were developed until the mobile phase migrated for a distance of ~60 mm was reached. It was found the complete analyte of electrospun PBS mats required less development time than the conventional TLC. It was found that developing time electrospun fibrous mats for TLC used was shorted than that of commercial TLC plate. In chromatography, efficiency (N) is a term that used to evaluate performance of separation. It related to the broadening of a sample band through the separation process. From the resulting investigation efficiency separation of TLC plates in Table 4.28, it was found that electrospun PBS fiber plates had efficiency separation of cholesterol for 7844 and oleic acid for 7200, whereas the commercial TLC plate had efficiency of cholesterol for 2844 and oleic acid for 3600, respectively. The plate numbers of electrospun PBS mat were higher than stationary phase of commercial TLC. It might due to fiber diameter of electrospun PBS fiber was smaller than particle size of silica gel which used to produce stationary phase of commercial TLC. It resulted in to increase the efficiency of separations without increasing the time of analysis. Therefore, the electrospun PBS mats showed higher efficiency and development times as compared to commercial available TLC plates. These results were similar to Clark *et al.* [103], Lu *et al* [106] and Su-ultra [108]. They described that efficiency of separation of electrospun TLC mats was much higher than that of commercial TLC plates.

4.5 Antibacterial efficiency

Developing antimicrobial nanofibrous materials from electrospinning process have recently gained much attention [30, 39, 41-42, 84-85, 146-148]. Two basic approaches, i.e., originally antimicrobial polymer and incorporation of exogenous biocide in the fibers are able to prepare the electrospun fibers with antimicrobial activity. The electrospun fibers containing antimicrobial agents have been widely studied [30, 41-42, 84-85, 146-148]. Quaternary ammonium compounds (QAC) is one type of exogenous biocides. They have been used in various fields as antimicrobial agents to inhibit the growth of microorganisms on the surface of materials including fibers, paints, filters, and packaging [41-42]. In recently, some quaternary ammonium compounds, i.e., benzyl trialkyl ammonium chloride (BTAAC) were used to improve electrospinnability of polymer solution [65, 127, 148-150]. Those compounds, i.e. BTMAC, BTEAC and BTBAC, were incorporated into polymer solution in order to change the electrical conductivity and surface tension of the solution, including also increase spinnability during the electrospinning of nanofibers [41-42, 65, 150]. Other researchers [41 and 148-150] used BTEAC as an antimicrobial agent for electrospun nanofibers. Poly(butylene succinate) (PBS) and its copolymers are commercially available aliphatic polyesters with interesting properties, including biodegradability, melt processability, good mechanical and thermal properties [26-27]. Because of their excellent mechanical properties and processability, they can be applied to a number of applications, such as packaging films, bags, flushable hygiene products, mulch films biomedical materials, and nonwoven electrospun PBS fibers. PBS [26-30]. Due to those of organic salts were able to use for improving the electrospinnability of PBS solution. It has antimicrobial characteristic properties. In order to characterize and compare efficiency antimicrobial property of electrospun PBS fibers which contained different organic salts. In this part, % loading of organic salts in PBS solution was fixed at 1% (w/v), used to prepare antimicrobial electrospun PBS nanofibers containing organic salts. The efficiencies of antimicrobial ability of the electrospun PBS fiber mats against *Staphylococcus aureus* (*S. aureus* ATCC 25923) and *Escherichia coli* (*E. coli* ATCC 25922) are summarized in Figure 4.21 and Table 4.29. Figure 4.21 shows the inhibition zone between electrospun PBS fibrous mats with and without organic salts after 24 hours of incubation. An antimicrobial efficiency of the electrospun fibrous mats was reported in this work. It was recognized the zone on the nutrient agar plate in contact with the specimen (contact zone). The clear area was generated around the electrospun fibrous mats. It was referred as zone of inhibition. The D values of zone inhibition of the electrospun PBS fibrous mats with different organic salts are summarized in Table 4.29. From the results, it was found that BTAAC salts-loaded PBS fibrous mats were able to inhibit the growth of *E. coli*, whereas the electrospun fibrous mats were not be able to inhibit the growth of *S. aureus*. The results demonstrated

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that those of the electrospun fibers could inhibit the growth of bacteria. However, it was found that the bacteria caused growth on the neat and the electrospun PBS fibrous mats with loading 1% (w/V) AAES as shown in Figure 4.21. It was shown that electrospun fibers could not inhibit the growth of bacteria.

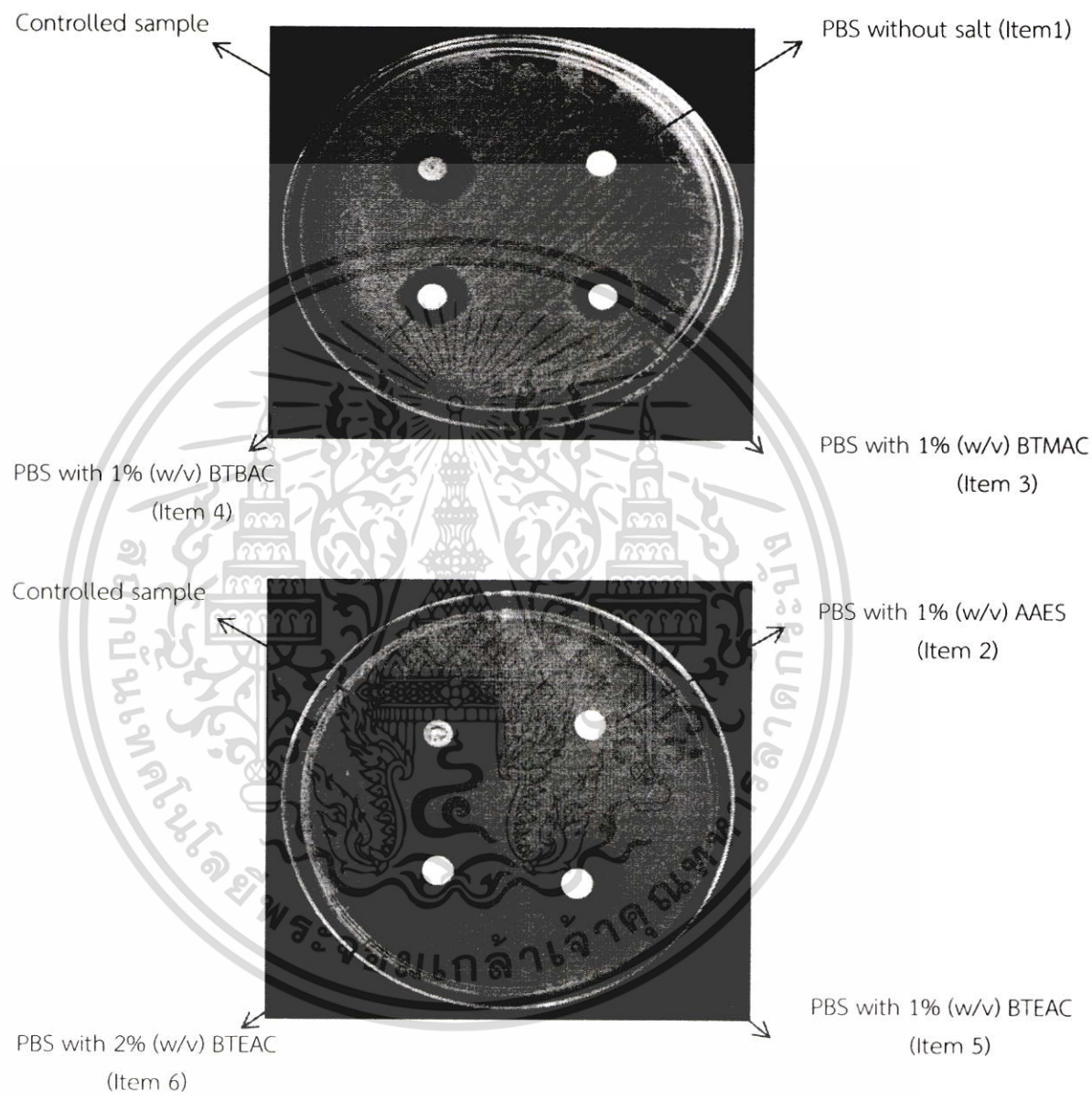


Figure 4.21 Photograph images of the inhibition zones of the electrospun PBS fibers mats with and without organic salts against *Escherichia coli* (*E. coli*)

Table 4.29 Summary of sizes of inhibition zones obtained from the electrospun PBS fibers with and without salts against *S. aureus* and *E. coli*

Item	Sample names	Zone diameter (millimeter)			
		<i>S. aureus</i>	Efficiency of antimicrobial	<i>E. coli</i>	Efficiency of antimicrobial
1	Electrospun pure PBS	0	Not active	0	Not active
2	Electrospun PBS with loaded 1%(w/v) AAES	0	Not active	0	Not active
3	Electrospun PBS with loaded 1%(w/v) BTMAC	0	Not active	8	Active
4	Electrospun PBS with loaded 1%(w/v) BTBAC	0	Not active	9	Active
5	Electrospun PBS with loaded 1%(w/v) BTEAC	0	Not active	11	Active
6	Electrospun PBS with loaded 2%(w/v) BTEAC	0	Not active	12	Active

As expected, the neat PBS fiber mats showed no activity against the tested microbes. However, different zone diameters of inhibition were observed around the electrospun PBS with 1% (w/v) BTAAC. Whereas 1% (w/v) AAES loaded PBS fibers was not able to see inhibition zone. The obtained results indicated that the inhibition zones depended on the chemical structures of salts. This reason might attribute to the effect of the quaternization degree on the hydrophobic/hydrophilic balance of the long chain structures [150-151]. It was known that BTAAC had antimicrobial activity comparable to other commonly used disinfectants [150-151]. Then inhibition zone of antimicrobial activity against of the electrospun PBS fiber with loaded 1% BTAAC was in range of 8-11 mm. As observed from the disc diffusion test, inhibition zone diameter of The 1% (w/v) BTEAC loaded in PBS fibers mats showed high potential of the antimicrobial activity against on *Escherichia coli* (*E. coil*). Moreover, it was found that the 2 % (w/v) BTEAC-loaded in PBS fibers mats showed highest inhibition of the antimicrobial activity of *Escherichia coli* (*E .coil*). Efficiency of antimicrobial activity of BTEAC loaded in electrospun PBS fibers against on *Escherichia coli* (*E .coil*) was similar to Kim *et al.* [41, 148-150]. They reported BTEAC loaded in electrospun PC fibers successfully inhibited the growth of *Escherichia coli*. Table 4.29 shows the inhibition zone of the electrospun PBS fibers mats with and without load organic salts. Antimicrobial mechanism of electrospun PBS fibrous mat with loading BTAAC can be explained as follows. The cellular membranes of most bacteria are negatively charged whereas the BTAAC are positive charges. Therefore, the lethal action of these

antimicrobial agents can be interpreted by the sequential manner in which the biocide target the cytoplasmic membranes of bacterial cells. This mechanism proposed in Figure 4.22. The following elementary processes were briefly summarized as the following modes of action [143 and 150-151]:

- 1) Adsorption onto the bacterial cell surface
- 2) diffusion through the cell wall
- 3) Binding to the cytoplasmic membrane
- 4) Disruption of the cytoplasmic membrane
- 5) Release of the cytoplasmic constituents such as K^+ ions, DNA, RNA; and fin
- 6) Death of the cell

In order to have a better understanding the mentioned mechanisms stroked the most cellular membranes of most bacteria. It can be summarized in Figure 4.22.

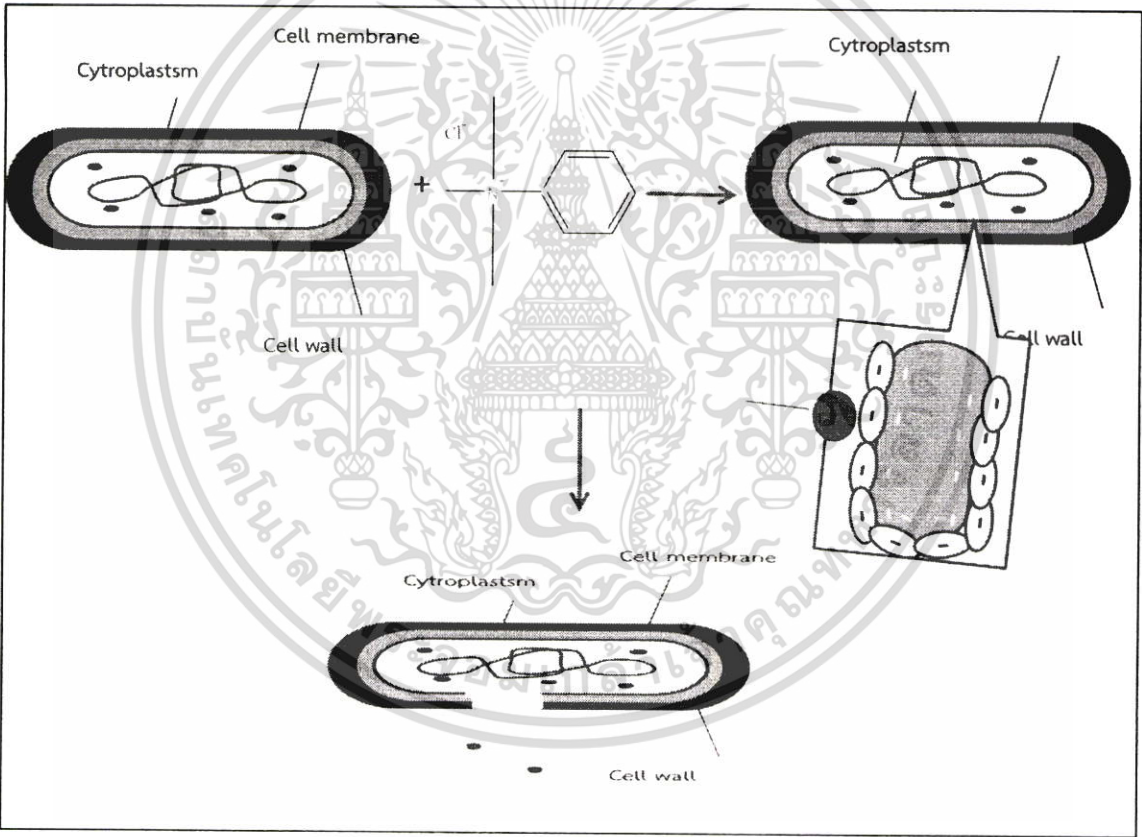


Figure 4.22 Possible mechanism of cations on benzyl trialkyl ammonium chloride loaded in electrospun fibers interacted anions of phospholipid on cellular membranes adapted from [148-150]

In case of electrospun PBS with BTAAC, antimicrobial activity against was pronounced more effective against bacteria *Escherichia coli* (Gram negative) than *Staphylococcus aureus* (Gram-positive). It might be due to peptidoglycan layer on cell membrane of gram positive bacteria which was higher than gram negative bacteria as shown in Figure 4.23. It might be contributed the cell membrane of

Staphylococcus aureus was difficult damaged by BTAAC as compared to *Escherichia coli* (Gram negative). Then, antimicrobial of electrospun PBS fibrous mats loaded BTAAC is more effectively against *Escherichia coli* than *Staphylococcus aureus*.

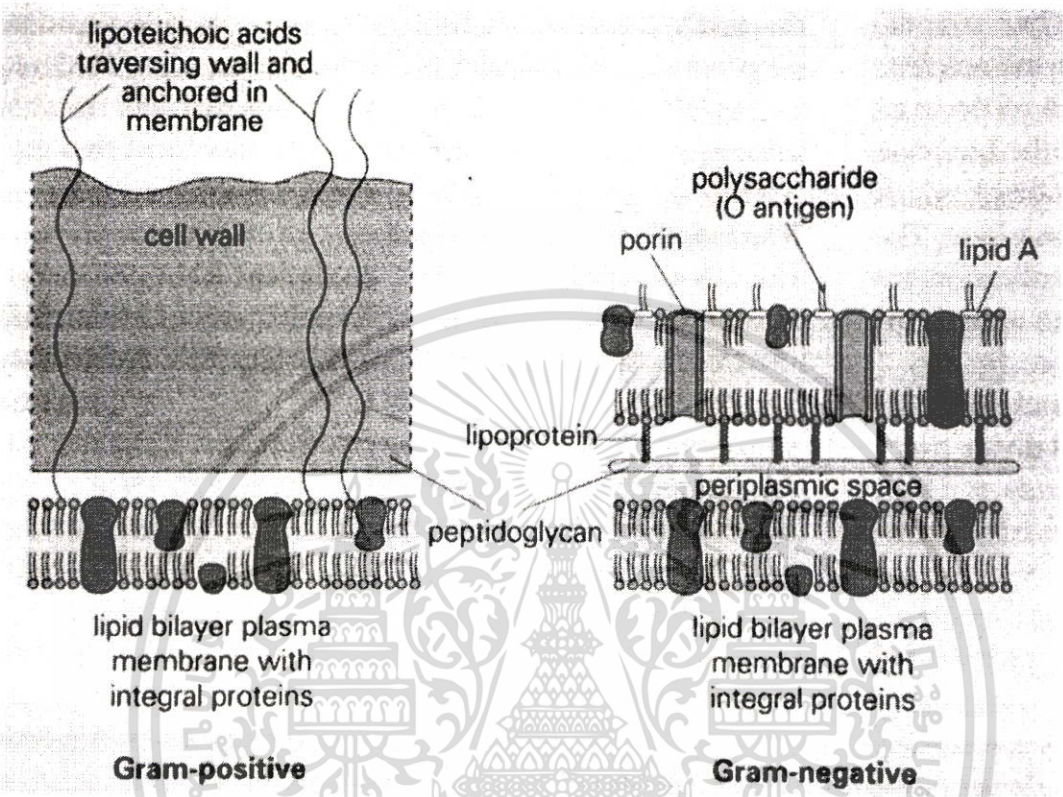


Figure 4.23 Comparison of cell walls between gram positive bacteria and gram negative bacteria [151]

Antimicrobial electrospun PBS fibers were prepared in this work using quaternary ammonium compounds (QAC). From the results it was found that the type and structure of organic salts was one of the factors that determined the antimicrobial activity against on the growth bacteria. The resulting antibacterial test, it was found that 1% (w/v) BTEAC or BTBAC- PBS nanofibers demonstrated successfully inhibited the growth of *Escherichia coli* as compared to electrospun PBS fibers obtained from the solution in CF with AAES or BTMAC and solution in 70:30 (W/V) CF:MeOH. However, those of the electrospun fibers did not show the antimicrobial activity against on *Staphylococcus aureus*.

Chapter 5

CONCLUSIONS

5.1 Conclusions

In this study, effects of solvent systems, solution concentrations, and addition of organic salts on electrospinnability of PBS and fiber morphology were investigated. In the case of the single-solvent systems, chloroform (CF) and dichloromethane (DCM) was chosen as a single solvent. However, electrospun PBS fibers obtained from single-solvent systems showed discrete beads and beaded fibers in every PBS concentrations because of low solution conductivities. Attempts to increase solution conductivity were carried out by adding other solvents with high dielectric constants (so called mixed solvent systems) and or organic salts to improve electrospinnability. It was found that the bead problems could be solved by the addition of MeOH as cosolvents and/or organic salts. The cosolvents and salts had significant effects on the solution conductivity and PBS fiber morphology. Electrospinnability and defects were greatly depended on the types of solvents, optimal ratios of the mixed-solvent systems and amounts of salts. Electrospinnability of the mixed-solvent system could be improved because of high dielectric constant of DMF or MeOH. As the MeOH loading was increased (from 0 to 30%), morphologies of electrospun PBS fibers were changed from beaded fibers to smooth fibers with decreasing average diameters. PBS concentrations had significant effects on the solution viscosity and PBS fiber morphology.

Effects of organic salts addition, i.e., alkyl ammonium ethyl sulfate (AAES) and benzyl trialkyl ammonium chloride (BTAAC), on the electrospinnability of PBS and fiber morphology were investigated. It was found that the bead problems could be removed by the addition of the organic salts. Type of the salts had significant affected on the solutions conductivity and fiber morphology. In case of PBS solution with AAES, conductivity of PBS solutions dramatically increased with loading the salts in the PBS solutions. However, at the same concentration of the salts, the addition of AAES in the PBS solution in DCM, the solution conductivity was higher than PBS solution in CF. Average diameters of electrospun fibers obtained from the solutions with AAES were decreased with increasing AAES concentrations. In this part, 1% (w/v) AAES was the optimum amount of salt for using to prepare bead free ultrafine fibers. Effects of salt concentrations and types on morphology and average fiber diameter were investigated. The average diameters of electrospun PBS fibers were decreased with increasing salt concentrations. It was found that morphology and average diameter of electrospun PBS fibers were significantly different between the salt types.

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Degree of crystallinity of each PBS fibrous mat which obtained from solution with and without salts were investigated. It was found that the additions of the AAES salt and MeOH as the cosolvent enhanced the percentage crystallinity of PBS. This suggested that the increased conductivity of polymer solutions resulted in a high degree of elongation of the jet yielding better chain orientation and increasing crystallization of PBS chains. Characterization of PBS fibers electrospun from solution with and without salts by using FT-IR spectroscopy was studied. It indicated that salts were trapped in the electrospun PBS fibrous non-woven mats. The effects of organic salts on the mechanical properties of electrospun fibrous non-woven mats were studied. It can be observed that the tensile strength and Young's modulus of electrospun PBS non-woven mats obtained from solution with salts were higher than that of solution without salt.

Application of electrospun PBS used as stationary phase for TLC was studied in this work using the electrospun fiber prepared from 70:30 (v/v) CF:MeOH. The results showed that the electrospun PBS fibrous mats could be used as the stationary phase for thin layer chromatography. Cholesterol and oleic acid in mixture analytes were used to evaluate separation efficiency. The efficiency of cholesterol and oleic acid performed on PBS fibrous plates were improved as compared with commercial TLC plates (silica gel). However, separation efficiency of the mixtures have depended the mat thickness, and analyte volume.

Efficiencies of antimicrobial ability of the electrospun PBS fiber mats against *Staphylococcus aureus* and *Escherichia coli* were studied in this work using organic salts as antimicrobial agent. It was found that the types of salt had significant effects on the antimicrobial efficiency. It was found that BTAAC loaded PBS fibrous mats were able to inhibit the growth of *E. coli*, whereas all the electrospun fibrous mats were not able to inhibit the growth of *S. aureus*. The 1% (w/v) BTEAC loaded in PBS fibers mats showed high potentials of the antimicrobial activity against on *Escherichia coli* (*E. coli*). However, no antimicrobial activity was detected in both the pure and 1% AAES loaded PBS mats.

5.2 Recommendations

1) In this work, it should be noted that the addition of different salt types into the PBS solutions leads to different morphologies and fiber diameters. This can be used in another interesting research topics which require no bead defect.

2) To understand the influence of the organic salts on the orientation of PBS fibers, aligned electrospun PBS fibers obtained from solutions with different salts can be studied using X-ray diffraction and polarized Fourier transform infrared spectroscopy.

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3) Stationary phase of TLC was fabricated by using electrospinning process. It was a new attractive technique which can be used to fabricate ultrathin layer chromatography (UTLC). It would be recommended to study in the another materials such as poly (lactic acid), poly (ethylene terephthalate) etc.

4) In this work, 70:30 v/v ratio of CF-MeOH was the best for preparing ultrafine fibers without bead defects from the electrospinning process. In case of evaluation antibacterial efficiency, the electrospun PBS fiber with loading other antimicrobial additives such as curcumin, mangosteen extracts and another quaternary ammonium salt should be studied in order to develop wound dressing materials.



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Academic Publications

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