PREPARATION AND CHARACTERIZATON OF MULTILAYERED ELECTROSPUN POLY(LACTIC ACID) AND POLY(BUTYLENE SUCCINATE) NON-WOVEN ULTRAFINE FIBROUS MATS

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Title	Preparation and Characterization of Multilayered Electrospun Poly(lactic acid) and Poly(butylene succinate) Non-woven Ultrafine Fibrous Mats
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Abstract

Nowadays, many researchers have been motivated to develop biodegradable products from renewable bio-based materials due to environmental problems from plastic wastes. The aim of this work was to study the preparation and characterization of multilayered electrospun Poly(lactic acid) or (PLA) and Poly (butylene succinate) or (PBS), non-woven ultrafine fibrous mats. Firstly, 12% (w/v) PLA fibers in 7:3 DMF-DCM and 12% (w/v) PBS fibers in 9:1 DCM-CB mixed solvent systems were prepared by electrospinning technique. The effects of fiber content, diameter, surface morphology, thermal and tensile properties on the multilayered electrospun PLA/PBS mats were characterized by a Scanning electron microscope, a Differential scanning calorimeter, and an Universal testing machine. It was found that, as concentration of PLA was increased, the average fiber diameters decreased with the smooth fibers and uniform size distribution being obtained, especially for 12% (w/v) of PLA. Furthermore, the glass transition temperature (Tg) and melting temperature (Tm) of the multilayered PLA/PBS ultrafine fibrous mats were very close to those of PLA and PBS with a decrease in % crystallinity. In tensile tests, Young's modulus, tensile strength and tear strength of the multilayered PLA/PBS ultrafine fibrous mats were higher than those of the virgin electrospun fibers. However, the

properties were decreased with increasing PBS fiber content. Nevertheless, elongations at break and at yield were increased. The improvement in toughness could be achieved by the addition of PLA fibers.

Keywords : Poly(lactic acid), Poly(butylene succinate), electrospinning

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Abbreviations

ASTM	:	American Standard for Testing and Materials
DCM	:	Dichloromethane
CB	:	Chlorobenzene
DMF	:	*N,N* Dimethylformamide
DSC	:	Differential Scanning Calorimeter
MPa	:	Mega pascal
PBS	:	Poly (butylene succinate)
PLA	:	Poly (lactic acid)
SEM	:	Scanning Electron Microscope
Tg	:	Glass Transition Temperature
Tm	:	Melting Temperature
UTM	:	Universal Testing Machine

Chapter 1

Introduction

1.1 Rational

In recent years, a numbers of research works has been focused on biodegradable polymers which are continuously increasing due to the problem of plastic waste. Poly(lactic acid) (PLA) and poly (butylene succinate) (PBS) are well-known biodegradable plastic and eco-friendly after their composting which have been studied with much interest for use in several applications specially in surgery, drug delivery and tissue engineering [1].

As a general rule, Poly(lactic acid) (PLA) exhibits predictable and reproducible mechanical and physical properties, such as tensile strength, young's modulus and degradation rate under controlled conditions [2]. Beside some properties like brittleness, low heat resistance, and a slow crystallization has been the mains obstacle to expand its use in various applications [3]. There are two main pathways by which PLA can be synthesized. The first involves polycondensation of aqueous lactic acid and the second involves ring-opening polymerization of cyclic lactide dimers. However, another biodegradable aliphatic polyester, PBS which has trade name as "BIONOLLE" exhibits high flexibility, excellent impact strength, and thermal resistance but still has been limited in its stiffness.

To date, PLA and PBS have been successfully fabricated into various products such as fibers and non-woven mats specially by electrospinning technique which is a simple and powerful technique for producing nanofibers from a wide variety of polymer with diameters in the range from several micrometers down to tens of nanometers. Besides, these important advantages of producing polymeric nanofibers are large surface areas, ease of functionalization, superior mechanical properties and ease of process as suggested by many experts in this field which are of considerable interest for various kinds of applications such as nanofibers reinforced composites [4], membranes for filteration [5], support for enzymes and catalysts [4] and biomedical applications such as scaffolds for tissue engineering, wound dressings and drug delivery [6] etc.

The set up of the electrospinning process consists of a bipolar high voltage source which is applied to the droplet of a fluid. A polymer solution or melt coming out from the tip of a small

opening needle is coupled to a syringe injector, acts as one of the electrodes. When the electric field reaches to a point beyond which electrostatic repulsion works to overcome the surface tension, a charged polymer jet is ejected and electrospray accelerates towards the collector screen to obtain randomly orientated or aligned nanofibers [7].

A number of studies showed electrospun PLA nanofibers through post-spinning orientation and using rotating collectors for scaffolds in the regeneration of cardiac, neural, bone and blood vessel tissues can be fabricated [8]. Similarly, PLA/LDHs [9] have been electrospun into nanofibers which solvents generally used are chloroform, chloromethane and N,N-dimethylformamide [10-11]. Other nanofibrous mats of poly(butylene succinate-co-butylene adipate) (PBSA) were prepared by electrospinning PBSA solutions in methylene chloride (MC) and MC/N,N-dimethylformamide (DMF) mixtures have also been successfully produced [12].

Due to the limited of PLA and PBS outlined above, our research focused on laminating of PBS and PLA as ultrafine fibrous nonwoven mats with enhanced mechanical properties while maintaining processibility. Howerever, the use electrospinning for the development of ultrafine fibrous non-woven mats of multilayered electrospun PLA with PBS have not yet been reported.

In this investigation, multilayered PLA and PBS ultrafine fibrous non-woven mats of various thickness were prepared by electrospinning. Several properties were examined and studied by different characterization techniques. Morphology of non-woven mats were analyzed by SEM images while mechanical properties were analyzed by Universal testing machine. In addition, thermal properties were also studied by Differential scanning calorimeter (DSC). All the properties of the non-woven mats were compared with electrospun virgin PLA and PBS polymers.

This study further aimed to reduce plastic waste in daily use by considering replacement with biodegradable PLA and PBS polymers and consequently to extend its application fields.

1.2 Objectives

The objectives of this research were:

1. To prepare the electrospun PLA, PBS and multilayered PLA/PBS ultrafine fibrous non-woven mats from mixed solvent systems.
2. To examine the preparation effects on morphological appearance of the electrospun PLA nanofibers in various concentrations and the multilayered PLA/PBS ultrafine fibrous non-woven mats in different thickness ratios.
3. To characterize the multilayered electrospun PLA/PBS ultrafine fibrous non-woven mats such as, mechanical properties.

1.3 Scopes of Study

The scopes of this research study can be divided into several parts as the following details.

1. Literature reviews of the theory and publication were necessitated in this special project.
2. Realization the basic experimental approach of an electrospinning.
3. To Study the concentration effects of electropun PLA nanofibers and the affecting thickness ratio of the multilayered electrospun PLA/PBS ultrafine fibrous non-woven mats on morphological appearance.
4. To analyze the % crystallinity of the multilayered electrospun PLA/PBS ultrafine fibrous non-woven mats.
5. To compare the mechanical properties of the multilayered electrospun PLA/PBS ultrafine fibrous non-woven mats such as tensile strength, tear strength, elongation at break and Young's modulus etc.

1.4 Expected Results

1. To succeed at the preparation of the multilayered electrospun PLA/PBS ultrafine fibrous non-woven mats by appropriate suitable conditions in electrospinning technique.
2. Mechanical properties of the multilayered electrospun PLA/PBS ultrafine fibrous non-woven mats can be gained.
3. Knowledge and information from this research can be applied with other electropun nanofibers.

Chapter 2

Theory and Literature Reviews

Poly(lactic acid) (PLA) has generated great interest as one of the most innovative materials being developed for a wide range of applications. The polymer is thermoplastic and biodegradable, which makes it highly attractive for biological and medical applications. It can be transformed by spinning into filaments for subsequent fabrication of desirable textile structures. Spinning may be accomplished by various routes, the fibers fabricated into various forms and used for implants and other surgical applications such as sutures, tissue engineering which is the most recent domain where poly(lactic acid) is being used and is found to be one of the most favorable matrix materials.

2.1 Characterization and Properties of PLA

Poly(lactic acid) (PLA) or poly(lactide) is a well-known biodegradable and the first trade good polymer produced from completely renewable resources like sugar beets, sugarcanes, corn, wheat and other starch-rich products that has been studied with much interest in the past few decades. PLA was first discovered by Carothersin 1932 [13].

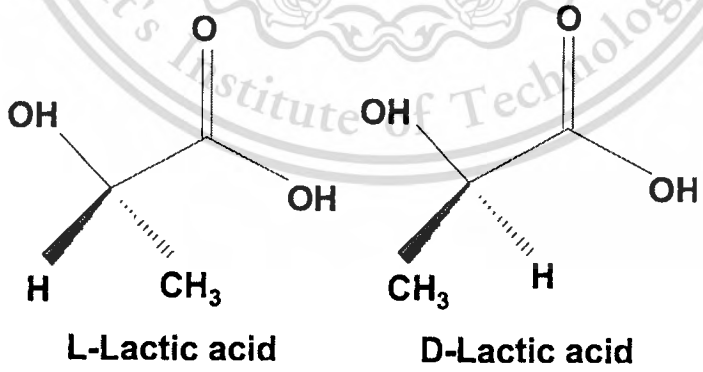


Figure 2.1 Optical isomers of lactic acid [14]

PLA involves the processing and polymerization of lactic acid monomer which exists two enantiomers as L-lactic acid and D-lactic acid as shown in Figure 2.1 [14]. There are two

main synthesis methods which PLA can be synthesized, the first one involves by polycondensation of aqueous lactic acid which is generally given the name poly(lactic acid), and a second one involves by ring-opening polymerization of cyclic lactide dimers, that is generally called poly(lactide) but these names are not much used throughout the literature [15]. However, most work has more focused on the ring-opening polymerization of lactide. Nowadays, Cargill Dow Polymers operates the world's largest PLA production unit.

Polymerization of lactic acid for making high molecular weight PLA can be achieved in two ways as shown in Figure 2.1: (1) Direct condensation which involves solvents under high vacuum. (2) Formation of the cyclic dimer intermediate (lactide) which is solvent free [14]:

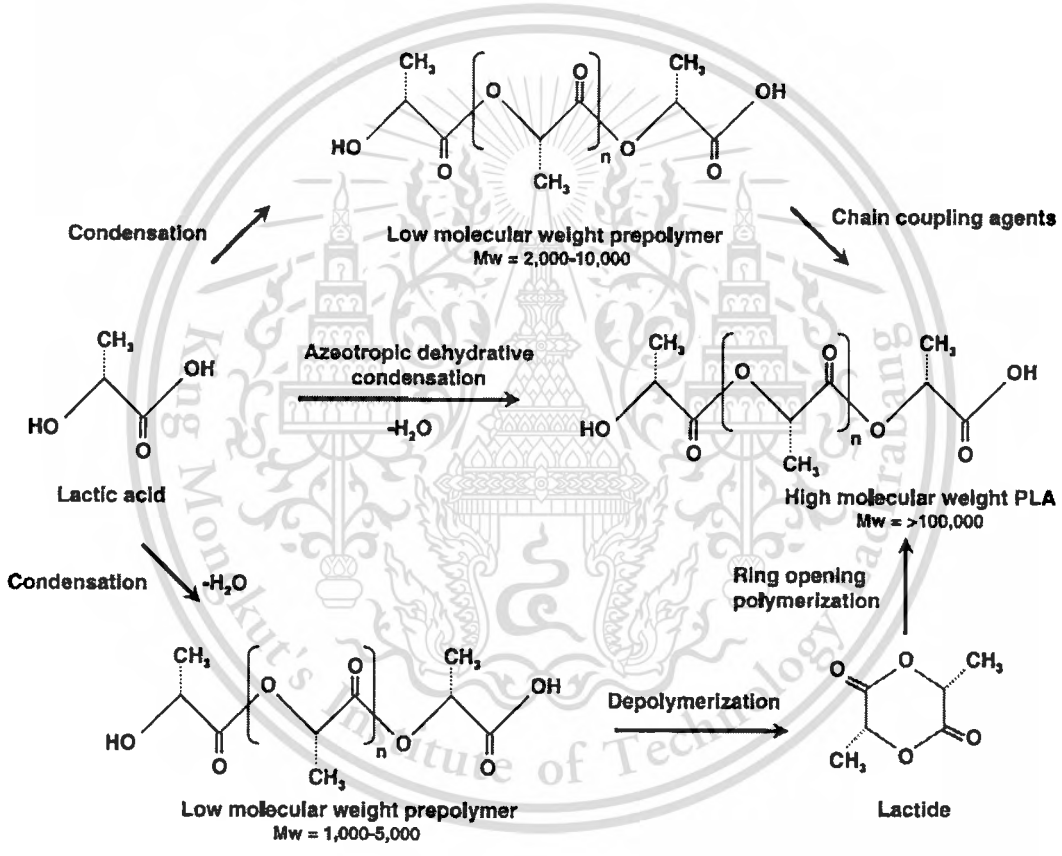


Figure 2.2 Synthesis of polylactic acid [16].

Poly(lactic acid) (PLA) is a linear aliphatic thermoplastic polyester which can be either amorphous or semi-crystalline, depending on the stereochemistry and thermal history; furthermore, in many modes of PLA behaves like PET but still also performs like PP. For amorphous PLAs is rigid and brittle due to the high glass transition (T_g) which determines the upper use temperature for most commercial applications, mostly in the range of 50-60 °C. For semi-crystalline PLAs, the glass transition temperature (T_g) is about 58 °C and melting

temperature (T_m) is between 130–230 °C by depending on structure that quit important for determining the use temperatures across various applications. Both of T_g and T_m are powerful affected by overall optical composition, primary structure, thermal history, and molecular weight [17].

Various advantages of PLA include high-strength and high modulus polymer, biocompatible and biodegradable, rapidly broken down thermally by hydrolysis and PLA also can tailor its physical properties by material modifications [18-20]. This fact is responsible for growing interest in PLA for many applications, as it is expected to reduce an impact on the environment caused by the production and utilization of petrochemical [21].

However, PLA also has some shortcomings which restrict its use, such as its inherent brittleness, low thermal stability, relatively high price, and the linearity of the molecules limits the range of physical properties. The most critical as such polymers generally have a relatively high glass transition temperature; moreover, the gas and water vapor barrier properties are not as good as those of the traditional polyolefins, the polymers are linear, every hydroxy or carboxylic impurity present during polymerization results in chain termination leading to low molecular weight products with poor chemical and mechanical stability so that would tend to limit the range of applications as well [22].

2.2 Characterization and Properties of PBS

Poly(butylene succinate); or PBS is a biodegradable synthetic aliphatic polyester with similar properties to PET which the trade name is "BIONOLLE". PBS is produced by the polycondensation of 1,4-butandiol with succinic acid that is generally blended with other compounds, such as starch (TPS) and adipate copolymers (to form PBS-A), to make its use economical.

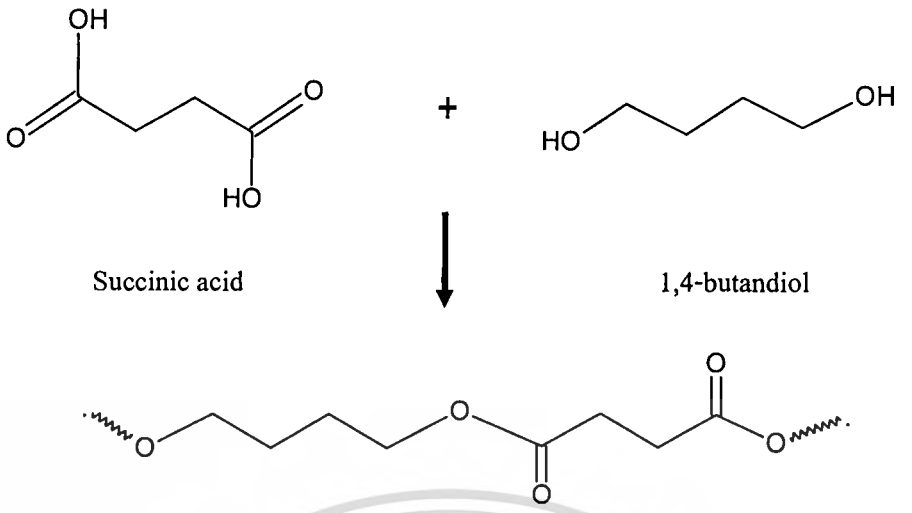


Figure 2.3 The polycondensation of 1,4-butandiol with succinic

PBS is hydro-biodegradable and begins to biodegrade via a hydrolysis mechanism. Hydrolysis occurs at the ester linkages and this results in a lowering of the polymer's molecular weight, allowing for further degradation by micro-organisms, a leading manufacturer of PBS polymers, quotes a degradation rate of 1 month for 50% degradation for 40 micron thick film in garden soil.

PBS have received growing interests in recent decades because of increasing global waste-plastic pollution which are biodegradable and easily decomposed in an acidic or basic condition and thus considered as promising polymers to solve the problem, has been investigated by many researchers [23]. Because of their excellent biodegradability, melt processability and thermal and chemical resistance, the application fields of their products via conventional melt processing techniques. Applications include mulch film, packaging film, bags and 'flushable' hygiene products. Especially those combined with the electrospinning process, may be extended further to textiles, medical treatment, environmental engineering and biotechnology and security application, etc. [24-25].

2.3 Electrospinning Process and Apparatus

At this presents, it is possible to produce fibers with diameters in the range from several micrometers down to tenths of nanometers and there are various approaches to producing nanofibers. However, in recent years, electrospinning technique is great, the cheapest and the most straightforward way to produce nanomaterials with a low-cost, high-value, high-strength fiber from a biodegradable and renewable waste product for easing environmental concerns which are of considerable interest for various kinds of applications and electrospun nanofibers are essential for the scientific and economic revival of developing countries [26-28].

2.3.1 Basic Experimental Approach

Electrospinning represents an attractive approach for polymer biomaterials processing through an electrically charged jet of polymer solution, with the opportunity for control over morphology, porosity and composition by using just simple equipment as shown in Figure 2.4 [29].

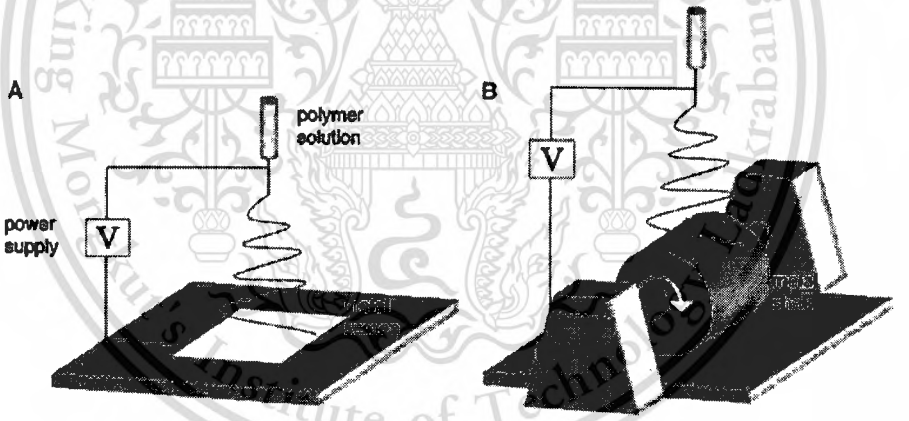


Figure 2.4 Electrospinning set-up [29]

The basic equipment requirements for demonstration of simple electrospinning are as follows [30]:

1. A viscous or a melt polymer solution.
2. An electrode that is hollow tubular or solid, is maintained in contact with the polymer solution.
3. A high-voltage DC generator connected to the electrode.
4. A grounded collecting screen to collect the nanofibers.

A simple experimental set up consist of a syringe which is carrying a few milliliters of a polymer solution. The viscosity of the solution is high enough to prevent it dripping from the syringe under gravity. The needle is mounted vertically a few centimeters (15-20 centimeters) above the grounded collecting screen or metal drum. A metal wire electrode that is touching the needle, is connected to the positive terminal of a high-voltage DC power supply unit and the negative one is connected to the metal drum or the grounded collecting screen [31]. Adjusting the voltage to 10-20 kV is required for let a droplet of the polymer solution be drawn out from the needle into a cone-shaped terminus and sprays downwards as a jet towards the metal drum in a range of nanoscale [32].

2.3.2 Basics Relevant to Electrospinning

Since electrospinning is basically the drawing of a polymer fluid, there are many different types of polymers and precursors that can be electrospun to form fibers. The materials to be electrospun will depend on the applications. Materials such as polymers and polymer nanofiber composites can be directly produced by electrospinning. Other materials such as ceramics and carbon nanotubes require post processing of the electrospun fibers.

2.3.2.1 Polymer

Polymers consist of long chain of molecule with repeating units called monomers that are mostly covalently bonded to one another. Polymers exhibit several properties that are attractive for many applications. Most polymers are inexpensive as they contain simple elements and they are relatively easy to synthesize.

Fundamental Classification of Polymer

There are basically two types of polymer under this classification, thermoplastic and thermoset. In thermoplastics, the linear polymers melt when heat is applied but solidifies when cooled. This heating and cooling can be repeated many times without affecting the properties. For thermosetting polymer, once an initial heat is applied, there is crosslinking between polymer chains. Subsequent application of heat would only degrade the polymer.

Polymer Crystallinity

In bulk polymer, there are usually both regions of crystalline and amorphous parts The ratio of the two regions would determine the properties of the polymer. A polymer is said to be

amorphous when the arrangement of the linear molecules is completely random. A crystalline polymer has its linear adjacent linear chains are aligned. Polymers that are of higher crystallinity show higher yield strength, modulus and hardness. When crystalline polymers are stretched, the polymer chains are oriented in the direction of the stress and destroy the spherulites structure. They also have better wear and chemical resistance. However, crystalline polymers are more brittle.

Polymer Molecular Weight

As polymer chains are made of repeating units, the molecular weight of the polymer is the sum of the molecular weight of the individual monomers. Generally, a higher molecular weight increases the polymer's resistance to solvent dissolution. The molecular weight of the polymer also has a direct influence on its viscosity.

Glass Transition Temperature (Tg)

The glass transition temperature is a very important property of polymers. This temperature defines the mobility state of the polymer molecules. Below its Tg, the amorphous polymer is brittle as the molecules are frozen but above Tg, the polymer is ductile and the molecular chains have sufficient thermal energy to slide. This causes the elastic modulus of amorphous polymers to decrease by several orders of magnitude at temperature above Tg. It is important to note that the mechanical behavior of the polymer at temperature above Tg is affected by the loading rate. Tg affects the mobility of polymer molecules, however, the motion of the molecular chain is not instantaneous. For slow loading rate, the molecular chain have time to move at temperature near Tg but if the loading rate is fast, there may not be enough time for the molecular chain to move thus increasing the effective Tg.

Synthetic Polymer

For synthetic polymer, there are generally two types, the ethenic polymers and the condensation polymers.

Natural Polymer

One of the greatest potential in electrospun fiber is in the area of bioengineering. For many biomedical applications, the materials used have to be biocompatible, thus natural polymers have a distinct advantage over synthetic materials. Since most natural polymer can be degraded by naturally occurring enzymes, it can be used in applications where temporary implants are

desired or in drug release. It is also possible to control the degradation rate of the implanted polymer by chemical cross-linking or other chemical modifications thus allowing greater versatility in the design of the implant.

2.3.2.2 Electrospun Polymer Fiber

Nowadays , there are many polymers that have been electrospun including custom made polymers. Electrospun fibers are commonly used in the field of tissue engineering due to their small diameters which are able to mimic natural extracellular matrix. Thus there are two groups of polymers that are commonly electrospun. These are the biodegradable polymers and natural polymers. Many different types of polymers from these two classes have been successfully electrospun which showed the versatility of electrospinning.

2.3.3 Parameters Affecting Nanofiber Quality

The parameters affecting electrospinning of polymer solution is concerned for the needy and the fibers may be broadly classified into polymer solution parameters, processing conditions which include the applied voltage, temperature and effect of collector, and ambient parameters.

2.3.3.1 Polymer Solution Parameters

Molecular Weight And Solution Viscosity

The molecular weight of the polymer represents the length of the polymer chain, which have an effect on the viscosity of the solution since the polymer length will determine the amount of entanglement of the polymer chains in the solvent. To maintain the continuity of the jet during electrospinning is to increase the viscosity of the solution, that means to increase the polymer concentration which is similar to increasing the molecular weight, the concentration is increased. That results in greater polymer chain entanglements within the solution. The polymer chain entanglements have a significant impact on whether the electrospinning jet breaks up into small droplets or resultant electrospun fibers contain beads [33]. A minimum viscosity for each polymer solution is required to yield fibers without beads [34-36]. At a low viscosity, it commonly finds beads along the fibers deposited on the collection screen. When the viscosity increases, there is a gradually alterable in the shape of the beads from spherical to spindle-like until a smooth fiber is obtained [35-37]; Moreover, increasing viscosity, the

diameter of the fiber also increases [38-42]. This is due to the greater resistance of the solution to be stretched by the charges on the jet [39].

Surface Tension

Bead formation in electrospinning can be induced by changing the surface tension of the solution [37-38]. The cause of surface tension has the effect of decreasing the surface area per unit mass of a fluid. When there is a high concentration of free solvent molecules, there is a greater tendency for the solvent molecules to meet and adopt a spherical shape due to surface tension.

However, a polymer solution can be controlled by selection of the solvent such as ethanol has a low surface tension thus it can be added to encourage the formation of smooth fibers [37-38] or can be added surfactant to the solution. The addition of surfactant was found to yield more uniform fibers even when insoluble surfactant is dispersed in a solution as fine powder, the fiber morphology is still improved [43].

Solution Conductivity

The Electrospinning involves stretching of the solution caused by repulsion of the charges at its surface. The conductivity of the solution is increased, more charges can be carried by the electrospinning jet which can increase the conductivity of the solution by the addition of ions lead to the critical voltage for electrospinning to occur is also reduced [44]. Solution prepared using solvents of higher conductivity generally yield fibers without beads while no fibers are formed if the solution has zero conductivity [39].

Dielectric Effect of Solvent

A solution with a greater dielectric property reduces the beads formation and the diameter of the resultant electrospun fiber [45]. Solvents such as N,N-Dimethylformamide (DMF) is added to a solution to increase its dielectric property to improve the fiber morphology [46]. However, if a solvent with a higher dielectric constant is added to a solution to improve the electrospinnability of the solution, the interaction between the mixtures such as the solubility of the polymer will also have an impact on the morphology of the resultant fibers.

2.3.3.2 Processing Conditions

Voltage

Generally, both high negative or positive voltage of more than 6kV is able to cause the solution drop at the tip of the needle to distort into the shape of a Taylor Cone during jet initiation [47]. At a higher voltage, it was found that there is a greater tendency for beads formation [41,40,48], the shape of the beads changes from spindle-like to spherical-like [48], and also encourage faster solvent evaporation to yield drier fibers [49]. At a lower voltage, the reduced acceleration of the jet and the weaker electric field may increase the flight time of the electrospinning jet. In this case, a voltage is close to the critical voltage for electrospinning which may be favorable to obtain finer fibers [50]. Nevertheless, the effect of high voltage is not only on the physical appearance of the fiber, it also affects the crystallinity of the polymer fiber. The electrostatic field may cause the polymer molecules to be more ordered during electrospinning thus induces a greater crystallinity in the fiber. An still more interesting, Increasing of voltage has increased the beads density, which at even the beads will join to form a thicker diameter fiber [51].

Feed rate

When the feed rate is increased, there is a increase in the fiber diameter or beads size. However, there is a limited of increasing in the diameter of the fiber due to higher feed rate [52]. A lower feed rate is more desirable as the solvent will have more time for evaporation [53] due to the greater volume of solution drawn from the needle tip, the jet will takes a longer time to dry. As a result, the solvents in the deposited fibers may not have enough time to evaporate given the same flight time. The residual solvents may cause the fibers to fuse together.

Temperature

The temperature of the solution has both the effect of increasing its evaporation rate and reducing the viscosity of the polymer solution which allows more even stretching of the solution. The fibers produced have a more uniform diameter.

Effect of Collector

The collector screen or drum should be made out of conductive material such as aluminum foil because when a non-conducting material is used as a collector, charges on the electrospinning jet will rapidly collect on the collector which will result in fewer fibers deposited [54-55]. Fibers that are collected on the non-conducting material usually have a lower packing density compared to those collected on a conducting surface. This is caused by the repulsive forces of the accumulated charges on the collector as more fibers are deposited. However, a rotating collector or drum has been used to collect aligned fibers, it assists the yield of fibers that are dry. This rotating collector will allow the solvent to have more time to evaporate [54-55] and also can increase the rate of evaporation of the solvents on the fibers which will cause to improve the morphology of the fiber.

Diameter of Syringe Orifice / Needle

A smaller internal diameter of the syringe orifice and the needle was found to reduce the clogging of polymer solution as well as the amount of beads on the electrospun fibers due to less exposure of the solution to the atmosphere during electrospinning [56]. Decreasing of the internal diameter of the orifice has caused a reduction in the diameter of the electrospun fibers. However, if the diameter of the orifice is too small, it may not be possible to extrude a droplet of solution at the tip of the orifice [50].

Distance Between Tip and Collector

When the distance between the tip and the collector is reduced, the jet will have a shorter distance to travel before it reaches the collector screen. But for some fibers forming, the electrospinning jet must be allowed time for most of the solvents to be evaporated, so the effect of varying the distance may or may not have a significant effect on the fiber morphology. However, beads were observed to form when distance was too short [40]. The formation of beads may be the result of increased field strength between the needle tip and the collector.

2.3.3.3 Ambient Parameters

The humidity of the environment will determine the rate of evaporation of the solvent in the solution. If it is high humidity, it will seem like water condenses on the surface of the fiber when electrospinning is carried out under normal atmosphere. As a result, this may have an influence on the fiber morphology especially the polymer dissolved in volatile solvents

[40,57]. At a very low humidity, a volatile solvent may dry very rapidly, so the electrospinning process may only be carried out for a few minutes before the needle tip is clogged [38]. Other ambient parameters are the composition of the air, which the different gases, will have different behavior under high electrostatic field and reduction in the pressure surrounding the electrospinning jet does not improve the electrospinning process. When the pressure is below atmospheric pressure, the polymer solution in the syringe will have a greater tendency to flow out of the needle and there causes unstable jet initiation.

2.3.4 Patterning

The ability to obtain one-dimensional (ID), two-dimensional (2D), and three-dimensional (3D) fiber architecture with controlled alignment and pitch will greatly increase the potential application of electrospun fibers. Cylinder Collector, The most basic form of getting aligned fibers rather than random mesh is through the use of a rotating mandrel as show in Figure 2.5 [58].

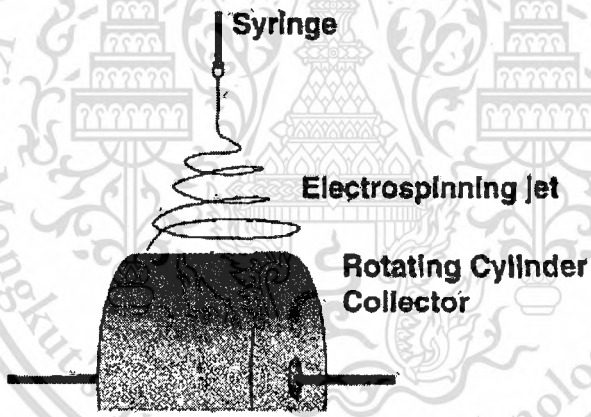


Figure 2.5 A rotating cylinder collector to obtain unidirectional nanofiber alignment along the rotating direction [58].

As the fibers are formed from the electrospinning jet, the mandrel that is used to collect the fibers is rotated at a very high speed up to thousands of rpm (revolution per minute). This method has been successful in obtaining aligned electrospun poly(glycolic acid) (PGA) (1000 rpm rotating speed) and type I collagen (4500 rpm rotating speed) fibers [59-60]. In electrospinning, the jet is traveling at a very high speed. As a result, to align the fibers around the mandrel, it is necessary that the mandrel is rotating at a very high speed so that the fibers can be taken up on the surface of the mandrel and wounded around it. A speed can be called as alignment speed. If the rotation of the mandrel is slower than the alignment speed, the fibers deposited will be randomly

oriented. As more fibers are collected on the mandrel, accumulation of charges may cause incoming fibers to be repelled resulting in less oriented fibers.

2.4 Characterization of Nanofibers and Mats

Characterization of nanofibers and mats are undertaken primarily to correlate test metrics with the useful properties of the material and to ensure consistent high quality of the product during manufacture. With single fiber measurements the intent is usually to generate fundamental data that allow a better understanding of the relationship between the structure and the properties of nanofibers. In principle there are a large number of different characterization techniques that can be used with nanofibers. With organic polymer nanofibers, the entire gamut of available polymer characterization techniques can be applied.

A modified electrospinning method has been provided by Wangnerbet al [61] for the creation of an elastomeric, fibrous sheet (fibrous composite sheet with to distance sub-micrometer fiber population: biodegradable poly(eater urethane) urea (PEUU) and poly(lactide-co-glycolide)(PLGA), where the PLGA was loaded with the antibiotic tetracycline hydrochloride(PLGA-tet) capable of sustained antibacterial activity in vitro. Composite sheet were flexible with breaking strains exceeding 200%, tensile strengths of 5-7 MPa, and high suture retention capacity. The blending of PEUU fibers markedly reduced the shrinkage ratio observed for PLGA-tet sheets in buffer from 50% to 15% while imparting elastomeric properties to the composites. In development of this materials , a new approach to two-stream electrospinning was used wherein one component stream provided for antibiotic release while the other provided mechanical properties deemed essential for the desired application.

2.4.1 Mat Porosity and Pore Size Distribution

The interstitial porosity of a nanofibrous mat is the fractional void space contained within it and is therefore a morphological property that is unrelated to the material characteristics of the nanofibers. It is the pore size distribution and three-dimensional geometry that determine the key properties such as filtration or scaffold performance of nanofibrous mats.

2.4.2 Nanofiber Diameter and Pore Size

Microscopic imaging is routinely used in the initial characterization of nanofibrous mats Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques are both particularly useful in understanding and quantifying fiber morphology. Depending on the particular instrument, resolutions of 1–20 nm are possible with SEM, and 0.1 nm for TEM, but both techniques essentially yield two-dimensional representations of nanofibers and pores.

2.4.3 Mechanical Properties of Mats

The techniques available to measure the mechanical properties of films and textile materials are well known and in most instances can be applied with some modification to nanofibrous mats. However, some caution in interpreting the data is warranted. The most common such technique is tensile property measurement using the same general experimental technique used with film or woven textile samples.

2.4.3.1 Single-Fiber Characterization

Characterization of individual nanofibers is critical to understanding their physics because invariably it is the fiber characteristics that govern the properties of their mats. But, their minute dimensions makes this a daunting task. Nanofibers of particular interest, those with dimensions smaller than the wavelength of light, are especially difficult to isolate or test. It is not practical to extract fiber-level information by manipulation of test data generated from even the best-characterized fiber mats.

2.4.3.2 Nanofiber Crystallinity

Differential scanning calorimeters are designed to hold a sample of the nanofiber sealed in a metal sample pan (usually made of aluminum) and a reference metal pan carrying no sample, at exactly the same temperature. The higher thermal capacity of the sample pan will demand more thermal energy relative to reference pan to attain a given temperature. As the temperature of the insulated enclosure holding the pans is slowly increased, the difference in power demand by sample and reference pans is accurately monitored as a function of temperature and yields thermal data on the nanofiber sample in the sample pan.

2.5 Potential Applications Area

2.5.1 Medical Applications

Biomedical applications is still the most intensely researched application area for electrospun nanofibers composites. Nanofibers are expected to contribute in diverse emerging medical areas such as organogenesis, genomic medicine, high throughput screening, rapid bedside clinical tests, and smart wound dressings.

Drug Release

Generally, drug uptake into the human body is faster with the smaller size of the drug and its coating material. Hence, drug delivery system has been developed using polymeric materials in the form of nano or micro particles, hydrogels and micelle [62]. Many researchers have recently focused on the usage of polymer nanofiber membranes which encapsulate medical drugs instead of conventional polymeric materials.

Tissue Scaffolds

Recently, electrospun polymer nanofibers have been identified as promising biodegradable matrices for supporting cell attachment and proliferation. With electrospun nanofibers shown to be a good candidate as tissue scaffold through the many successes in tissue culture, the artificial blood vessel scaffold also produced by using electrospinning, tubes of diameter as small as 1.27 mm has been fabricated for application as nerve guidance channel.

Bone

Biodegradable polymers often have been combined with bioceramics to produce materials for bone repair such as PGA, PLA and PLGA that have found application as recordable sutures [63], bone fixation screws and plates, They have been widely investigated as bone graft substitutes with positive results [64] An improvement in the mechanical properties of PCL has been achieved by co-polymerization with PLA, enabling its use for orthopedic applications, such as the repair of bone defects.

Nerve

Electrospinning provides a straightforward way to fabricate fibrous polymer scaffold for neural tissue engineering. The potential of nanofibrous porous scaffold is prepared by phase

separation using poly(lactic acid) with a similar structure of natural ECM in nerve tissue engineering [65]. In a recent study, nerve guidance channel was fabricated by electrospinning poly(L-lactide- co-glycolide) biodegradable polymer nanofibers onto a Teflon mandrel [66].

Affinity Membrane

Affinity membrane was developed to permit the purification of molecules based on physical/chemical properties or biological functions rather than molecular weight/size. Rather than operate purely on the sieving mechanism, affinity membrane based its separation on the selectivity of the membrane to 'capture' molecules, by immobilizing specific ligands onto the membrane surface.

2.5.2 Industrial Applications

Composite Reinforcement

Fiber reinforced polymer composite materials have been utilized in aerospace, automobile, sports items and electrical products. Fillers used in reinforcing fillers and must be of small enough average particle size and of adequate surface compatibility with the matrix to effectively. The choice of reinforcement and matrix polymer is dependent on the required mechanical performance of the products and the whole productive cost.

2.5.3 Materials Applications

Polymer Battery

The important properties of polymer nanofiber batteries are (1) Ion Conductivity, (2) Interfacial Resistance and (3) Electrochemical stability. Conductive polymers such as polyvinylidenefluoride (PVdF) [67-68], polyacrylonitrile (PAN) [67-69], poly(vinyl chloride) (PVC) [70] and poly(methyl methacrylate) (PMMA)[71-72] have been utilized as gel condition with electrolyte solution.

Sensors

Benefits of sensors is to transform physical or chemical responses into an electrical signal.

- Gas Sensors

Considering to use quartz crystal microbalances (QCM) sensors with electrospun nanofibers [73]. It is acknowledged that QCM sensors are widely used to detect the mass change

in the presence of coating material which reacts with the target gas. He further tried to improve the sensitivity of QCM sensors at lower concentration of NH^3.As a result, sensitivity of QCM sensors was improved up to 30 ppb level of NH^3.

- Chemical Sensors

Benefits of chemical sensors is to detect certain chemical component or a change of pH (potential of hydrogen) in a material system. To modify the conventional piezoelectric sensors [74], so called Thickness Shear Mode (TSM) sensors using electrospun nanofibrous membrane. Poly-lactic acid-co-glycolic acid (PLAGA) nanofibers were deposited on a sensing interface of TSM sensors and characterization under different liquid loading.

- Biosensors

Biosensors are the device which can detect or monitor the biological change of the human body. The fabricated polyvinylpyrrolidone (PVP) nanofiber sensor incorporated with urease (urea decomposition enzyme) to detect urea, which can be used to check kidney and liver function problems [75].

Hybrid Compound for Cosmetics

The advantage of new hybrid compounds for cosmetics is the release of active ingredients for applications related to skin care and protection. Based on the encapsulation of active organic components within porous silica microcapsules. Sol-gel Technology Ltd. Located in Bet Shemesh, Isreal provides a safe solution by encapsulating the active organic UV filters in silica micro-capsules.

Hybrid Material for Protective and Decorative Coatings

Hybrid materials have occurred in the automotive coating. Hybrid coatings provide coloration, scratch-resistance, protection from UV, and chemical resistance for the substrate. DuPont with Generation 4 has developed a complex mixture of two hybrid polymer cross-linked simultaneously during to form a polymer network. This network is partially grafted and partially interpenetrated as a decorative coating for the automotive industry.

2.5.4 Nanofiber Mats Applications

Filtration is the leading nonbiomedical application of electrospun nanofibers. Another emerging application area for nanofibers is in sensors for sense chemical and biological agents

including the growing number of toxic industrial chemicals (TICs). In nearly all application areas the fragility of organic nanofibers and their temperature sensitivity limits their use. In catalysis applications, for instance, the substrate gas streams that need to be processed or the liquid-phase reactions that need to be catalyzed are at relatively high temperatures. The use of inorganic nanofibers, including metal and metal oxide nanofibers, can therefore be of particular value in such applications.

2.5.4.1 Air Filtration

Nanofiber mats, because of the small fiber diameter, are very well suited for air filtration providing that sufficiently low solidity and mechanical strength can be obtained. The range of particle sizes that need to be separated from an air stream can be quite broad, ranging from environmentally relevant large particles such as PM-10 (particulate matter with aerodynamic diameter smaller than 10mm), all the way down to engineered nano-particles only several nanometers in diameter.

Filters with Nanofibers

The effectiveness of incorporating a nanofiber layer on conventional filter media has been recognized for some time in the air filter industry. Typically, these applications have been for dust removal and the media has demonstrated robustness for a wide range of applications.

2.5.4.2 Nanofiber Sensors

It is reasonable to expect the sensitivity of a sensor that involves surface interaction with analyze molecules to increase with increasing surface area per unit mass of the sensing material. The high specific surface area of nanofibers therefore suggests the possibility of more efficient and rapid sensor performance, particularly when sensing mechanism is via a surface reaction

Gravimetric Sensors

Sorption and surface adsorption of chemical agents by a mat of polymer nanofibers can be detected gravimetrically using quartz crystal microbalance (QCM) detectors. The mass sensor is essentially a circular quartz crystal with thin metal electrodes deposited on either side of it.

2.5.4.3 Inorganic Nanofibers

Nanofibers that are made of inorganic materials such as inorganic polymers, metals, or metal oxides are of interest in semiconductor or electronic materials, photonic materials, aerospace applications, catalysis, and high temperature sensor applications. Inorganic nanofibers are use in a wide range of operating temperatures.

2.6 Literature Reviews

The first recorded observation of electrospraying was in the late 1500s, William Gilbert set out to describe the behavior of magnetic and electrostatic phenomena which his work has been an early example of what would become the modern scientific method.[76] However, the first description of a process recognizable as electrospinning was in 1902 when J. F. Cooley filed a United States patent entitled "Apparatus for electrically dispersing fibers" [77].

An overview of Poly(lactic acid) fiber was reported by B. Guptaa, N. Revagadea and J. Hilbornb [78], They studied the chemistry of poly(lactic acid) and spinning process of poly(lactic acid) fibers.

H. Zhou, T. Green and Y. Joo were found that melt electrospun PLA sub-micron fiber mats with no residual solvent may serve as better filter media and tissue scaffolds.[79]

Y. Liu, J. He and J. Yu studied preparation and morphology of Poly(butylene succinate) nanofibers via electrospinning which the morphology of the fibers were studied on different weight concentrations of PBS/CF solution and were spun with different diameters of needle-orifice. From the results, when the weight concentration equals 8%, the electrospinning process was very difficult and had only a few fibers. As the concentration was increased, the efficiency was high and the process became more easy. However, the morphology of the fibers was more uniform when they were spun with a larger diameter of the needle-orifice.[80]

Characterization and processing of biodegradable polymer blends of poly(lactic acid) (PLA) with poly(butylene succinate adipate) (PBSA). were studied by S. Lee and J. Lee [81]. They investigated thermal, rheological, morphological and mechanical properties of a binary blend of PLA and PBSA. The blends were extruded and their molded properties were examined. It was found that the rheological properties of the blends changed remarkably with composition while the tensile strength and modulus of blends decreased with PBSA content. Interestingly, the impact strength of PLA/ PBSA (80/20) blend was seriously increased higher than the rule of

mixture. Morphology of the blends also showed a typical sea and island structure of immiscible blend. The effect of the blend composition on the biodegradation was also investigated by DSC thermograms indicated that the thermal properties of PLA did not change noticeably with the amount of PBSA. Immiscibility was checked with thermal data. In the early stage of the degradation test, the highest rate was observed for the blend containing 80 wt% PBSA.

In 2008, V. Guarino and Co-workers [82] used poly(lactic acid) fiber-reinforced poly(caprolactone) scaffolds for bone tissue engineering, In the detail, they found that for a new type of composite material for bone regeneration which were composed of a porous PCL matrix reinforced with continuous PLA fibers. They were fabricated by the synergic use of filament winding and phase inversion/salt leaching technique.

A. Iwatake, M. Nogi and H. Yano [83] studied successfully in the topic of cellulose nanofiber-reinforced polylactic acid, the reinforcement of polylactic acid (PLA) using microfibrillated cellulose (MFC) with the goal of making sustainable green-composites.

In 2009, A. Nakagaito and coworkers [84] concerned about production of microfibrillated cellulose (MFC)-reinforced polylactic acid (PLA) nanocomposites from sheets which were obtained by a papermaking-like process. In the detail of research, a new process to produce MFC/PLA composites was compression molding which was found uniformly dispersed MFC and PLA fibers. A procedure similar to papermaking was developed. However, the fabrication of cellulose nanofiber-reinforced composites has been so far problematic due to difficulties in obtaining good dispersion of hydrophilic cellulose fibers in a hydrophobic polymer matrix.

In 2009, L. Suryanegara, A. Nakagaito and H. Yano [85], studied the effect of crystallization of PLA on the thermal and mechanical properties of microfibrillated cellulose-reinforced PLA composites, demonstrated that MFC could extend the application of PLA, particularly for products exposed to high temperature.

E. Jeong, S. Im, J. Youk were reported that biodegradable Poly(butylene succinate) ultrafine polymer were continuously electrospun for the first time from preparing of PBS solutions in chloroform (CF)/2-chloroethanol (CE) (7/3, w/w), CF/CE (6/4, w/w), dichloromethane (DM)/CE (7/3, w/w), DM/CE (6/4, w/w), and CF/3- chloro-1-propanol (9/1, w/w). the result of annealed ultrafine PBS fibers exhibited a lamellar stack morphology containing crystalline and amorphous layers and also had very high crystallinity with their average diameters were in the range of 125–315 nm. [86]

Compatibility of biodegradable poly (lactic acid) (PLA) and poly (butylene succinate)(PBS) blends for packaging application was studied by A. Bhatia and Coworkers [87], which Poly (lactic acid) (PLA) and poly (butylenes succinate) (PBS) are both biodegradable polymers. Blends of PLA and PBS were prepared by using a laboratory-scale twin-screw extruder at 180°C. Morphology showed a clear phase difference trend depending on blend composition. MDSC thermograms of the blends indicated that the glass transition temperature (Tg) of PLA did not change much with the addition of PBS. However, PLA/PBS blend of up to 80/20 composition showed that partial miscible between the two polymers. Tensile strength, modulus and percentage (%) elongation at break of the blends decreased with PBS content. Rheological resulted miscibility between the two polymers for PBS composition less than 20% by weight. PBS reduced the brittleness of PLA, thus making it a contender to replace plastics for packaging applications.

Chapter 3

Experimental Details

3.1 Chemicals

1. Poly(lactic acid) (PLA), Nature Works LLC Co., USA
2. Poly (butylene succinate) (PBS), Showa HighPolymers Co.,Ltd., Japan
3. *N,N* Dimethylformamide (DMF; analytical grade), Labscan Co.,Ltd.,Thailand
4. Dichloromethane (DCM; analytical grade), Labscan Co.,Ltd.,Thailand
5. Chlorobenzene (CB; analytical grade), Labscan Co.,Ltd.,Thailand

3.2 Apparatus

1. High voltage DC power supply
(model UC5-30P, Gamma High Voltage Research, USA)
2. 20 Gauge stainless steel needle
3. Rotating cylinder collector
4. Aluminum foil
5. Glass bottle with a tighten cap
6. 50 ml glass syringe
7. Magnetic stirrer and magnetic bar
8. Balance
9. Stop watch

3.3 Instruments

1. LEO 1455 VP Scanning electron microscope
2. Differential scanning calorimeter (DSC; Perkin Elmer DSC-2)
3. PEACOCK micrometer
4. Universal testing machine (UTM, LLOYD Instrument; 100N)

5. Brookfield DV-III viscometer

3.4 Procedure

3.4.1 Electrospinning of Polylactic acid (PLA) and Poly (butylene succinate) (PBS)

Part A Preparation of polylactic acid (PLA) and poly(butylene succinate) (PBS) solutions

1. To obtain electrospinnable solutions, pure PLA pellets were dissolved in mixed-solvent system of 7:3 (v/v) DCM-DFM mixtures. The varying concentrations of PLA were prepared by increasing in increments of 2% (w/v) starting at 8-14%.
2. Pure PBS pellets were also dissolved in 9:1 (v/v) DCM-CB mixtures at fixed concentration of 12% (w/v).
3. These solutions were vigorously stirred with a magnetic stir bar for at least 4 hours in a sealed glass bottle at room temperature.
4. To investigate viscosity of the spinning solution, a Brookfield DV-III viscometer following the ASTM D 2857-87 standard test method was used.

Figure 3.1 Polylactic acid (PLA) and poly (butylene succinate) (PBS) solutions

Part B Setup Of Electrospinning Process

1. Electrospinning process was carried out at room temperature. 50 ml glass syringe was filled with the as-prepared PLA and as-prepared PBS solutions. The gauge-20 stainless steel needle with a 1 cm-long blunt-ended was selected as the nozzle. In order to minimize solution dripping at the tip of the nozzle, both the syringe and the nozzle were tilted close to 45° from a horizontal baseline.

2. A rotating cylinder collector was covered with a piece of flat aluminium sheet which was used as a collective screen.

3. A high voltage DC power supply (model UC5-30P, Gamma High Voltage Research, USA) was used to charge the spinning solutions by connecting the emitting electrode of positive polarity to the nozzle and the grounding electrode to the collective screen. The applied voltage was fixed in 20 kV with a 18 cm working distance.

4. The fibers were collected on a grounded rotating cylinder collector which fixed speed of rotation (92 rpm).

5. The thickness ratios of electropun PLA, PBS and Multilayered electrospun PLA/PBS non-woven ultrafine fibrous mats as shown in Figure 3.3 and Table 3.1.

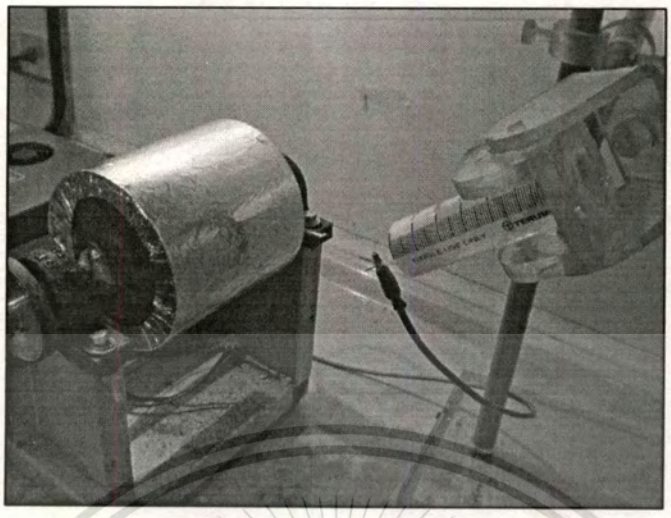


Figure 3.2 Experimental set up for electrospinning technique

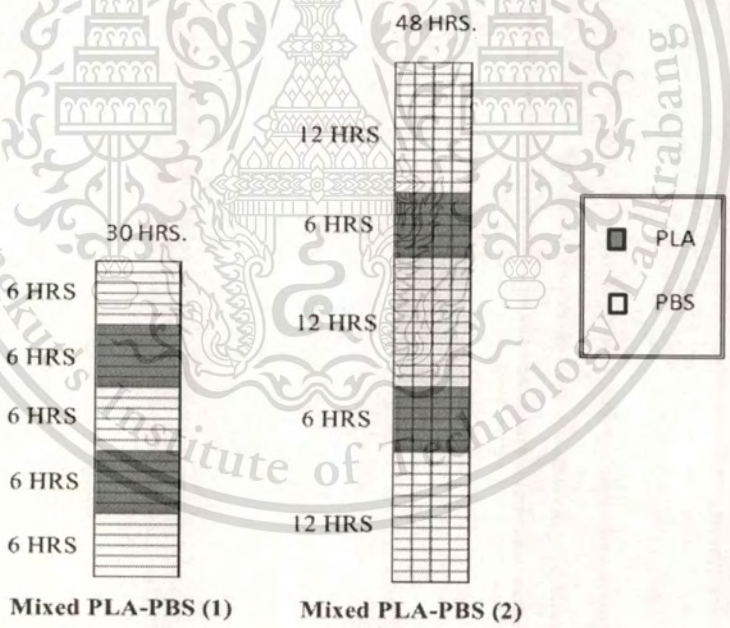


Figure 3.3 The amount of time ratios of electropun PLA and PBS fibrous mats

Table 3.1 The thickness ratios of electropun PLA and PBS fibrous mats

Samples	Electropun Nonofibrous Mats	Collection Time (h.)		Thickness (mm.)
1	PLA	~23		1.9
2	PBS	~38		1.9
3	Mixed PLA/PBS (1)	PBS	~6	0.3
		PLA	~6	0.5
		PBS	~6	0.3
		PLA	~6	0.5
		PBS	~6	0.3
4	PLA	~34		2.8
5	PBS	~56		2.8
6	Mixed PLA/PBS (2)	PBS	~12	0.6
		PLA	~6	0.5
		PBS	12	0.6
		PLA	~6	0.5
		PBS	~12	0.6

3.4.2 Characterization of Electrospun Polylactic acid (PLA) and Poly (butylene succinate) (PBS) Fibers

Part A Morphology Testing

1. To characterize morphological appearance of the fibers, the electrospun PLA, PBS, and multilayered PLA/PBS fibers were imaged on a LEO 1455 VP scanning electron microscope (SEM) to view microscopic features. Samples were coated with a thin layer of gold prior to imaging.

2. The diameter of the individual fibers in the electrospun PLA, PBS, and multilayered

PLA/PBS fibrous mats were analyzed by measuring over 100 fibers from randomly recorded SEM micrographs using an image analysis software (SemAfore®4.0).

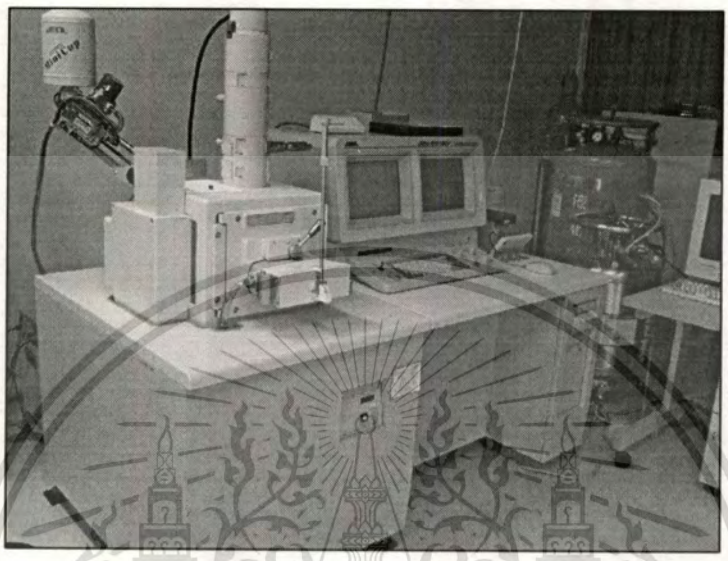


Figure 3.4 Scanning Electron Microscope

Part B Physical Properties Testing

1. A differential scanning calorimeter (DSC) was used to investigate thermal behaviors (Tm, Tg, % crystallinity) of the electrospun PLA, PBS and multilayered PLA/PBS fibrous mats. The weight of each specimen was set at approximately 10 mg.

2. For both untreated fibers and pure pellets were placed in an aluminium pan. The samples were then enclosed within the aluminium pans and scanned immediately, maintaining a static air flow of 20 mL/min. Dynamic scans of 12% (w/v) PLA, 12% (w/v) PBS and multilayered PLA/PBS samples were carried out at 10 °C/min with a scanned temperature range from 50 °C to 180 °C.

Part C Mechanical Properties Testing

1. Tensile testing

The mechanical properties were analyzed using a universal testing machine (UTM LLOYD Instrument) according to ASTM D 882. All of the UTM measurements were carried out at room temperature. Tensile specimens were prepared by cutting the rectangular shape. The dimensions of the ultrafine fibrous mat used were 15 mm x 80 mm (width x thickness) and 40 mm. of a gauge length. Five to eight specimens were tested in both machine direction (MD) and transverse direction (TD) at the conditions as followed :

- Load cell 100 N
- Cross head speed 10 mm/min
- Gauge length 40 mm

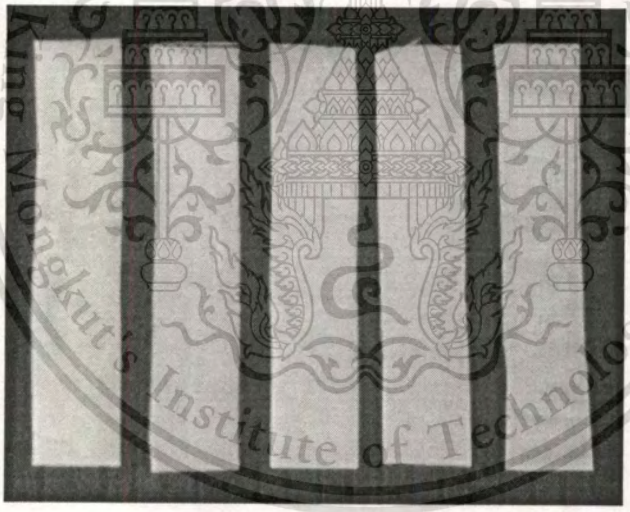


Figure 3.5 Samples of tensile testing

Tensile Strength

From tensile testing, tensile strength (TS) was calculated by the equation,

TS = F/A

Where, TS = tensile strength (MPa)

F = force at yield or at break (N)

A = initial cross-section area of the test specimen (mm^2)

Elongation at Break

The elongation at break (EB) was obtained by the equation,

%EB = $((L-L_0)/L_0) \times 100$

Where, %EB = elongation at break (%)

L = the distance between gauge marks at break (mm)

L_0 = the initial distance between gauge length (mm)

Young's Modulus

Young's modulus (E) was experimentally determined from the initial slope of a stress-strain curve by dividing the tensile stress by the tensile strain,

E = tensile stress / tensile strain

Where, E = Young's modulus

Elongation at Yield

The percentage elongation at yield was obtained by the difference between the elongation of the specimen at the start and at the finish of discontinuous yielding.

Tensile Stress at Yield

The stress at which material strain changes from elastic deformation to plastic deformation, causing it to deform permanently.

Tear Strength

Tear strength specimens were prepared by using ASTM Die C knife-block with pressure cutting machine. Five specimens were tested in both machine direction (MD) and transverse direction (TD) at the conditions as follows,

- Load cell 100 N
- Cross head speed 10 mm/min
- Gauge length 50 mm

Calculate the resistance to tear from the maximum force registered by the testing machine and the thickness of the specimen.

Tear Strength = F / t

Where, F = force (N)

t = specimen thickness (mm)

Figure 3.6 Samples of tear strength testing

3.5 Experimental Flow Chart

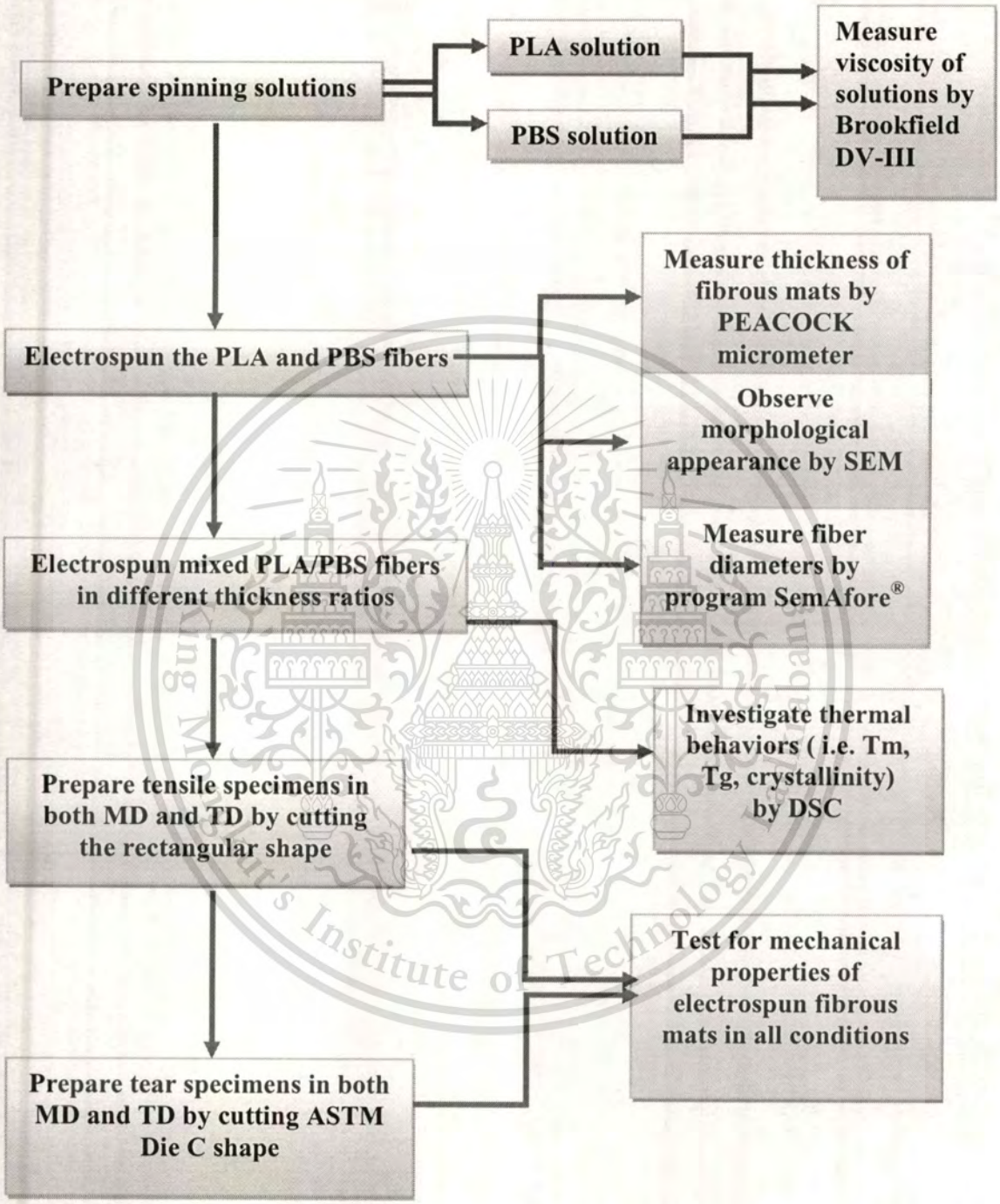


Figure 3.7 Schematic diagram of the experimental procedures

Chapter 4

Results and Discussion

Poly(lactic acid) (PLA) and poly (butylene succinate) (PBS) ultrafine fibrous non-woven mats were fabricated by electrospinning technique which is a feasible way to produce sub-micron scale fibers. In this work, firstly, PLA was electrospun at concentration 8% (w/v) to 14% (w/v) using 7:3 (v/v) DCM-DFM mixed-solvent system to investigate the effect of concentration on fiber diameters. The DCM-DMF mixture was selected as the solvent for the organic phase because DCM is an excellent solvent for PLA while DMF is an excellent solvent for electrospinning probably due to its high dielectric constant. Secondly, 12% (w/v) of PLA was chosen to electrospinning with 12% (w/v) PBS in 9:1 (v/v) DCM-CB mixtures at various thickness ratios. It was easy to make non-woven mats with this electrospinning conditions. Finally, fiber morphologies, thermal and mechanical properties of the prepared non-woven mats were characterized.

4.1 Processing Conditions and Fiber Morphologies

In order to investigate viscosity of the PLA and PBS spinning solution, a Brookfield DV-III viscometer following the ASTM D 2857-87 standard test method was used. It was found that the viscosity values of 12% (w/v) PLA and 12% (w/v) PBS solutions were 125 cP and 220 cP, respectively.

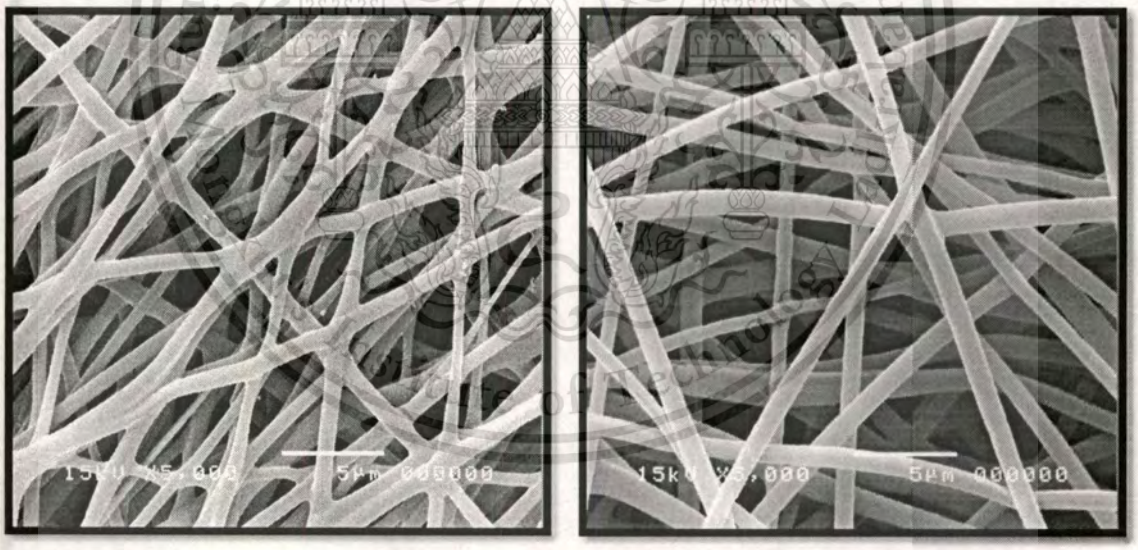
4.1.1 Effect of Processing Parameters on Fiber Diameter

The morphology of electrospun ultrafine fibrous non-woven mats on SEM images changed with PLA concentration. The electrospinning technique was carried out under an electrical potential of 20 kV that was applied over a collection distance of 18 cm. Figure 4.1 shows SEM images of the obtained fibers for four different concentrations of electrospun PLA in 7:3 (v/v) DCM-DFM mixtures (i.e., 8, 10, 12, and 14 % (w/v)).

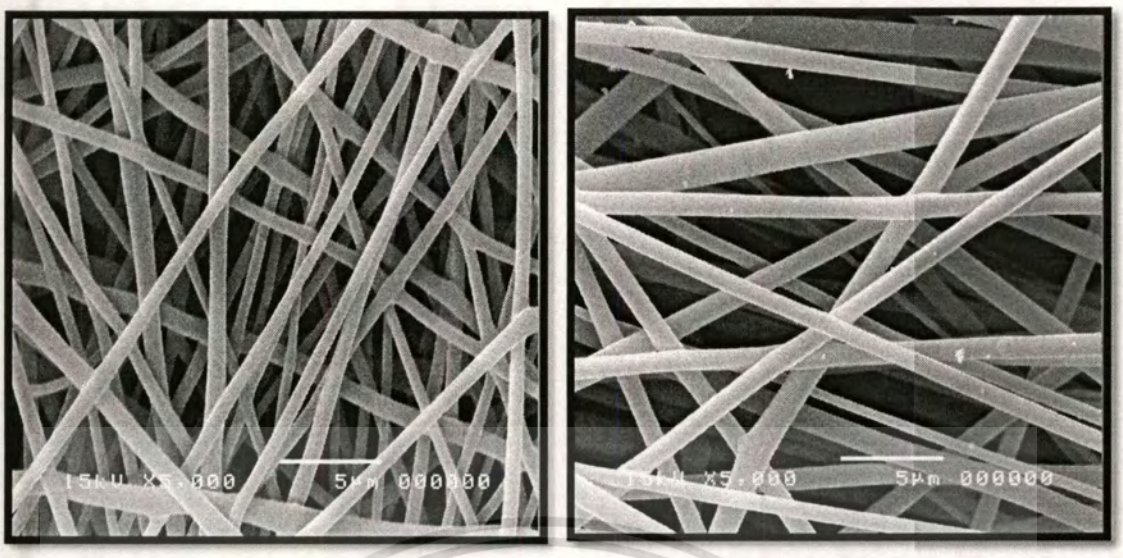
At 8% (w/v) solution (Figure 4.1a), fibers were random conformation which the fibers diameter was about 150 nm and a large proportion of electrospun fibers were ribbon-shaped as well as branching and web-like structures. It was noted that some ribbons possess lines that run

parallel to the length of the fibers. This effect can be explained by fast evaporation of the solvent during the electrospinning process, leading to the formation of a solid skin that shrinks and collapses upon the evaporation of the remaining solvent. Branching was observed due to instabilities of the electrospinning jet. Splitting of the ribbons into nanowebs was probably fast phase separation between polymer and solvent, the solvent rich region being apparently transformed into pores.

As the concentration was increased to 14% (w/v), The average fiber diameter was approximately 125 nm to 145 nm. and fibers still were random conformation. The number of fibers which were ribbon-shaped began to disappear until only uniformly cylindrical fibers and with a consequent increase in the fiber diameter (Figure 4.1b-d). It can be seen that all fibers are smooth and no formation of beads was observed along the fibers. This increase in average diameter is common as the concentration increases. However, in the case of biaxial fibers like ribbons the diameters are also influenced by the tilt angle of the ribbons. Therefore, the largest visible width of the fibers can be seen in Figure 4.2.



(a) (b)



(c) (d)

Figure 4.1 SEM micrographs of the concentration series for PLA electrospun from the various concentrations: (a) 8, (b) 10, (c) 12, (d) 14% (w/v) (5000X magnification)

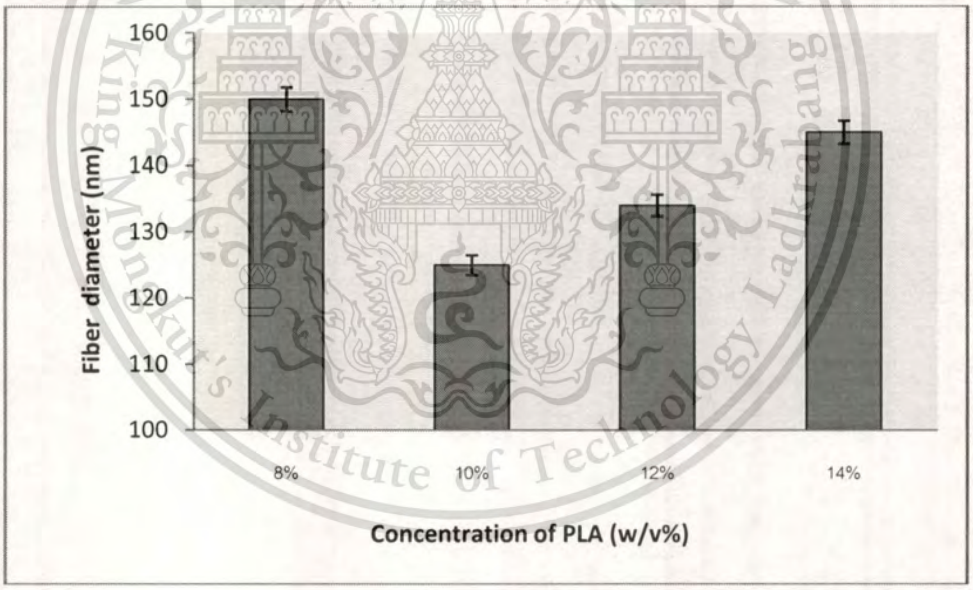


Figure 4.2 Average fiber diameter of electrospun PLA as a function of concentration

Due to the distribution of the concentration series for PLA electrospun, the fiber diameters are allowed in a broad range between 89 to 203 nm which the highest frequency distributions (mode) are the range between 136 to 138 nm for 12% (w/v) and the range between 152 to 164 nm for 8% (w/v) as presented in Figure 4.3.

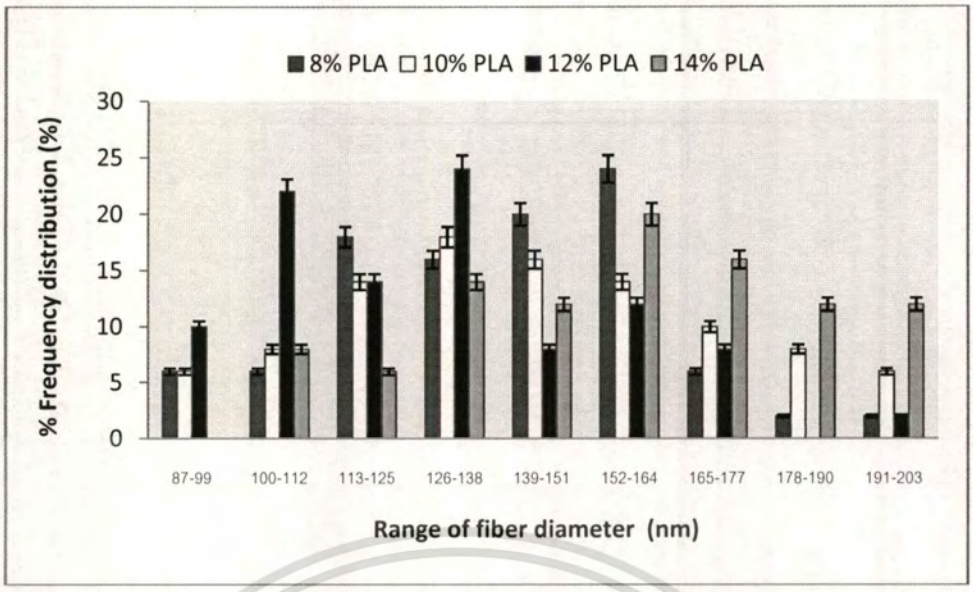


Figure 4.3 The distribution of the electrospun PLA fiber diameters as a function of concentration

4.1.2 Influence of the Mat Preparation

To study the effect of multilayered electrospun PLA/PBS ultrafine fibrous non-woven mats, the electrospun PBS fiber mats were laminated with PLA fiber mats at various thickness ratios as shown in Table 4.1. At formula 1, the thickness ratio was fixed at 0.19 mm with 0.3 mm of PBS fibers in every PBS layers. Whereas formula 2, the thickness ratio was about 0.28 mm with 0.6 mm of PBS fibers in every PBS layers.

Table 4.1 The thickness ratios of electropun PLA and PBS fibrous mats

Samples	Electropun Nonofibrous Mats	Collection Time (h.)		Thickness (mm.)
1	PLA	~23		1.9
2	PBS	~38		1.9
3	Mixed PLA/PBS (1)	PBS	~6	0.3
		PLA	~6	0.5
		PBS	~6	0.3
		PLA	~6	0.5
		PBS	~6	0.3
		Mix.	~30	1.9
4	PLA	~34		2.8
5	PBS	~56		2.8
6	Mixed PLA/PBS (2)	PBS	~12	0.6
		PLA	~6	0.5
		PBS	12	0.6
		PLA	~6	0.5
		PBS	~12	0.6
		Mix.	~48	2.8

Morphological appearance of the fibrous mats after lamination were observed the fiber formation efficiency which were compared with the virgin electrospun PLA and PBS fibers. Selected SEM images are shown in Figure 4.4. Evidently, PLA fibers were smooth with the diameters of these fibers approximately 219 nm (Figure.4.4a). They also show the uniform fibers with a small difference in their size distribution as shown in Figure 4.6. Similarly, at the top most layer, only smooth fibers were obtained in PLA/PBS fiber mats (Figure.4.4c). The average diameters of these fibers range between 200-220 nm, with an extremely uniform size distribution (Figure 4.6) and without any bead formation. In addition, electrospun PBS fibers were preformed (Figure 4.3b). The diameters of the fibers range between 131 nm and 291 nm, with an high variation size distribution and a small proportion of electrospun fibers (Figure 4.4). However,

only the electrospun PBS and multilayered PLA/PBS fiber mats which were shown aligned conformations but PLA fibers were perform random conformation. This aligned conformation can be explained by higher viscosity of PBS solution which was easier to perform fibers without unstable and vibration of electrospun fibers. Moreover, speed of rotation which wasn't matched with electrospun were also affected with fibers come out.

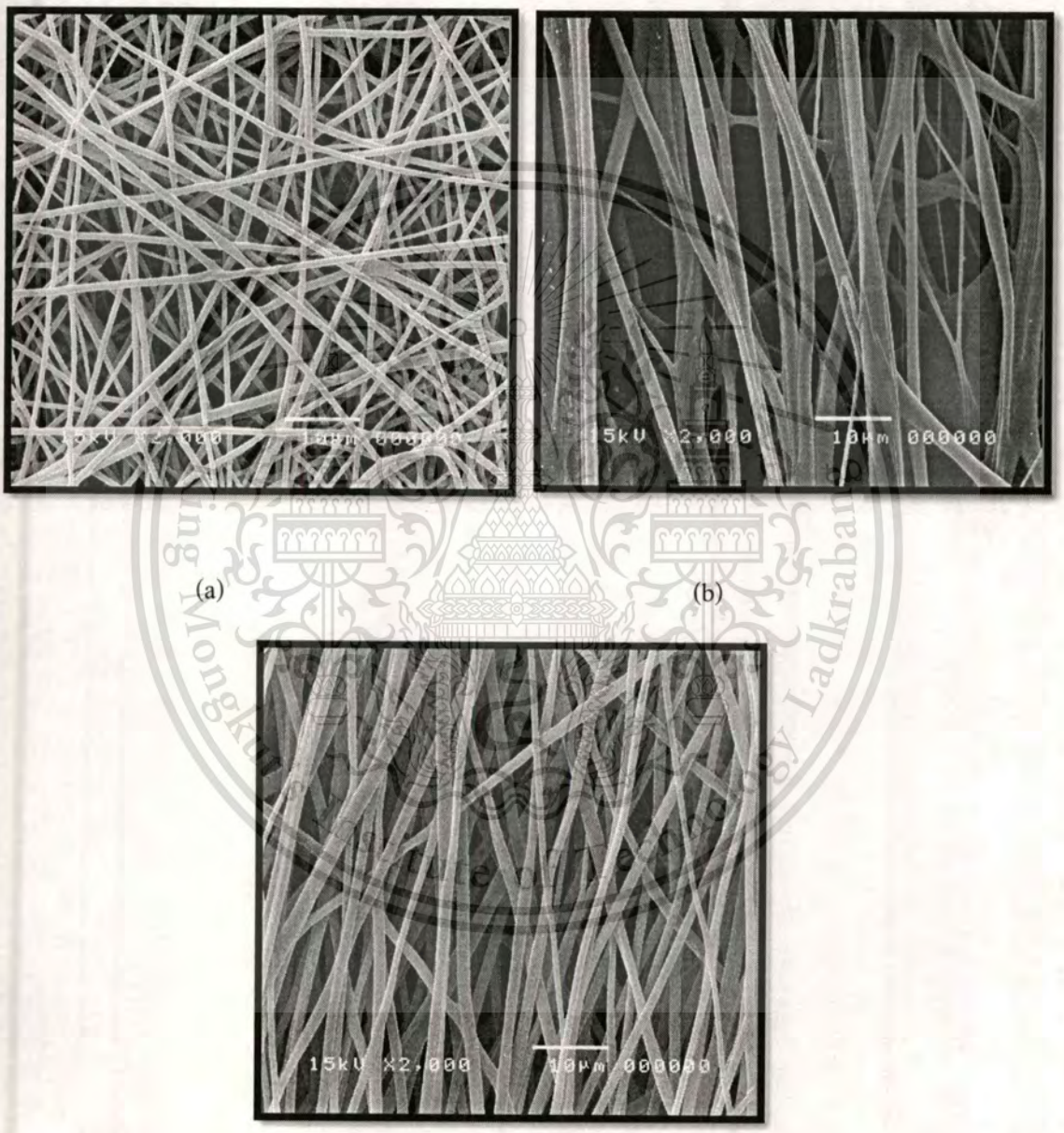


Figure 4.4 SEM micrographs of the PLA, PBS and PLA/PBS electrospun ultrafine fibers; (a) PLA fibers, (b) PBS fibers, (c) PLA/PBS fibers (2000X magnification)

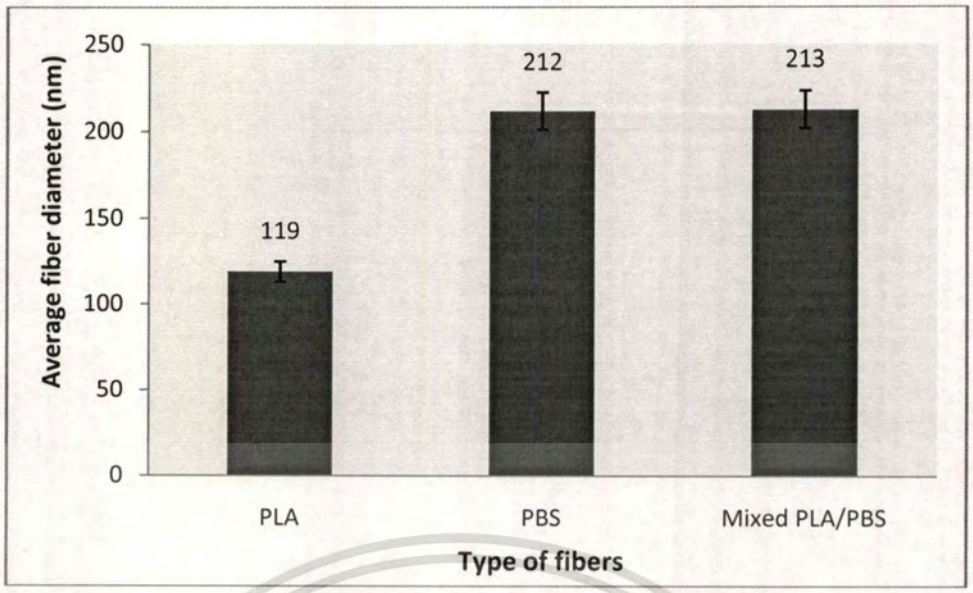


Figure 4.5 Average fiber diameter of electrospun PLA, PBS and Multilayered PLA/PBS fibrous mats

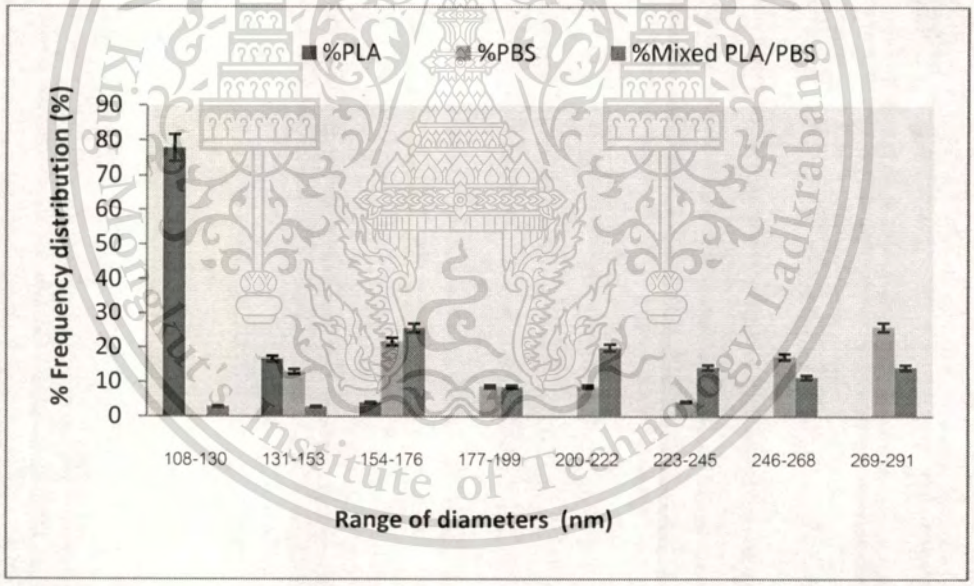


Figure 4.6 The distribution of the electrospun PLA, PBS and Multilayered PLA/PBS ultrafine fibrous diameter

After electrospinning, the thickness of the electrospun fiber mats was measured by PEACOCK® micrometer. The average thickness of the PLA electrospun fiber was found to be much higher than PBS when the electrospinning time was increased, as shown in Figures 4.7 and

4.8. The reason for this phenomenon might be that the solvent of PBS, 9:1 DCM-CB mixtures, was evaporated quickly at the exit orifice of the needle.

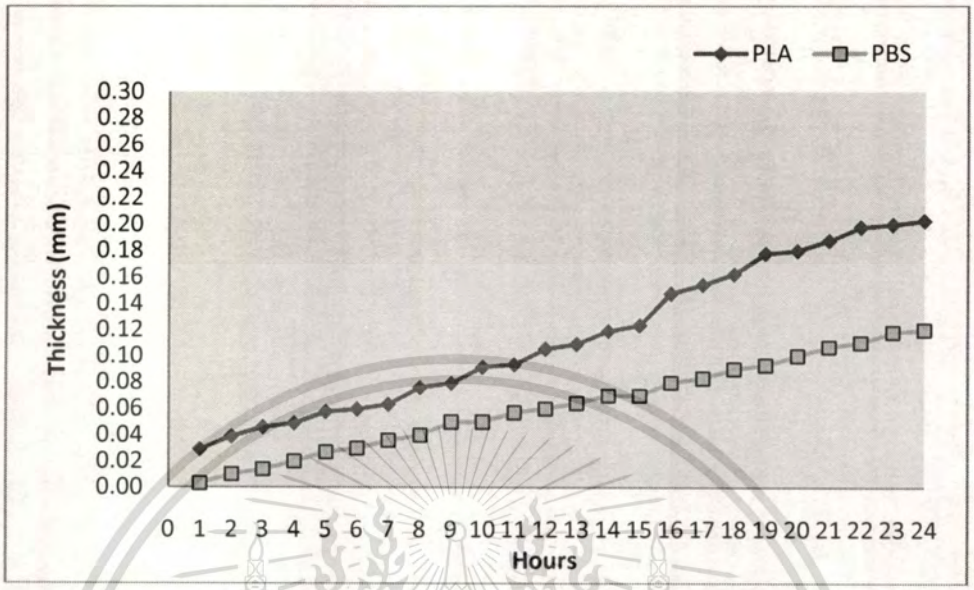


Figure 4.7 Average thickness of the electrospun PLA and PBS ultrafine fibrous mats as a function of electrospinning time

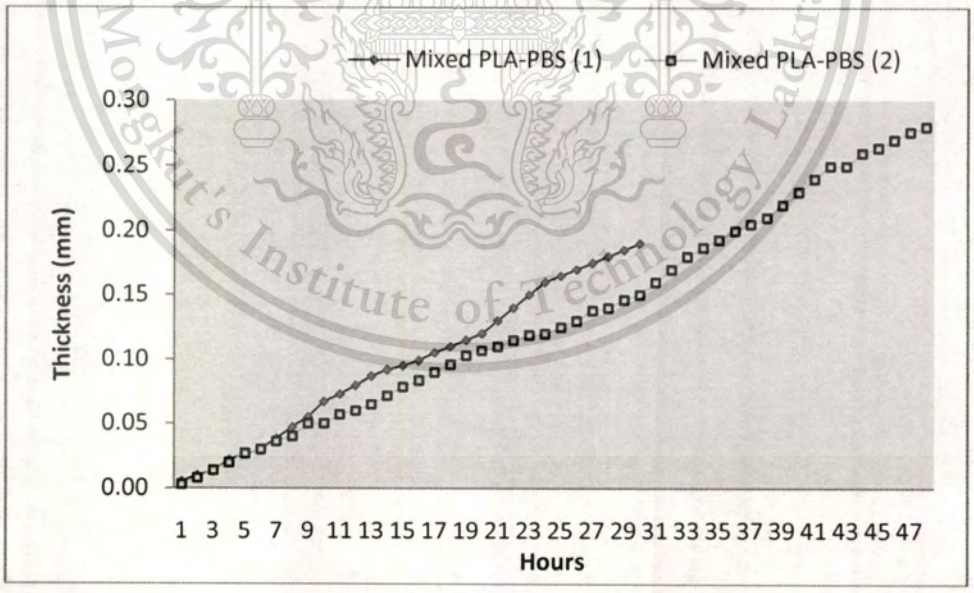
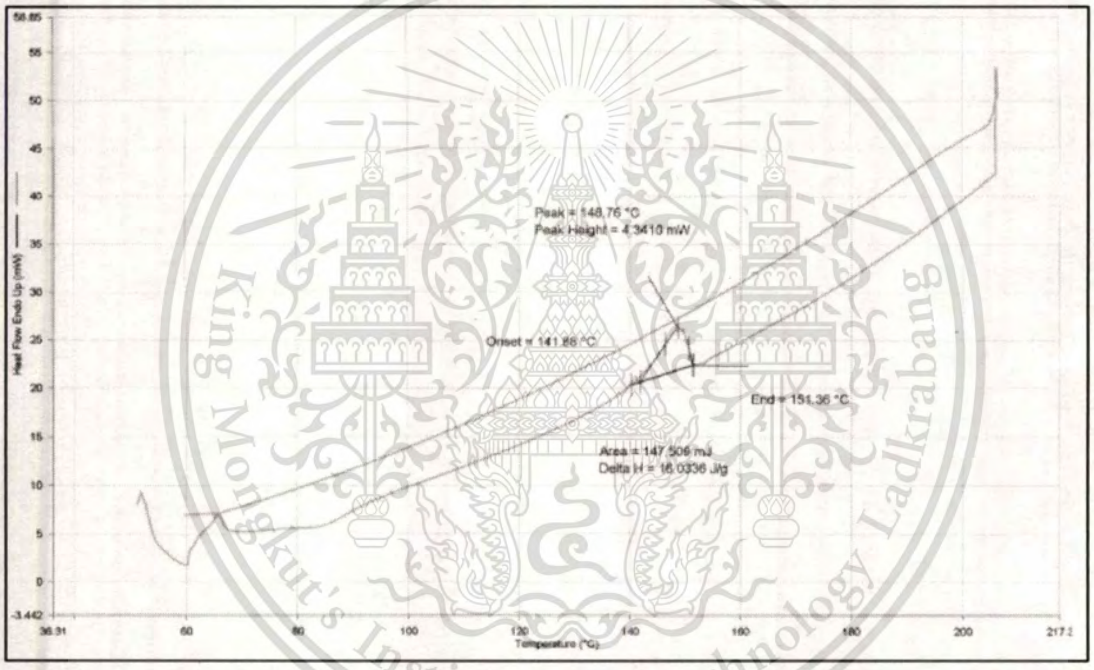


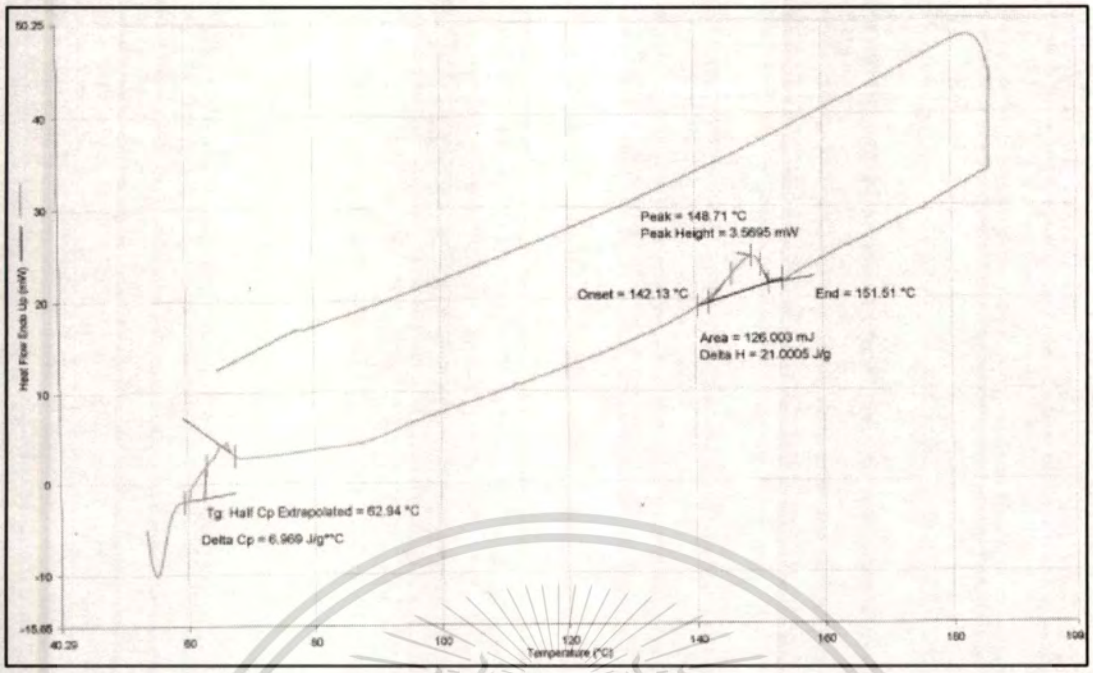
Figure 4.8 Average thickness of electrospun multilayered PLA/PBS fibrous mats as a function of electrospinning time

4.2 Thermal Properties And Crystallization

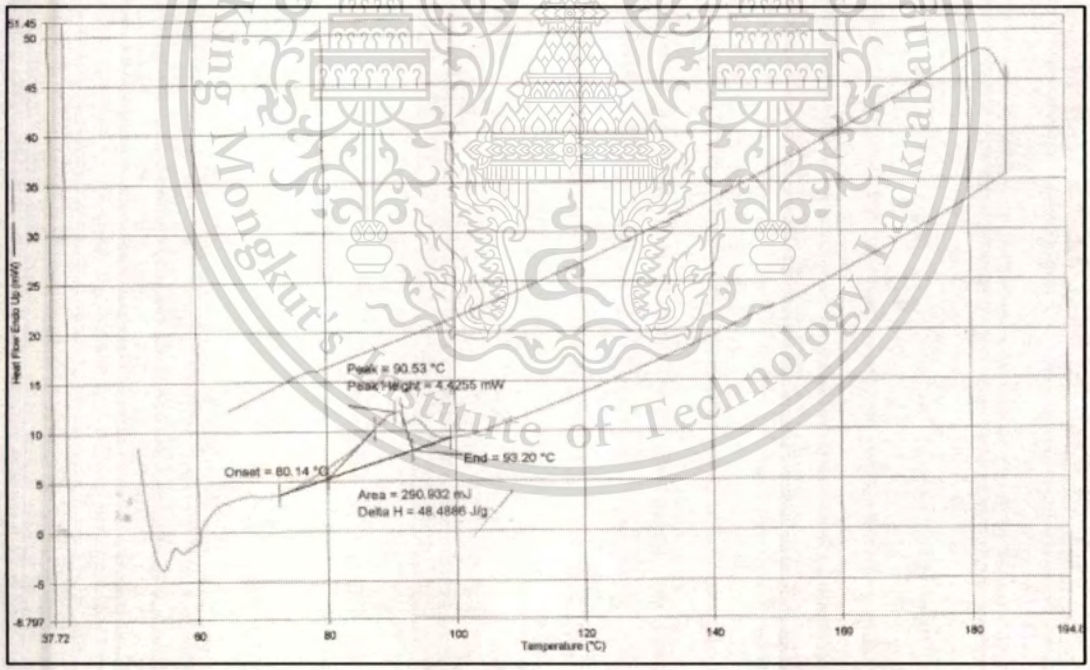
Thermal properties of the multilayered PLA/PBS ultrafine fibrous mats were investigated by Differential Scanning Calorimeter (DSC) which was used to characterize the melting and glass transition temperatures of the PLA and PBS in both pellets and electrospun ultrafine fiber forms. The electrospun ultrafine fibers were fabricated under the condition of 12% (w/v). Each specimen was heated from 50-180 ^{O}C at a rate of 10 ^{O}C min^{-1} which are recorded the melting and glass transition temperatures, the enthalpies of fusion (ΔH_f^0) as well as the corresponding apparent degree of crystallinity values as shown in Figures 4.9 and Table 4.2, respectively



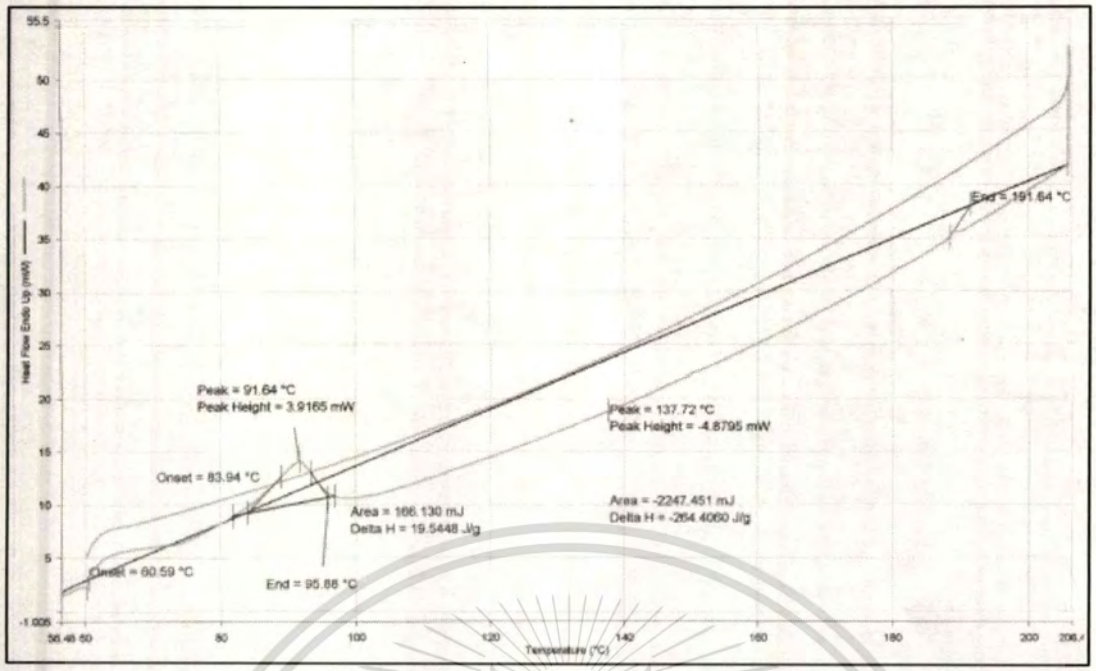
(a)



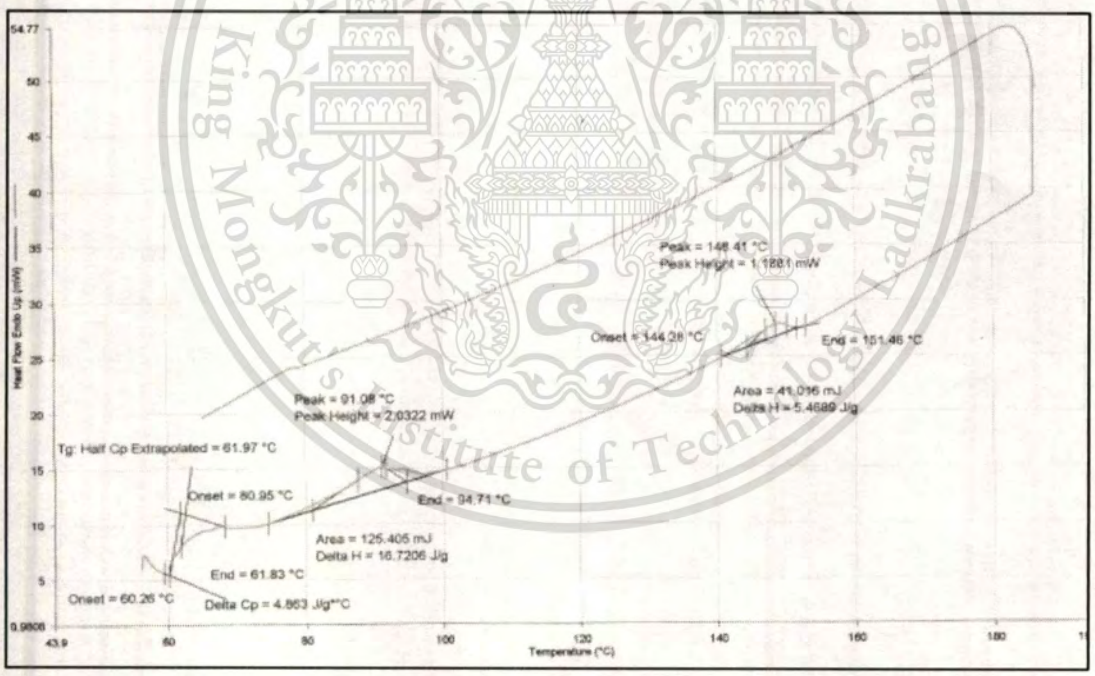
(b)



(c)



(d)



(e)

Figure 4.9 DSC thermograms of PLA, PBS and multilayered PLA/PBS ultrafine fibers: (a) PLA pellets, (b) PLA fibers, (c) PBS pellets, (d) PBS fibers, (e) multilayered PLA/PBS ultrafine fibers

Table 4.2 Thermal properties of PLA, PBS and multilayered PLA/PBS ultrafine fibers

Type of Polymer	Tm °C	Tg °C	Delta H (J/g)	% Crystallinity
PLA pellet	148.8	-	16	17.2
PLA fibers	148.7	62.9	21.0	22.6
PBS pellet	90.5	-	48.5	24.3
PBS fibers	91.6	-	19.5	9.8
PLA/PBS fibers	91.1	-	16.7	35.5
	148.4	62.0	5.5	10.3

As shown in Figure 4.9, the multilayered electrospun PLA/PBS fibers were compared with those of virgin PLA and PBS in forms of pellet and electrospun fibers. They are found that PLA and PBS pellets showed typical Tm and Tg behaviors which PLA was observed the peak of Tg at ~ 63 °C and the peak of Tm at ~149 °C. Similarly, PBS was reported the peak of Tm around 91 °C, while the Tg and Tm of the electrospun PLA, PBS and multilayered PLA/PBS ultrafine fibers are very close to those of PLA and PBS pellets.

Moreover, % crystallinity of the multilayered PLA/PBS fiber mats after electrospinning process was studied. Table 4.2 shows % crystallinity of electrospun PLA, PBS and multilayered PLA/PBS ultrafine fibers which are 17.2% and 22.6% of virgin PLA pellets and fibers, 24.3% and 9.8% of virgin PBS pellets and fibers and 4.0% of PBS and 3.1% of PLA in multilayered PLA/PBS fibrous mats, respectively. % crystallinity was calculated based on the following equation;

$$x = \frac{\Delta H_f}{\Delta H_f^0} * 100\%$$

Where ΔH_f is the heat of fusion and ΔH_f^0 is the heat of fusion for 100% crystallinity. In order to compare with the results in open literature, we calculated its crystallization based on the heat of fusion for PLA being 93 J/g and for PBS being 200 J/g [80]. The reasons for decreasing in % crystallinity were mainly the different methods used and the viscosity of polymer solution especially when polymer were collected on the rotating collector.

4.3 Mechanical Properties

Electrospinning process was used to produce multilayered electrospun PLA/PBS fibrous mats. In order to study mechanical properties, i.e., tensile strength, % elongation at break, Young's modulus and tear strength were characterized by using Universal Testing Machine (UTM) at room temperature (25 °C). All tests were done according to ASTM D638 standard. For these investigations both machine (MD) and transverse (TD) directions , the thickness of multilayered PLA/PBS fibrous mats in both formulas were about 0.19 mm and 0.28 mm. Tensile tests were carried out with a crosshead speed of 10 mm/min and load cell 100 N. Property values were reported to show an average of the results for tests run of 8 specimens. Figure 4.10 (a-f) shows the various tensile properties of multilayered PLA/PBS ultrafine fibrous mat (formula 1) which was compared to those of virgin PLA and PBS ultrafine fibrous mats in both machine (MD) and transverse (TD) directions. It required about 0.19 mm of thickness to obtain the fiber mat. Figure 4.10 (a-f) are found that the addition of PBS was steadily increased the Young's modulus, tensile strength, tensile stress at yield and tear strength, but was reduced % elongation at break and % elongation at yield. In machine direction (MD), the tensile strength values were increased regularly from 3.45 MPa of virgin PLA and 0.82 MPa of virgin PBS ultrafine fibrous mats to 4.35 MPa of multilayered PLA/PBS mats. Interestingly, the multilayered PLA/PBS fiber mats can be seen that is much stiffer and stronger than virgin PBS mat. Similar to the Young's modulus and tensile stress at yield of the multilayered PLA/PBS mats increased slightly with the PLA content. The strength gain was about 3 times higher compared to the virgin PBS mat. The improvement rate of tensile modulus being higher than that of the tensile strength which was almost 4 times. Moreover, toughness of multilayered PLA/PBS mats were decreased as the PLA fibers were added. This is likely caused by extremely brittle of the PLA fibers. However, the growth in stiffness of the multilayered PLS/PBS fibrous mats holds true only in machine direction

(MD) because of rotating collector were used to collect aligned fibers which most of fibers were aligned in machine direction (MD). So that the tensile test could not be predicted in transverse direction (TD). Nonetheless, the present of multilayered PLA/PBS fibers seem to deliver good ultrafine fiber mat which enhanced toughness with increasing PBS content to the multilayered PLA/PBS fiber mats.

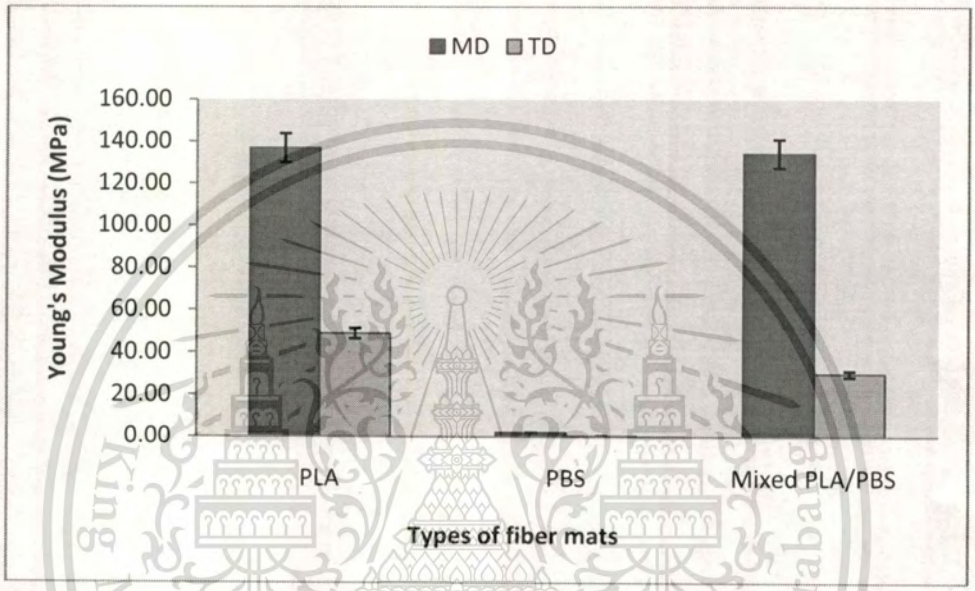


Figure 4.10 (a) Young's modulus of electrospun PLA, PBS and multilayered PLA/PBS ultrafine fibrous mats (Formula 1)

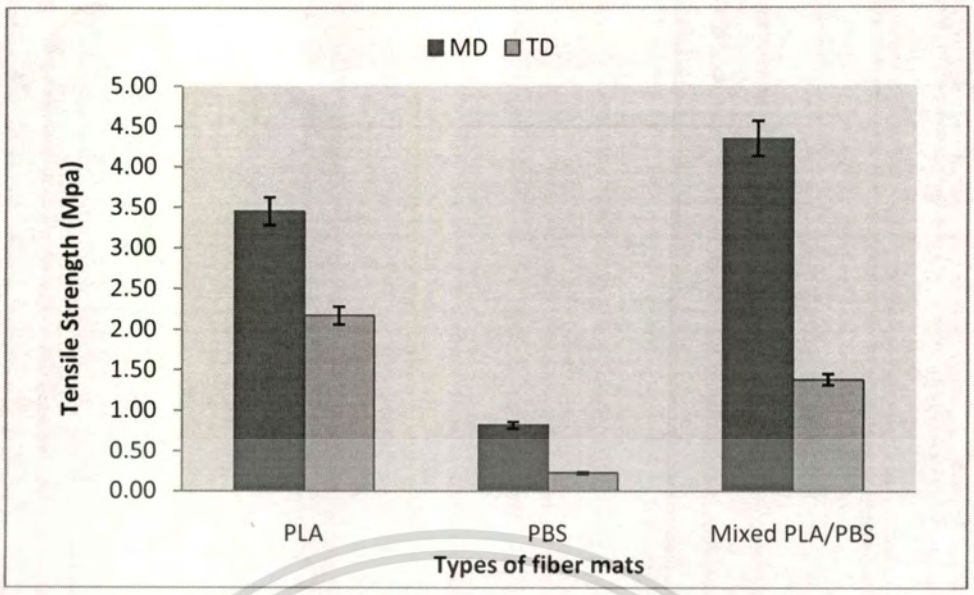


Figure 4.10 (b) Tensile strength of electrospun PLA, PBS and multilayered PLA/PBS ultrafine fibrous mats (Formula 1)

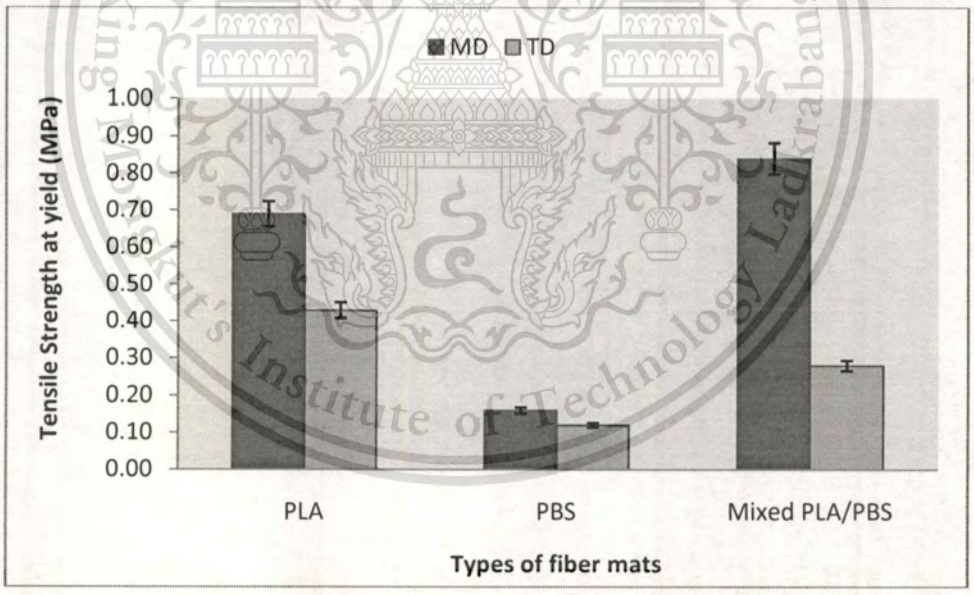


Figure 4.10 (c) Tensile stress at yield of electrospun PLA, PBS and multilayered PLA/PBS ultrafine fibrous mats (Formula 1)

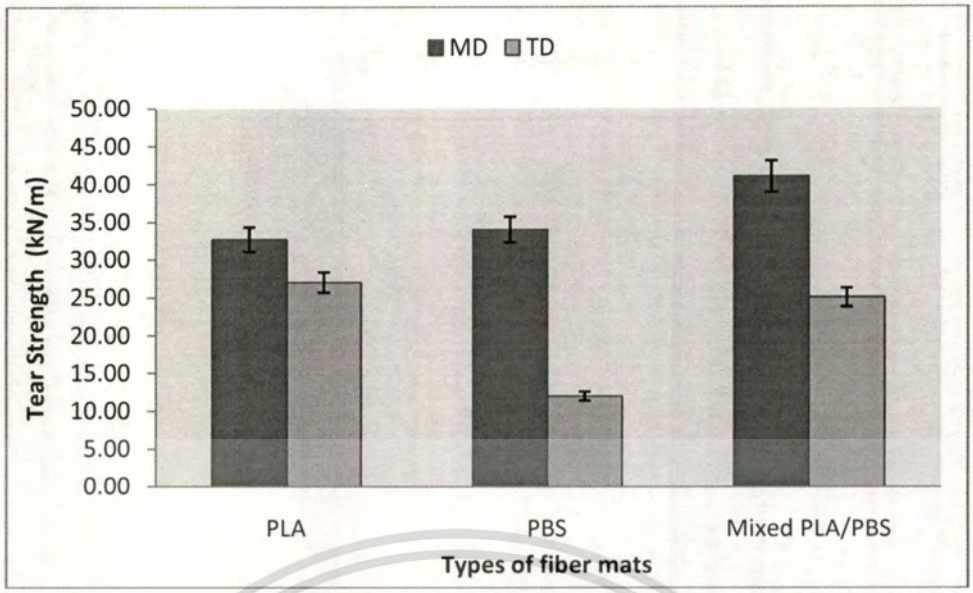


Figure 4.10 (d) Tear strength of electrospun PLA, PBS and multilayered PLA/PBS ultrafine fibrous mats (Formula 1)

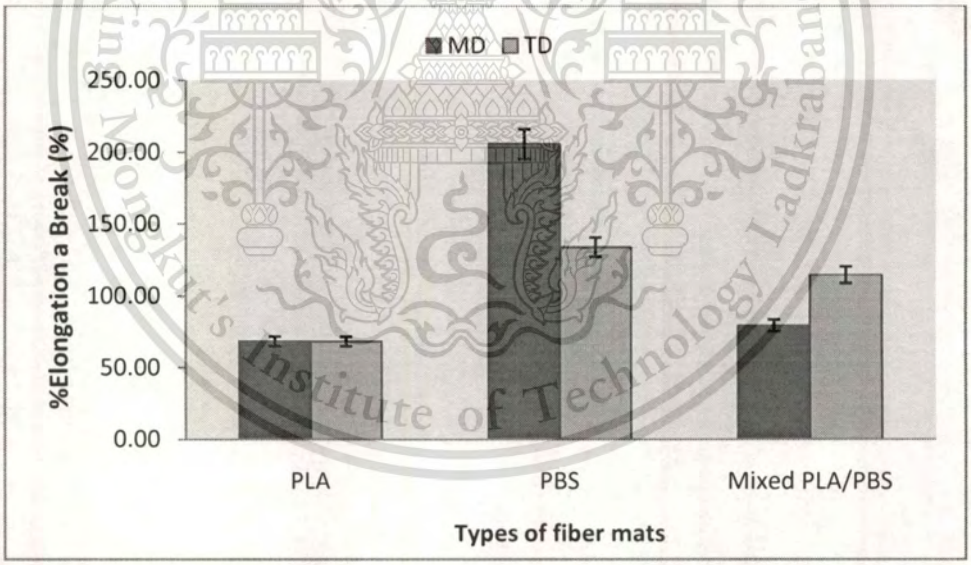


Figure 4.10 (e) % Elongation at break of electrospun PLA, PBS and Mixed PLA/PBS ultrafine fibrous mats (Formula 1)

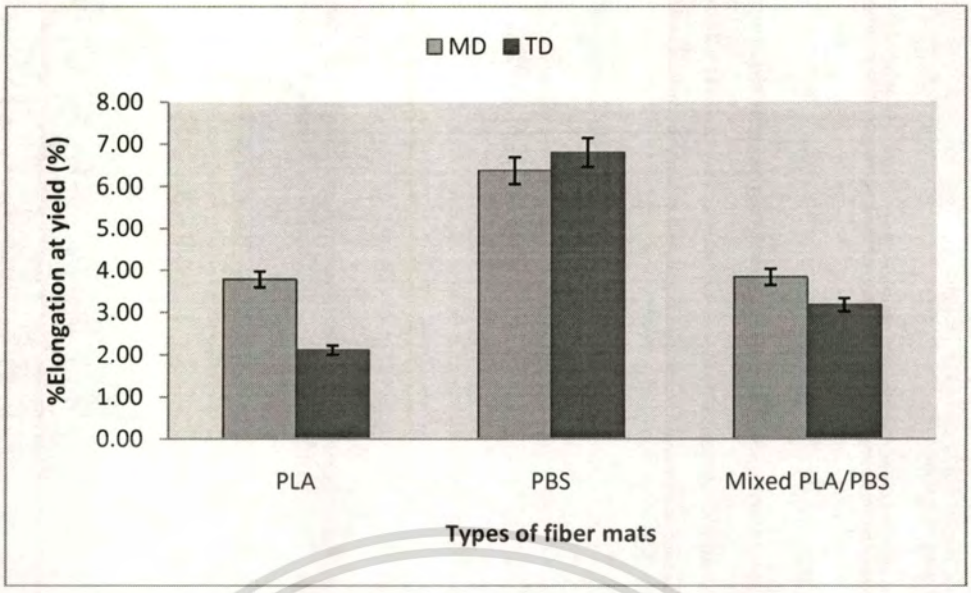


Figure 4.10 (f) % Elongation at yield of electrospun PLA, PBS and multilayered PLA/PBS ultrafine fibrous mats (Formula 1)

Besides, the tensile properties of multilayered PLA/PBA fibrous mats as a function of PBS contents are presented in Figure 4.11 (a-f). The Young's modulus, tensile strength, tensile stress at yield and tear strength are slightly decreased which can be reported inversely from Figure 4.10 due to the addition of PBS. Therefore, % elongation at break and % elongation at yield are gained with the enhancement in toughness. However, it could be noted that the increase of fiber contents is able to maintain the tensile properties in both machine (MD) and transverse (TD) directions.

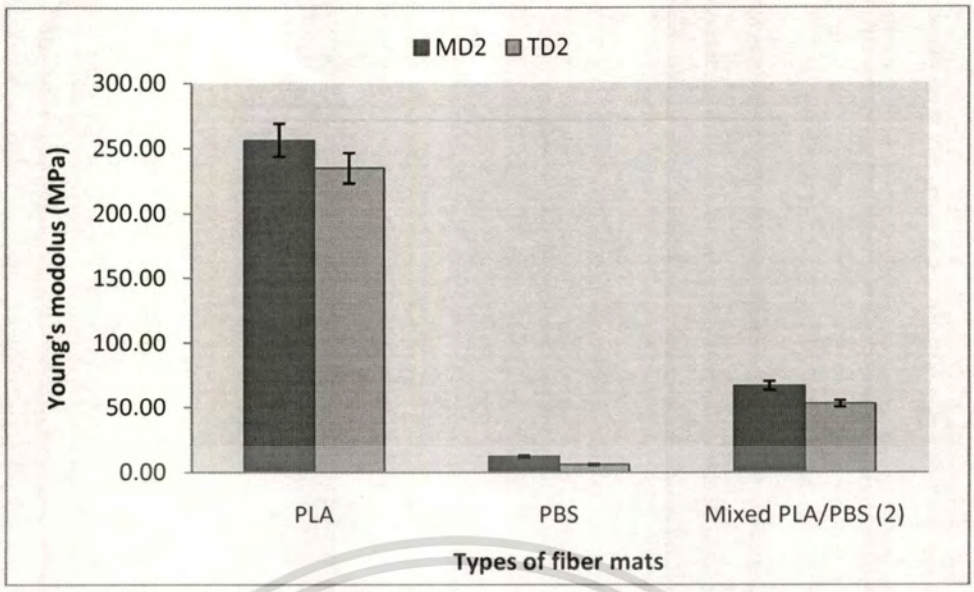


Figure. 4.11 (a) Young's modulus of electrospun PLA, PBS and multilayered PLA/PBS ultrafine fibrous mats (Formula 2)

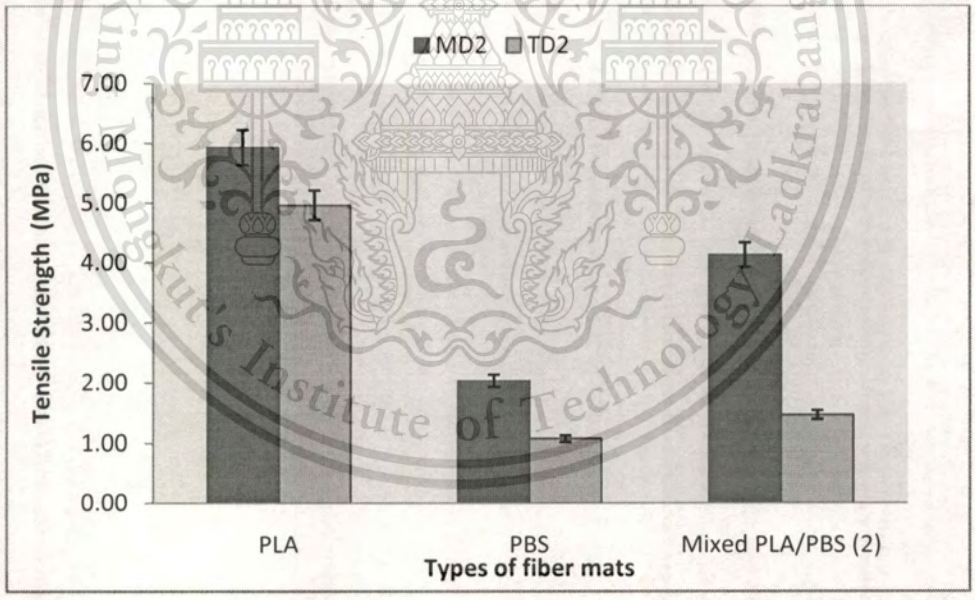


Figure 4.11 (b) Tensile strength of electrospun PLA, PBS and multilayered PLA/PBS ultrafine fibrous mats (Formula 2)

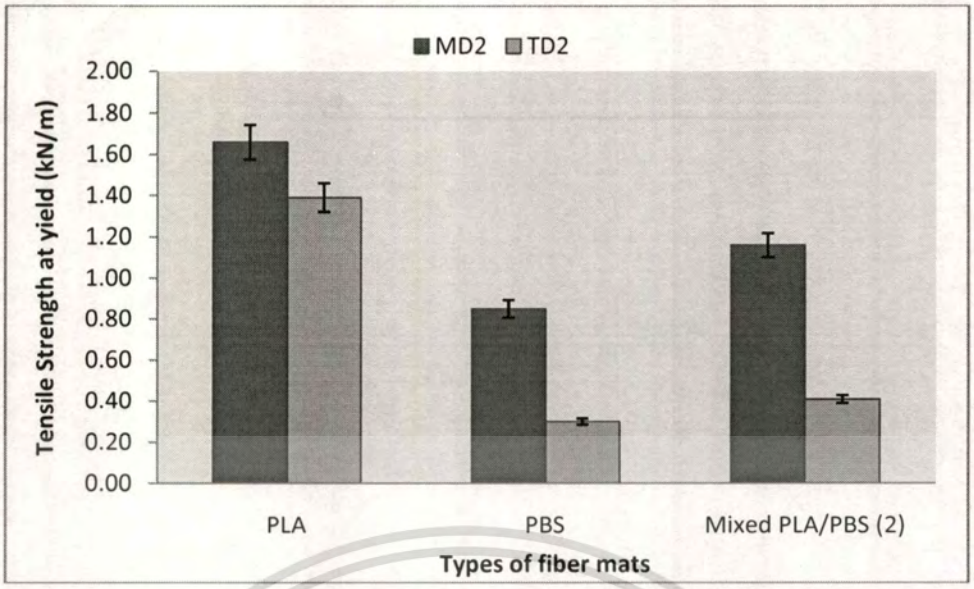


Figure. 4.11 (c) Tensile stress at yield of electrospun PLA, PBS and multilayered PLA/PBS ultrafine fibrous mats (Formula 2)

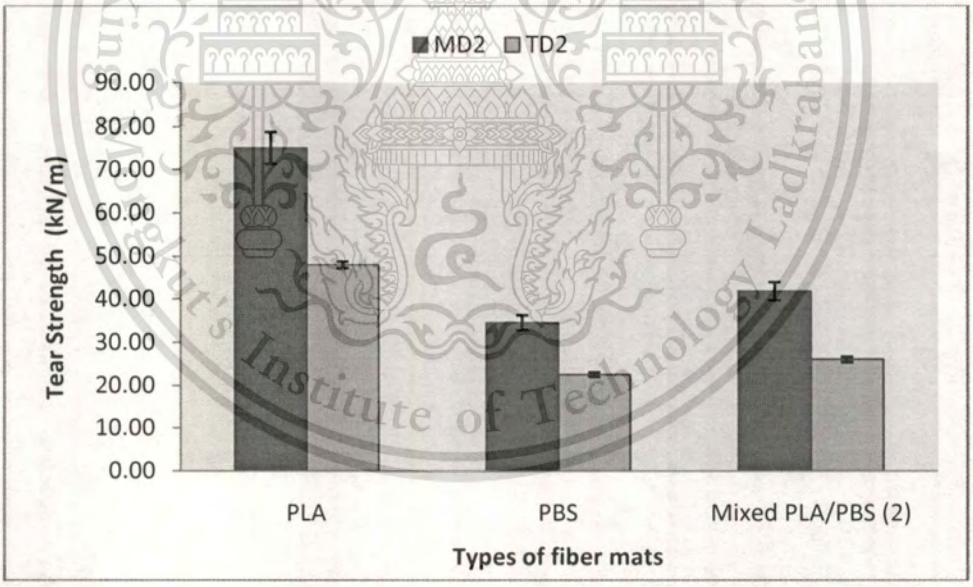


Figure 4.11 (d) Tear strength of electrospun PLA, PBS and multilayered PLA/PBS ultrafine fibrous mats (Formula 2)

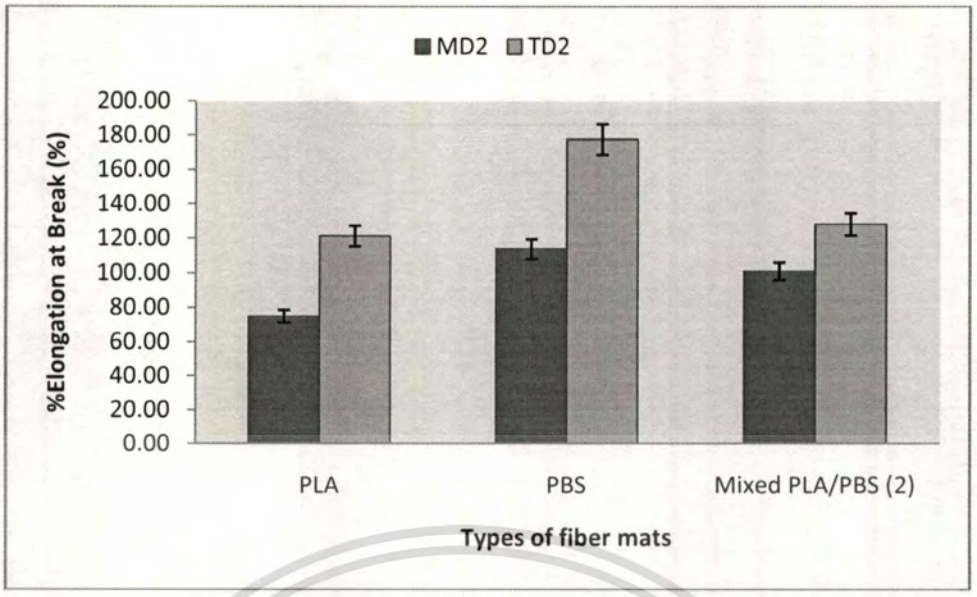


Figure 4.11 (e) % Elongation at break of electrospun PLA, PBS and multilayered PLA/PBS ultrafine fibrous mats (Formula 2)

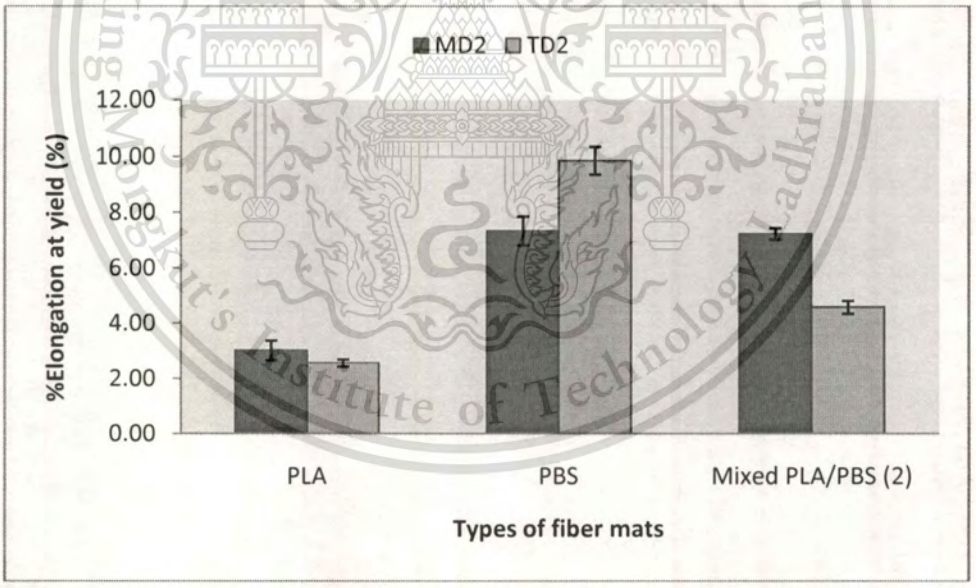


Figure 4.11 (f) % Elongation at yield of electrospun PLA, PBS and multilayered PLA/PBS ultrafine fibrous mats (Formula 2)

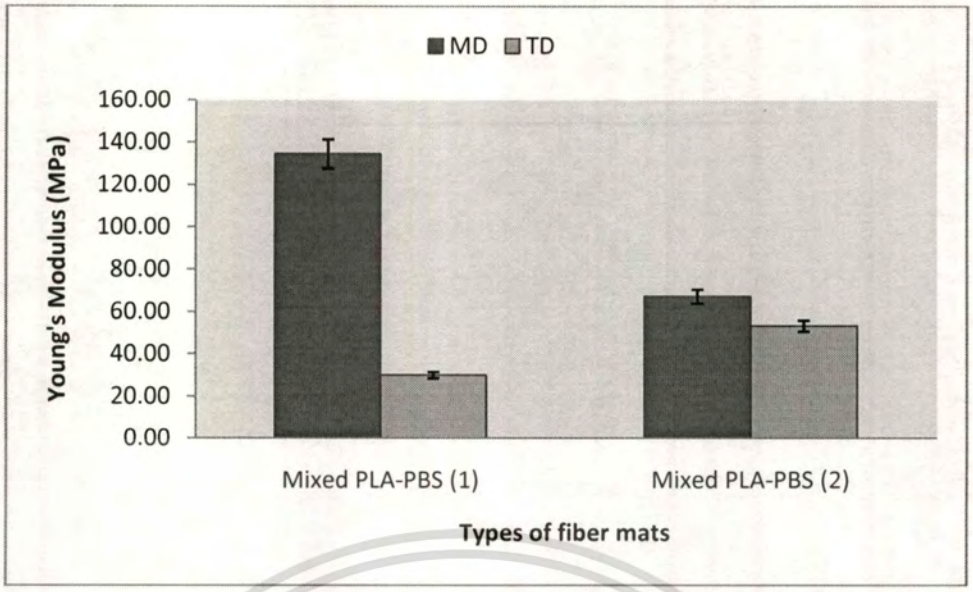


Figure. 4.12 (a) Young's modulus of electrospun Formula 1 and Formula 2

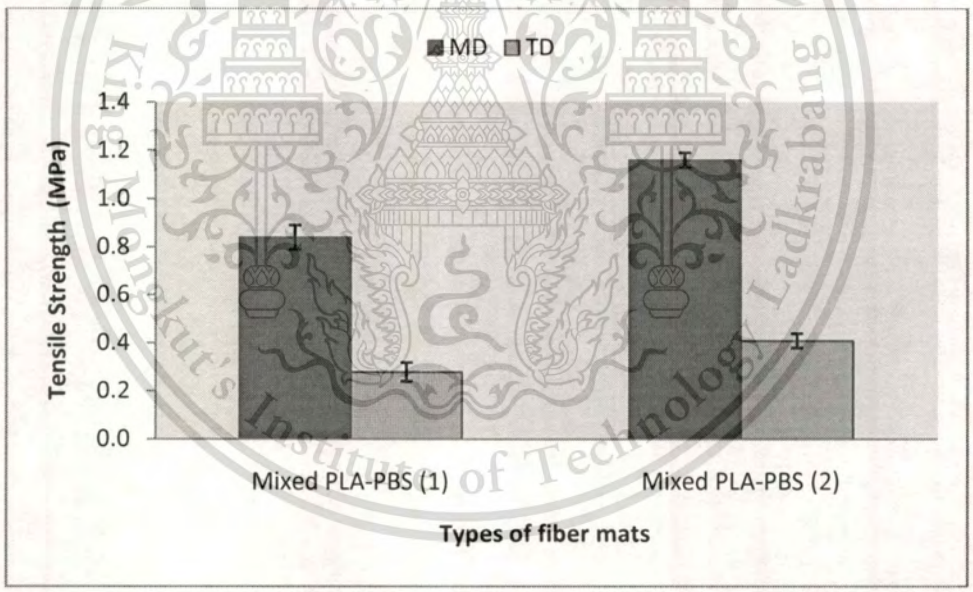


Figure 4.12 (b) Tensile strength of electrospun Formula 1 and Formula 2

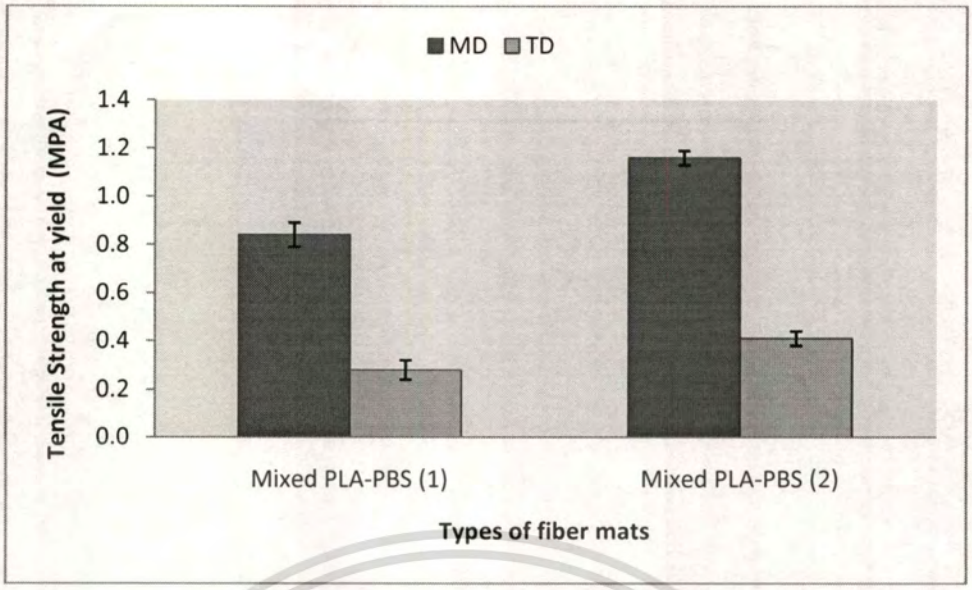


Figure. 4.12 (c) Tensile stress at yield of electrospun Formula 1 and Formula 2

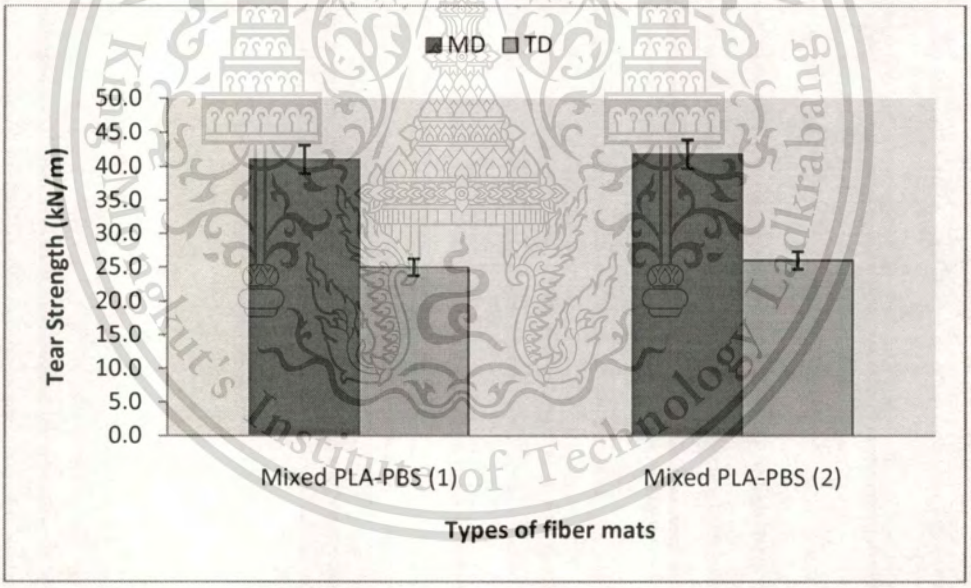


Figure 4.12 (d) Tear strength of electrospun Formula 1 and Formula 2

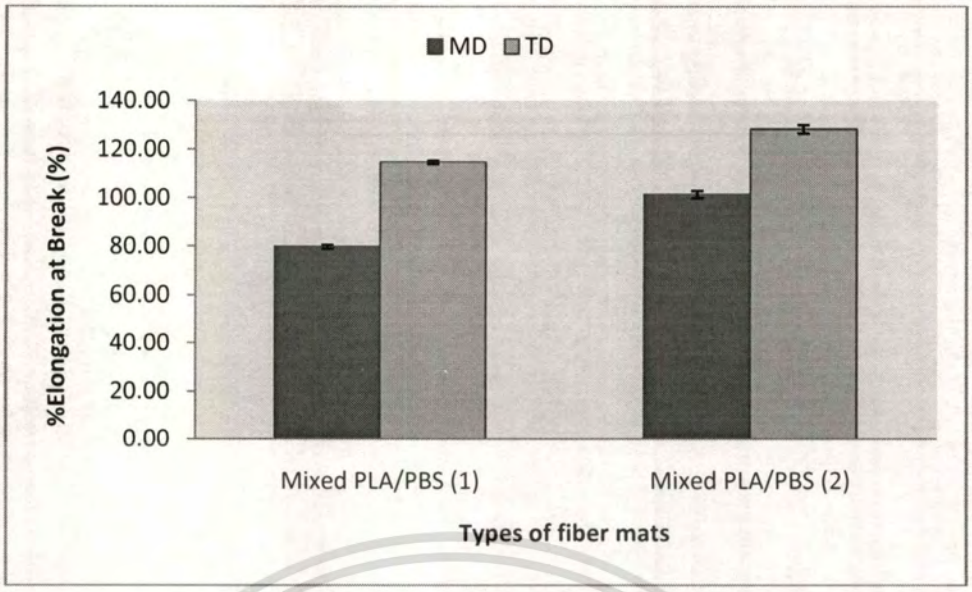


Figure 4.12 (e) % Elongation at break of electrospun Formula 1 and Formula 2

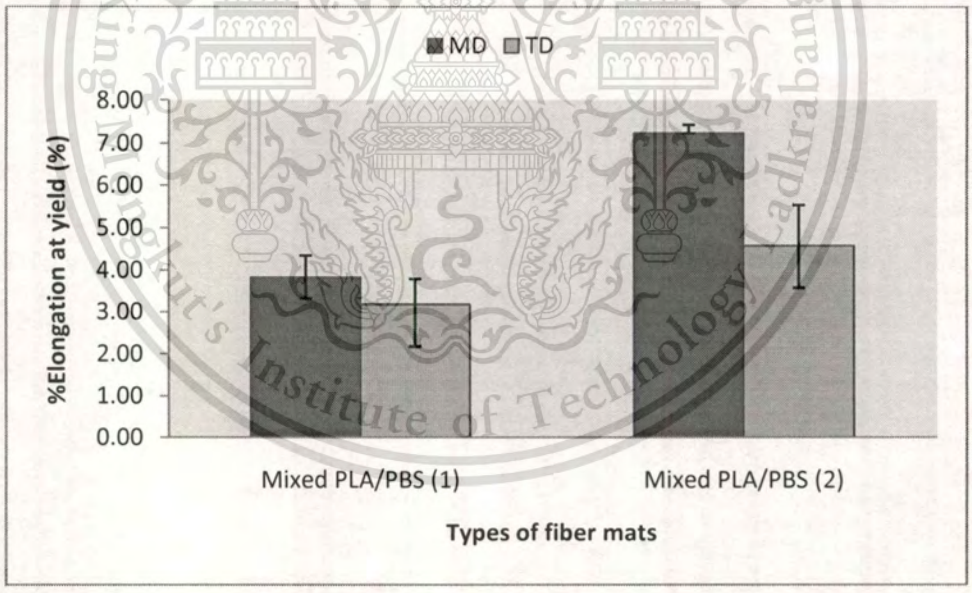


Figure 4.12 (f) % Elongation at yield of electrospun Formula 1 and Formula 2

Effects of increasing PBS fiber thickness in multilayered electrospun PLA/PBS mat, the mechanical properties were investigated as shown in Figure 4.12(a-f). As previous mentioned, the decreases in both Young's modulus and tensile strength resulted in improvement in the % elongation at break and % elongation at yield. Their can be predicted that an approximately linear

relationship between the elongation and the fiber content is obtained since the presence of PBS fibers contributes more effectively to enhance the toughness than to enhance the tensile strength in multilayered PLA/PBS mats. However, tear strengths of the higher PBS contents in multilayered PLA/PBS mats showed very close values to the lower ones (Figure 4.12d). This phenomena might be caused by the higher PLA loading obtained.

Chapter 5

Conclusion

5.1 Conclusion

In this work, electrospinning technique process was successfully used to fabricate mixed electrospun PLA/PBS ultrafine fibrous mats. At 8% - 12% (w/v) of PLA, the effects on the fibers morphology were studied. Moreover, 12% (w/v) PLA and 12% (w/v) PBS in mixed-solvent systems were prepared to consider the influence of the mat preparation, fiber morphologies, thermal and also mechanical properties of the ultrafine fibrous mats. The following conclusions can be made from this investigation.

5.1.1 Processing Conditions and Fiber Morphologies

Electrospinning of 8 % - 12% (w/v) of PLA, was fixed at electrostatic DC potential of 20kV with a 18 cm working distance. The average fiber diameters were approximately 150, 125, 134 and 145 nm, respectively. At low concentrations, a large proportion of fibers were ribbon-shaped. As the concentration was increased to 14% (w/v), the fibers became to obviously smooth and were random conformation with a consequent increase in the fiber diameter. The distribution of PLA electrospun fiber diameters was in a broad range between 89 to 203 nm.

Morphological appearance of the mats after lamination was compared with the virgin electrospun PLA and PBS fibers. PLA fiber surfaces were smooth with the diameters of ~219 nm which showed a small difference in their size distribution. The electrospun PBS fibers, very few small beads with uniform fibers were preformed which the diameters of the fibers range between 131nm - 291 nm. On the other hand, only smooth fibers were obtained in PLA/PBS fiber mats. The average diameters of these fibers ranging between 200-220 nm, with an extremely uniform size distribution. However, the average thickness of the PLA electrospun fiber was found to be much higher than PBS when the electrospinning time was increased. However, only the electrospun PBS and multilayered PLA/PBS fiber mats which were shown aligned conformations but PLA fibers were perform random conformation.

5.1.2 Thermal Properties And Crystallization

From DSC thermograms, PLA was observed the peak of Tg at ~ 63 °C and the peak of Tm at ~149 °C. Similarly, PBS was reported the peak of Tm around 91 °C, while the Tg and Tm of the electrospun PLA, PBS and multilayered PLA/PBS ultrafine fibers were very close to those of PLA and PBS pellets. The % crystallinity of electrospun PLA fibers, PBS fibers and mixed PLA/PBS ultrafine fibers were 22.6%, 9.8% and 4.0% of PBS and 3.1% of PLA in multilayered PLA/PBS fibrous mats, respectively.

5.1.3 Mechanical Properties

Mechanical properties values of multilayered PLA/PBS ultrafine fiber were compared to those of virgin PLA and PBS ultrafine fiber mats. At 0.19 mm of fixed thickness, was found that the addition of PBS increased the Young's modulus, tensile strength, tensile stress at yield and tear strength but reduced elongation at break and at yield. The toughness of the multilayered fiber mats was decreased as the PLA fibers were added. However, the increase in stiffness of multilayered PLS/PBS fibrous mats was slightly increased when PBS were particularly designed to mix with virgin PLA fibers.

When PBS fibers were added twice, the tensile properties of multilayered PLA/PBS fibrous mats were presented which the Young's modulus, tensile strength, tensile stress at yield and tear strength were slightly decreased. It can be predictable that an approximately linear relationship between the % elongation and the PBS fiber content was obtained.

5.2 Suggestion for Future Work

From the previous conclusion, the following recommendations for the future studies can be proposed as follows:

1. Electrospun PLA ultrafine fiber reinforced composites with PBS as a resin should be studied which can be analyzed for possibility of various applications.

2. The biocompatible properties of electrospun PLA/PBS fiber mats should be concerned to analyze possibility using in medical applications.

3. Even multilayered electrospun PLA/PBS ultrafine fibrous mats are flexible, the effect of other ratios should be tested.

4. The potential use of multilayered electrospun PLA/PBS ultrafine fibrous mats should be evaluated as biomedical mask.

5. This useful information concerning their use as improving mechanical properties in polymer composites.

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Appendix A

The Tables of Electrospun

PLA, PBS and Multilayered PLA/PBS fibrous mats Data

Table A-1 Mechanical properties of PLA, PBS and Multilayered PLA/PBS fibers Data (formula 1)

	Tensile Strength of PLA, PBS and Multilayered PLA/PBS (1) (MPa)					
	PLA (1) MD	**PLA (1) TD**	**PBS (1) MD**	**PBS (1) TD**	**Mixed (1) MD**	**Mixed(1)TD**
Average	3.45	2.17	0.82	0.23	4.35	1.38
SD	0.81	0.100	0.280	0.050	0.03	0.19
SD error	3.45 ±0.36	2.17 ±0.04	0.82 ±0.13	0.23 ±0.02	4.35 ±0.01	1.38 ±0.09

	Modulus of PLA, PBS and Multilayered PLA/PBS (1) (MPa)					
	PLA (1) MD	**PLA (1) TD**	**PBS (1) MD**	**PBS (1) TD**	**Mixed (1) MD**	**Mixed(1) TD**
Average	136.91	48.87	2.06	0.43	134.49	29.95
SD	0.70	0.440	0.300	0.280	0.23	0.56
SD error	136.91 ±0.31	48.87 ±0.20	2.06 ±0.13	0.43 ±0.13	134.49 ±0.10	29.95 ±0.25

	Tensile Stress at yield of PLA, PBS and Multilayered PLA/PBS (1) (MPa)					
	PLA (1) MD	PLA (1) TD	PBS (1) MD	PBS (1) TD	Mixed (1) MD	Mixed(1) TD
Average	0.69	0.43	0.16	0.12	0.84	0.28
SD	0.16	0.020	0.060	0.010	0.05	0.04
SD error	0.69 ±0.07	0.43 ±0.01	0.16 ±0.03	0.12 ±0.00	0.84 ±0.02	0.28 ±0.02

	Tear Strength of PLA, PBS and Multilayered PLA/PBS (1) (kN/m)					
	PLA (1) MD	PLA (1) TD	PBS (1) MD	PBS (1) TD	Mixed (1) MD	Mixed(1) TD
Average	32.7	27.00	21.3	15.60	9.9	25
SD	0.39	0.06	0.35	0.05	0.67	0.13
SD error	32.70 ±0.17	27.00 ±0.03	34.00 ±0.16	12.00 ±0.02	41.00 ±0.30	25.00 ±0.06

	%Elongation at Maximum load of PLA, PBS and Multilayered PLA/PBS (1) (%)					
	PLA (1) MD	PLA (1) TD	PBS (1) MD	PBS (1) TD	Mixed (1) MD	Mixed(1) TD
Average	68.52	68.39	205.7	133.95	79.81	114.65
SD	0.84	0.88	0.27	0.21	0.74	0.65
SD error	68.52 ±0.38	68.39 ±0.39	105.70 ±0.12	133.95 ±0.09	79.81 ±0.33	114.65 ±0.29

	%Elongation at yield of PLA, PBS and Multilayered PLA/PBS (1) (%)					
	PLA (1) MD	PLA (1) TD	PBS (1) MD	PBS (1) TD	Mixed (1) MD	Mixed(1) TD
Average	3.79	2.12	6.37	6.8	3.84	3.18
SD	0.50	0.410	0.960	0.650	0.51	0.62
SD error	2.79 ±0.22	2.12 ±0.18	6.37 ±0.43	6.80 ±0.29	3.84 ±0.23	3.18 ±0.28

Table A-2 Mechanical properties of PLA, PBS and Multilayered PLA/PBS fibers Data (formula 2)

	Tensile Strength of PLA, PBS and Multilayered PLA/PBS (2) (MPa)					
	PLA (2) MD	**PLA (2) TD**	**PBS (2) MD**	**PBS (2) TD**	**Mixed (2) MD**	**Mixed(2)TD**
Average	5.93	4.96	2.04	1.08	4.13	1.47
SD	0.61	0.86	0.33	0.11	0.09	0.09
SD error	4.96 ±0.27	5.93 ±0.39	3.04 ±0.15	1.08 ±0.05	4.13 ±0.04	1.47 ±0.04

	Modulus of PLA, PBS and Multilayered PLA/PBS (2) (MPa)					
	PLA (2) MD	**PLA (2) TD**	**PBS (2) MD**	**PBS (2) TD**	**Mixed (2) MD**	**Mixed(2) TD**
Average	256.46	234.79	12.5	6.1	67.08	53.16
SD	0.65	0.510	0.412	0.040	0.94	0.27
SD error	256.46 ±0.29	234.79 ±0.23	102.08 ±0.18	35.19 ±0.02	67.08 ±0.42	53.16 ±0.12

	Tensile Stress at yield of PLA, PBS and Multilayered PLA/PBS (2) (MPa)					
	PLA (2) MD	**PLA (2) TD**	**PBS (2) MD**	**PBS (2) TD**	**Mixed (2) MD**	**Mixed(2) TD**
Average	1.66	1.39	0.85	0.3	1.16	0.41
SD	0.45	0.240	0.010	0.030	0.03	0.03
SD error	1.39 ±0.20	1.66 ±0.11	0.85 ±0.00	0.30 ±0.01	1.16 ±0.01	0.41 ±0.01

	Tear Strength of PLA, PBS and Multilayered PLA/PBS (2) (kN/m)					
	PLA (2) MD	PLA (2) TD	PBS (2) MD	PBS (2) TD	Mixed (2) MD	Mixed(2) TD
Average	75.05	48.06	34.53	22.56	41.83	26.04
SD	0.18	0.74	0.26	0.51	0.06	0.66
SD error	75.05 ±0.08	48.06 ±0.33	22.56 ±0.12	34.53 ±0.23	41.82 ±0.03	26.04 ±0.30

	%Elongation at Maximum load of PLA, PBS and Multilayered PLA/PBS (2) (%)					
	PLA (2) MD	PLA (2) TD	PBS (2) MD	PBS (2) TD	Mixed (2) MD	Mixed(2) TD
Average	74.92	121.3	113.83	177.55	101.26	128.3
SD	0.55	0.55	0.99	0.91	1.53	1.77
SD error	74.92 ±0.25	68.39 ±0.25	105.70 ±0.44	133.95 ±0.41	79.81 ±0.69	114.65 ±0.79

	%Elongation at yield of PLA, PBS and Multilayered PLA/PBS (2) (%)					
	PLA (2) MD	PLA (2) TD	PBS (2) MD	PBS (2) TD	Mixed (2) MD	Mixed(2) TD
Average	3.02	2.57	7.34	9.86	7.24	4.58
SD	0.36	0.500	0.520	0.62	0.200	0.970
SD error	2.79 ±0.16	2.12 ±0.22	7.34 ±0.23	9.86 ±0.28	7.24 ±0.09	4.58 ±0.43

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