SURFACE MODIFICATION OF NYLON-6 ELECTROSPUN FIBER MAT WITH SILVER NANOPARTICLES USING LAYER-BY-LAYER METHOD

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A Thesis Submitted in Partial Fulfillment of the Requirements
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การดัดแปรผิวของแผ่นเส้นใยอิเล็กโทรสปันไนลอน-6 ด้วยอนุภาคระดับนาโนเมตรของเงิน โดยใช้วิธีเลเยอร์บายเลเยอร์

นางสาวศิขรินทร์ เอี่ยมธรรมรักษ์

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SIKHARIN IAMTAMMARUK: SURFACE MODIFICATION OF NYLON-6 ELECTROSPUN FIBER MAT WITH SILVER NANOPARTICLES USING LAYER-BY-LAYER METHOD. ADVISOR: ASSOC.PROF.NONGNUJ MUANGSIN, Ph.D., CO-ADVISOR: RATTHAPOL RANGKUPAN, Ph.D., STEPHAN T. DUBAS, Ph.D., 103 pp.

The goal of this research was to modified the surface and embed silver nanoparticles on the surface of nylon-6 electrospun fibers via layer-by-layer (LbL) assembly to improve the antibacterial properties of fiber mats. Effect of polyelectrolyte concentration and deposition time of polycationic poly(diallyl dimethyl ammonium chloride) and polyanionic poly(styrene sulfonic acid) on the surface treated with sodium hydroxide (NaOH) and untreated surface were investigated. Due to negative charge induction on fiber surface by NaOH, the NaOH treatment reduced minimum polyelectrolyte concentration and deposition time required for building up uniform LbL layers on fiber mats from 5 to 1 mM and 40 to 10 mins, respectively. Diameter of NaOH treated fiber modified with 1 to 15 LbL bilayers increased from 166 to 410 nm, while that of pristine fibers modified with bilayers remained relatively constant. Selected LbL modified nanofiber mats were embedded with Ag nanoparticles (AgNPs), capped with poly (4-styrenesulfonic acid-co-maleic acid). AgNPs LbL-modified fiber mats exhibited anti-microbial activities against *Escherichia coli* and *Staphylococcus aureus* (AATCC100 standard testing method) with percent reduction in the range of 31.71 to 99.99 percent.

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ศิขรินทร์ เอี่ยมธรรมรักษ์ : การดัดแปรผิวของแผ่นเส้นใยอิเล็กโทรสปันไนลอน-6 ด้วยอนุภาคระดับนาโนเมตรของเงินโดยใช้วิธีเลเยอร์บายเลเยอร์ (SURFACE MODIFICATION OF NYLON-6 ELECTROSPUN FIBER MAT WITH SILVER NANOPARTICLES USING LAYER-BY-LAYER METHOD) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ.ดร.นงนุช เหมืองสิน , อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ดร.รัฐพล รังกุพันธุ์, ดร.สเตฟาน ที ดูบาส, 103 หน้า

งานวิจัยนี้มีวัตถุประสงค์เพื่อ ดัดแปรสภาพพื้นผิวเส้นใยอิเล็กโทรสปันไนลอน -6 ด้วยการตรึงอนุภาคนาโนเงินโดย ใช้เทคนิคเลเยอร์บายเลเยอร์ เพื่อเพิ่มคุณสมบัติในการต่อต้านเชื้อแบคทีเรีย จากการ ศึกษาการสะสมชั้นฟิล์มบาง แบบสลับของ พอลิไดอัลลิลไดเมทิลแอมโมเนียมคลอไรด์ และพอลิสไตรีนซัลโฟนิค แอซิด บนเส้นใยที่มีการปรับสภาพพื้นผิวด้วยสารละลายโซเดียมไฮดรอกไซด์และไม่มีการปรับสภาพพื้นผิว เพื่อหาสภาวะการเตรียมฟิล์มที่เหมาะสม พบว่าการปรับสภาพพื้นผิวด้วยโซเดียมไฮดรอกไซด์ ช่วยลด ความเข้มข้นและระยะเวลาการเคลือบฟิล์ม ที่ต้องใช้ในการเตรียมฟิล์มที่มีความสม่ำเสมอลงจาก 5 เป็น 1 มิลลิโมลาร์ และ 40 เป็น 10 นาที ตามลำดับ เมื่อเทียบกับเส้นใยที่ไม่มีการปรับสภาพเนื่องจากโซเดียมไฮดรอกไซด์ เหนี่ยวนำให้เกิดประจุลบบนพื้นผิวของแผ่นเส้นใย ทั้งนี้การสะสมจำนวนชั้นของฟิล์มบางตั้งแต่ 1 ถึง 15 ชั้นคู่ บนแผ่นเส้นใยที่ปรับสภาพพื้นผิวด้วย โซเดียมไฮดรอกไซด์ทำให้ขนาดเส้นใยเพิ่มจาก 166 เป็น 411 นาโนเมตรในขณะที่การสะสมฟิล์มบางบนเส้นใยที่ไม่มีการปรับสภาพพื้นผิวทำให้ขนาดเส้นใยเพิ่มขึ้นเล็กน้อย เมื่อทำการติด อนุภาคนาโนเงินที่เคลือบด้วยพอลิ -4-สไตรีนซัลโฟนิค แอซิดโคมาเลอิคแอซิด บนผิวของแผ่นเส้นใยที่มีชั้นฟิล์มบางเพื่อเพิ่มคุณสมบัติการต่อต้านเชื้อแบคทีเรีย พบว่าแผ่นเส้นใยที่ผ่านการปรับสภาพพื้นผิวด้วยอนุภาคเงินนาโนโดย ใช้กระบวนการเลเยอร์บายเลเยอร์มีสมบัติการต่อต้านเชื้อแบคทีเรียเอสเชอริเชีย โคไล และสแตปฟิโลคอคคัส ออเรียส (มาตรฐานการทดสอบ AATCC100) โดยสามารถลดปริมาณเชื้อลงได้ในช่วงร้อยละ 31.71 ถึง 99.99

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ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม……..……

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LIST OFABBREVIATIONS

%	percentage
g	gram
L	microliter
mol	micromole
aq	aqueous
cm	centimeter
cm^{-1}	unit of wave number
^{o}C	degree Celsius (centrigrade)
FTIR	Fourier Transform Infrared Spectrophotometer
h	hour
kV	kilovolt
M	concentration in molar
mM	millimolar
mg	milligram
min	minute
mL	milliliter
mL/h	milliliter per hour
MW	molecular weight
nm	nanometer
pH	Potential of Hydrogen ion
ppm	part per million
r^{2}	correlation coefficient
SD	standard deviation
SEM	Scanning Electron Microscope
T$_{m}$	melting temperature
UV-vis	Ultraviolet-visible
LbL	layer-by-layer assembly

TEM	Transmission Electron Microscope
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometer
SPR	Surface plasmon resonance
S. aureaus	*Staphylococcus aureus*
E. coli	*Escherichia coli*
PSS	poly(4-styrenesulfonic acid)
PDADMAC	poly(diallyldimethylammoniumchloride)
PSS-co-MA	poly (4-styrenesulfonic acid-co-maleic acid)
$AgNO_3$	silver nitrate
$NaBH_4$	sodium borohydride
NaCl	sodium chloride
NaOH	sodium hydroxide

CHAPTER I

INTRODUCTION

1. Introduction

In the recent years, nanostructure material formation was interest significantly. Most of researches focus on development of embedded nanoparticles on polymer fibrous membrane for biomedical industrial. Because of the fibrous membrane has a tidy property with low weight materials, high porosity and large specific area. These benefit properties make the polymer nanofibers to be optimal candidates for many applications in protective clothing, wound dressing, sensor, biocatalyst, tissue engineering, drug delivery system and antimicrobial in biology [1-3]. However, the nanoparticles have many types that can be immobilized on the fibers to enhance the functionalities of materials in numerous applications. Especially, development of antibacterial and antibiotic on textile material is attracting to considerable.

Electrospinning process has become develop and applied widely technique with cost effective production for fabricate polymer fibers in range nanometer to submicron which high porosities and large surface areas and continuous surface area better than other materials [4-7]. Nylon-6 fiber is outstanding characteristic in textile commercial and industry due to it is offer with low cost, good chemical resistance, excellent mechanical and thermal properties. Nowaday, almost of material use in filtration applications prefer the nylon-6 fibrous membrane. Aussawasatien and coworker [8] was fabricated electrospun nylon-6 membrane with high porosity and small diameter then successfully removed microparticles approximately 90% efficiency. But considerable in antimicrobial application to experience bioactive functionality of nylon-6 is lack which not suitable for antimicrobial activity. Therefore, attempts to modified surface of nylon-6 fibrous to improve antibacterial interaction on fibrous membrane.

Difference approaches have focused on to form thin film layer for incorporate metallic particles to improve surface of materials. These including Langmuir-Schaefer method, plasma, electroless plating, chemical surface functionalities and layer-by-layer assembly [9-12]. All of method can be prepare thin film on the surface successfully but it is difficultly method and limited to flat surface whereas, layer-by-layer (LbL) assembly increasing popular in the last years as a simple, versatile and low cost technique to develop the surface for many applications such as sensors, catalyst and biomedical application [13-15]. It makes surface coating of alternate polycation and polyanion polyelectrolyte layers on broad range of substrates to build thin film multilayer structure and immobilized the nanoparticles on substrate easily. Most studies have been proposed on polyelectrolytes in fully charge state is proceeds smoothly as molecular thin layers and highly specific like poly(dimethyldiallylammonium chloride) (PDADMAC), poly(4-styrene sulfonic acid) (PSS) and so on [16-18]. Furthermore, PDADMAC and PSS have strong ionic charge and also independent of pH solution so we can use them for prepared system in widely range pH solution.

The versatility of invent layer-by-layer assembly method is well understood with alternate deposition of polycation and polyanion. However, a study of parameters is importance in order to obtain a quality of control film growth on fibrous substrate. Recent studies have reported that layer by layer parameter have significant influent the morphology of materials. The processing parameter is implies the need careful adjustment in order to control film growth such as concentration of polyelectrolyte and period of immerse polyelectrolyte on substrate. Interestingly, this research used layer-by-layer assembly for funtionalized surface of electrospun nylon-6 to increase surface properties for widely application. But surface of electrospun nylon-6 does not have any charge to interact with polyelectrolyte, thus be induce surface to produce negative charge by hydrolysis reaction with sodium hydroxide (NaOH) [19] for greater interaction with positive charge of PDADMAC and negative charge of PSS in the alternating adsorption.

The metallic silver nanoparticles has been recognised for antimicrobial activity over 100 years. Nowadays, consumer products to contain nanomaterials become favor nanosilver component products. They have been used not only against environmental problems but also include medical devices, food packaging materials, food supplements, room sprays, cosmetics, water disinfectants and textile industry [20-22]. Generally preparation of silver nanparticles that have a problem such as aggregrate of silver nanoparticles affect on loss concentration. The capping agent of a copolymer PSS-co-MA intention to introduce the use of both benefits as an efficient stabilizing on the silver nanoparticles and pH dependent polyelectrolyte for the layer assembly of these particles into thin films. The advantages presented by this copolyelectrolyte is inherent to the presence of sulfonic functional groups, allow the assembly of polyelectrolyte even at low pH and the stock solution of Ag:PSS-co-MA for prepare silver nanoparticles remain stable several months [23]. Interesting, silver nanoparticles stabilized with PSS-co-MA copolymer has been extensively used as a finishing agent for textiles to impart antimicrobial properties.

The goal of this research is to enhance antibacterial property of nylon-6 electrospun nanofibers by embedding the surface of the nanofibers with silver nanoparticles via layer-by-layer assembly process and to characterize physical property and anti-bacterial property of the modified nanofibers. We also investigated effect of alkali treatment and LbL process parameters, i.e. polyelectrolyte concentration and deposition time on LbL film formation. Lastly, we investigated effect of silver nanoparticles amount embedded in LbL film on antibacterial property.

1.1 Objectives of this research

1. To enhance antibacterial property of nylon-6 electrospun nanofibers by embedding the surface of the nanofibers with silver nanoparticles via layer-by-layer assembly process
2. To characterize physical property, chemical property and antibacterial property of modified nanofibers.

CHAPTER II

BACKGROUND AND LITERATURE REVIEWS

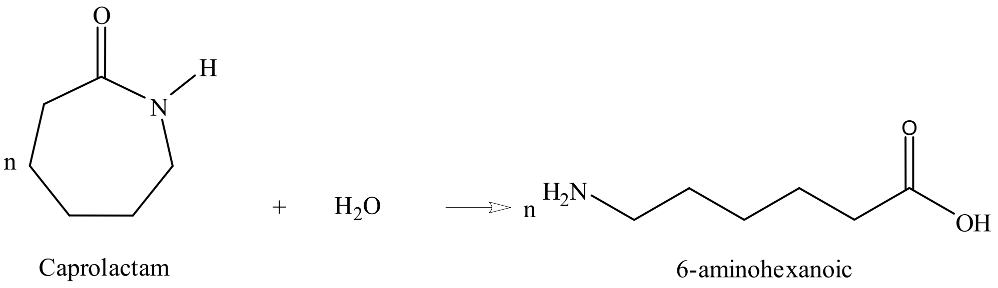
2. Background and literature reviews

2.1 Nylon-6 fibers

The first synthesis fiber is produced from nylon-6 which become to the most popular types among nylon use in commercially textile products since 1938 and still more than 90 percent of polyamide used in the global textile market. Characteristic of nylon consist of amide groups in the backbone chain refers to polyamide that derived from diamine and dicarboxylic acid consist of amide linkage that show -NH-CO- repeating unit. The most of manufacture nylon fibers could be made from 2 methods as follow [24]:

1. The condensation polymerization.
2. The hydrolytic polymerization of lactam which involve partial hydrolysis of the lactam to an amino acid.

The condensation of nylon derived from amine and carboxylic acid group. There are identified in term Nylon x where x is the number of carbon atoms in the monomer. In the case of nylon-6, the synthesis of nylon-6 is produce from caprolactam monomer which a white chip solid and melting point 68 ^{o}C is carried out the polymerization under anhydrous condition via anionic polymerization using hydride, hydroxides or alcoholates acted as catalyst. Water, acid or bases could be used to initiate the reaction. In the industries were usually add 5-10% of water for catalyse the reaction involved intiated ring opening of the caprolactam follow by condensation of aminocaproic acid. Moreover, the direct addition polymerization of caprolactam could be form nylon-6 in the reaction (equation 2.3). The way of nylon-6 formation represented in equation (2.1)-(2.3).



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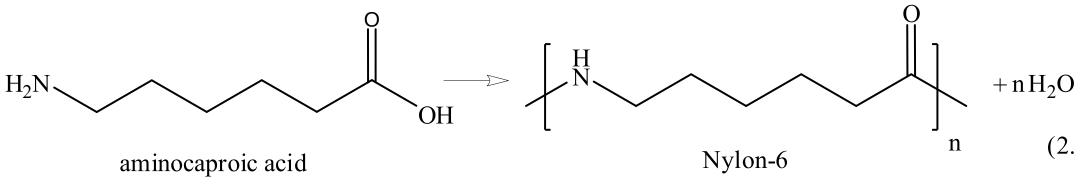

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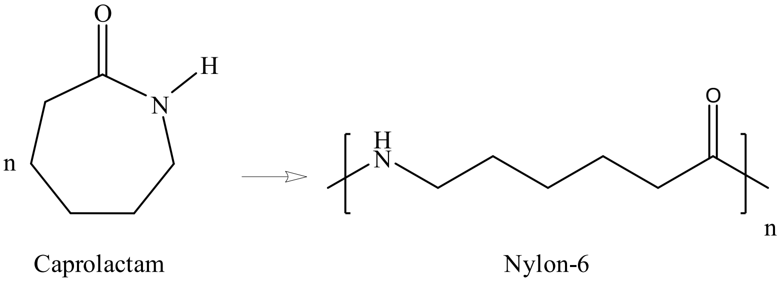


(2.3)

The equipment for preparation of nylon polymers is usually provided in three steps. The first step is monomer preparation, which is designed to controlled monomer composition. In the next step combined the additive such as pigment, stabilizer and light degradation into the polymer before extrusion. After that fed the monomer through polymerization reactor where is the caprolactam monomer is heated to around 250-280 °C for 12-24 hours at atmosphere pressure and then polyamide were forming under controlled condition. The polymerization of nylon-6 may be batch or continuous process. Although, batch polymerization was used in the previous production. In the present, continuous polymerization is become popular process of the production due to it give cheaper process and high quality product.

2.1.1 Nylon fiber production

Nylon-6 is the one of the greatest commercial synthesis polymers used as fibers both alone and blends with the other fibers which important applied in high performance wipes, synthetic suede, heat insulators, battery separators, clothing, paper, engineering plastic and synthetic fiber. Because it has many advantage offer with smooth, more silk-like handle, dimensional stability fabric, wrinkle resistance, biodegradable, biocompatible, long lasting fabric, dye ability in wide range of dye, abrasion resistance, extremely chemical resistant to hydrocarbons aromatic strong acids, bases, phenols and good thermal properties.

2.1.1.1 Conventional fiber production

The processing of commercial nylon fiber production consisted of fiber extrusion and fiber drawing. Melt extrusion is the most popular economical process for fibers formation including aliphatic nylon-6 fibers. This process is required a stable polymer in molten condition. In the initial stage, polymer pellets flow into chip hopper and pass to the extruder or heated grid to melt them at a temperature of 250-260 ^{o}C. After that, the molten polymer is fed through to a metering pump, an important instrument part to control linear density of final spun yarn, at controlling condition with temperature of 280-300 ^{o}C and pressure 50-70 MPa. In the second step, molten polymer is feed passes to the extrusion heads which contain a filter and a spinneret to spun into a yarn at speed above 1,000 m/min. Normally spinneret are made of stainless steel in circular shape with typical diameter of 100-400 µm. The spinneret a many small holes which correspond to the number of fibers require in final product. The polymer streams are draw via take up reel and moved to cool air quenching stream where fibers solidify at temperature 18-20 ^{o}C, an relative humidity 55-65 %.At this stage, is solidify into fibrous form with fiber The filament is complete to the solidification state in fibrous insuffient tensive properties since the fibers axis and theirs crystalline are too low. Finally, drawing process is necessary for desire balance the properties of filament yarn. The yarn is move from extrusion section to pass around spin roll of drawing process which difference speed of roller. After drawing process the filament yarn is wind up on package for industrial application. A schematic diagram of nylon fibers production with an extrusion and drawing line is shown in figure 2.1.

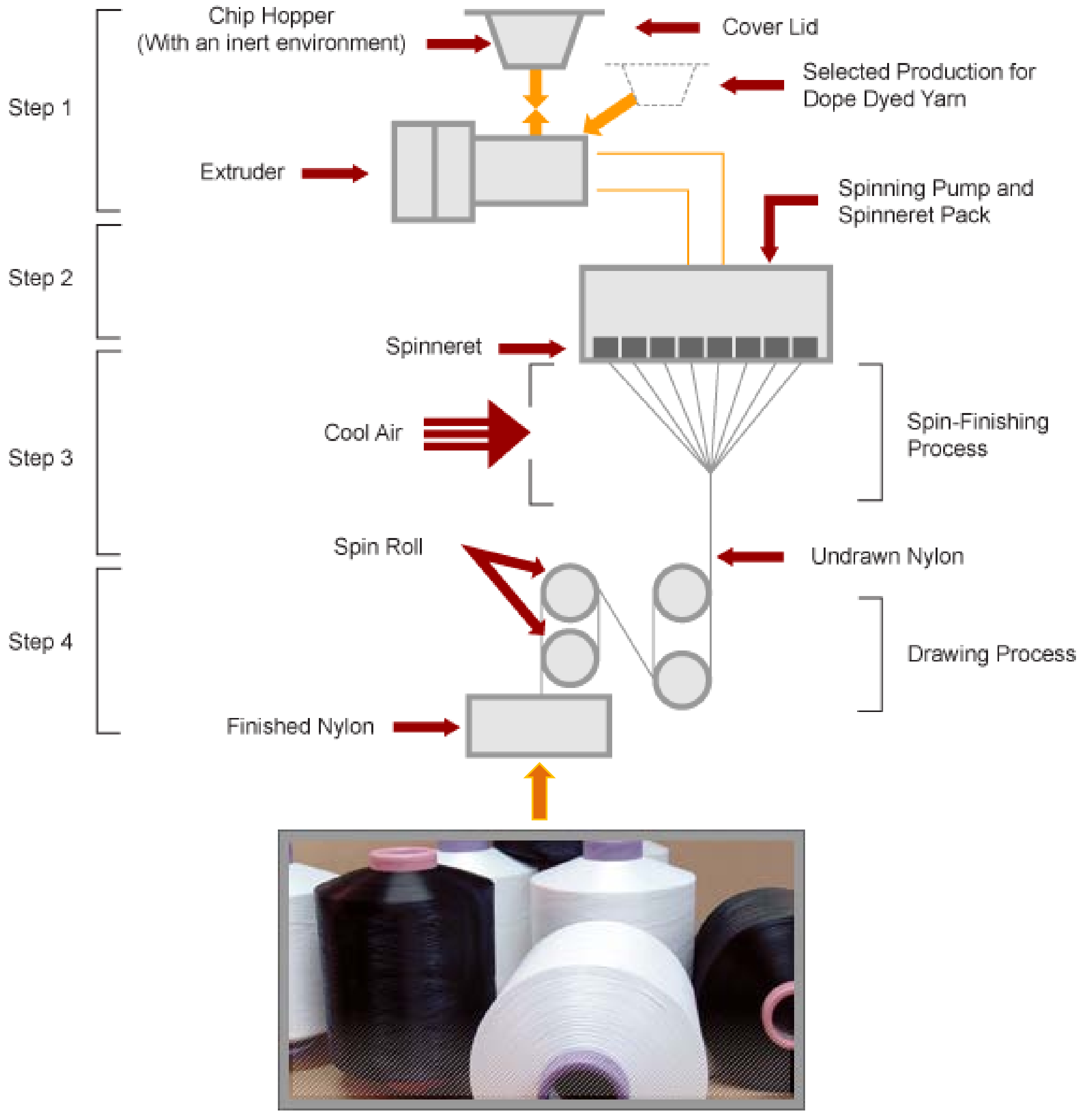


Figure 2.1 Manufacturing process of nylon-6 filament yarn.

2.1.1.2 Non-conventional fiber production

An innovative of fibers formation a smaller diameter textile fiber is become interesting in field science, engineering and technology in the recent years. Previously methods using for produce small fibers in range micrometer to nanometer such as spunbonding process, melt blowing and electrospinning process which comparison of fiber processing and fiber diameter in table 2.1.

Table 2.1 Comparison of fiber processing and fiber diameter

Process of fibers production	Fiber diameter (nm)
Spunbond	5,000-25,000
Melt blowing	2,000-15,000
Electrospinning	100-10,000

Spunbond process

In generally, material of spunbond process usually used a high molecular weight and broad molecular weight distribution polymers to produced fiber webs for example polyamide, polypropylene, polyurethane and polyethylene terephthalate.

The principle of spunbond process produce from integrated process combining fiber spinning, web formation and bonding extrude. The spun fibers onto a collecting wire mesh belt results of bonding the fibers during flow air jets. The first step, fed the polymer into the extruder and the pellet become to melt and homogeneous. The molten polymers pass into a filter system and spinning pump. The molecular orientation increasing and apply heated rolls or hot needles to the melt polymer to binding fibers and fuse the fibers together. Finally, the filaments yarns are twist around and deposited a random nonwoven on the collecting belt to obtain 5 to 25 micrometer. After cooling, the filament wound. Spun bond nonwoven webs products are applied in medical field, upholstery materials, construction and carpet backing.

Melt blowing process

Melt blowing is a one-step process for producing nonwoven fiber mats from polymers or resins via high velocity air blow. Melt blowing fibers generally have diameters in the range of 2 to 15 micrometer. A characteristic property of fibers from this technique is differences from other fabrics such as degree of porosity, softness and opacity.

The melt blowing process is consists of the extruder, metering pumps, die assembly, web formation, and winding. The principle of this technique is follow a high velocity air blows molten thermoplastic from extruder die tip and draws a molten polymer resins with heated onto conveyor and transform the polymer resins to nonwoven fibers. In some ways the process is similar to the spun-bond process but melt-blown fibers is much finer and fibers diameter production in range micrometer. The supporting market segments are widely used the melt-blown filament in many products such as medical product, sanitary, oil adsorbents, hot melt adhesive and electronical.

Electrospinning process

Electrospinning process introduce a new level of prepare ultra-fine fibers in nanoscale with specific excellent properties and smooth fibers like skin which attract for many application. The advantage of this process is simple, easy to process control, inexpensive, safety, widely used of materials including polymer both natural and synthetic polymers [25-27].

In 2005 Kalayci explain the mobility of an ion in the polymer solution of electrospinning process depends on electrostatic force. The major equipment processing requirements for demonstration the electrospinning are as follow:

1. A viscous polymer solution or melt polymer solution.
2. A high voltage DC power supply.
3. A collector that has an opposite charge to collect the fibers.

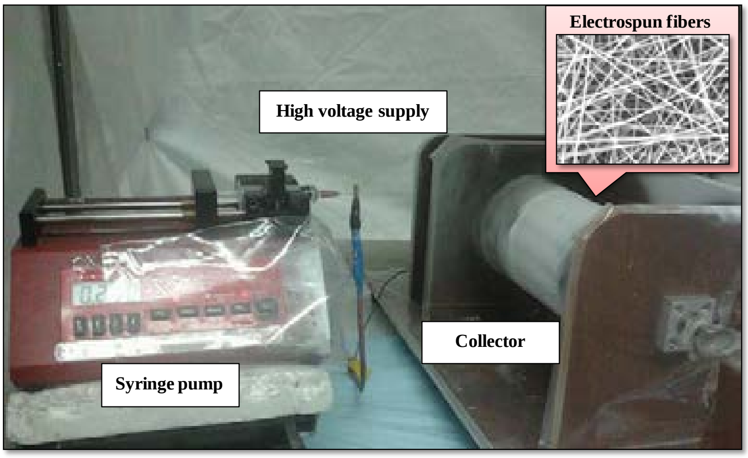


Figure 2.2 A set up of electrospinning process

A basis of experimental set up the electrospinning method is using a high voltage to generate the polymer solution in the syringe as the electrical charged jet of polymer solution. The charge droplet of polymer solution is the initial step for electrospinning. Typically, a polymer solution is pumped at low flow rate into capillary tip where is carrying a positive charge. In the absence of electric field, the droplets form at the end of capillary and fall under the gravity.

In 1969, Taylor was found the deformation of small charged droplets from a sphere transform to ellipsoid under increasing the electric field until the repulsive electrostatic forces on the solution overcomes the surface tension. These effect results in transform the droplet of the polymer solution at a capillary tip generate to Taylor cone due to ejection of solution charged jet [28].

The elongatation droplet assumes a cone-like-shape and a narrow jet of fluid was eject from its point “Taylor’s cone”. It was formed at a critical voltage (V_c) applied to a droplet at the end of a capillary of length h and radius R (Taylor 1969). The equation as follow:

$$Vc = \left(\frac{2L}{h}\right)^2 \left(\ln\left(\frac{2h}{R}\right) - 1.5\right)(0.117\pi RT) \qquad (2.4)$$

Taylor determine from the equilibrium between surface tension and electrostatic forces when the half angle of the cone was 49.3^{o}. The equation 2.4 decides for high surface tension liquids to require high electric field to obtain a critical voltage for electrostatic processing which induce a corona discharge forming.

The fluid jet travels in air towards a grounded collector which the solvent evaporates to formation randomly dry non-woven fibers mat on a collector. The quality of electrospun nanofibers is affected on morphology by various of material and process for example concentration of solution, voltage, feed rate, distance between tip to collector, solvent system, conductivity of solution and temperature.

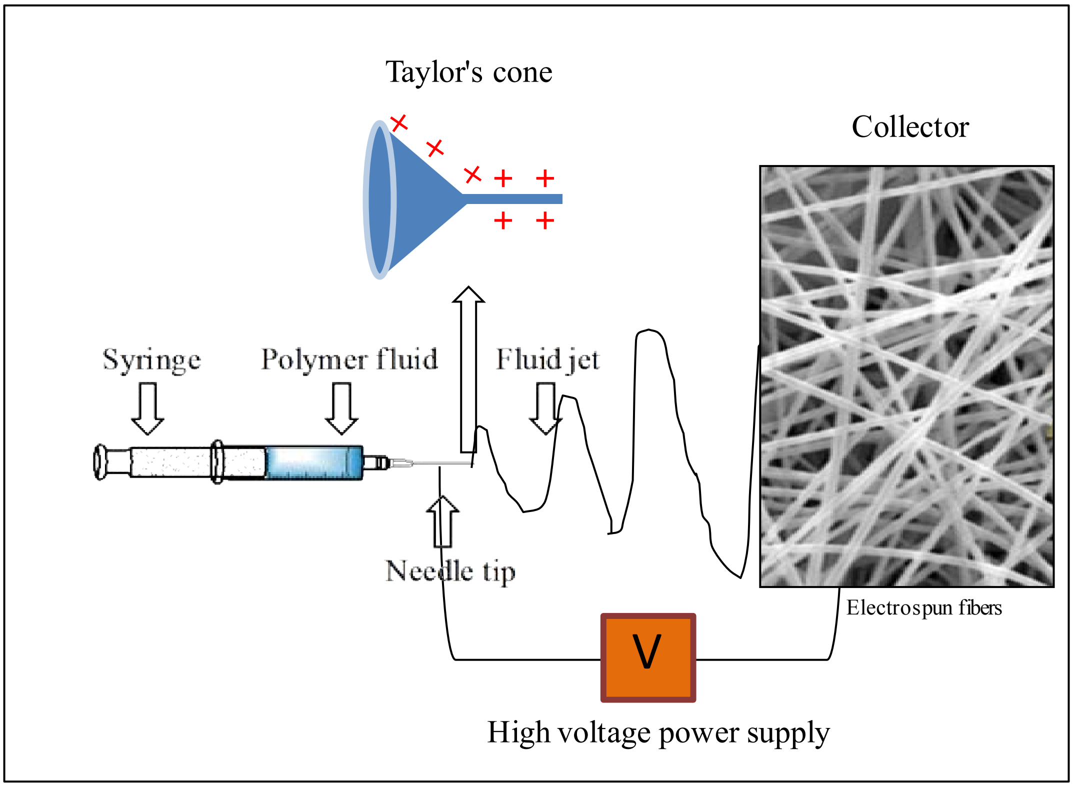


Figure 2.3 Taylor’s cone formation of solution at a capillary tip of electrospinning process.

Application of electrospun fibers

Nonwoven electrospun fibers mat composed have a large surface area to volume ratio, very small fibers diameter in range 100-1,000 nm, small pore size, uniform and continuous fibers. So, electrospun fiber is interesting in a wide range of important applications such as scaffold for tissue engineering, sensor, would dressing, drug delivery, catalyst, reinforcing fibers in composite materials, membrane for filtration, etc [29-31].

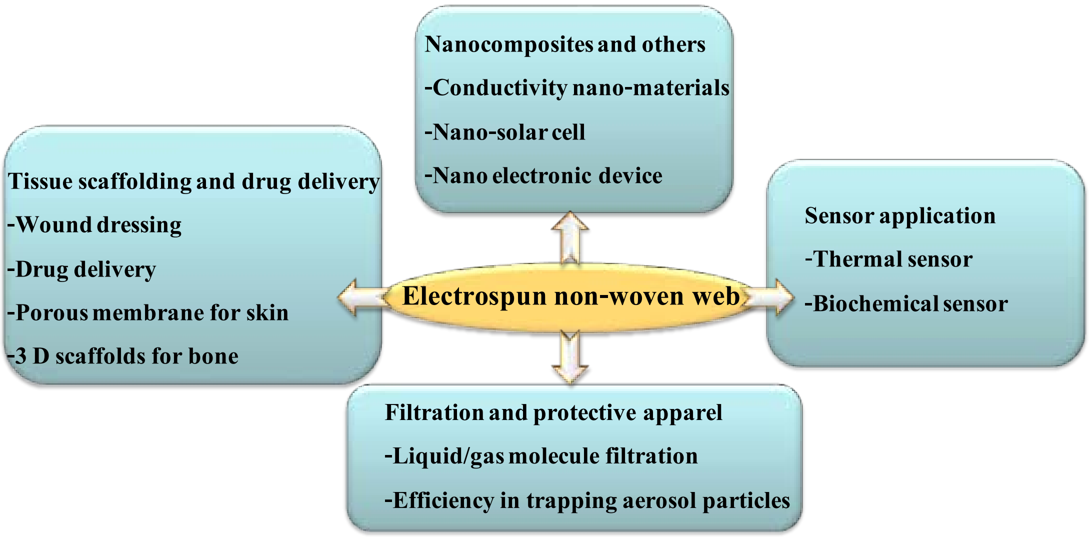


Figure 2.4 Application of electrospun nanofibers

2.1.2 Properties of nylon-6

In generally, the properties of fibers consider in three categories such as geometric, physical and chemical properties. Furthermore, this works also consider the biological properties of fibers.

2.1.2.1 Geometric properties

Molecular structure

Nylon-6 structure is linear chain polymer orientation along the fibers axis, the repeating unit of nylon-6 is consist of carbon, hydrogen and nitrogen elements (Figure 2.5(a)). The end-to-end of amide repeating units must be form hydrogen intermolecular attraction between molecule and their structure also provide inflexibility. This arises from the polarity of the C-O and N-H bonding. Nylon-6 has a regular repeating units join end to end that can form hydrogen bonds interactions between polymer chains. These occur from the intermediate polarity of the carbon-oxygen and nitrogen-hydrogen bond of molecules (Figure 2.5(b)).

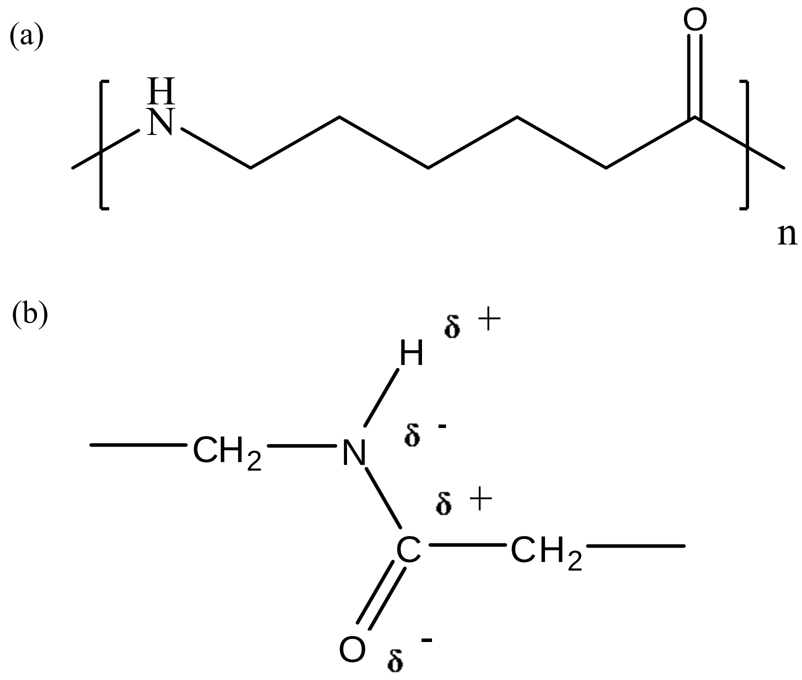


Figure 2.5 (a) Molecular structure of nylon-6, (b) partial dipole moment of nylon-6

Crystallinity

The structure of nylon-6 fibers demonstrate a semi crystalline polymer that consist of crystalline and amorphous phases. Nylon-6 structure is a linear aliphatic polyamides which the amide (-CONH-) group represents a strong intermolecular hydrogen bonding able to mostly crystallize and exhibit a common crystalline α and γ forms (Figure 2.6). The orientation of crystalline structure is influence on the nylon 6 properties such as optical, mechanical and thermal properties [33-34]. Generally, the structure of nylon-6 in α-form crystal comprises of extended nylon 6 chains which the adjacent chains are antiparallel. The γ-form crystal is composing of plated chains which the chains are arranged in parallel. Crystalline of α- and γ-forms of nylons can controll by processing conditions to obtain various percentages of its form, for example nucleation is seed the melt polymer to produce uniform size smaller than spherulites structure. Another advantage to obtain from nucleation is decrease time of processing.

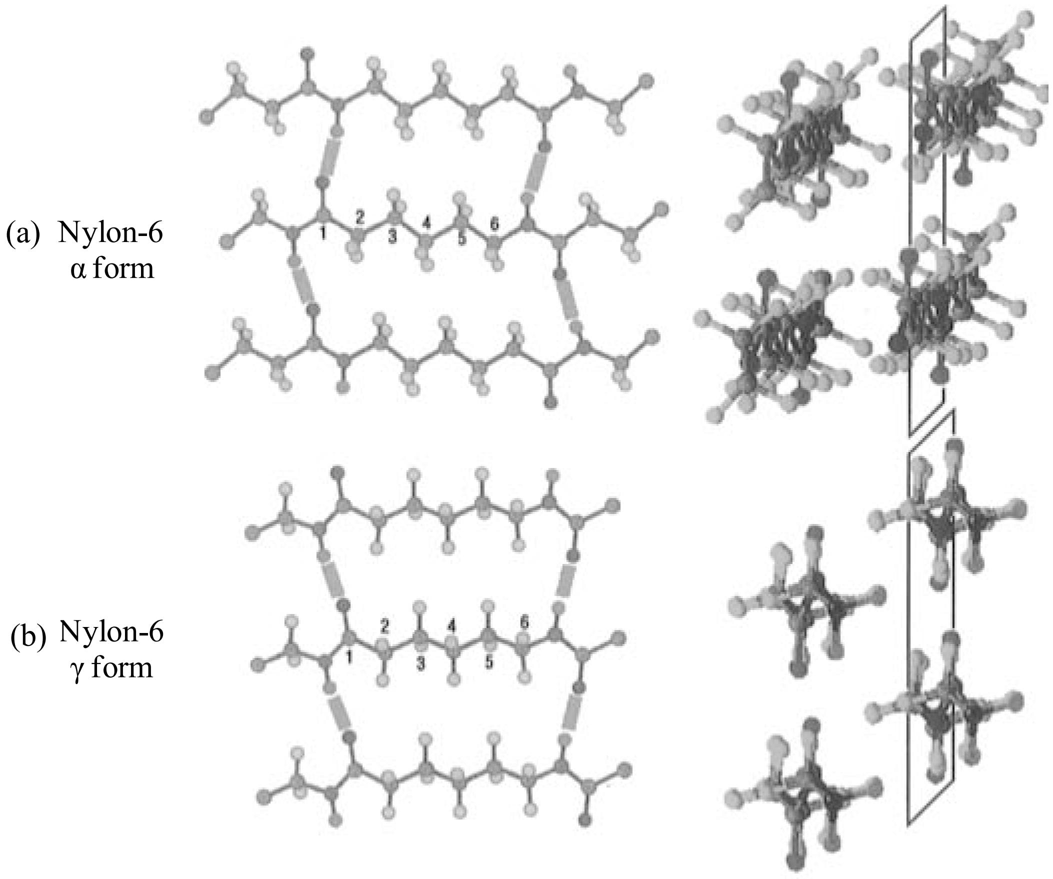


Figure 2.6 Structures of nylon-6 represent (a) α form and (b) γ forms. The left side shows the hydrogen bonds planes and the right side shows the chain axis [33].

2.1.2.2 Physical Properties

Nylon-6 has a cylindrical in shape which good dimensional stability at medium temperature. The surfaces of fibers are smooth and without any wrinkles or creasing after recovery and represent a high abrasion. Absorbance ability of nylon-6 fiber is too low because moisture regain of it is estimate 4%, so soak fiber is dries rapidly after laundering [24].

The nylon-6 fibers are uniform in diameter and it has an advantages with high mechanical strength that represent tensile strength of dry nylon-6 at 20 °C is typically 76-97 MPa, density (70 ^{o}F) 1.13 g/cc, it has a high elasticity fibers that relative with high elongation at break 24-40%, high tenacity about 4.2-5.8 gpd and excellent toughness, softening point, good wear resistance, high rigidity, low young modulus and soft touch that appreciate for flexible packaging. Because of these superior performances, nylon-6 has already replaced some materials being used for mechanical parts such as glass fiber reinforced, transformer housing, junction box, hair straightened housing, fabrics, bridal veils, carpets, musical strings and rope, machine screws, gears, connector, electric tool handle, vehicle wheel, sporting equipment.

2.1.2.3 Chemical properties

Effect of organic and inorganic solvent

Nylon-6 is resistance to the most of organic and inorganic solvent for example benzene, chloroform, acetone, esters ethers including oil. It is inert to alkaline and chemical corrosion resistance. Nylon-6 can be dissolves in formic acid, phenol, cresol and strong mineral acids for example sulfuric acid, nitric acid and hydrochloric acid.

Effect of sunlight

Storage of the nylon-6 fibers might be avoid the sunlight because when prolong exposure nylon-6 fibers to the sunlight for a few weak, It will lose of strength and finally it almost decomposed. Another influence such as detergent and bleach do not effect on the fibers

Dye ability

The nylon fiber is exhibit polar characteristics from -COOH and -NH_2 functional groups that affinity for dye adsorption on fibers with almost any type of dye. Dye diffusion into nylon-6 fibers is independent on dye concentration but depend on electrostatic and hydrophobic interactions between dye and fibers. The dye could be use organic and inorganic but inorganic dye is widely usage more than organic dye because of its give a higher color, thermal stability and light fastness, which fundamental requirement. Furthermore, metal complex dyes are associates with carboxylic groups or amine groups in the nylon-6 structure to give light fastness and excellent washing for example chromium, silver and cobalt. The dye is normally applied via dyeing or printing in processing operations. Although, There have been many attempts to improve the dye ability of nylon for more staining especially in consumer products.

The dye ability of small fibers is difference in some respects from the fibers of normally linear density. The nylon-6 nano-microfibers are a greater surface reflection arising from the increasing surface area to interaction with pigment. Therefore, comparison of dye adsorption at same concentration on nano-micro fabric and the fibers of normally linear density that occur a smaller nylon-6 fiber apparently lighter shade and lower wash fastness than conventional linear density fibers.

Thermal properties

The thermal behavior of nylon-6 and fibers are importance for manufacture in various applications. The amide linkages in the nylon-6 structure has offer enhance the melting point of its higher than polyethylene because polyethylene has a weak intermolecular interaction (van der waals) and then the melting point is low about 120 ^{o}C (218 ^{o}F). Nylon-6 has a melting point about 215-220 ^{o}C (419-428 °F), heat deflection temperature (66 psi) about 188 ^{o}C (370 ^{o}F), specific heat 0.40 BTU/lb-^{o}F, thermal conductivity 1.67, glass transition temperature: 47^{o}C and excellent thermoform ability. The thermal properties of nylon-6 is high enough for versatile application such as flame retardant, relays accessories, transformer housing, plug, cable ties, wire jacket, film packaging, automotive, electronically and resist accidental fusing.

The maximum servicing temperature for long period time of nylon-6 fibers without damage is about 149 ^{o}C (300 ^{o}F). When the temperature increasing to about 177-205 ^{o}C (350-400 ^{o}F) obtain nylon-6 fibers transform to soft, strength decrease and discolor. While the nylon-6 synthetic fibers is in the flame, observe its melts and burn which forming a white smoke like fishy odor. Then extinguish the flame by blowing. Remove the specimen from the flame that obtain yellowish bead residue.

2.1.2.4 Biological properties

The most of microorganism such as bacteria, virus and fungal including insects are produce the mildew that attack on nylon-6 finished textile but its do not affecting on nylon-6 fibers. Although, nylon-6 fibers is exhibit highly resistant to the microorganism but it does not have any properties to destroy the microorganism [35].

2.2 Introduction of layer-by-layer assembly

In the past decade micro and nanometer scale has the most important in science and nanotechnology, especially in textile application. Several techniques have become available which can be used to produce uniform films of functional coating on fibrous membrane. Layer-by-layer assembly is one of the most important technique of thin film deposition to provide imparts almost type of special functionalities on surface such as organic, inorganic, particles on the surface substrate to form special hybrid structures with simple, low cost production, the thickness of thin film layers can be controlled in range nanometer to submicron, no restriction in the shape or size of substrates and widely used for many substrates including fibers membrane [36].

The requirement of layer-by-layer adsorption is the presence of appreciate surface properties [37]. Especially, the properties of adsorbed layers depend on the nature of the substrate. In generally, silicon wafers, glass slide, quartz, mica were used as substrates for coated. Surface charge is not the only factor that may affect on the multilayer adhesion. The surface character could also affect on adhesion properties.

The polyelectrolyte commonly used as a material in the layer-by-layer deposition process. Polyelectrolytes are polymers carried out positive or negative charged ion groups on the structure. These polyelectrolytes can be distributed the counterions attraction onto the opposite charged surface of polyelectrolyte. Strong polyelectrolyte such as poly(diallyldimethylammonium) and polystyrene sulfonate are dissociated into macroion and counterion in aqueous solution. The advantage of PDADMAC and PSS were soluble in the widely range of pH (0-14). However weak polyelectrolyte for example poly(acrylic acid), poly(elthylene imine) are usually classified as dissociated a polyion system only in a limited pH range. This is remain undissociates polyacid in the acid range or undissociates polybase in the alkaline range.

Layer-by-layer deposition of polyelectrolyte involved alternately oppositely charge deposition of polycation and polyanion of polyelectrolytes on substrate. The polyelectrolyte exhibit an extremely charge density on surface which readily to interaction. This method driven by covalently, hydrogen bonding, electrostatic and vanderwaals interaction to construct the stability thin films. The structures of multilayer thin film can be generating with special properties such as optical, magnetic and electrical [36]. The basis of layer-by-layer assembly processing describe as follows (figure 2.7):

(1) Frabrication of oppositely charged polyelectrolyte on a charged substrate to construct the first monolayer

(2) Following wash cycle step to remove excess of charge and contamination of polyelectrolyte colloidal

(3) The coated structure of substrate already deposited other opposite charge polyelectrolyte layers and self assembly multilayer structure is formed [37].

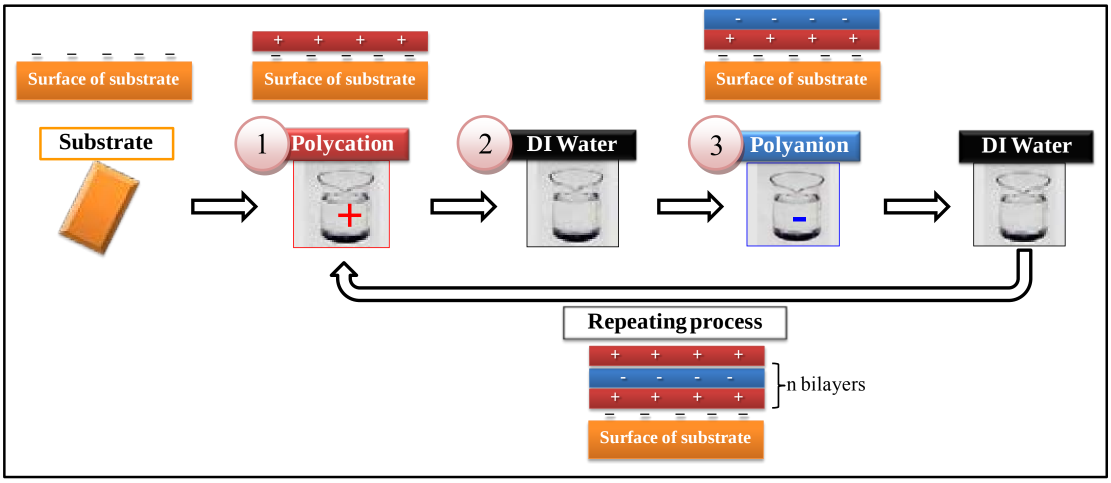


Figure 2.7 Layer-by-layer deposition process

The first step of deposition polyelectrolyte onto a substrate is a quickly process in a few seconds on domain. The next step, follow a slower process due to rearrangement of the coated substrate. During the second step, diffusion of polyelectrolyte chains might occur that cause to increase the film growth. The level of coverage on the coated substrate is saturated with deposition time. Moreover, polyelectrolyte interactions are responsible for layer construction as evidenced from surface thermodynamic. These effect responses to wettability confirm by contact angle measurement on polymer coated substrates [9, 38].

2.2.1 Processing parameter for control the growth of polyelectrolyte film

The polyelectrolyte thin film formation can be finely tuned by environmental conditions, including polymer concentration, deposition time and ionic strength of salt;

Polyelectrolyte concentration

The polyelectrolytes concentration act as the important variables for film growth. Polyelectrolytes are polymers represent the ionizable groups [35–37]. The ionized groups of polyelectrolyte can dissociate in the polar solvents which forming charges on polymer chains and release the counterions in solution. Electrostatic interactions between charges lead to the surface charge density increases. The surface charge density increases even further, the chains in the adsorbed layer form a concentrated polyelectrolyte solution with thickness increasing.

The entropic of counterion in the dilute polyelectrolyte solution is high and almost of counterions leaves polymer chains and freedom in solution. In contrast, the high polymer concentration, the entropic of counterion contain decreases resulting in a gradual increase in the number of condensed counterions.

The number of deposited layer pairs was the important step of thin film formation. The growth of film is based on the diffusion of the polyelectrolytes through the whole film on the layer pair deposition step. Layer thickness for the polycation and polyanion combination as a function of the number of deposition layer. Eventually, the thickness represented a linear or steady-state depends on layer number. For example, multilayers of PAH and PSS construct have been reported as linearly growing systems.

Deposition time of polyelectrolyte

The polyelectrolyte multilayer assemble with variables of deposition time is necessary for processing. The kinetic controlled adsorption of polyelectrolyte must lead to over compensation of surface charge. The long time of polyelectrolyte deposite on substrate results in polyelectrolyte chain assemble cover the surface of substrate increasing. Because counterions of polyelectrolyte are effective for leading to electrostatic interactions between ionized groups on the polymer backbone [38].

Ionic strength of salt

The charge inversion plays an important role in the layer-by-layer assembly technique. The amount of charge on surface can be tune by adjust ionic strength of salt in the solution. The ionic strength of salt influence on the electrostatic interactions of polyelectrolyte coating. The low concentrations of salt occurred the weak electrostatic interactions between polyelectrolytes film layer and caused the destruction of polyelectrolyte nanofilms. In generally, the salt concentration increase during the assembly can lead a transition from a linear growth regime to an exponential growth regime for some systems.

Previous studied of Guzman and et.al [39] were combination of polycation poly (diallyldimethylammonium chloride) (PDADMAC) with polyanionic poly(sodium styrene sulfonate) (PSS). The low salt concentrations (0.1 M) was correspond the average thickness per layer being assembled only 7 nm due to polyelectrolyte segments were efficient at seeking out surface charge. The increased of salt concentration to over 0.5 M result in thickness increased to around 25 nm, cause enhanced the ionic strength of polyelectrolyte adsorbed on substrate.

2.2.2 Application of layer-by-layer assembly

Layer-by-layer assembly can be effective on planar surfaces and geometries as well. The particles widely use for fabricate the three dimensional structures for advanced fabrication of two dimensional films. This offers a wide range of opportunities of non-covalent tuning of the chemical and physical properties of the surface of colloidal particles.

Layer-by-layer assembly method offers advantages to other methods of biomaterial, encapsulation and drug delivery system. For example drug delivery application is produce for controll, sustain or trigger release systems of small encapsulate drug molecules [39-40]. Fluorescein dye release from polyelectrolyte capsules relative with the number of film layers that use to determine the extent of diffusion resistance and encapsulated core dissolution, also relevant to drug delivery systems. Tailored release systems minimize side-effects due to lower systemic drug concentrations, prolonged duration of drug action and protection of active ingredients in hostile physiological environments.

2.3 Introduction of silver nanoparticles

Nanoparticles have very promising benefits to society with their development in science, engineering and technology. One important approach of nanoparticles are exhibit a very small particles size which often in range 10-100 nm (figure 2.8). Because of the material becomes a tiny size that results in high specific surface area, surface reactivity and surface to volume ratio which enhances the material to interact with other particles[41].

The interesting properties of silver nanoparticles demonstrate widely available application such as nanoparticles actually proven to be a good catalyst in the catalytic industry, sensor, anti-reflective optical coatings and antibactericidal. Silver nanoparticles become popular to use in numerous industrial, commercial, medical and science research because it has a unique optical, ductile and excellent conductor of electrical and thermal properties which high melting point and boiling point about 961.93 and 2,212 ^{o}C, respectively. In biology and medical, silver nanoparticles have attracted to define new types of cost-effective of antimicrobial materials. One important use of silver nanoparticles as efficient agent to resistance many type of germs [42-43]. In recent years silver nanoparticle are display a strong antimicrobial material various parts of consumer and pharmaceutical products. For example of this is addition of nanosilver to clothes and socks for inhibition and destroy the bacteria associated with body and foot odor resistant. Furthermore, silver nanoparticles become widely everyday life available containing electronic products, room spray, food packaging and detergent for enhance antibacterial properties of products.

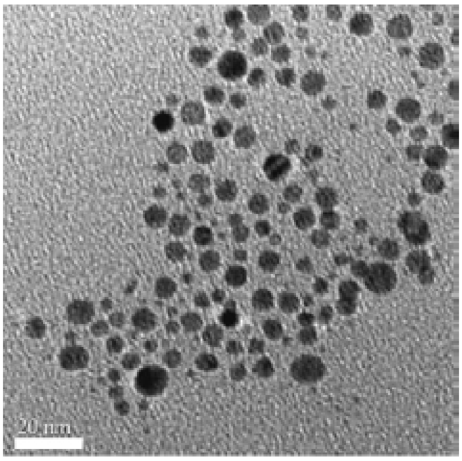


Figure 2.8 TEM images of silver nanoparticles [23]

2.3.1 Synthesis of Silver Nanoparticles

The method for prepared silver nanoparticles can be synthesis from many methods such as photochemical method, electrochemical, gamma irradiation, electron irradiation, microwave processing, laser ablation and chemical reduction etc. Properties of silver nanoparticles are different from their bulk materials such as silver metal is dark gray but colloidal silver nanoparticles synthesis show clear yellow.

Organic and inorganic agent reduction

The most method for synthesis of silver nanoparticles is common use chemical reduction because of simple and low cost effective [44-45]. Silver nitrate usually create silver ion precursor for silver nanoparticles production. In general, silver nitrate use as solvent of silver metal that will be making an anion associated with the silver nanoparticles synthesis processes. After silver nitrate dissolve, it separate into two ion parts such as a positive silver ion (Ag^+) and a negative nitrate ion (NO_3^-). Organic and inorganic agents are widely using for reducing agents for example sodium borohydride, sodium citrate, ascorbate, hydrogen gas, hydrazine, ethylene glycols, ascorbic acid, aliphatic amines, sorbital, dimethylformamide and

Tollen’s reagent. The reducing agent act as reduce silver ions (Ag^+) to metallic silver particles (Ag) formation in the solution which ions reducing via receive an electron from a donator (equation 2.5) and reduction of silver ion (Ag^+) to silver nanoparticles by using sodium borohydride represent in equation 2.6 [46].

$$Ag^+ + e^- \longrightarrow Ag^0 \qquad (2.5)$$

$$Ag^+ + BH^-_4 + 3H_2O \longrightarrow Ag^0 + B(OH)_3 + 3.5H_2 \qquad (2.6)$$

Generally, silver nanoparticles have an inclined behavior to agglomerate. Stabilizer is take advantage to control of the synthesis of nanosilver which stabilize particle growth, prevent agglomerate, aggregrate and losing surface properties of metal particles. The interesting reasonable is stabilized silver particles with polymer to form utilized the protective shell cover the particles for example poly(vinylpyrrolidone), poly(ethylene glycol), poly(vinyl alcohol), poly(methacrylic acid) and poly (4-styrenesulfonic acid-co-maleic acid). The polymer has long chains to incorporation onto nanoparticles at the end of chain polymer readily. If there is not enough stabilizer to cover the surface that result in interaction between the freedom of the polymers and particles decrease then finally effective of polymer to act as a stabilizer to cover the surface of particles decrease [47-48].

Organometallic reduction

Organometallic reduction method also use for silver nanoparticles synthesis with advantage of system is nontoxic, inexpensive and does not require external heating source. Previous reported of Fernandez and coworker were used $AgClO_4$ organometallic treated $NBu_4[Ag(C_6F_5)_2]$ complex to form nanoparticles $Ag(C_6F_5)$ precursor which is further converted to 10 nm silver nanoparticles [49]. These radicals reduce silver salts without use of external reducing or capping agents.

Ultra violet light reduction

Ultra violet light is well-known as reducing method for prepared metal ion particles. Source of ultra violet radiation using a mercury discharge lamp for expose the colloidal silver. The silver salt solution readily to interact with ultra violet radiation by using photosensitive agent which excited from absorption ultra violet radiation to generates silver radical. After that, the reduction of silver ion to silver particles forms with shape and size distribution in range 30-40 nm. The size of silver nanoparticles depends on power of laser which low laser powers at short irradiation times produced silver nanoparticles at approximately 20 nm. In addition, high irradiation power produce smaller nanoparticles at approximately 5 nm. The advantages of this procedure is simple, cost effective and avoid the chemical stress to the material. Disadvantage is high exposure time processing [50-51].

Microwave assisted synthesis

The size of silver particles from microwave assisted synthesis depends on the concentration of reducing and stabilizing agent such as carboxymethyl cellulose, poly N-vinylpyrrolidone, polyol, ethylene glycol, starch. The advantage of this method is nanoparticles were monodispersed silver nanoparticles and size-controll silver nanoparticles can be rapidly synthesis under microwave irradiation and nanoparticles stable for several months without any visible change [52], respectively. Size distribution of the silver nanoparticles production is strongly dependent on the states of silver cations in the initial reaction solution.

2.3.2 Silver nanoparticles properties and application

The utilizing of silver nanoparticles such as optical, conductivity and antimicrobial is interesting to incorporate into various application and technologies including consumer products. The silver nanoparticles are desirable for important application such as electrical and sensor, catalyst and antibacterial products.

Optical properties

The optical response of metal nanoparticles presence a strong absorption band which different from the spectrum of the bulk metal. The optical properties of silver nanoparticles are unique effect on extinction such as absorption and scattering light that widely use for analyte by localized surface plasmon resonance frequency (LSPR) (figure 2.9). The principle of localized surface plasmon resonance is based on measurement of small refractive index changing due to the oscillation of metal electron, for example gold, copper and silver. When exposed the radiation on silver that result in excite the electron to oscillate at the frequency of the occurrence irradiation. The localization of peak absorption depends on the particle size, shape and local external dielectric environment such as coating, polarization of surrounding medium and supporting substrate. The size and shape of particles are the important factor to determine the spectroscopic properties. The small metal particles and spherical shape are features to well define peak of the absorption spectra because of it exhibit a symmetry form. Moreover, the surface plasmon resonance does not respond to metallic smaller than 2 nanometer. This is due to the predominating quantum effect.

The appearance color of metal particles depends on dimension and shape of the particle which is different from any dye and pigment. Thus, the silver nanoparticles appearance yellow color characteristic localized surface plasmon resonance absorbance (LSPR) position a sharp peak at wavelength 400 nm [53-56].

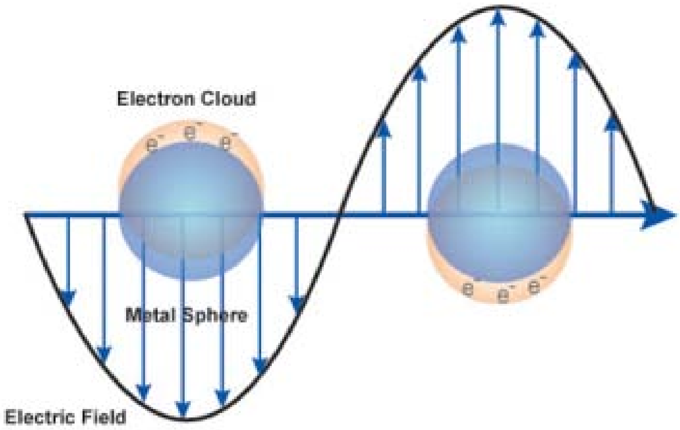


Figure 2.9 Surface plasmon resonance of metal particles [54].

Catalytic properties

The silver nanomaterial is interest for catalyst in the industrial production. The high surface area of silver nanoparticles provides a high surface energy which encourages surface reactivity to exhibit a good activity for catalytic application. For example silver nanoparticles and silver nanocomposites use as oxidation catalysts to catalyze ethylene oxididation, carbon monoxide oxidation, benzene oxidation and photodegradation of gaseous acetaldehyde. In addition, nanosilver use as nanocomposite or supporter catalyst such as silver immobilized on silica spheres to catalyze the reduction of dyes, catalyst supporter to accelerate the decomposition of nitroden dioxide. The silver nanoparticles catalyze the three-component coupling reaction of aldehyde, alkyne, and amine with high yield, save time of processing and materials.

Electronics and sensor

The properties of silver nanoparticles has a high electrical, high sensation and conductivity that interesting properties to development various electronics device such as single electron transistors, electrical connectors, nanowires, optoelectronics, subwavelength optics, active waveguides, micro interconnects, integrate circuits and integral capacitors in optical devices and sensors applications [57-58]. Silver inks are use for replace wires and act as flat wires in printed circuit boards. The advantage of silver inks are also use to repair circuit breaks in print circuit boards with highly density recording devices. Moreover silver nanomaterials use for intercalation materials of batteries and integral capacitors.

Antimicrobial properties

Silver nanoparticles are well known materials that have a higher antibacterial ability than other metals. In the past decade silver have a great purposed performance in antimicrobial agent that is toxic to many type of fungi, viruses and bacteria for example *Staphylococcus aureus, Bacillus cereus, Escherichia coli, Pseudomonas aeruginosa, Serratia marcescens, Aspergillusniger* and *Penicillium phoeniceum* and *Klebsiella pneumonia* [59-61]. Silver has long been use as a disinfectant to treat pots, spoon, bowl, vassel including wounds due to it has an amphiphilic hyperbranch macromolecules base on metallic ions bond on several macromolecular that exhibit killing the microbial cell.

The strong antimicrobial activity of silver nanoparticles is a reason for increasing the incorporated silver into many products in the present for use in widely range of manufacture consumer products for example personal and care, medical, cosmetic, wastewater treatment, textile and composite materials for antibacterial application [35, 62, 63].

In the present mechanisms of silver nanoparticles to effect on antimicrobial in many part way which proposed to described as follow:

1. Adherence of silver particles on surface of bacteria to change the membrane properties of it. Previous study have been report mode of action the silver nanoparticle to degrade lipopolysaccharide molecules via collect the nanoparticles to forming pits at internal membrane, resulting in to enhance permeability of liquid, nutrient and oxygen .

2. Silver nanoparticle penetrate to inside the bacterial cell that cause of DNA damage

3. Dissolution of silver releases silver ions (Ag^+) to act as antimicrobial describe in Figure 2.9. Nanosilver may dissociate to form silver ions able to interact with sulfydryl (-SH) groups of proteins within microorganisms of bacteria and possibly phospholipids associated with the proton pump of bacterial membranes hence inhibition of respiratory processes and DNA uncoil. This results in a collapse of the membrane causing a disruption of cellular metabolism and then silver nanoparticles have to be effective to inhibition of bacterial growth and they were eventually cell death.

Generally, physicochemical properties play an important role in the antimicrobial activity of silver. Espeacially, silver particle at the nanoscale provide a small size, high surface area and increase the surface reactivity that easily interact with other particles that results in enhance their antibacterial efficiency properties when compared with the bulk material. Previous study was demonstrated a relationship between size of silver nanoparticles and antibacterial properties. Xu and coworker were found the particle smaller than 10 nanometer was a great toxic to bacteria cell [64]. Furthermore, silver nanoparticles ranging from 1 to 10 nm exhibit an alternate favours the viruses cell binding to glycoproteins instead of binding to host cells. The smaller particles has a larger surface area which easily to reach in the nuclear content of bacteria. Hence, this was proved the silver in the nanoscale more efficient in the antibacterial against.

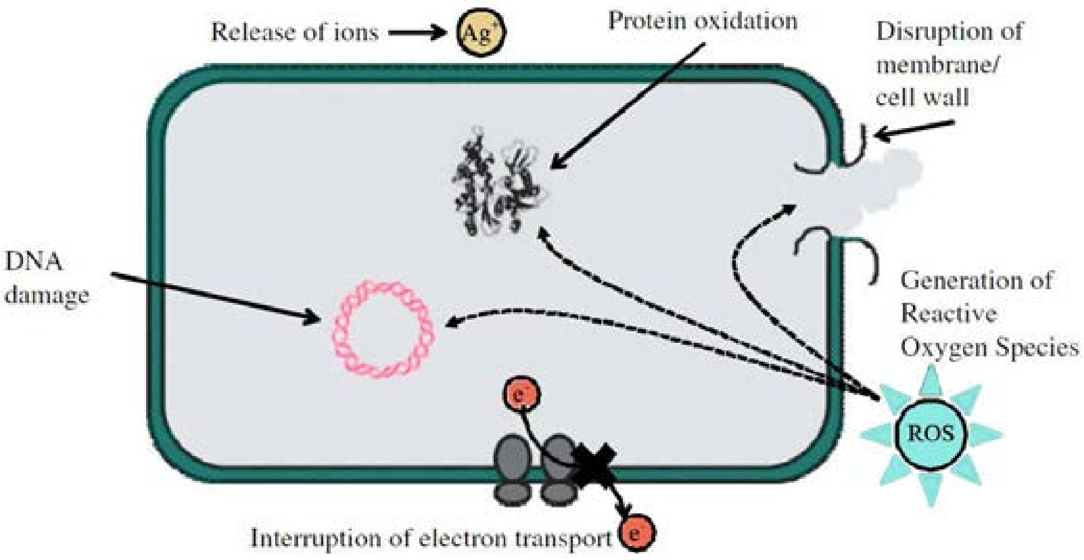


Figure 2.10 Mechanism of silver nanoparticles act as antimicrobial activity (Method 3) [60]

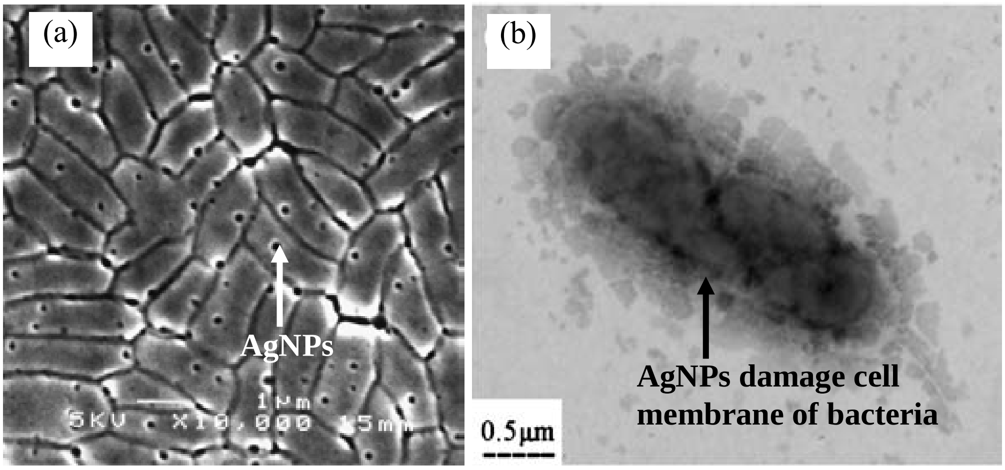


Figure 2.11 SEM image of damage *E. coli* cells treated with silver nanoparticles , TEM image of E.coli cells treated with silver nanoparticles 50 µg/ml [59].

2.3.3 Other Industrial Applications

Silver nanoparticles utilize in the specified industrial process. Nanosilver use as based paper against the proliferation of bacteria in hospital. In addition, the antibacterial properties of nanosilver encourage for many application such as commercial water purification systems, sanitary tubing and interior of automobiles.

Silver nanoparticles also use for wood preservation to resist mildew and mold. Silver nanoparticles combine with titanium dioxide in spraying product to enhance facilities in the office. The nanosilver proposes for future applications including business stationery, envelopes, brochures and other materials.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals and Materials

Nylon-6 pellets $(C_6H_{11}NO)_n$, Mw 22,000) were used to prepare polymer solution for electrospinning process. Poly(diallyldimethylammoniumchloride) (PDADMAC, 20wt% in water $(C_8H_{16}ClN)_n$, Mw 200,000–350,000), poly(4-styrenesulfonic acid), (PSS, $C_8H_7NaO_3S)_n$, Mw 70,000) and poly (4-styrenesulfonic acid-co-maleic acid) (PSS-co-MA, $(C_{12}H_{10}Na_2O_7S)_n$, Mw 200,000) were purchased from Sigma Aldrich, USA, and to be used for thin film construction by layer-by-layer technique.

Sodium hydroxide (NaOH, Mw 39.99) and sodium chloride (NaCl, Mw 58.44) were purchased from Carlo Erba, Italy. Silver nitrate ($AgNO_3$, Mw 169.87) (Merck KGaA, Germany). Sodium borohydride ($NaBH_4$, Mw 37.83) (Labchem, Australia). Crystal violet ($C_{25}N_3H_{30}Cl$, Mw 407.9 g/mol) cationic dye and erythrosine ($C_{20}H_6I_4O_5Na_2$, Mw 879.9) anionic dye were supplied from Sigma Aldrich, USA. Formic acid 99 vol% ((CH_2O_2), Mw 46.03) and nitric acid 65% (HNO_3, Mw 63.01) was purchased from Carlo Erba, Italy. All chemicals and materials were used as received without further purification or modification.

3.2 Preparation of solutions

3.2.1 Preparation of 24 wt% nylon-6 solution

An appropriate amount of nylon-6 was dissolved in formic acid 99% 10 ml to obtain homogeneous solution with concentration 24 wt% for prepared the electrospun nylon-6 fibers.

3.2.2 Preparation of poly(diallyldimethylammoniumchloride), PDADMAC solution

PDADMAC was used as positively charged polyelectrolyte. A solution of PDADMAC was dissolved in double deionized water to obtained 10 mM of stock solution. The solution ionic strength was adjusted with sodium chloride at concentration of 1 M. After that the PDADMAC stock solution was diluted in range of 0.1-10 mM for testing.

3.2.3 Preparation of poly (4-styrenesulfonic acid) sodium salt, (PSS) solution

The anionic stock solution of PSS at concentration 10 mM in double deionized water was prepared. The ionic strength of the solution was adjusted with sodium chloride at concentration 1 M. Finally dilute the PSS stock solution to appreciate concentration in range 0.1-10 mM for testing.

3.2.4 Synthesis of silver nanoparticles

The synthesis of silver nanoparticles was carried out by dissolving 1 mM of silver nitrate in distillation water. Sodium borohydride solution with concentration of 5 mM was used as reducing agent for stabilized the particles. The anionic PSS-co-MA acted as a capping agent was mixed with varied concentration 0.005, 0.01, 0.05, 0.1 and 0.5 mM for remain the particles stable in several months.

3.3 Nylon-6 fibers preparation by electrospinning process

Non-woven nylon-6 nanofibers were prepared via electrospinning process (figure 3.1). In short, appropriate amount of nylon-6 solution was filled in a plastic syringe, which placed in a syringe pump to regulate solution flow rate. The syringe was equipped with a blunt needle tips, which acted as a spinnerette. A high voltage power supply was used to establish electrical potential different between the spinnerette and fibers collecting plate made of an aluminium sheet. All fibers were prepared under a fixed potential different of 25 kV with 10 cm collecting distance at 0.2 mL/h solution flow rate .

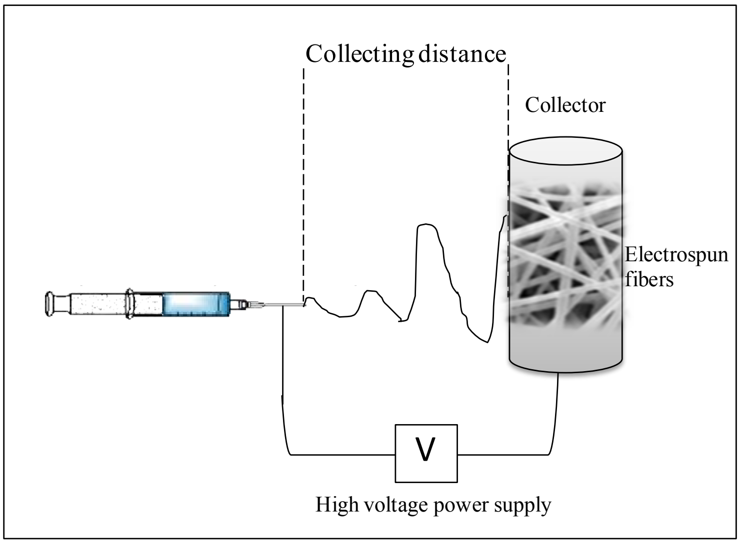


Figure 3.1 Schematic of electrospinning setup.

3.4 NaOH treatment of nylon-6 electrospun fibers mat

In order to determine a suitable alkali treatment condition for the nylon-6 electrospun fiber mats, as prepared mats were immersed in NaOH solutions with concentration 0.1 to 10 M for 5 to 90 minutes. The treated fiber mats were then rinsed in distilled water for 3 times to get rid of NaOH and air dried for 24 hours prior to further characterization to determine optimized treating condition for subsequent experiment.

3.5 Surface modification of fibers by layer-by-layer technique

Surface of NaOH treated and as prepared fiber mats were modified with polyelectrolyte multilayers thin film consisted of alternating layers of cationic polyelectrolyte, PDADMAC and anionic polyelectrolyte, PSS. The films were constructed via layer-by-layer deposition method. To determine optimized LbL processing condition, i.e. polyelectrolyte concentration, deposition time and number of film layers. The fiber mats were alternately immersed into a PDADMAC and PSS solution bath of various concentration (0.1 to 10 mM) under various deposition time (5 to 90 minutes). After each round of polyelectrolyte deposition, excess solution on the fiber mats was washed out by dipping in a double distilled water for 5 minutes. Fiber mats of subsequent experiment were modified with LbL films using the optimized LbL process parameters (figure 3.2).

3.6 Immobilization of Silver nanoparticles on layer-by-layer modified nylon-6 nanofibers

The concept of silver nanoparticles embedding on electrospun nanofiber mats was illustrated in figure 3.3. Briefly, the electrospun fiber mats, with the size approximately 5 by 5 cm, were placed on a wire frame and dipped into mixtures of silver nitrate solution and PSS-co-MA, which used as a capping agent to prevent agglomeration of silver nanoparticles. Mixing ratio between silver ions and PSS-co-MA was varied from 1:0.005, 1:001, 1:0.05, 1:0.01, 1:0.5 mM. Embedding time was varied from 5 minutes to 24 hours. After silver nanoparticles functionalization, the mats were air dried and stored in plastic bags at room temperature for further testings.

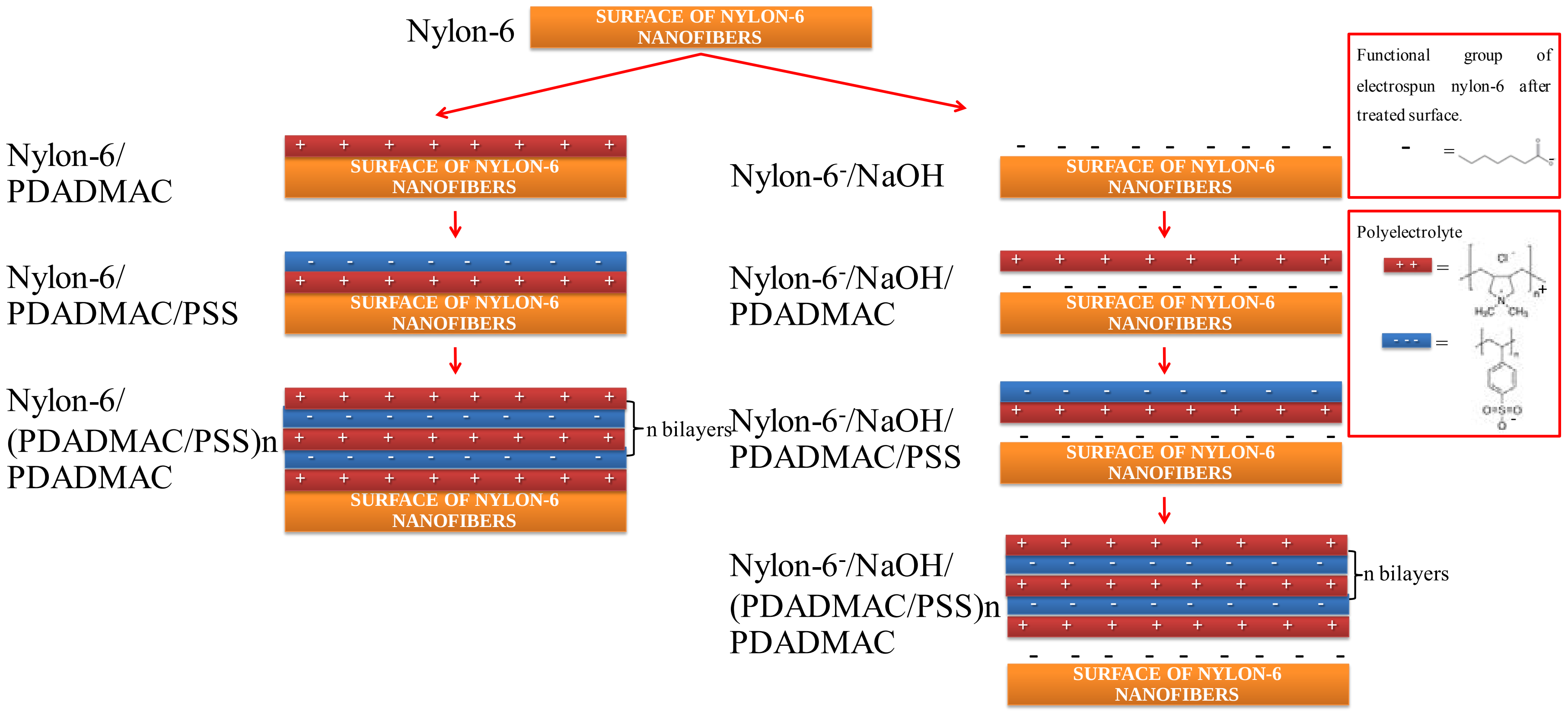


Figure 3.2 Step of surface modification of nylon-6 electrospun nanofibers via layer-by-layer technique

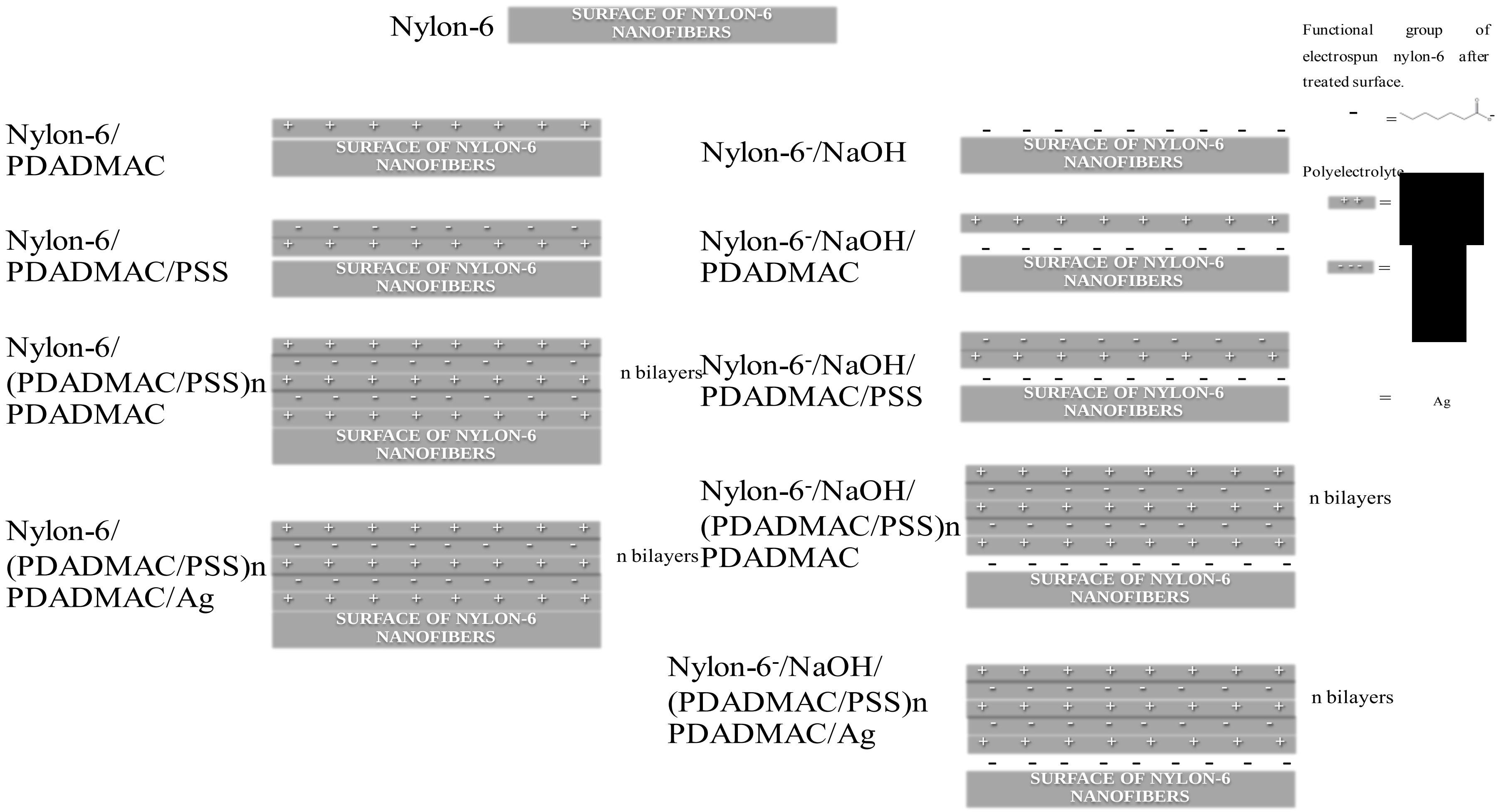


Figure 3.3 Step of immobilization of silver nanoparticles modified nylon-6 nanofibers via layer-by-layer assembly.

3.7 Characterization

3.7.1 Chemical properties

3.7.1.1 Ultraviolet-Visible (UV–vis) Spectroscopy

A quantitative value for color adsorption on electrospun nylon-6 nanofibers were carried out on a Perkin Elmer Lambda 800 UV-visible spectrophotometer. Crystal violet was used as cationic dye for testing negative charge on surface of electrospun (NaOH, PSS) and erythrosine used as anionic dye for testing cationic charge of PDADMAC on electrospun. The dyes were dissolved in double distillation water at concentration 40 μM heated 60 ^{o}C. The amount of crystal violet and erythrosine absorbed on surface of electrospun nylon-6 were determined by UV–vis spectroscopy at wavelength 585 nm and 525 nm, respectively.

3.7.1.2 Fourier-Transformed Infared Spectra (FT-IR)

The Functionalities of electrospun nylon-6 nanofibers improvement surface with PDADMAC and PSS film were characterized by Perkin-Elmer attenuated total reflectance Fourier transform infrared (Perkin-Elmer ATR-FTIR) use for investigated functionalities of sample were scanned over a wavenumber range of 400–4000 cm^{-1} at resolution of 4 cm^{-1}.

3.7.1.3 Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES)

Qualitative of silver in solutions were measured by using Inductively Coupled Plasma-Optical Emission Spectrometer (Thermo Scientific, ICAP 6500 ICP-OES). Electrospun electrospun nylon-6 fiber mats were dissolved in concentrated nitric acid 96 % for 48 h, and serial dilutions of the acidified samples were evaluated Inductively coupled plasma

3.7.2 Morphology

3.7.2.1 Color scanning and image analysis

Uniformity and extent of charge induction on the surface of fiber mats, obtained from NaOH treatment and LbL surface modification process, were followed indirectly by dyeing the mats with a dye with opposite charge and, then, analyzed using a color scanner and a simple image analysis protocol. Briefly, an image of dried fiber mat was captured using Epson Me 340 series photo scanner under following scanning parameters, i.e. professional mode, 24 bit color image type, 300 dpi resolution and JPEG image format. The relative intensity of RGB components of the obtained image was then determined.

Accordingly, the relative intensity of RGB component in a scanned image could define as the chromaticity level [1]. The percent of red chromaticity level (% r) and percent of blue chromaticity level (% b) is average red and blue chromaticity level of all pixels respectively can be calculated as

$$\% r = \left(\frac{R}{R+G+B}\right) \times 100 \quad \text{———} \quad (1) \qquad \% b = \left(\frac{B}{R+G+B}\right) \times 100 \quad \text{———} \quad (2)$$

where :

R, G and B are the average red, green, blue chromaticity level of all pixels, respectively.

3.7.2.2 Scanning Electron Microscope (SEM)

The size and morphology of uncoated and coated electrospun nylon-6 fibrous membranes with polyelectrolyte PDADMAC and PSS were examined by scanning electron microscopy (SEM, JEOL, JSM-5800LV).

3.7.2.3 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDX)

The qualitative silver composition embedded on the LbL-coated electrospun nylon-6 membranes was characterized by EDAX (SEM, JEOL, JSM-5800LV).

3.7.2.4 Transmission Electron Microscope (TEM)

Particles size and distribution of silver nanoparticles deposited on surface of electrospun nylon-6 and electrospun nylon-6 fibrous membranes treated surface with NaOH were observed with transmission electron microscope (TEM, TECNAI 20 TWIN).

3.7.3 Physical properties

3.7.3.1 Mechanical properties

The mechanical properties of the electrospun nylon-6 nanofibers, layer-by-layer coated electrospun treated surface with NaOH and untreated surface of electrospun were used universal testing machine (UTM; COMPECH, QC 508-BZ) determined. Five of specimens were tested at room temperature which prepared in a standard dumbbell shape according to ASTM D 638, crosshead speed of 10 mm/min with a 50 N load cell.

3.7.3.2 Contact angle measurement

Surface thermodynamic properties of electrospun nylon-6 nanofibers, electrospun treated surface with NaOH before and after surface improvement with PDADMAC and PSS were characterized by standard contact angle goniometer with drop instrument (OCA 150 plus, TECHNAI). Sample tested for five droplets of water on newly prepared surface.

3.7.4 Antibacterial testing

The antibacterial behavior of silver nanoparticles immobilized on electrospun were evaluated against *Escherichia coli* (*E. coli,* Gram-negative bacterium) and *Staphylococcus aureus* (*S. aureaus*, Gram-positive bacterium). Nylon fiber mats was cut the circular in diameter 3.8 cm for antibacterial testing.

3.7.4.1 Percentage reduction of bacteria

The antibacterial properties of nylon-6 nanofiber mats embeded silver nanoparticles on surface according to a modified AATCC 100 test method. The sample was replaced in flask containing 0.5 ml of bacteria (approximately 10^5 Colony forming Units). After 1 hours shaking, 1 ml of the bacteria mixture was diluted with deionized water. The dilute solution 0.1 ml was placed onto a solid agar using the spread plate method. After incubated at $37^{o}C$ for 24 hours, the number of viable bacteria was counted. The results corrected with the dilution factor and expressed as number of colony forming unit (CFU) per milliliter. The percent reduction of bacteria evaluate by the following.

$$R = \frac{(C - A)}{C} \times 100$$

where:

R = Reduction percentage

A = The number of bacteria recovered from the inoculated treated test specimen swatches in the jar incubated over the desired contact period.

C = The number of bacteria recovered from the inoculated untreated control specimen swatches in the jar immediately after inoculation (at “24 hours” contact time).

3.7.4.2 Zone of inhibition

The electrospun nylon-6 nanofibers modified surfaces with silver nanoparticles were prepared in size diameter 3.8 centimeter to examined against the bacteria cell. The electrospun nanofibers mats were tested on nutrient agar plates, which were inoculated with *Escherichia coli* (*E. coli*) and Staphylococcus aureus (S. aureus) as the intended test bacteria. An antimicrobial efficiency of the mat was then recognized with the zone on the nutrient agar plate in contact on the sample (contact zone) was free of bacteria. If necessary, additionally a bacterial free zone (inhibition zone) was formed at the edge of the fiber mats. The antimicrobial efficiency evaluated by measure the radius of vacancy the sample. If there would be no growth of the bacteria that could obtain clear zone on the dish specimens.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Electrospun nylon-6 nanofibers properties

4.1.1 Morphology of electrospun nylon-6 nanofibers

The electrospun nylon-6 fibers, which prepared from 24 wt% of nylon-6 solution in 99%vol formic acid, were generated using 25 kV of applied voltage, a flow rate of 0.2 ml/h and a collecting distance of 10 cm. The morphology of fibers was observed under scanning electron microscope (SEM) and transmission electron microscope (TEM). The surface of nylon-6 fibers was uniform and smooth along the fibers electrospun (Figure 4.1).

The average fiber size and fiber size distribution were obtained from SEM micrograph analysis. The average fiber size for each sample was calculated from the size at least 50 individual fibers segment. Under specified processing condition, the average fiber size was 163±19 nm, with fiber segment size ranging from 125 to 225 nm (Appendix A).

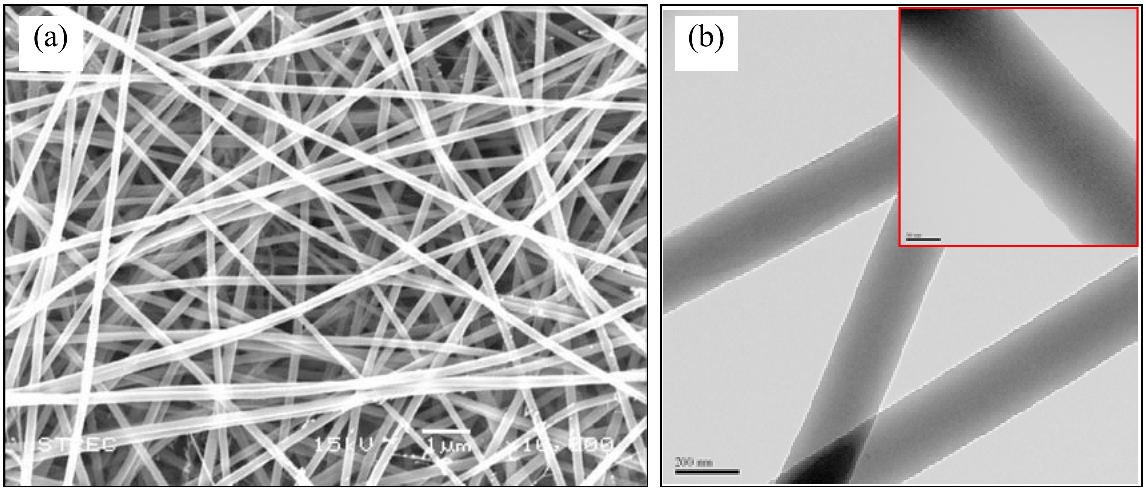


Figure 4.1 Morphology of nylon-6 electrospun nanofibers were examined by (a) SEM and (b) TEM micrographs.

4.1.2 Surface thermodynamic properties

Table 4.1 showed the water contact angle value of the as spun-nylon-6 nanofiber, which has the average contact angle about 120.6±1.5°.

Table 4.1 Illustrate contact angle of electrospun nylon-6 fibers

No	Contact angle (°)
1	119.0
2	119.4
3	122.6
4	122.0
5	120.1
Average	120.6 ± 1.5

The results suggested that the as-spun fiber mat had poor wettability, which might arise from the curvature of the nanofiber. In order to embed silver nanoparticles on electrospun surface with hydrophilic properties, it was necessary to impart hydrophilic structure and wettability of nylon-6 fibers by suitable surface modification technique. In this study, a multilayers assemble of polyelectrolyte thin films was used because of its simplicity, low cost and effectiveness.

The polyelectrolyte had the moisture absorbed character cause hydrophilic properties on surface substrate. Especially, strong polyelectrolyte such as poly(diallyldimethylammonium), (PDADMAC) and poly(4-styrenesulfonic acid), (PSS) generated a lot of charge and counter ion thin film. Therefore, in this research was used polycation PDADMAC and polyanion PSS modified surface of nylon-6 electrospun to generate hydrophilicity of fibers.

4.2 Layer-by-layer thin film formation

The properties of nylon-6 fiber mats showed hydrophobic properties resulted in low dye absorption on the fiber surface. To improve their hydrophilicity, the layer-by-layer thin film technique was used to modify the surface of the mats.

Generally, film formation mechanism in layer-by-layer method relied on electrostatic interaction between the substrate-polyelectrolyte and polycation-polyanion of polyelectrolyte. Based on chemical structure, nylon-6 can be considered no surface charges to interact with polyelectrolyte. To induce surface charges on the fiber, the mats were treated with alkaline and solvents hydrolysis. Hydrolysis reaction of sodium hydroxide (NaOH) [19] on amide group caused a chain scission at –CONH– position and generated a negative charge of –COO$^-$ group (Figure 4.2). These anionic charges provide anchoring point for positively charged poly(diallyldimethylammonium), (PDADMAC) to interact via electrostatic attraction, resulting in enhanced deposition of PDADMAC on the fiber mats. PDADMAC layer, in turn, interacted strongly with negatively charged poly(4-styrenesulfonic acid), (PSS).

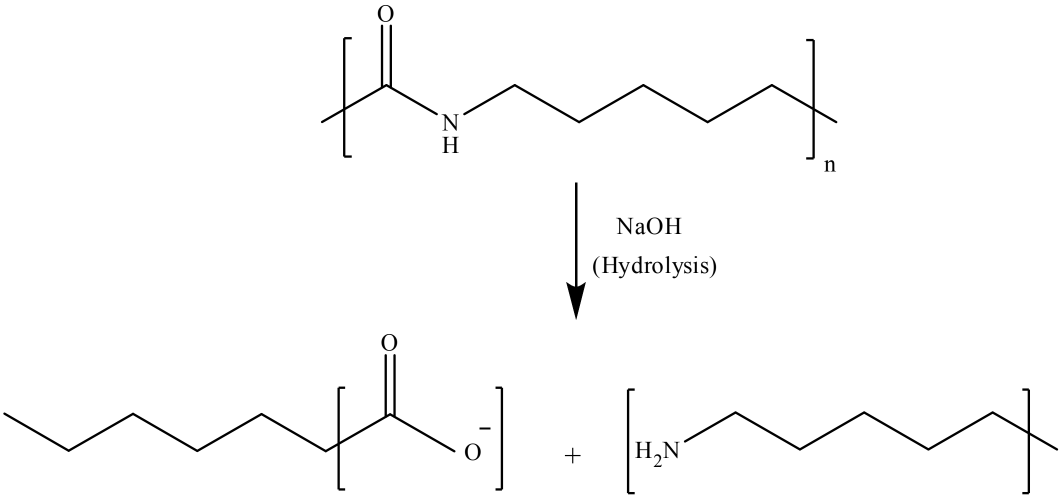


Figure 4.2 Hydrolysis reaction on surface of electrospun nylon-6 fibers.

In this section, preparation of polyelectrolyte poly(diallyldimethylammonium) (PDADMAC) and poly(4-styrenesulfonic acid) (PSS) assemble on nylon-6 fibrous substrate via layer-by-layer technique. The parameter of layer-by-layer deposition that effect on thin film formation such as concentration of polyelectrolyte, deposition time and number of bilayer thin film are reported.

4.2.1 Ultraviolet-visible (UV–vis) spectroscopy and image analysis.

For the most applications, thickness and uniformity of LbL film deposited on the substrate is crucial for homogeneous property of final product. While there are several techniques that can be used to follow the progress of LbL film formation and thickness of the film such as elipsometry, atomic force microscopy, these techniques often require an expensive instrument, are fairly difficult to perform for novice user and usually take a measurement of a very local space of the substrate.

In this study, we have developed an indirect method to track down LbL film formation and uniformity of the film using either a simple UV-Vis spectrophotometer or a regular photoscanner. The concept of the method is based on the absorption of a dye, containing charges with opposite polarity onto the substrate surface. Crystal violet and erythrosine dye, cationic and anionic dye respectively, were used as an absorption marker in the study. The chemical structures of both colorants were represented in figure 4.3.

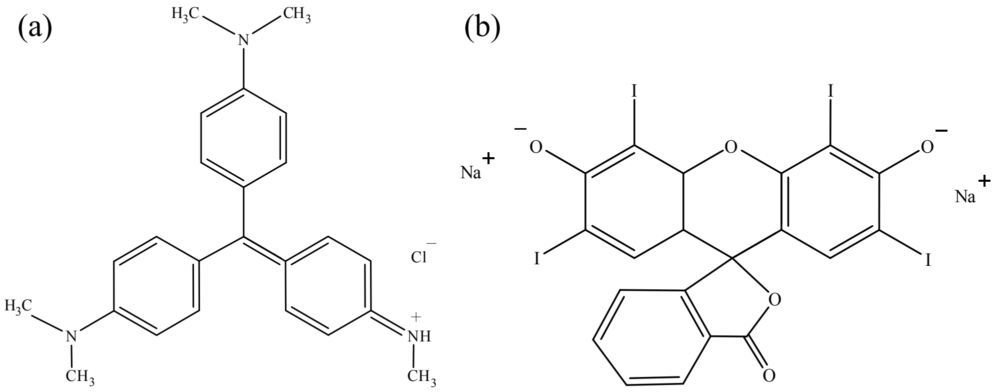


Figure 4.3 Chemical structures of (a) crystal violet and (b) erythrosine.

UV-visible spectroscopy and image analysis were interest for investigated the effect of concentration and contact time of polyelectrolyte PDADMAC and PSS on surface electrospun nylon-6.

The UV-Vis spectrum or the color of the sample with adsorbed dye was measured and compare to a calibration curve that had been correlate with other direct measurement of film thickness. While the method developed here is not suitable to measure exact thickness of the film as those methods mentioned previously, it is simple to do and does not required expensive equipment. Moreover, its measurement area is much larger than other techniques, and thus, it can be used to measure the property of the substrate in global scale.

The adsorption intensity of crystal violet and erythrosine were measured by UV-Visible spectroscopy at wavelength 585 nm and 525 nm (Figure 4.4), respectively. A linear calibration curve obtained from absorption of dye solutions with difference concentrations was shown in Fig. 4.4-4.5. The precision of calibration UV measurement were expressed as a correlation coefficient R-squared (R^2) closer to 1.00 ($R^2 > 0.98$).

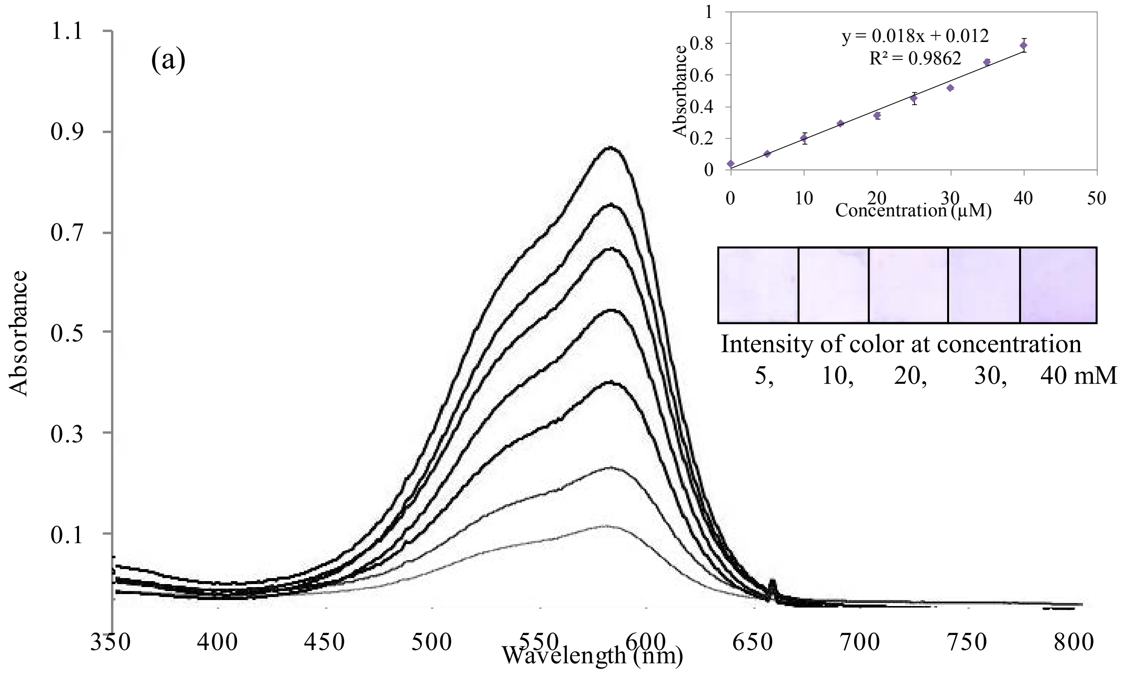


Figure 4.4 Absorption spectra and calibration curve of crystal violet.

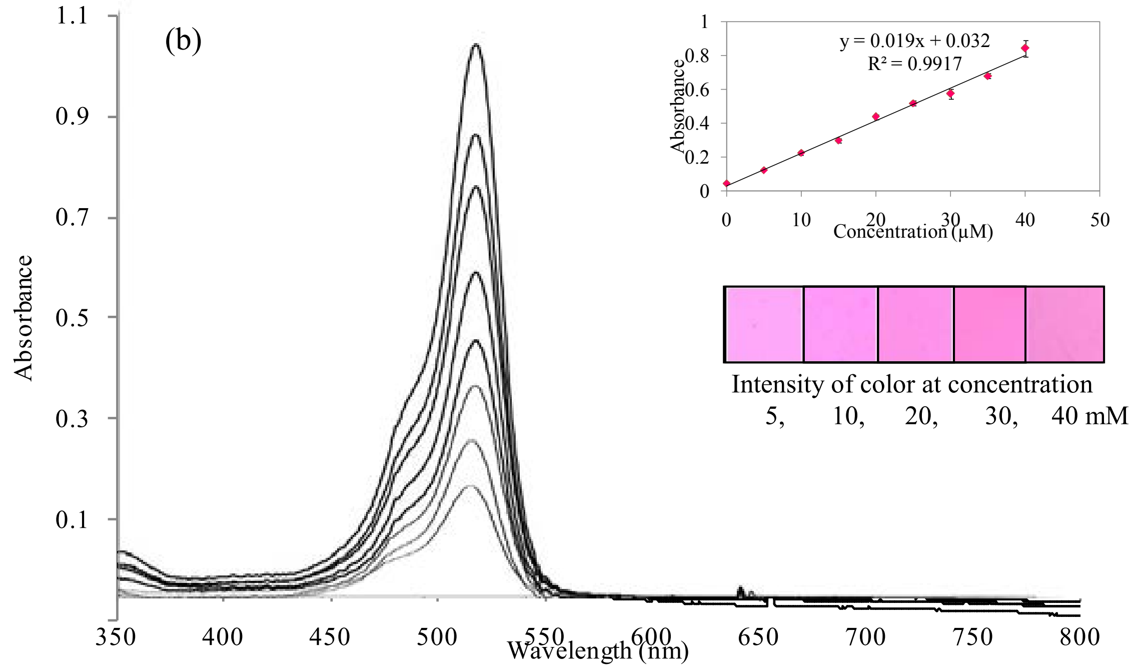


Figure 4.5 Absorption spectra and calibration curve of erythrosine.

Determination of dye adsorption ability on fiber surface was investigated from the absorbance values of crystal violet and erythrosine. The absorption ability appearanceed as a function of concentration and deposition time of NaOH, PDADMAC and PSS layers. Similarly, the digital image analysis represented color adsorption ability on surface of electrospun. The results were also tendency as results of UV absorbance.

First step, pre-treatment surface of electrospun nylon-6 in NaOH solution and then deposited of polycation poly(diallyldimethylammoniumchloride) as a primer on electrospun nylon-6 substrate via the layer-by-layer process.

The results of UV measurements showed progressive relation graph (Figure 4.6) among concentration of crystal violet and concentration, dipping time of NaOH treated surface of electrospun. Absorption ability of crystal violet on electrospun could observe by image analysis, which same trend of results from UV measurement. The appreciate concentration was obtained at concentration 1 M 25 minutes that expected surface of electrospun nylon-6 could coverage with NaOH completely.

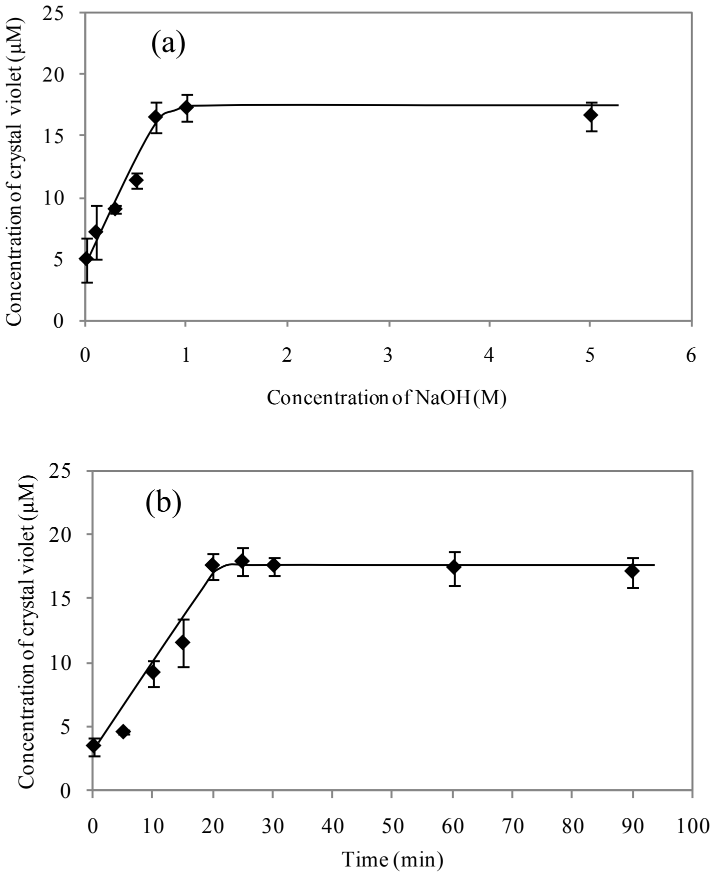


Figure 4.6 The effects of NaOH treated on electrospun nylon 6 and color absorption ability on nylon-6 electrospun nanofibers (a) effect of concentration and (b) effect of dipping time of NaOH solution.

The effect of PDADMAC modified surface of electrospun nylon-6 was investigated from erythrosine adsorption. From digital image analysis, the initial adsorption of erythrosine color on untreated electrospun nylon-6 was represented percentage of color intensity about 37.90±0.65%. Finally, color adsorption ability reach to stable at concentration of PDADMAC 5 mM with percentage of red about 41.91±0.10%. From these results, the percentage of red on fibers mat treated with NaOH was presented the stable concentration of PDADMAC adsorbed lower than as-spun fibers. (40.54±0.06% at concentration of PDADMAC 1 mM). Because surface of electrospun appearance negative charge from $-COO^-$ group which enhanced the interaction of positive charge of polyelectrolyte PDADMAC on negative charge of substrate.

From Table 4.2 represents the concentration of erythrosine adsorbed on electrospun. The effect of concentration represented different behavior among first and second slope. The first slope, NaOH treated surface of electrospun enhance the concentration of erythrosine rapidly. This was due to surface of electrospun represented the negative charge via removed hydrogen to form carboxyl group of nylon-6 (Figure. 4.3). The results in enhanced electrostatic interaction among a positive charge of polymer chain and negative charge of treated surface nylon-6. The second slope gradually increased and finally, it was become to stable, caused layer of PDADMAC and PSS surface coverage completely (concentration 1 mM).

The effects of deposited time of PDADMAC and PSS on electrospun were investigated. Electrospun nylon-6 treated and untreated surface with NaOH were dipped in the polycation polyelectrolyte (PDADMAC) for appropriate time ranging from 5 to 90 minutes. Table 4.2 demonstrated dipped times as short as 10 minutes for NaOH treated surface system was sufficient to obtain maximum deposition of the polyelectrolyte film.

Moreover, increased in dipped time did not improve the erythrosine and crystal violet adsorbed on sample because the deposition process was completed. The color adsorption ability on electrospun nylon-6 with varied deposition time of PDADMAC and PSS determined from digital image analysis. The appreciate condition determined from digital image analysis was obtained as the same trend from UV absorption data. The stable color adsorbed on NaOH treated surface of electrospun was remain at 10 minutes with the percentage of red about 41.28±0.06 % and percentage of blue was 44.37±0.07%, respectively.

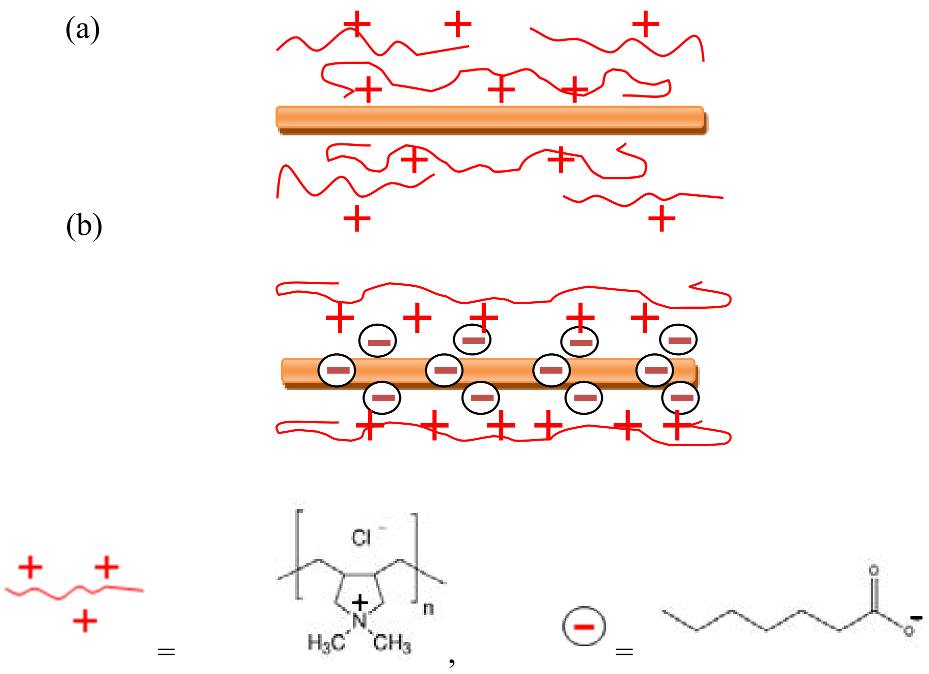
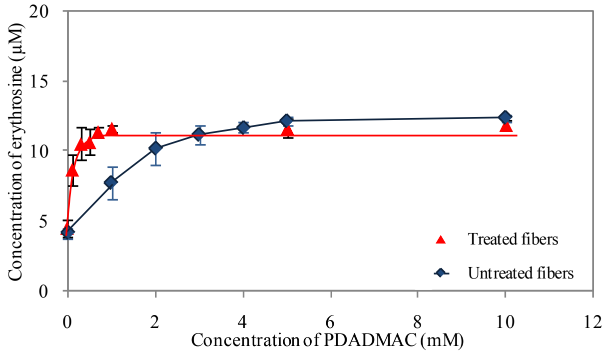
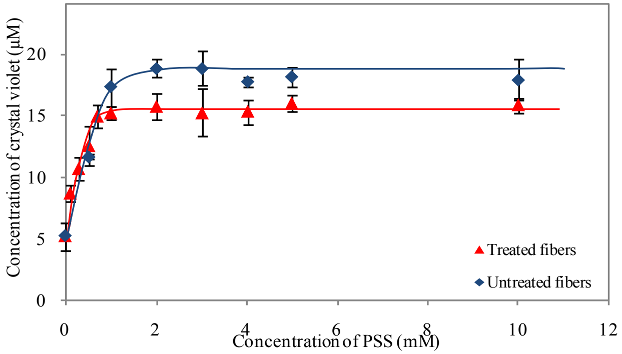
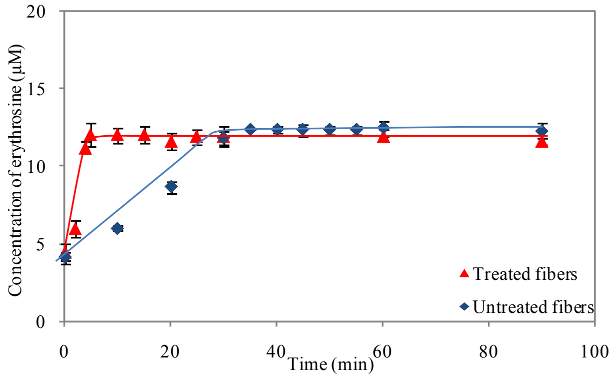
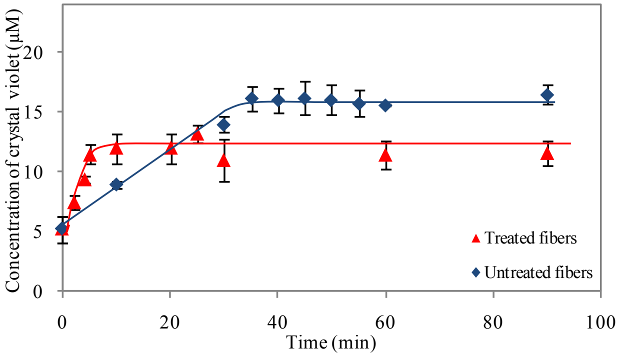


Figure 4.7 Comparison of polyelectrolyte chain assembly on surface electrospun nylon-6 fibers (a) untreated surface and (b) treated surface with NaOH solution.

Table 4.2 Representative of color absorption ability on nylon-6 electrospun measurement by UV-vis spectrometry and image analysis. The effect of concentration and deposition time for polyelectrolyte coated on electrospun nylon 6 fibers treated and untreated surface with NaOH.

Effect	Polyelectrolyte	
	PDADMAC	PSS
Concentration		
Kinetic		

Comparison NaOH treatment surface of electrospun with pristine fibers that observed the concentration and time for use polyelectrolyte was lower than untreatment surface. This suggested surface of electrospun nylon-6 had a negative charge from NaOH hydrolysis reaction. Results in polyelectrolyte formed electrostatic attraction quickly diffused to coverage the treated surface. Whereas the color adsorption on untreated surface was slightly increased as a function of concentration and kinetic. Because the surface of electrospun nylon-6 did not sufficient charge to interact with polyelectrolyte. Therefore, pre-treated surface of substrate was an important step for modification of surface substrate, which enhanced polyelectrolyte adsorption ability.

4.2.2 Fourier-transformed Infared Spectra (FT-IR)

FT-IR spectra provided evidence the layer-by-layer deposition of PDADMAC and PSS films on electrospun nylon-6. From Figure 4.8 indicated the intensities of polyamide characteristic of the stretching vibration C=O at 1640 cm^{-1} region. Absorption intensity at 3298 and 1539 cm^{-1} were represented the N-H stretching and vibration in the amine group respectively. The absorption band around the 2850-2930 cm^{-1} region was characteristic of C-H stretching of an alkyl group in nylon-6 and PDADMAC. The spectra (Figure 4.8) showed a broad band around 3200-3500 cm^{-1}. These exhibited $-COO^-$ vibration on surface of electrospun nylon-6 due to the interaction of NaOH hydrolysis reaction to form carboxylate ion. Absorption intensity peaks confirmed the layer-by-layer growth. The attributed peak of the ring vibrational of SO_3^{2-} group of PSS represented at 1189 and 1032 cm^{-1}. An identical of FT-IR spectra characteristic to the functional groups of PDADMAC and PSS were adsorbed on nylon-6 electrospun nanofibers successfully.

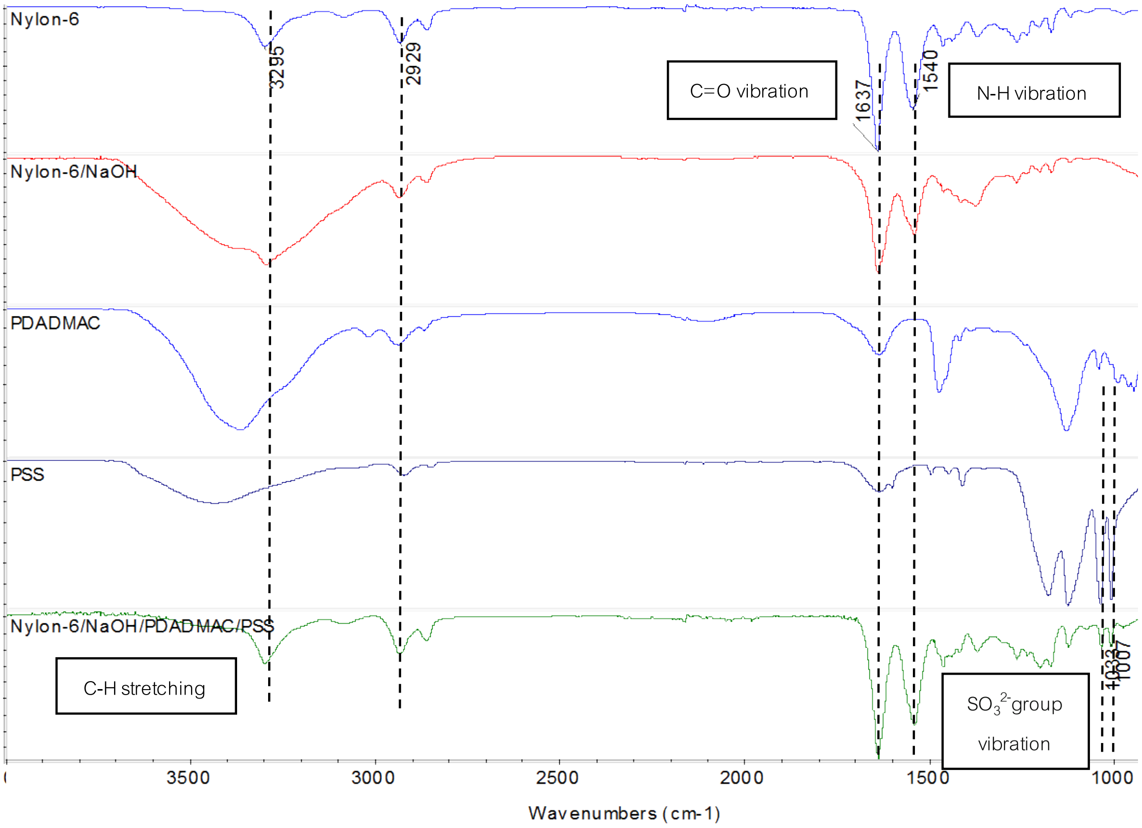


Figure 4.8 FT-IR spectrum of surface modification of electrospun with polyelectrolyte.

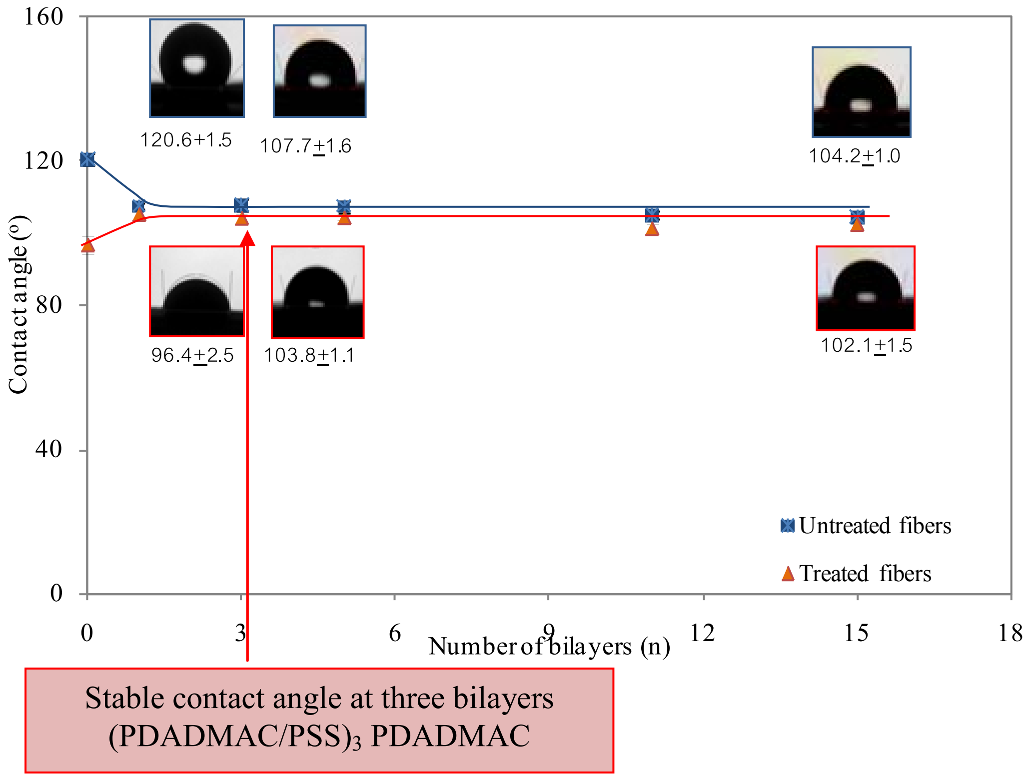
4.2.3 Surface thermodynamic properties

The surface of electrospun nylon-6 represented hydrophobic structure with highly water contact angle about 120.6±1.5° (Table 4.3). The polyelectrolyte thin film assemble on the electrospun nylon-6 substrates could generate the charge on substrate. This results in imparted a hydrophilic surface (Figure 4.9). Table 4.3 showed the value of water contact angle of polyelectrolyte PDADMAC and PSS coated fibers from one up to fifteen bilayers. All of bilayers polyelelctrolyte PDADMAC and PSS showed higher hydrophilic surface than nylon-6 fibers. Becuase the characteristic of polyelectrolyte had a high charge density, hydrophilic properties and high moisture absorption.

NaOH treated surface of as-spun fibers represented lower contact angle than nylon-6 fibers (96.4±2.5°). The NaOH hydrolysis reaction induced the chain scission of polyamide in nylon-6 structure to form –COO$^-$ group which enhance the hydrophilic properties on surface of nylon-6. And then alternative deposited of PDADMAC and PSS on surface of electrospun treated with NaOH. The results indicated the contact angle increased from 96.4±2.5° to 102.1±1.5 ° when increased the number of film deposited. The contact angles occur was due to –COO$^-$ group of surface treated with NaOH represented more polar than PDADMAC and PSS structure.

Table 4.3 The water contact angle of surface electrospun nylon-6 fibers modified surface with varied number of PDADMAC and PSS bilayers (Nylon-6/(PDADMAC/PSS)$_n$)

Number of bilayers (n)	Water contact angle (degree) of Nylon-6/(PDADMAC/PSS)$_n$	Water contact angle (degree) of Nylon-6/NaOH/(PDADMAC/PSS)$_n$
-	120.6±1.5	96.4±2.5
1	107.4±0.8	104.9±1.5
3	107.7±1.6	103.8±1.1
5	107.5±1.6	104.0±0.8
11	105.1±1.1	101.0±1.1
15	104.2±1.0	102.1±1.5



Stable contact angle at three bilayers (PDADMAC/PSS)$_3$ PDADMAC

Figure 4.9 Effect of PDADMAC/PSS bilayers numbers on contact angle for pristine and NaOH treated nylon-6 fiber.

Contact angle analysis represented wettability of PDADMAC and PSS bilayers coated fabric depend on the number of polyelectrolyte. After three LbL bilayers deposition, the contact angle of both NaOH treated and as-spun fiber mat became stable at approximately 104-107^{o} with no significant changes (*p-value*<0.05). The number of bilayers deposition increased did not change hydrophilicity of the mats. Therefore, it was concluded that coating with three bilayers of PDADMAC and PSS was sufficient for wettability improvement of the mats.

4.2.4 Morphology of film formation on electrospun fiber mats

From TEM image was described the morphology of surface electrospun nylon-6 and treated electrospun with NaOH solution. The surface of electrospun nylon-6 fibers were uniform and smooth like surface treated with NaOH. However, the surface of electrospun nylon-6 modified with polyelectrolyte observed roughness surface. Because of the layer-by-layer assemble involved polyelectrolyte PDADMAC and PSS adsorption on electrospun nylon-6 substrate to construct the ultrathin coatings (figure 4.10).

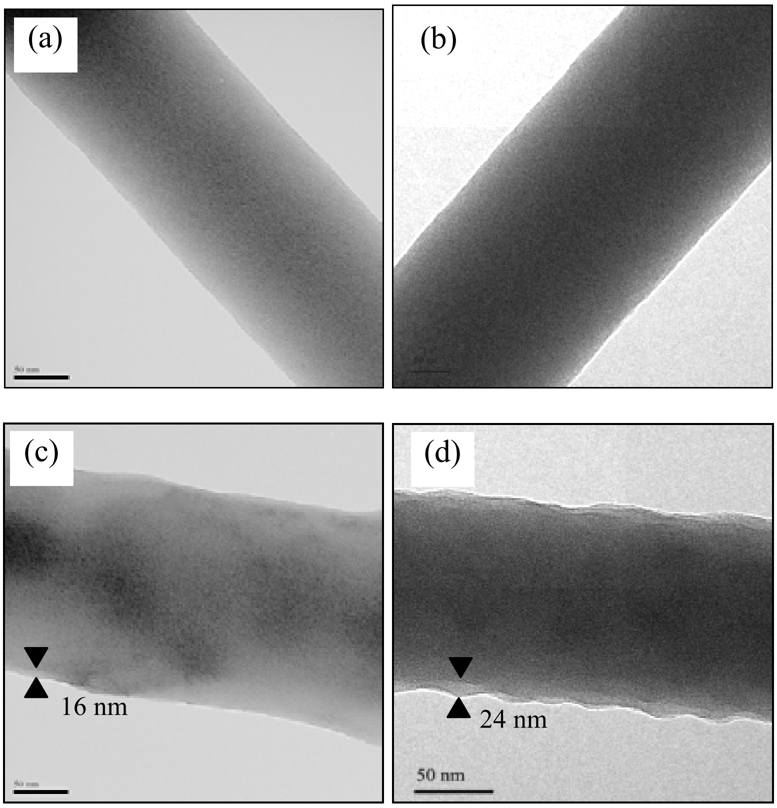


Figure 4.10 TEM image of (a) electrospun nylon-6 fibers, (b) Nylon-6/NaOH, (c) Nylon-6/ (PDADMAC/PSS)$_3$ and (d) Nylon-6/NaOH/(PDADMAC/PSS)$_3$

Morphology and diameter of electrospun nylon-6 investigated from SEM image (Figure 4.11). The relative of fibers diameter and number bilayers appearanced the fibers diameter of pristine fibers with coated nylon-6 fibers from 1 bilayers to 15 bilayers slightly increasing from 166 to 202 nm (Figure 4.12). Whereas the NaOH treated surface of electrospun represented the fiber diameter rapidly increasing from 166, 255, 275 nm and up to 411 nm, respectively. Because NaOH hydrolyzed surface of nylon-6 to negatively charged species forming successfully. These resulted in rapidly deposition of PDADMAC and PSS thin film layers on electrospun fiber mats.

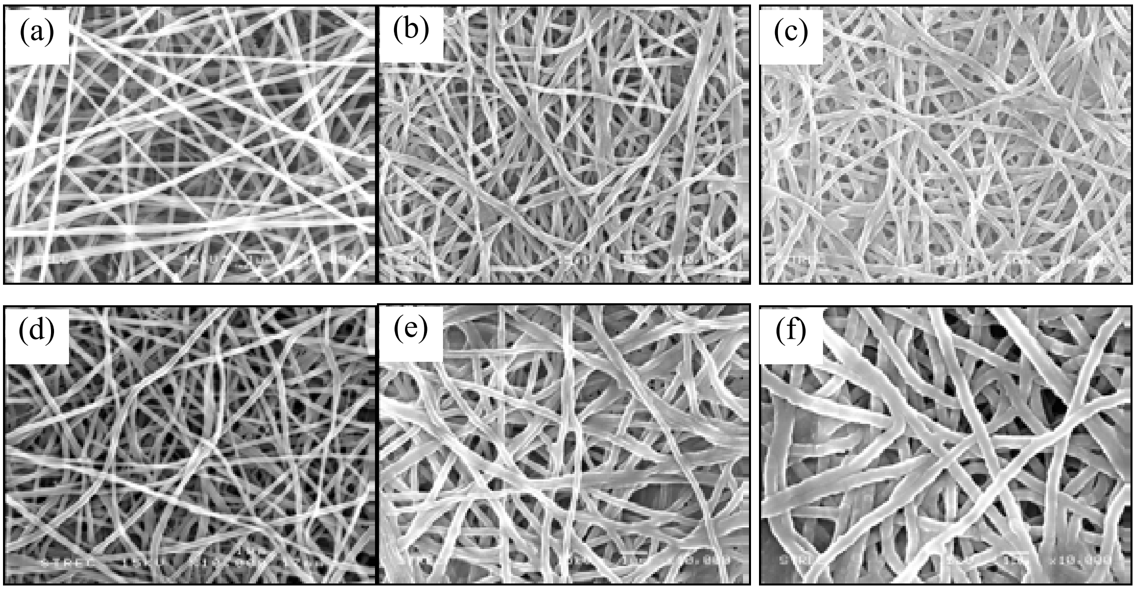


Figure 4.11 SEM images of polyelectrolyte multilayer coated electrospun nylon 6 fibers with different number bilayers of PDADMAC and PSS

(a-c) untreated surface, (a) electrospun nylon 6 nanofibers, (b) 1 bilayer, (c) 15 bilayers.

(d-f) treated surface with NaOH, (d) electrospun nylon 6 nanofibers and (e) 1 bilayer and (f) 15 bilayers.

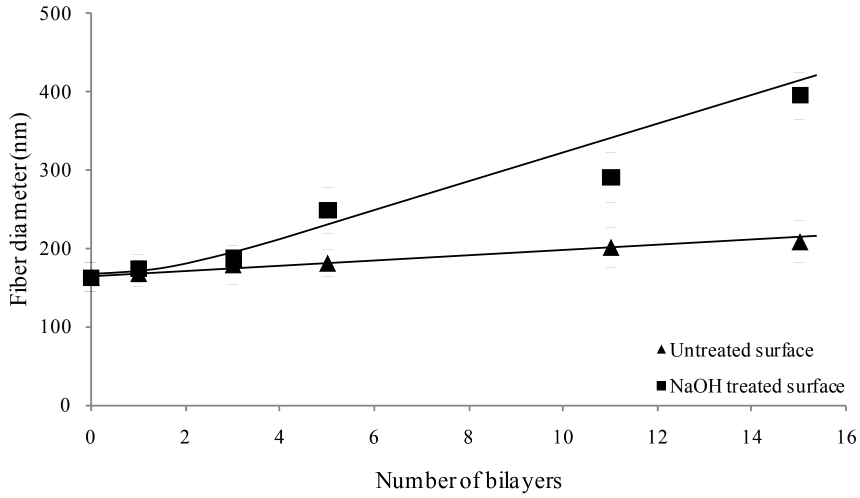


Figure 4.12 Relationship of fibers diameter and number bilayers of polyelectrolyte PDADMAC and PSS assembly on electrospun surface substrate.

4.2.5 Physical properties

The tensile testing behavior of the nonwoven electrospun nylon-6 fiber mats were evaluated by the effect of young's modulus, tensile strength and elongation at break. The strength of fibers influenced on homogeneous distribution of their chemical structure and properties of composite materials.

The mechanical properties of nonwoven fibers probably considered with the fibers oriented in the direction of crosshead displacement. The strain was applied to the electrospun nylon-6 fibrous mats, the junctions and cohesions between the fibers were broken results in low young's modulus and tensile strength at 47.3±7.3 MPa and 5.3±1.0 MPa, respectively. But it represented high elongation at break approximately 21.6±7.6% of nylon-6 electrospun nonwoven mats (Table 4.4).

Obviously, tensile strength of nylon-6 fibrous increased after treatment surface with NaOH. This could due to a surface roughness generated after alkali treatment surface which increased inter fiber friction. The roughness increased inter-fiber lacking and prevented each fiber from slipping from nearby fibers, and led to a more rigid fiber mat as a whole. The increased rigidity resulting lower elongation at break of NaOH treated fiber mats compare to that of pristine fiber mats.

Moreover, the effect of surface hydrolysis results in enhanced the adsorption of polyelectrolyte layers (UV and SEM results). The following method could enhance the mechanical properties because polyelectrolyte induce the formation of thin film layer coating network which dense, hard and protect any small cracks and other defect on nylon-6 nonwovenfibers (Table 4.4). The mechanical properties such as Young's modulus, tensile strength and elongation at break increased as a function of the number of bilayers of PDADMAC and PSS coated nylon-6 fiber mats. From figure 4.13 appearanced young's modulus, tensile strength and elongation at break of electrospun nylon-6 modified surface with PDADMAC/PSS increased from 47.3±7.3 MPa, 5.3±1.0 MPa, 21.6±7.6% to 116.3±4.7 MPa, 15.4±2.9 MPa , 47.1±4.1% (fifteen bilayers), respectively. The results of polyelectrolyte assemble on fiber mats were dominant to improve the mechanical properties of nylon-6 fibers. The mechanical properties of assemble thin film layers on nylon-6 fibers were increased until three bilayers, it reached to sustain that confirm the polyelectrolyte layer coverage on the surface of fibers completely thus be greatly modified at this stage (figure 4.13).

Table 4.4 Mechanical properties of nylon-6 nonwoven fiber mats treated surface with NaOH and untreated fibers including effect of PDADMAC/PSS coated on nylon-6 fiber mats with varied number of bilayers from one to fifteen bilayers.

Number of bilayers	Young modulus (MPa)		Tensile strength (MPa)		Elongation at break (%)	
	Untreated	NaOH	Untreated	NaOH	Untreated	NaOH
0	47.3±7.3	56.8±8.3	5.3±1.0	14.4±3.4	21.5±7.6	14.6±3.3
1	116.6±9.7	160.7±3.2	14.9±2.6	22.3±1.9	43.9±2.6	51.0±1.9
3	119.2±1.8	176.0±7.1	15.2±1.4	24.8±1.9	47.1±1.1	54.3±2.9
5	117.5±4.6	171.2±9.8	15.2±2.0	24.2±2.7	45.9±1.9	53.3±2.6
11	115.9±7.3	179.9±4.6	15.8±1.0	23.2±1.9	46.4±3.7	53.7±2.5
15	116.3±4.7	172.0±3.7	15.4±2.9	24.3±1.9	47.1±4.1	54.4±3.7

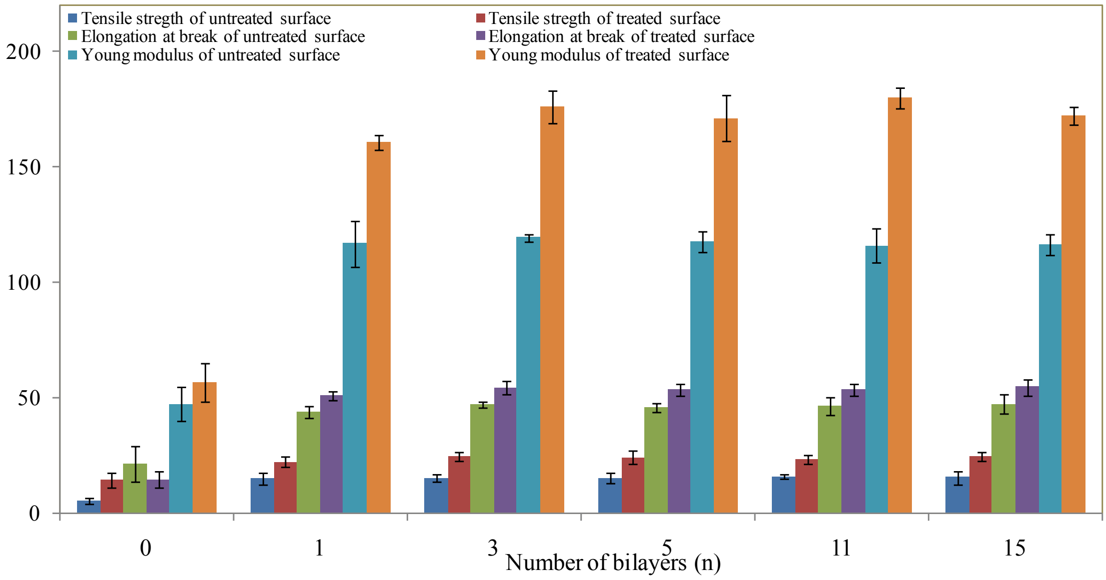


Figure 4.13 Relationship the number of polyelectrolyte PDADMAC and PSS bilayers with young modulus, tensile strength and elongation at break of treated and untreated surface electrospun.

4.3 Silver nanoparticles assembly

In this section, discussed on immobilize the silver nanoparticles on surface of electrospun nylon-6 following layer-by-layer assembly to invistigated the effect of concentration of capped agent and kinetic of silver deposition. PSS-co-MA capped on silver nanoparticles represented a strong charge and weak charge in structure which enhanced the stability and flexibility of film. Therefore, this work used PSS-co-MA acted as capped nanosilver deposited on the outmost surface of electrospun nylon-6 which was PDADMAC layer.

4.3.1 Ultraviolet-Visible spectroscopy

The layer-by-layer deposition of the silver nanoparticles considered as the particles absorbed in range of light wavelength through the surface plasmon resonance effect. The amount of silver nanoparticles embeded on the fibers provided from the reflectance data which widely used to measure variation of absorbance from the particles deposited on textile.

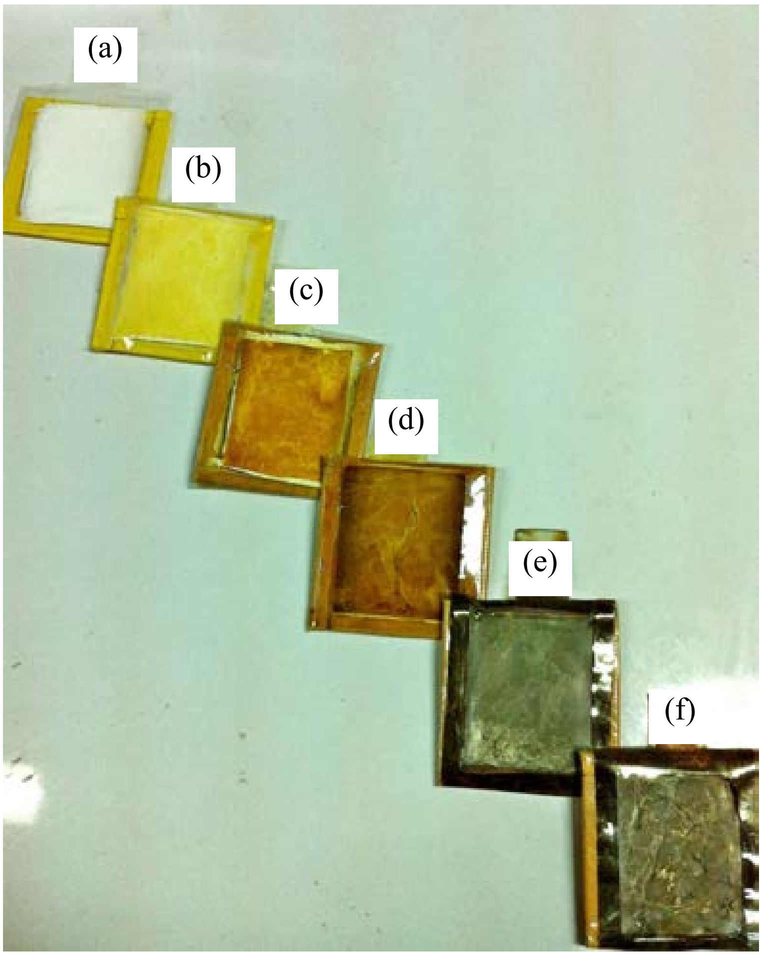


Figure 4.14 Representative the color of fibers mats (a) electrospun nylon-6 mats and Ag:PSS-co-MA varied concentration coated fibers (b) 1:0.5 mM, (c) 1:0.1 mM, (d) 1:0.05 mM, (e) 1:0.01 mM and (f) 1:0.005 mM.

The growth of spherical silver nanoparticles assemble on a substrate investigated from surface plasmon resonance (SPR) at wavelength 420 nm. The slow rate of silver nanoparticles deposition related to the surface properties of nylon-6 fibers. The as-spun fibers posse a lower charge density than NaOH treated surface of electrospun nylon-6. Results in the silver nanoparticles were deposited through interaction with cationic PDADMAC layer on electrospun treated surface of fibers faster than untreated surface due to treated surface induced the polyelectrolyte adsorption more than untreated surface. This was the major reason of treated surface had a higher deposition of silver nanoparticles than untreated surface at the same time.

Time-dependent increase in the intensity of the plasmon resonance (420 nm) was observed the silver nanoparticles formation. Illustrate in figure 4.14-4.15 represented the absorbance value of the nylon-6 fibers as a function of kinetic deposited layers of (PDADMAC/PSS)$_3$/PDADMAC/Ag. Obviously, the absorbance value of silver nanoparticles immobilized on surface of untreated electrospun nyln-6 fibers slightly increasing to constant absorbance about 18 hours. Comparison of treated nylon-6 fibers that found silver nanoparticles rapidly reach to stable absorbance at 12 hours. The results of surface treatment via NaOH hydrolysis enhance the polelectrolyte adsorption to more surface charge. The charge on surface of fibers induced a higher deposited of silver nanoparticles which provide higher silver adsorbed at all of ratio treated nylon-6 fibers and then led to increase the absorbance value.

The kinetics of silver nanoparticles assemble on fibers affect to enhance the particles adsorption ability. This behavior follow electrostatic interaction of PSS-co-MA capped nanosilver and PDADMAC at the surface nylon-6. The single-layer adsorption of silver nanoparticles gradual increased as amount with the time. It was certainly sustain due to silver nanoparticles coated reach to stable state which cover surface completely.

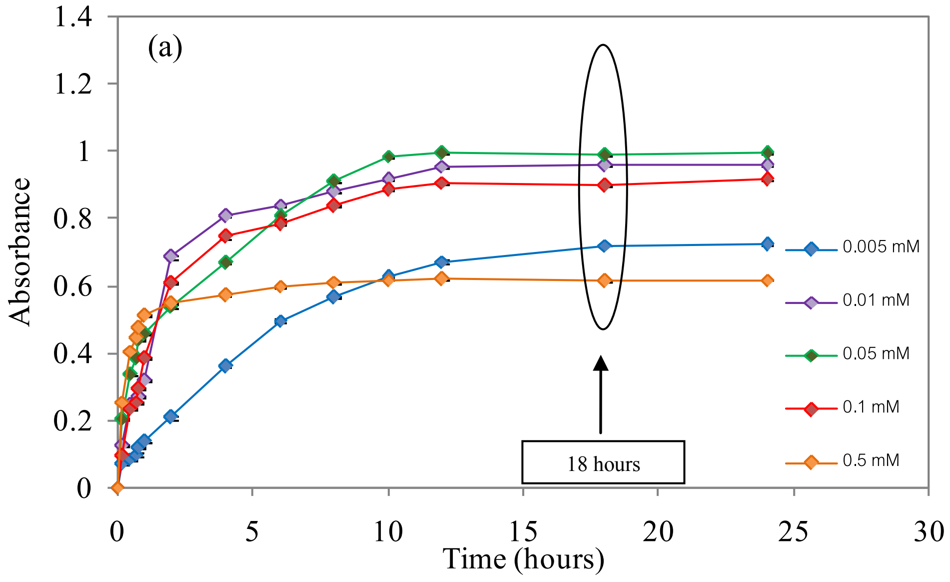


Figure 4.15 Relationship of absorbance and kinetic of silver immobilized on (a) electrospun nylon-6 substrate, (b) NaOH treated surface of nylon-6 fibers with varied ratio of Ag:PSS-co-MA 1:0.005, 1 :0.01, 1:0.05, 1:0.1 and 1:0.5 mM.

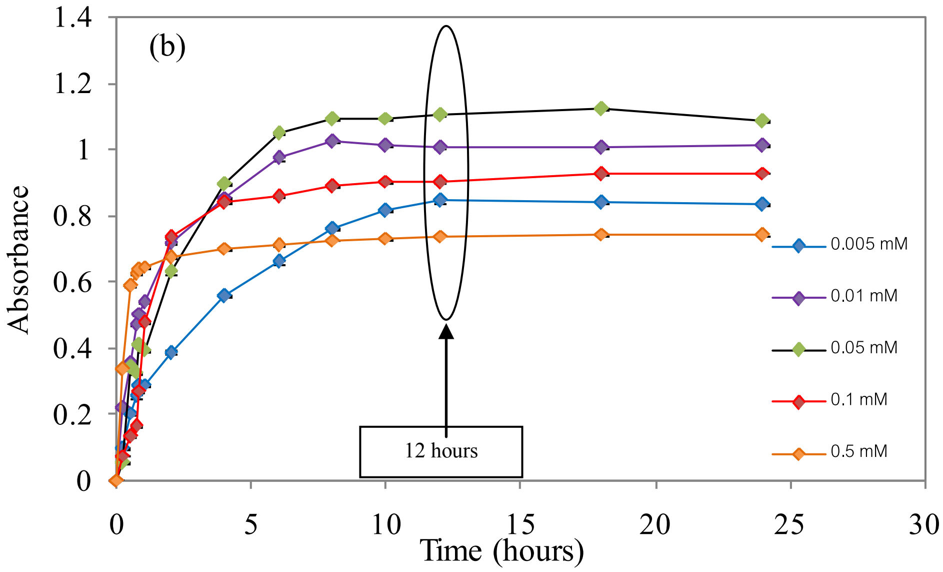


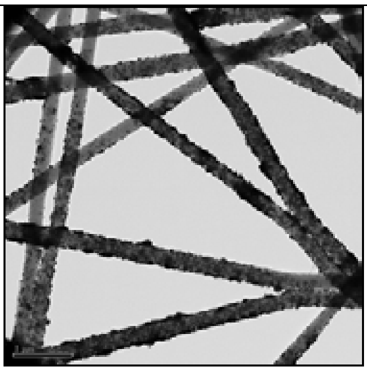
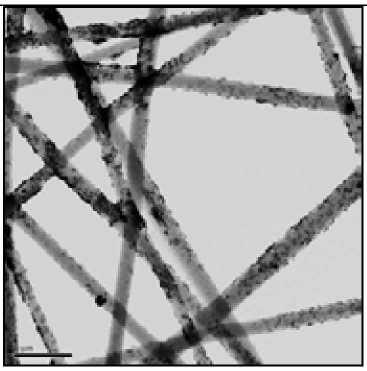
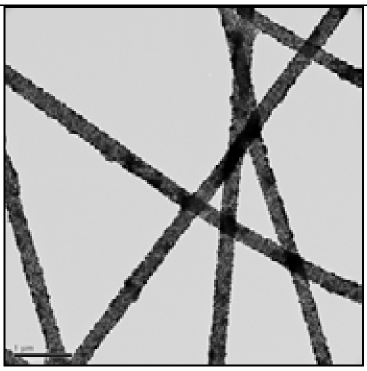
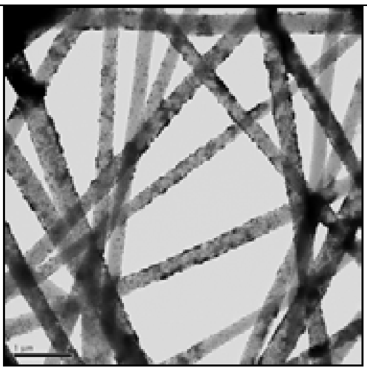
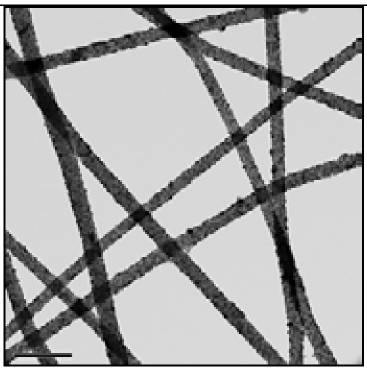
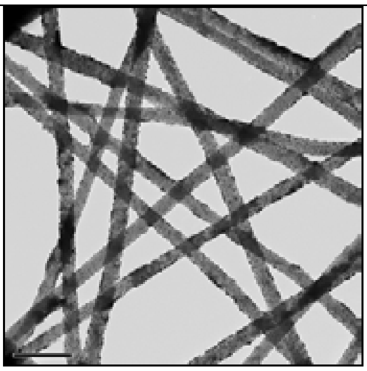
Figure 4.15 Relationship of absorbance and kinetic of silver immobilized on (a) electrospun nylon-6 substrate, (b) NaOH treated surface of nylon-6 fibers with varied ratio of Ag :PSS-co-MA 1:0.005, 1:0.01, 1:0.05, 1:0.1 and 1:0.5 mM.

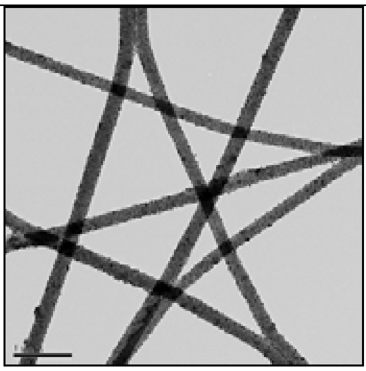
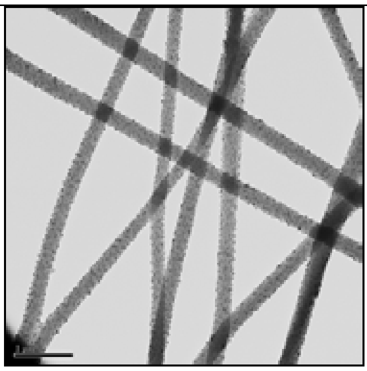
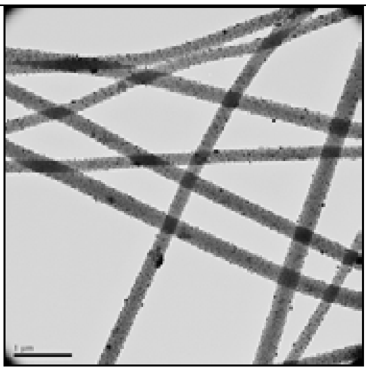
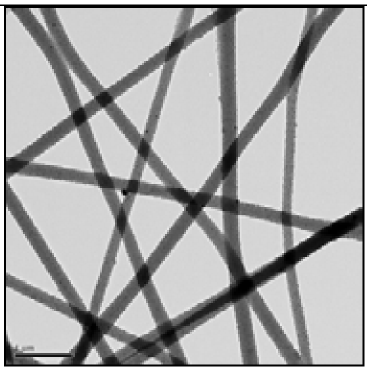
4.3.2 Transmission Electron Microscope (TEM)

Morphology of electrospun immobilized surface with silver nanoparticles were illustrate in Table 4.4-4.5. The assembly of PSS-co-MA covered the silver nanoparticles and embedded on surface of electrospun nylon-6 was basis on electrostatic interactions. The outmost thin film layer represented the positive charge of PDADMAC utilized for immobilized of silver nanoparticles capped with PSS-co-MA via layer-by-layer deposition. Because of silver capped with PSS-co-MA represented a strongly negative charged of sulfonate group and weakly charged of carboxylate group in structure which enhance electrostatic attraction of the nanosilver with PDADMAC films on nylon-6 electrospun substrate.

The capped agent of PSS-co-MA covered the surface nylon-6 fibers influence on adhesion of particles and morphology. Obviously, the ratio of PSS-co-MA ratio increased (constant concentration of silver) that appeared the homogeneous distribution of silver nanoparticles on surface of nylon-6 fibers (Table 4.5). For the reason that higher capped of PSS-co-MA represented strongly charged and weakly charged in structure which enhance stability and flexibility of film coated the particles. The capped agent acted as prevent the particles to aggregate and agglomerate. In addition, it enhanced the particles to interact with opposite charge of polymer, high adhesion and distribution on surface of electrospun greater than low concentration of PSS-co-MA such as 1:0.005 and 1:0.01 mM.

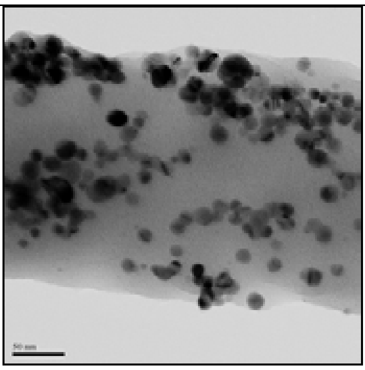
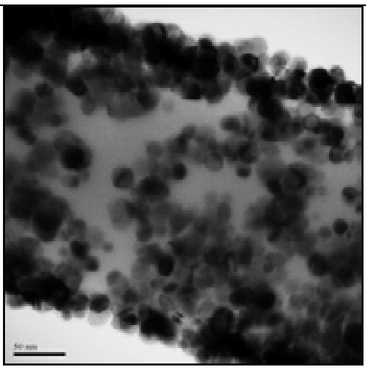
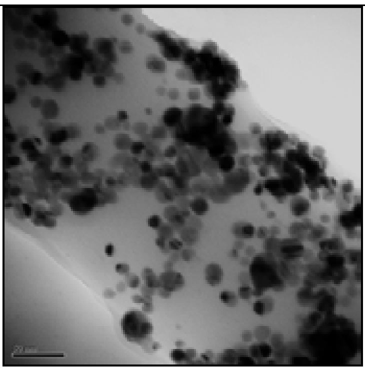
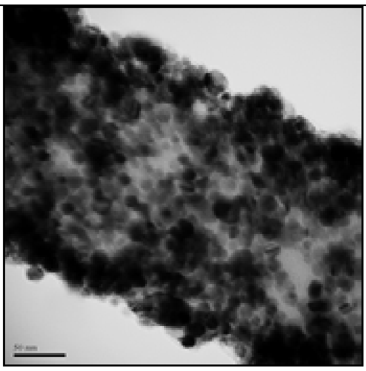
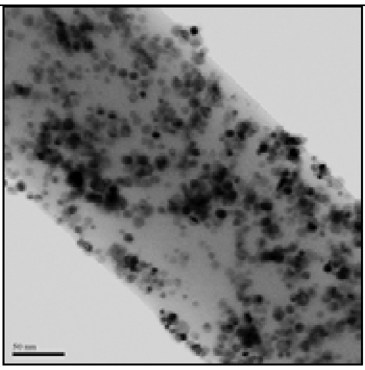
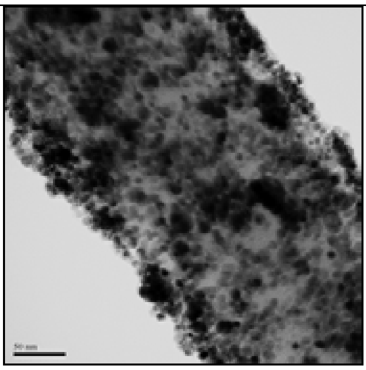
Table 4.5 Morphology and distribution of silver nanoparticles at varied concentration of Ag:PSS-co-MA immobilized on electrospun nylon-6 and NaOH treated surface of electrospun at magnificent 3500x.

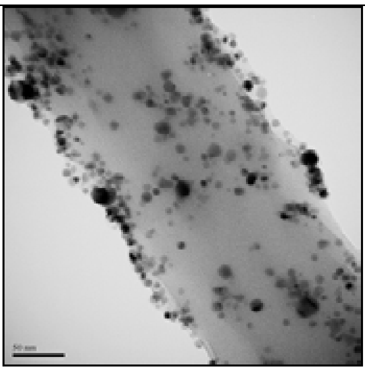
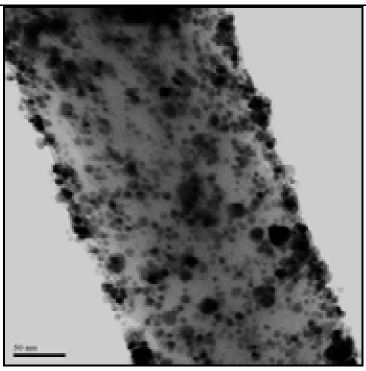
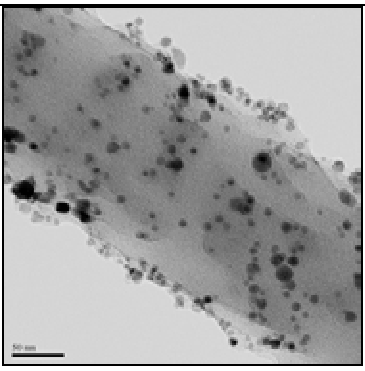
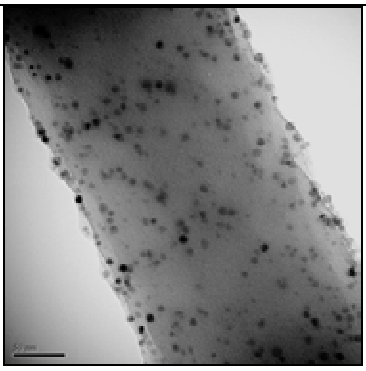
Ratio of Ag:PSS-co-MA (mM)	TEM image of Nylon-6/ (PDADMAC/PSS)$_3$/AgNPs	TEM image of Nylon-6/NaOH/ (PDADMAC/PSS)$_3$/AgNPs
1:0.005		
1:0.01		
1:0.05		

Ratio of Ag:PSS-co-MA (mM)	TEM image of Nylon-6/ $(PDADMAC/PSS)_3$/AgNPs	TEM image of Nylon-6/NaOH/ $(PDADMAC/PSS)_3$/AgNPs
1:0.1		
1:0.5		

The size of silver nanoparticles observed from TEM micrograph (Table 4.6). That occurred average diameter of particles decrease when increase ratio of PSS-co-MA from 0.005, 0.01, 0.05, 0.1 and 0.5 mM to appear particles size approximately 14.56±3.86, 12.62±2.30, 7.43±1.53, 5.81±1.21 and 4.97±1.21 nm. The reason of silver nanoparticles capped with low PSS-co-MA concentration occurred a bigger size than high concentration of silver colloidal. Because of the particles close packing and lower inter-particle repulsion that tend to agglomorate.

Table 4.6 Morphology of silver nanoparticles at varied concentration of Ag:PSS-co-MA immobilized on electrospun nylon-6 and NaOH treated surface of electrospun at magnificent 62000x.

Ratio of Ag:PSS-co-MA (mM)	TEM image of Nylon-6/ $(PDADMAC/PSS)_3$/AgNPs	TEM image of Nylon-6/NaOH/ $(PDADMAC/PSS)_3$/AgNPs
1:0.005		
1:0.01		
1:0.05		

Ratio of Ag:PSS-co-MA (mM)	TEM image of Nylon-6/ (PDADMAC/PSS)$_3$/AgNPs	TEM image of Nylon-6/NaOH/ (PDADMAC/PSS)$_3$/AgNPs
1:0.1		
1:0.5		

4.3.3 Qualitative analysis of silver nanoparticles embedded on fiber mats

The amount of silver particles embedded on surface of electrospun were analyzed by ICP-OES. The electrostatic interaction of oppositely charged species of anionic PSS-co-MA, which encapped around the silver nanoparticles, and cationic of PDADMAC caused these polymers to self assemble into a thin film, resulting in silver nanoparticle deoposition on the LbL modified electrospun fiber. Depending on the concentration of capping agent, the amount of silver nanoparticles deposited on the fiber were not the same, and this could affect other properties of the fiber mats.

Quantitative analysis for amount of silver nanoparticles deposited on the fiber mats was determined by ICP-OES, as shown in table 4.7. The results showed that the amount of silver nanoparticles deposited on the fiber mats increased as the concentration of capping agent decreased from 0.5 to 0.1 and 0.05 mM, which had the maximum deposition. However, after reaching maximum silver deposition at the capping concentration of 0.05 mM, the amount of silver deposited on the fiber mats declined gradually, as the capping concentration lowered to 0.01 and 0.005 mM. The results for both LbL modified nanofiber and LbL modified NaOH treated-nanofibers were having the same trend, although it was more prominent for LbL modified NaOH treated-nanofibers.

From visual observation, as shown in figure 4.16, silver nanoparticles appeared to look like a metallic film at low capping concentrations (0.01 and 0.005 mM), while the films prepared at high capping concentration appeared to be yellowish-reddish in color. The TEM images in table 4.6 also revealed that the nanoparticles with lower capping agent aggregate more than that with high capping agent concentration (0.1 and 0.5 mM). These results suggested a lower intermolecular particle repulsion between the capped nanoparticles at low capping concentration.

Table 4.7 Amount of silver nanoparticles at various Ag: PSS-co-MA ratio immobilized on nylon-6 electrospun fiber mats modified surface with $(PDADMAC/PSS)_3$ and NaOH treated electrospun fiber mats modified surface with $(PDADMAC/PSS)_3$.

Ratio of Ag: PSS-co-MA (mM)	Concentration of silver ion (ppm)		
	Untreated surface nylon-6 fibers	Treated surface nylon-6 fibers	Pure nylon-6 fibers
0.5	339.94 ± 4.24	366.54 ± 4.96	304.81 ± 3.18
0.1	657.5 ± 5.05	919.86 ± 6.23	351.36 ± 5.34
0.05	927.06 ± 6.56	1902.36 ± 5.67	775.66 ± 4.9
0.01	884.76 ± 5.93	1161.96 ± 4.87	647.97 ± 5.41
0.005	878.96 ± 3.26	1084.99 ± 5.98	554.3 ± 3.31

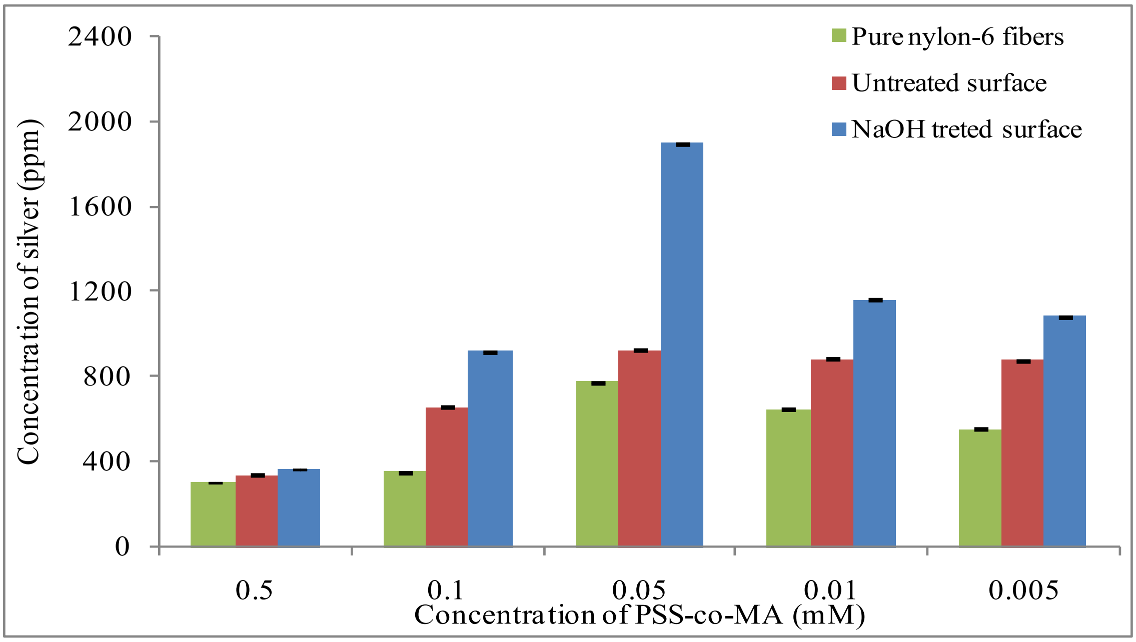


Figure 4.16 Effect of concentration of PSS-co-MA act as capped silver nanoparticles and concentration of silver ion embeded on electrospun nylon-6.

4.3.4 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDX)

The composition of silver elemental immobilized on surface of electrospun nylon-6 fibrous treated with NaOH indicated from the combination of SEM and EDX spectrum. The treated surface of the nylon-6 fiber mats with ratio of Ag:PSS-co-MA 1:0.005, 1:0.05 and 1:0.5 mM apparenced the silver composition on surface electrospun nylon-6 approximately 7.40, 20.33 and 1.81 %, respectively (Table 4.8). The result represented the silver composition on surface was depend on ratio of capped agent. The ratio of Ag:PSS-co-MA 1:0.05 mM showed the highest silver composition at 20.33 ± 1.46 % relate to ICP-OES data.

Table 4.8 Illustration of silver composition embedded on surface of electrospun nylon-6 fibrous treated with NaOH against the concentration of PSS-co-MA capped silver nanoparticles

Concentration of PSS-co-MA (mM)	Percentage of AgNPs embeded on electrospun nylon-6
0.005	7.40 ± 0.54
0.05	20.33 ± 1.46
0.5	1.81 ± 0.26

4.3.5 Antibacterial testing

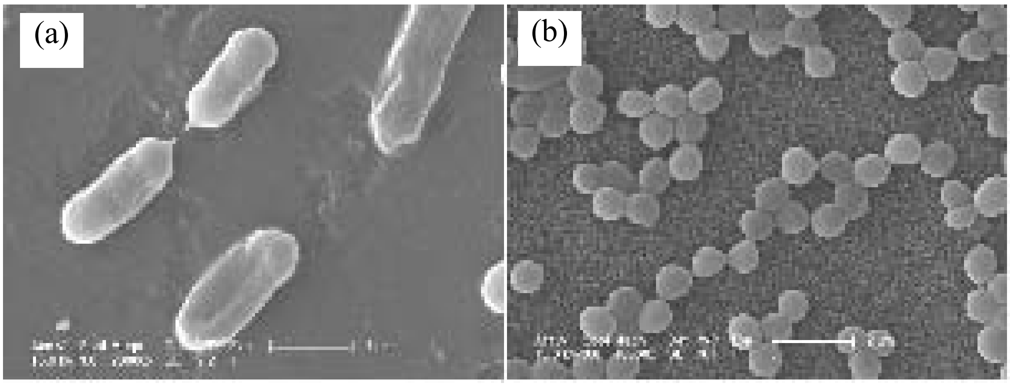


Figure 4.17 SEM micrographs of (a) gram negative of *Escherichia coli* (*E. coli*) and (b) gram positive of *Staphylococcus aureus* (*S. aureaus*) bacteria cell [68].

In the past decade silver acted as a good antibacterial agent, non-toxic and natural inorganic metal. It was attractive materials to use in different kind of fibers. The antimicrobial activity of nylon-6 electrospun fiber mats incorporated with silver nanoparticles was interested to investigate in this work. The antimicrobial propertiy of the modified nylon-6 fabrics against gram negative of *Escherichia coli* (*E. coli*) and gram positive of Staphylococcus *aureus* (*S. aureaus*) were investigated by (i) percentage reduction of bacteria and (ii) zone of inhibition.

4.3.5.1 Percentage reduction of bacteria

The antimicrobial tested was according AATCC 100 standard testing method on textile material.

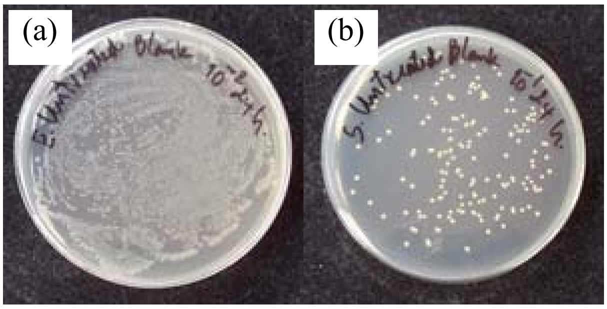


Figure 4.18 Blank of nylon-6 electrospun for *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureas*) testing 3.6 x 10^6 and 2.0 x 10^6 CFU/sample .

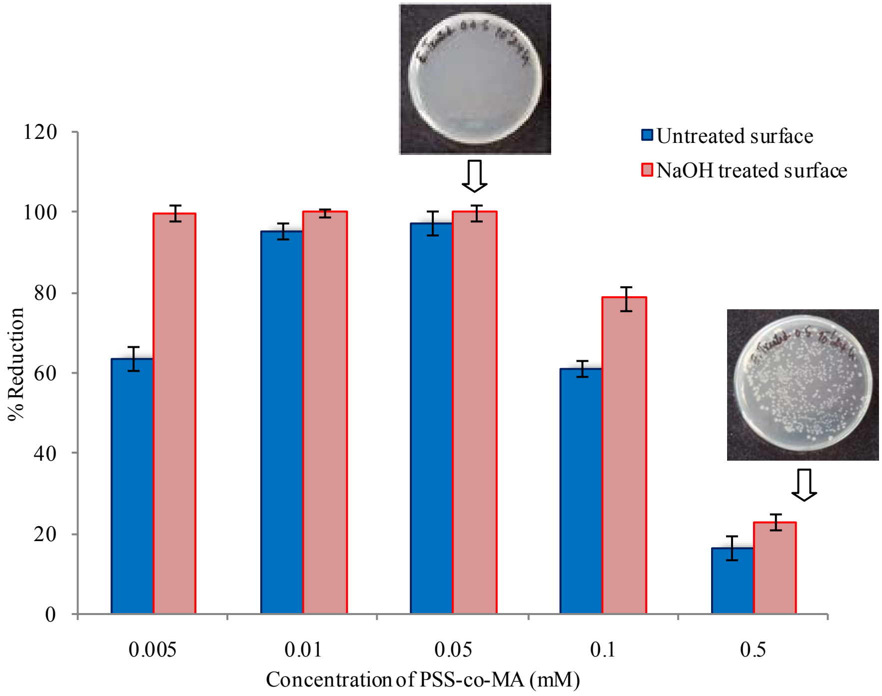


Figure 4.19 Percentage reduction of electrospun nylon-6 fiber mats immobilized the silver nanoparticles with different PSS-co-MA concentrations 0.005, 0.01, 0.05, 0.1 and 0.5 mM against Gram-negative *Escherichia coli (E. coli)* according AATCC 100.

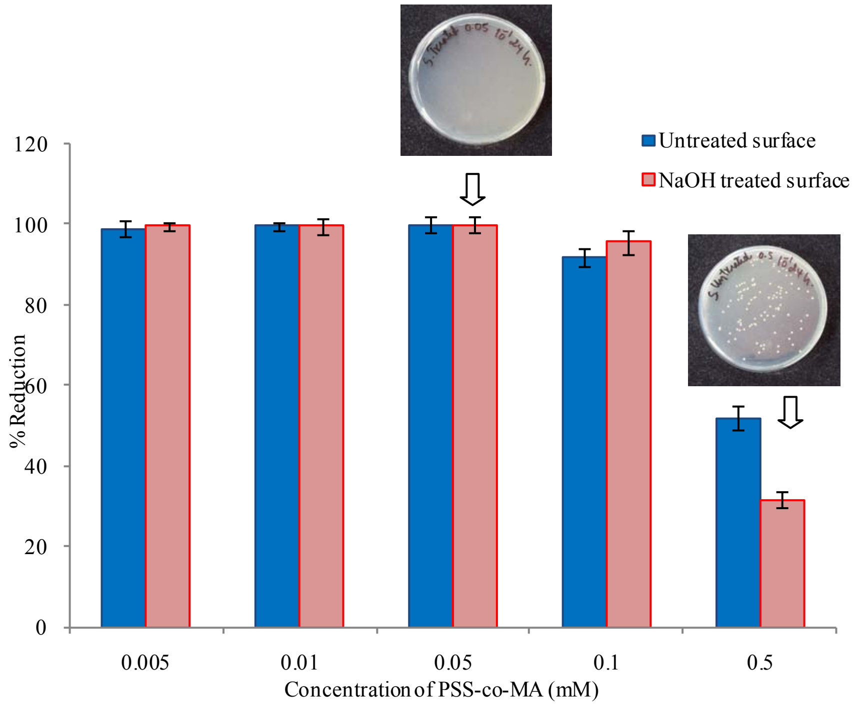


Figure 4.20 Percentage reduction of electrospun nylon-6 fiber mats immobilized the silver nanoparticles with different PSS-co-MA concentrations 0.005, 0.01, 0.05, 0.1 and 0.5 mM against *Staphylococcus aureus* (*S. aureas*) according AATCC 100.

The antimicrobial efficiency was summarized in figure 4.19-4.20. The percent reduction of bacteria was calculated which percent of inhibition bacteria cell as a function of chemical properties of surface and PSS-co-MA capped silver particles. Nylon-6 electrospun fibers used as a blank for testing which represented no bacterial effects (figure 4.18).

The antimicrobial activity correlation of PSS-co-MA capped nanosilver immobilized on surface of electrospun nylon-6 fibers. The percentage reduction of bacteria on fibers showed clearly demonstrated. The most of samples represented antibacterial activity which no bacterial growth or less (Figure 4.19-4.20). From ICP-OES result, the moderate concentration of PSS-co-MA 0.05 mM yield the highest of silver nanoparticles deposition on the fiber mat results in enhanced the antibacterial effects to 99.99 % reduction both gram negative of *Escherichia coli* (*E. coli*) and gram positive of *Staphylococcus aureus* (*S. aureas*).

4.3.5.2 Zone of inhibition

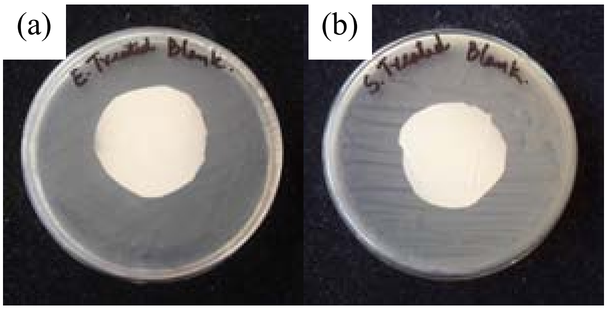


Figure 4.21 Blank of nylon-6 electrospun for *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureaus*) testing (38 cm).

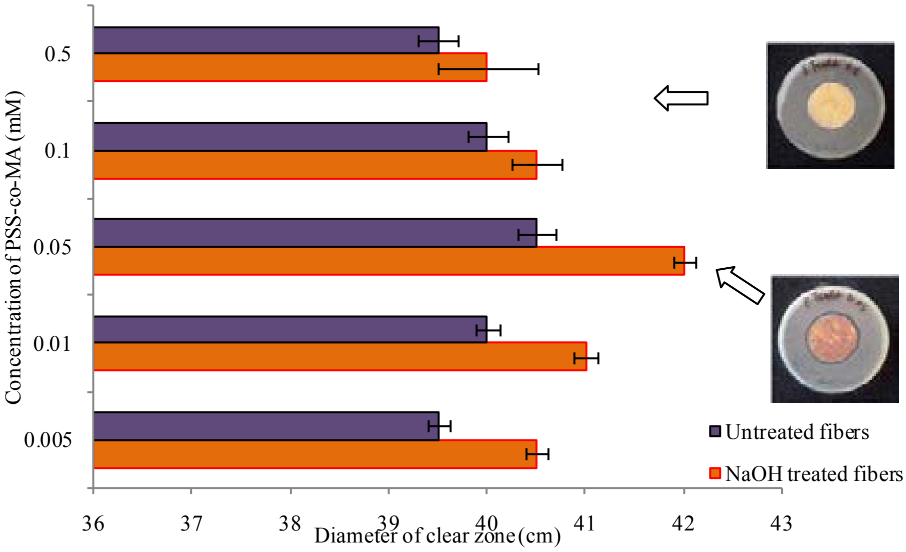


Figure 4.22 Bacteria inhibition zone of electrospun nylon-6 fiber mats immobilized the silver nanoparticles with different PSS-co-MA concentrations 0.005, 0.01, 0.05, 0.1, 0.5 mM against Gram-negative *Escherichia coli (E. coli).*

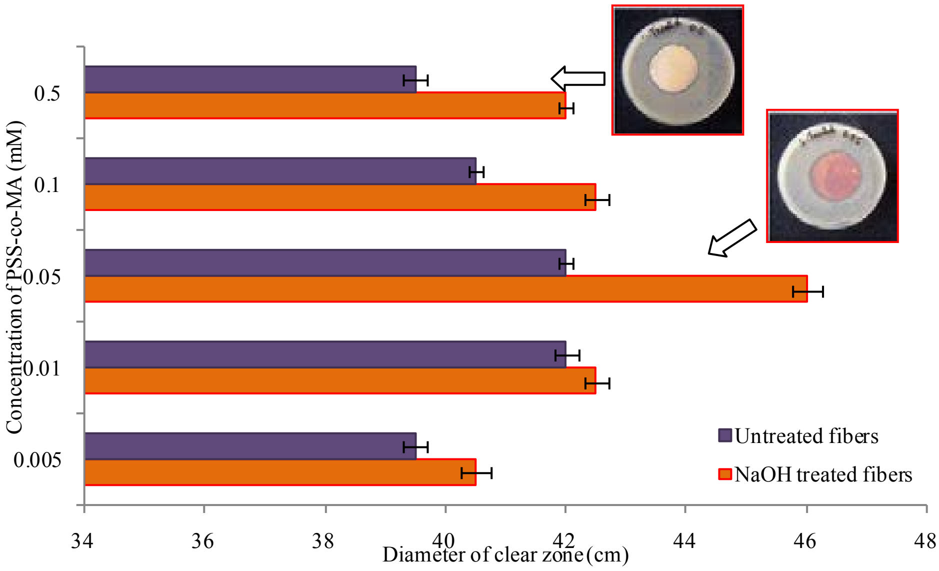


Figure 4.23 Bacteria inhibition zone of electrospun nylon-6 fiber mats immobilized the silver nanoparticles with different PSS-co-MA concentrations 0.005, 0.01, 0.05, 0.1, 0.5 mM against Gram-positive *Staphylococcus aureus* (*S. aureas*).

The efficiency of antibacterial from zone of inhibition (Figure 4.21-4.22) represented the same trend at all of condition. All of results confirmed the electrospun nylon-6 fibers modified surface with PDADMAC/PSS and silver nanoparticles could enhance the antibacterial properties of electrospun nylon-6 successfully.

The reason of the silver impregnated on surface of electrospun nylon-6 led to the silver oxidation and readily to react on sulfhydryl (-SH) groups on the cell wall of bacteria by replaced the hydrogen atoms, caused in the coupling of the sulfur atoms to form silver-S-S-bonds on bacteria membrane cell. Finally, bacteria cell death. Furthermore, from the results that found at the same concentration of capping agent NaOH treated surface to form more charge. There were gave a higher antibacterial efficiency than untreated surface that can be confirm the treatment surface was important step for desire surface of substrate and enhanced chemical, physical and antibacterial properties.

CHAPTER V

CONCLUSION AND SUGGESTION

5.1 Conclusion

In this research, surface of nylon-6 electrospun nanofiber mats were modified with layer-by-layer polymeric thin films and embedded with silver nanoparticles to enhance anti-bacterial properties of the mats. The layer-by-layer (LbL) thin films composed of alternate layers of poly(diallyldimethyl ammonium chloride), PDADMAC and poly(4-styrene sulfonic acid), PSS. Effect of polyelectrolyte concentration, deposition time and sodium hydroxide surface treatment prior to LbL formation were investigated. Uniformity of polyelectrolyte coverage on nanofibers surface was followed by measuring dye absorption with a UV-Vis spectroscopy and a photoscanner. The results from both analysis showed similar trends. Interestingly, sodium hydroxide (NaOH) treatment of fiber mats was reduced polyelectrolyte concentration and deposition time to build a uniform layer from 5 mM 40 minutes to about 1 mM 10 minutes. Film thickness, as confirmed by SEM micrographs, of NaOH treated fiber mats with 1 to 15 bi-layers were increased from 166 nm to about 410 nm, while that of pristine fiber remained relatively constant. After surface modification with polyelectrolyte, PDADMAC/PSS, it was found that the hydrophilicity of the treated mats was improved, as the water contact angle was changed from 120.6^{o} to 104.2^{o}. Silver nanoparticles were immobilized on the fiber mats modified with 3 LbL bilayers. Effect of capping agent, poly(4-styrenesulfonic acid-co-maleic acid), PSS-co-MA, concentration on silver nanoparticles deposition and the antibacterial property of the mats were investigated. Depending on Ag: PSS-co-MA ratio, the reduction of *Escherichia coli (E. coli)* and *Staphylococcus aureus* (*S. aureaus*) bacteria cell of the mats were in the range of 20-99.99% and 20-99.99%, respectively. The Ag: PSS-co-MA of 1:0.05 mM showed the highest antibacterial efficiency against both *E. coli* and *S. aureaus bacteria* cell, respectively.

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APPENDICES

APPENDIX A

Electrospun nylon-6 fibers diameter distribution

The fiber diameter of nylon-6 electrospun nanofibers and treated surface of fibers with various layers of polyelectrolte via layer-by-layer assembly are represent in Table 1-12A. The relation of fiber diameter and percentage of frequency to show distribution of fiber diameters is illustrate in Figure 1-12A.

Table 1A Fiber diameter of electrospun nylon-6 measured from SEM micrograph.

Fiber diameter (nm)	Frequency	% Frequency
0-25	0	0.0
25-50	0	0.0
50-75	0	0.0
75-100	0	0.0
100-125	0	0.0
125-150	1	1.4
150-175	18	25.7
175-200	33	47.1
200-225	16	22.9
225-250	2	2.9
250-275	0	0.0
275-300	0	0.0
300-325	0	0.0
325-350	0	0.0
Total	70	100.0

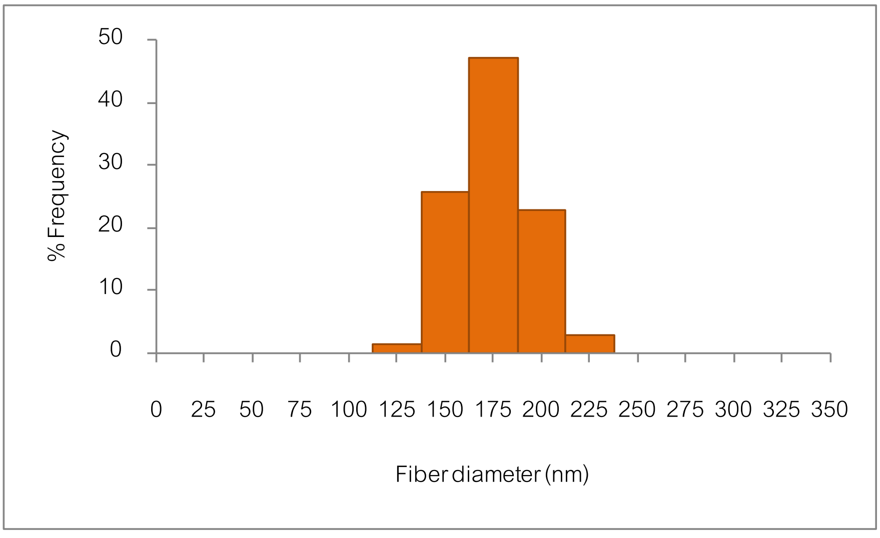


Figure 1A The diameter distribution of electrospun nylon-6 fibers

Table 2A Fiber diameter of electrospun nylon-6 functionalized surface with 1 bilayer of poly(diallyldimethylammoniumchloride) and poly(4-styrenesulfonic acid) sodium salt (Nylon /PDADMAC/PSS) measured from SEM micrograph.

Fiber diameter (nm)	Frequency	% Frequency
0-25	0	0.0
25-50	0	0.0
50-75	0	0.0
75-100	0	0.0
100-125	0	0.0
125-150	0	0.0
150-175	11	14.5
175-200	38	50.0
200-225	26	34.2
225-250	1	1.3
250-275	0	0.0
275-300	0	0.0
300-325	0	0.0
325-350	0	0.0
350-375	0	0.0
375-400	0	0.0
400-425	0	0.0
425-450	0	0.0
Total	76	100.0

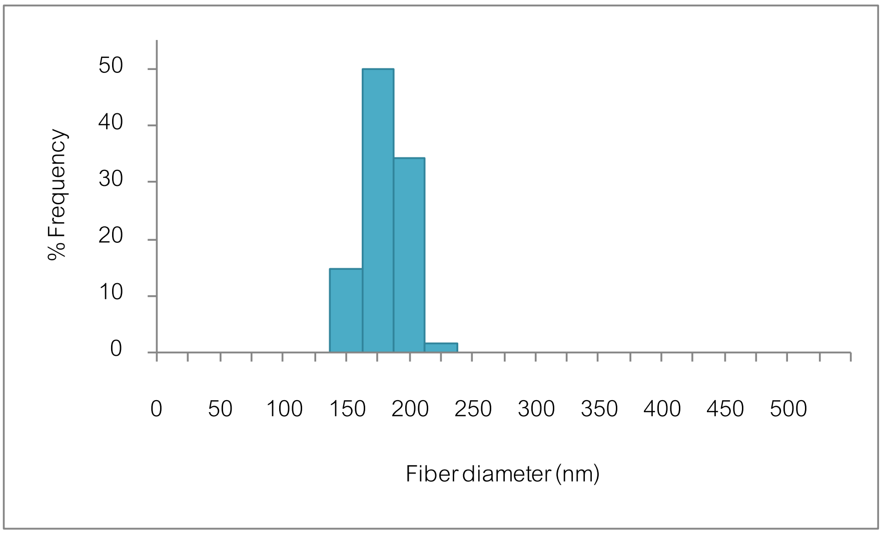


Figure 2A The diameter distribution of Nylon-6 /PDADMAC/PSS.

Table 3A Fiber diameter of electrospun nylon-6 functionalized surface with 3 bilayers of poly(diallyldimethylammoniumchloride) and poly(4-styrenesulfonic acid) sodium salt (Nylon /(PDADMAC/PSS)$_3$) measured from SEM micrograph.

Fiber diameter (nm)	Frequency	% Frequency
0-25	0	0.0
25-50	0	0.0
50-75	0	0.0
75-100	0	0.0
100-125	0	0.0
125-150	0	0.0
150-175	7	10.6
175-200	25	37.9
200-225	28	42.4
225-250	2	3.0
250-275	2	3.0
275-300	1	1.5
300-325	1	1.5
325-350	0	0.0
350-375	0	0.0
375-400	0	0.0
400-425	0	0.0
425-450	0	0.0
450-475	0	0.0
Total	66	99.9

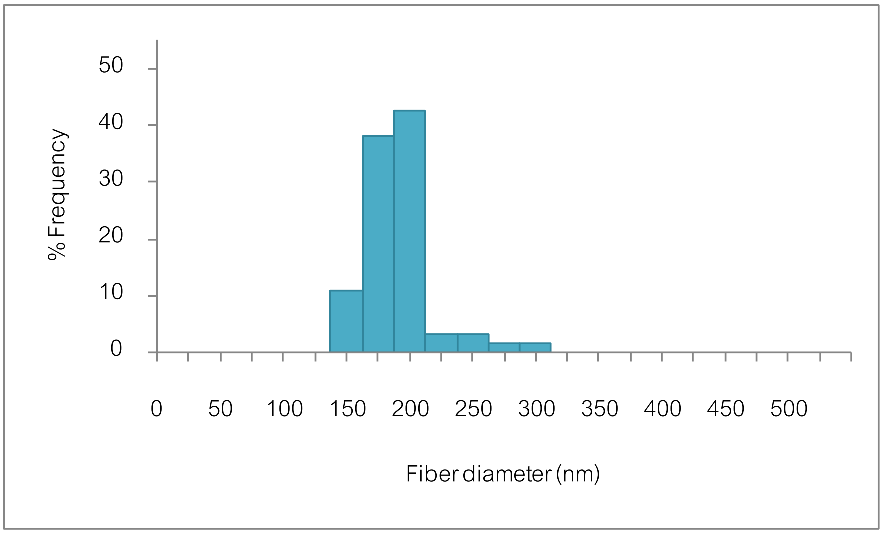


Figure 3A The diameter distribution of Nylon-6 /(PDADMAC/PSS)$_3$.

Table 4A Fiber diameter of electrospun nylon-6 functionalized surface with 5 bilayers of poly(diallyldimethylammoniumchloride) and poly(4-styrenesulfonic acid) sodium salt (Nylon /(PDADMAC/PSS)$_5$) measured from SEM micrograph.

Fiber diameter (nm)	Frequency	% Frequency
0-25	0	0.0
25-50	0	0.0
50-75	0	0.0
75-100	0	0.0
100-125	0	0.0
125-150	0	0.0
150-175	2	2.3
175-200	36	41.4
200-225	36	41.4
225-250	11	12.6
250-275	2	2.3
275-300	0	0
300-325	0	0
325-350	0	0
350-375	0	0
375-400	0	0
400-425	0	0
425-450	0	0
450-475	0	0
Total	87	100

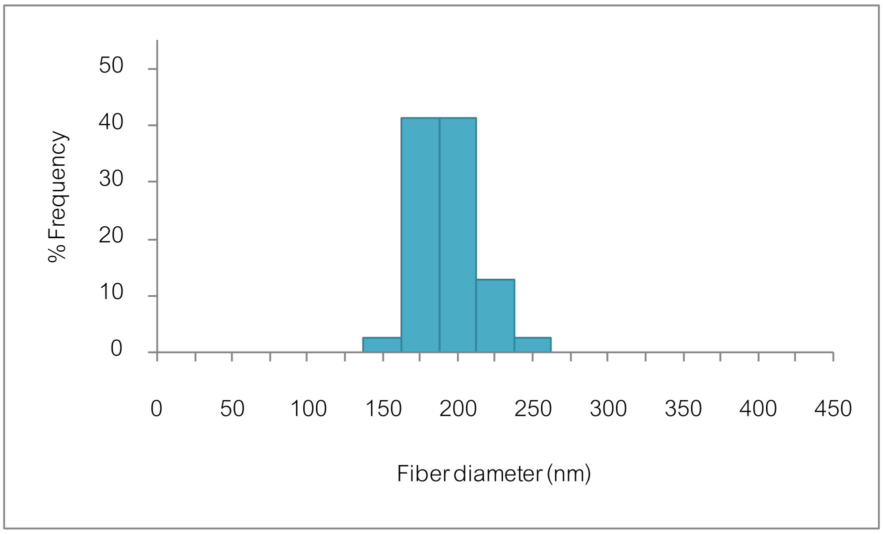


Figure 4A The diameter distribution of Nylon-6 /(PDADMAC/PSS)$_5$.

Table 5A Fiber diameter of electrospun nylon-6 functionalized surface with 11 bilayers of poly(diallyldimethylammoniumchloride) and poly(4-styrenesulfonic acid) sodium salt (Nylon /(PDADMAC/PSS) $_{11}$) measured from SEM micrograph.

Fiber diameter (nm)	Frequency	% Frequency
0-25	0	0
25-50	0	0
50-75	0	0
75-100	0	0
100-125	0	0
125-150	0	0
150-175	0	0
175-200	12	13
200-225	35	38
225-250	35	38
250-275	5	5.4
275-300	4	4.3
300-325	1	1
325-350	0	0
350-375	0	0
375-400	0	0
400-425	0	0
425-450	0	0
450-475	0	0
Total	92	99.7

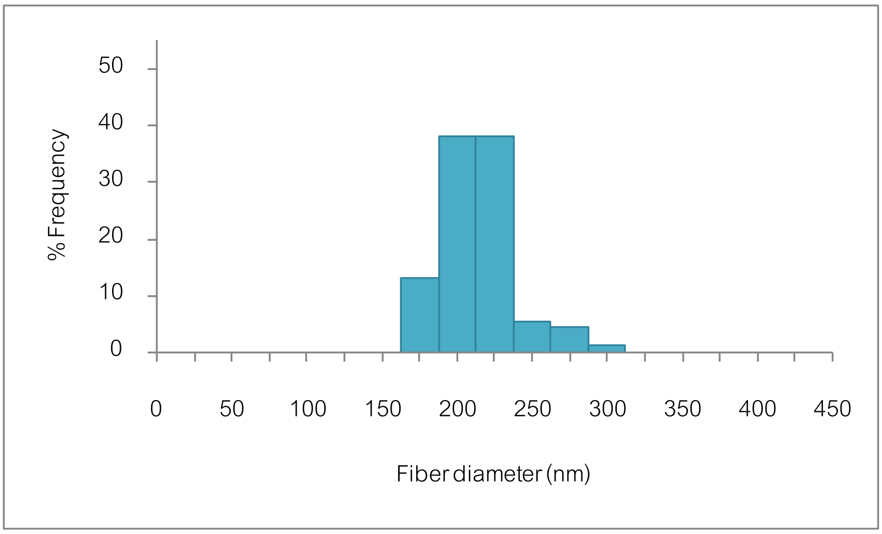


Figure 5A The diameter distribution of Nylon-6 /(PDADMAC/PSS)$_{11}$.

Table 6A Fiber diameter of electrospun nylon-6 functionalized surface with 15 bilayers of poly(diallyldimethylammoniumchloride) and poly(4-styrenesulfonic acid) sodium salt (Nylon /(PDADMAC/PSS)$_{15}$) measured from SEM micrograph.

Fiber diameter (nm)	Frequency	% Frequency
0-25	0	0
25-50	0	0
50-75	0	0
75-100	0	0
100-125	0	0
125-150	0	0
150-175	0	0
175-200	8	7.5
200-225	40	37.7
225-250	36	34
250-275	13	12.3
275-300	5	4.7
300-325	2	1.9
325-350	2	1.9
350-375	0	0
375-400	0	0
400-425	0	0
425-450	0	0
Total	106	100

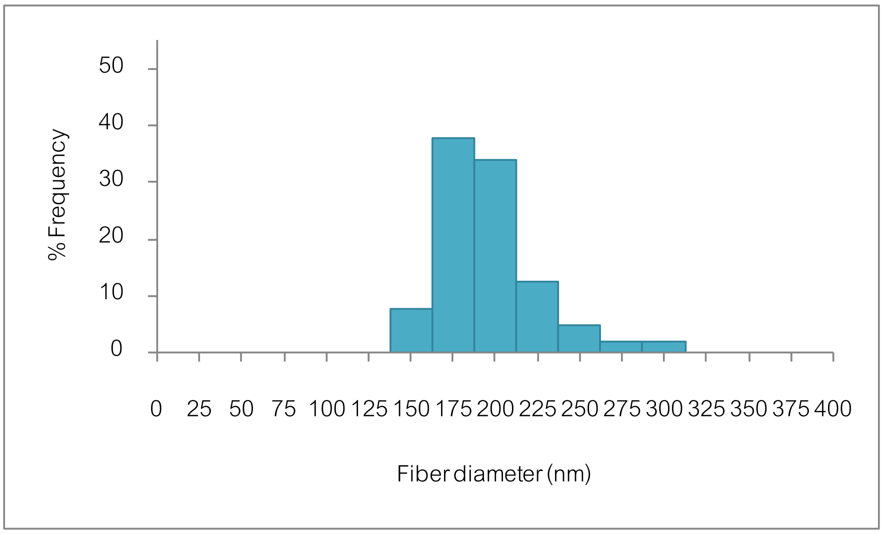


Figure 6A The diameter distribution of Nylon-6 /(PDADMAC/PSS)$_{15}$.

Table 7A Fiber diameter of electrospun nylon-6 treated surface with sodium hydroxide solution (Nylon/NaOH) measured from SEM micrograph.

Fiber diameter (nm)	Frequency	% Frequency
0-25	0	0
25-50	0	0
50-75	0	0
75-100	0	0
100-125	0	0
125-150	1	1.4
150-175	18	25.7
175-200	33	47.1
200-225	16	22.9
225-250	2	2.9
250-275	0	0
275-300	0	0
300-325	0	0
325-350	0	0
Total	70	100

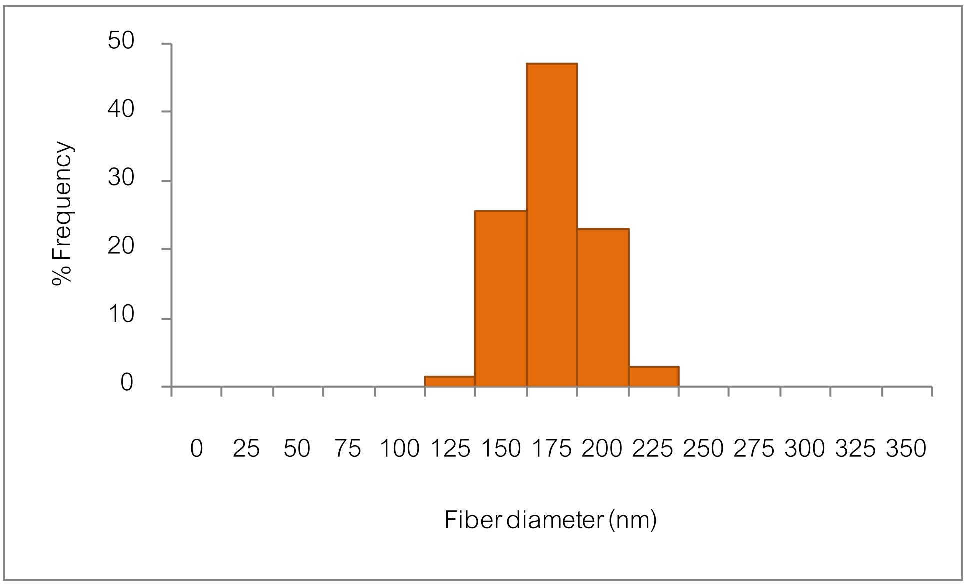


Figure 7A The diameter distribution of Nylon-6 /NaOH.

Table 8A Fiber diameter of electrospun nylon-6 treated surface with sodium hydroxide solution and functionalised surface with 1 bilayers poly(diallyldimethylammoniumchloride) and poly(4-styrenesulfonic acid) sodium salt (Nylon /NaOH/PDADMAC/PSS) measured from SEM micrograph.

Fiber diameter (nm)	Frequency	% Frequency
0-25	0	0
25-50	0	0
50-75	0	0
75-100	0	0
100-125	0	0
125-150	0	0
150-175	7	7
175-200	51	51
200-225	34	34
225-250	7	7
250-275	1	1
275-300	0	0
300-325	0	0
325-350	0	0
350-375	0	0
375-400	0	0
400-425	0	0
425-450	0	0
Total	100	100

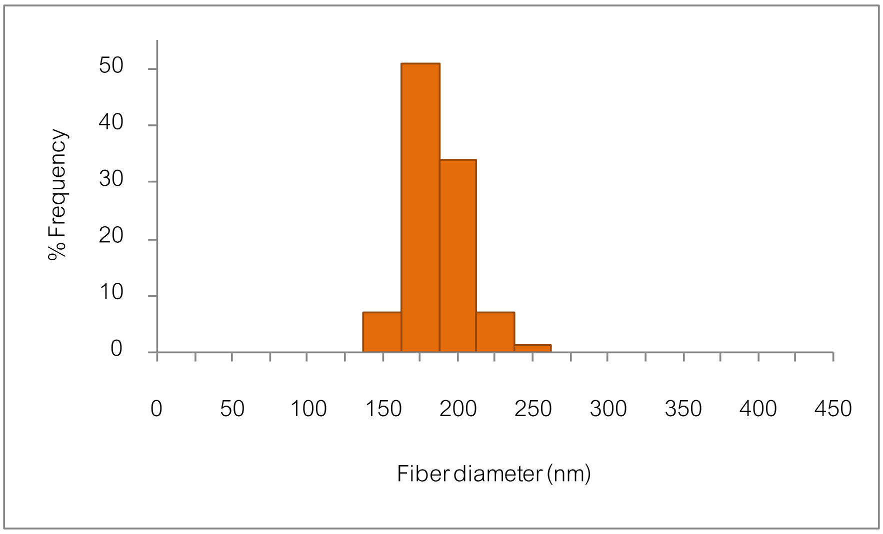


Figure 8A The diameter distribution of Nylon-6 /NaOH/PDADMAC/PSS.

Table 9A Fiber diameter of electrospun nylon-6 treated surface with sodium hydroxide solution and functionalised surface with 3 bilayers poly(diallyldimethylammoniumchloride) and poly(4-styrenesulfonic acid) sodium salt (Nylon /NaOH/(PDADMAC/PSS)$_3$) measured from SEM micrograph.

Fiber diameter (nm)	Frequency	% Frequency
0-25	0	0
25-50	0	0
50-75	0	0
75-100	0	0
100-125	0	0
125-150	0	0
150-175	2	1.8
175-200	40	36.7
200-225	47	43.1
225-250	10	9.2
250-275	3	2.8
275-300	5	4.6
300-325	2	1.8
325-350	0	0
350-375	0	0
375-400	0	0
400-425	0	0
425-450	0	0
Total	109	100

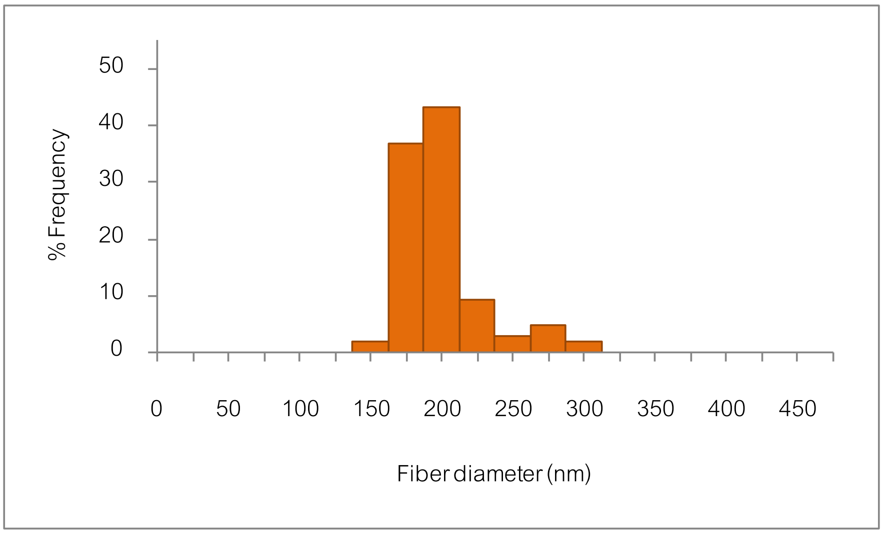


Figure 9A The diameter distribution of Nylon-6 /NaOH/(PDADMAC/PSS)$_3$.

Table 10A Fiber diameter of electrospun nylon-6 treated surface with sodium hydroxide solution and functionalised surface with 5 bilayers Poly(diallyldimethylammoniumchloride) and poly(4-styrenesulfonic acid) sodium salt (Nylon /NaOH/(PDADMAC/PSS)$_5$) measured from SEM micrograph.

Fiber diameter (nm)	Frequency	% Frequency
0-25	0	0
25-50	0	0
50-75	0	0
75-150	0	0
150-175	0	0
175-200	0	0
200-225	5	5.8
225-250	13	15.1
250-275	29	33.7
275-300	19	22
300-325	7	8.1
325-350	9	10.5
350-375	2	2.3
375-400	2	2.3
425-450	0	0
450-500	0	0
500-525	0	0
525-550	0	0
550-575	0	0
Total	86	99.8

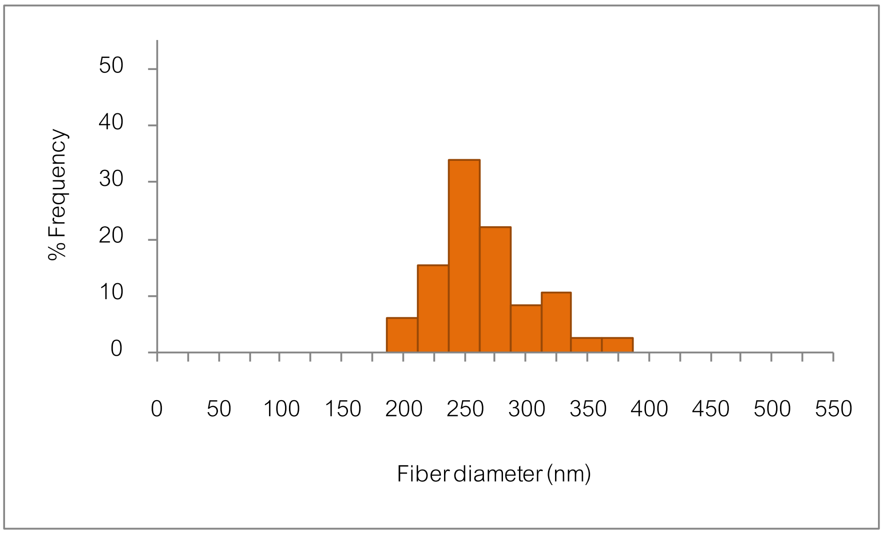


Figure 10A The diameter distribution of Nylon-6 /NaOH/(PDADMAC/PSS)$_5$.

Table 11A Fiber diameter of electrospun nylon-6 treated surface with sodium hydroxide solution and functionalised surface with 11 bilayers Poly(diallyldimethylammoniumchloride) and poly(4-styrenesulfonic acid) sodium salt (Nylon /NaOH/(PDADMAC/PSS) $_{11}$) measured from SEM micrograph.

Fiber diameter (nm)	Frequency	% Frequency
0-25	0	0
25-50	0	0
50-200	0	0
200-225	1	1.3
225-250	4	5
250-275	19	23.8
275-300	21	26.3
300-325	20	25
325-350	5	6.2
350-375	5	6.2
375-400	3	3.7
400-500	0	0
500-600	0	0
600-625	0	0
Total	80	100

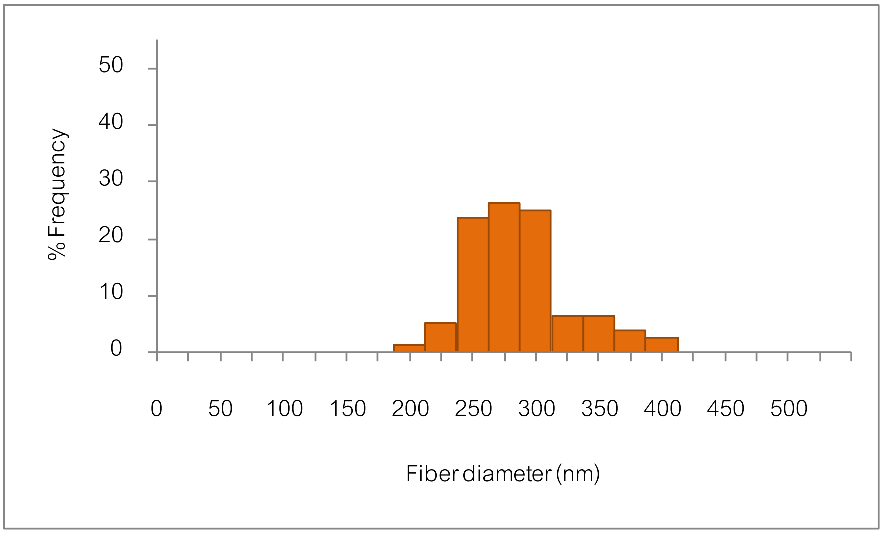


Figure 11A The diameter distribution of Nylon-6 /NaOH/(PDADMAC/PSS)$_{11}$.

Table 12A Fiber diameter of electrospun nylon-6 treated surface with sodium hydroxide solution and functionalised surface with 15 bilayers Poly(diallyldimethylammoniumchloride) and poly(4-styrenesulfonic acid) sodium salt (Nylon /NaOH/(PDADMAC/PSS) $_{15}$) measured from SEM micrograph.

Fiber diameter (nm)	Frequency	% Frequency
0-25	0	0
25-50	0	0
50-200	0	0
200-300	0	0
300-325	0	0
325-350	1	1.8
350-375	5	8.9
375-400	4	7.1
400-425	16	28.6
425-450	11	19.6
450-475	8	14.2
475-500	8	14.2
500-525	1	1.7
525-550	2	3.5
550-575	0	0
575-600	0	0
600-700	0	0
Total	100	99.6

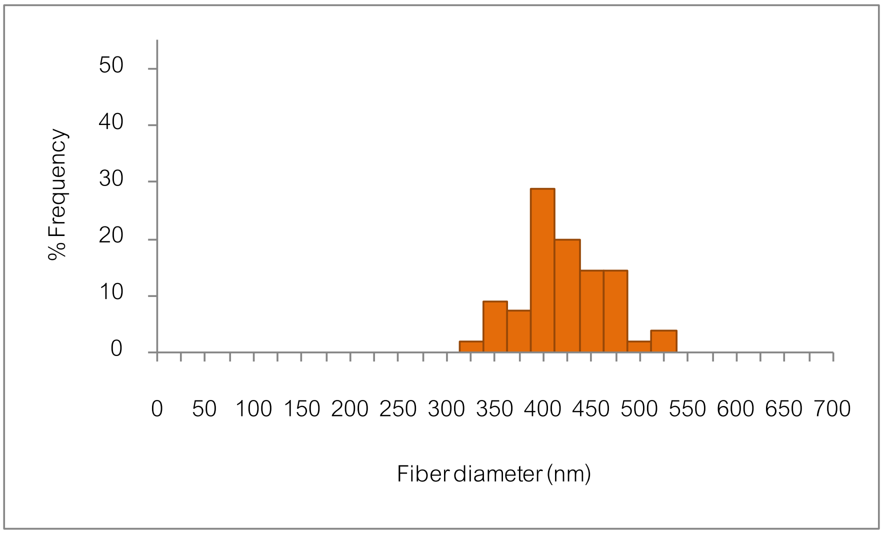


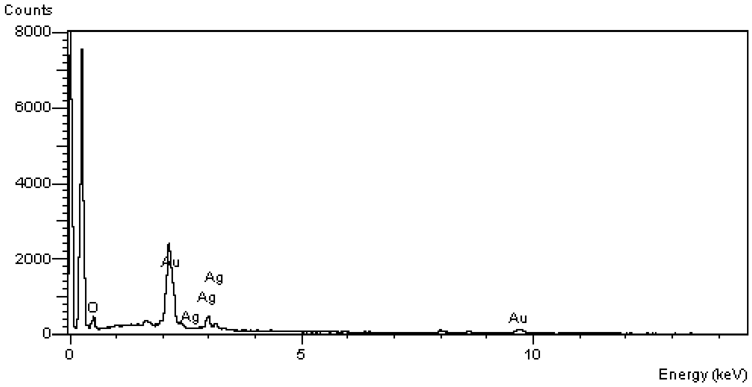
Figure 12A The diameter distribution of Nylon-6 /NaOH/(PDADMAC/PSS) $_{15}$.

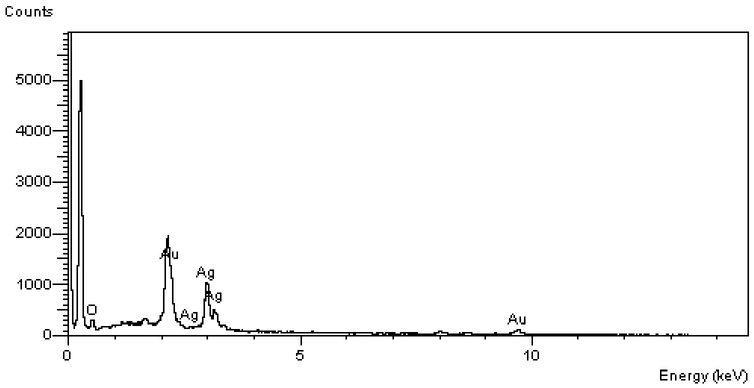
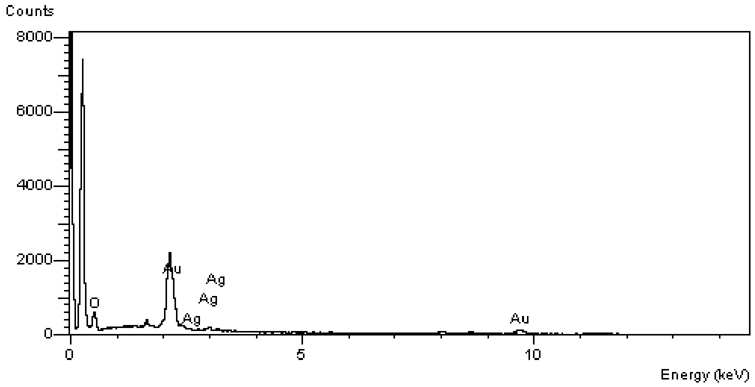
APPENDIX B

The composition of silver elemental on surface of electrospun nylon-6

The composition of silver elemental immobilized on surface of electrospun nylon-6 fibrous treated with NaOH indicated from the combination of SEM and EDX spectrum is presented in Table 1B.

Table 1B Illustrate the composition of silver elemental on electrospun nylon-6 fibers.

Ratio of Ag:pSS-co-Maleic acid (mM)	SEM-EDX spectrum of the nylon-6 fiber mats containing silver nanoparticles (Nylon/NaOH/(PDADMAC/PSS)$_3$/AgNPs)
1:0.005	

1:0.05	Counts 5000 4000 3000 2000 1000 0 O Au Ag Ag Ag Au 0 5 10 Energy (keV)
1:0.5	Counts 8000 6000 4000 2000 0 O Au Ag Ag Ag Au 0 5 10 Energy (keV)

APPENDIX C

Percentage reduction of bacteria on electrospun nylon-6 fibers and composited nylon-6membrane

The antimicrobial activity of nylon-6 electrospun fiber mats incorporated with silver nanoparticles was investigated. This work was used according AATCC 100 standard testing method on textile material. The silver immobilized on surface of nylon-6 fabrics against gram negative of *Escherichia coli* (*E. coli*) and gram positive *Staphylococcus aureus* (*S. aureaus*), respectively. The samples were incubated at 37°C for 24 h to evaluate percent reduction of bacteria by the following :

$$R = \frac{(C - A)}{C} \times 100$$

where:

R = Reduction percentage

A = The number of bacteria recovered from the inoculated treated test specimen swatches in the jar incubated over the desired contact period

C = The number of bacteria recovered from the inoculated untreated control specimen swatches in the jar immediately after inoculation (at "24 hours" contact time)

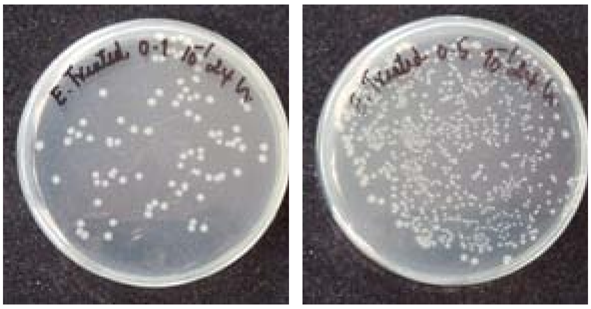
Table 4.8 Illustrate the percentage reduction of sample effect on *Escherichia coli* cell.

Test Microorganisms	**Sample**	**The number of bacteria CFU/Sample (0 h)**	**The number of bacteria CFU/Sample (24 h)**	**% Reduction (C at 0 h)**	**% Reduction (C at 24 h)**
Escherichia coli (-)	Untreated Blank	3.1×10^6	3.6×10^6	-	-
	0.005	-	1.3×10^6	58.06	63.87
	0.01	-	1.7×10^5	94.51	95.27
	0.05	-	1.0×10^5	96.77	97.22
	0.1	-	1.4×10^6	54.83	61.11
	0.5	-	3.0×10^6	0	16.67
	Treated Blank	3.6×10^6	3.9×10^6	-	-
	Treated 0.005	-	1.0×10^4	99.72	99.74
	Treated 0.01	-	1.0×10^3	99.97	99.97
	Treated 0.05	-	1.0×10^2	99.99	99.99
	Treated 0.1	-	8.3×10^5	76.94	78.71
	Treated 0.5	-	3.0×10^6	0	23.07

Untreated Blank Untreated 0.005 Untreated 0.01 Untreated 0.05

Untreated 0.1 Untreated 0.5

Treated Blank Treated 0.005 Treated 0.01 Treated 0.05



Treated 0.1 Treated 0.5

Figure 1C. The number of *Escherichia coli* bacteria presented in sample with varied concentration of PSS-co-MA at “24 hours” which incubated at 37°C for 24 hours.

Table 4.8 Illustrate the percentage reduction of sample effect on *Staphylococcus aureus* (*S. aureaus*) cell.

Test Microorganisms	**Sample**	**The number of bacteria**	**The number of bacteria**	**% Reduction (C at 0 h)**	**% Reduction (C at 24 h)**
Staphylococcus aureus (+)	Untreated Blank	3.9×10^5	2.0×10^6	-	-
	0.005	-	1.9×10^4	95.12	99.05
	0.01	-	7.0×10^3	98.2	99.87
	0.05	-	1.0×10^2	99.99	99.99
	0.1	-	1.6×10^5	58.97	92
	0.5	-	9.6×10^5	0	52
	Treated Blank	3.0×10^5	8.2×10^5	-	-
	Treated 0.005	-	1.0×10^3	99.68	99.87
	Treated 0.01	-	1.0×10^3	99.68	99.87
	Treated 0.05	-	1.0×10^2	99.99	99.99
	Treated 0.1	-	3.4×10^4	89.37	95.85
	Treated 0.5	-	5.6×10^5	0	31.71

Untreated Blank Untreated 0.005 Untreated 0.01 Untreated 0.05

Untreated 0.1 Untreated 0.5

Treated Blank Treated 0.005 Treated 0.01 Treated 0.05

Treated 0.1 Treated 0.5

Figure 2C. The number of *Staphylococcus aureus* bacteria presented in sample with varied concentration of PSS-co-MA at “24 hours” which incubated at 37°C for 24 hours.

APPENDIX D

The bacteria inhibition zone of electrospun nylon-6 fibers

The bacteria inhibition zone of electrospun nylon-6 fiber mats immobilized with the silver nanoparticles as different of PSS-co-MA concentrations 0.005, 0.01, 0.05, 0.1, 0.5 mM against Gram-negative *Escherichia coli (E. coli).* And *Staphylococcus aureus* (*S. aureaus*), respectively were studied.

Table 4.8 Illustrate the bacteria inhibition zone of sample effect on *Escherichia coli* cell and *Staphylococcus aureus* cell.

Sample	Clear Zone (mm.)	
	Staphylococcus aureus	*Escherichia coli*
Untreated blank	38	38
Untreated 0.005	39.5	39.5
Untreated 0.01	42	40
Untreated 0.05	42	40.5
Untreated 0.1	40.5	40
Untreated 0.5	39.5	39.5
Treated blank	38	38
Treated 0.005	40.5	40.5
Treated 0.01	42.5	41
Treated 0.05	46	42
Treated 0.1	42.5	40.5
Treated 0.5	42	40

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