FABRICATION AND CHARACTERIZATION OF PVA/ZINC ACETATE NANOFIBERS BY ELECTROSPINNING METHOD

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ABSTRACT

Local-made electrospun machine is firstly constructed. Poly Vinyl Alcohol/Zinc acetate (PVA/Zinc acetate) composite fibers of different molarities 0.2 M, 0.3 M, 0.4 M, 0.5 M are formed on Aluminium-foil substrate by electrospinning technique. Electrospun Poly Vinyl Alcohol/Zinc Oxide (PVA/ZnO) submicron fibers of 0.2 M ~ 0.5 M are successfully formed by calcinations at high temperatures. Scanning Electron Microscopy (SEM) analysis is carried out to examine the fiber diameter and microstructural properties of both micron fibers.

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CHAPTER I

OBJECTIVE AND MOTIVATION

This research deals with the fabrication construction and the production of electrospinning apparatus. Sol-gel process is used to produce the polymer solution. The surface morphology of prepared nanofibers is characterized by Scanning Electron Microscopy (SEM). The overall objectives of this work are to develop a suitable processing methodology to produce ZnO fibers with properly controlled interconnectivity by using electrospinning in combination with the sol-gel technique.

Nanotechnology has shown astounding prospects and progress in recent years and it is viewed as a high-end tool for numerous technological advancements. The objective of this thesis is to explore the possibility of using nanotechnology to create high performance nanomaterials. The process for producing polymeric nanofibers and the effect of process parameters over its structure and morphology has been analyzed.

Research work reported in this thesis has exploited the electrospinning nanotechnology to develop high performance nanofiber webs that have advanced applications. The motivation to this thesis has been the on going development in the field of nanotechnology and the interesting properties of nanostructures. Nanotechnology offers the advantage of increased sensitivity, selectivity and response time.

The potential of nanofiber materials have motivated this present research to carry out research on the electrospinning of a few polymer fibers and then investigation of fiber properties. Results obtained will hopefully lead to furthering the current understanding of electrospinning of nanofibers [1].

1.1 The Role of Nanofibers

A number of amazing characteristics arise when polymer fiber materials shrink in diameter from micrometres to sub-microns or nanometres. Among their important properties, two that stand out are a very large ratio of surface area to volume, and superior mechanical performance (stiffness and tensile strength) compared to any other known fiber-material form. These outstanding properties make polymer nanofibers optimal candidates [2].

Fibers with a diameter of between 100 nm-500 nm are generally classified as nanofibers. These fibers can be made from a wide variety of materials ranging from metals to ceramics to polymers. What makes nanofibers of great interest is there extremely small size. With higher surface area to volume ratios and smaller spaces between individual fibers than larger fibers, nanofibers offer an opportunity for use in a wide variety of applications. Increased awareness of the current and the potential applications of nanofibers have in recent years accelerated the research and development of these structures [3].

Up to date, polymer composites reinforced with electrospun nanofibers have been developed mainly for providing some outstanding physical (e.g. optical and electrical) and chemical properties while keeping their appropriate mechanical performance and less work has been done on the development of electrospun polymer nanofiber reinforced composites.

First of all, not sufficient quantity of uniaxial and continuous nanofibers has been obtained and could be used as reinforcements. The non-woven or randomly arranged nanofiber mats generally cannot result in a significant improvement in the mechanical properties of the composites with their reinforcement. Another reason may be that polymers yielding these fibers are generally considered as less suitable for structural enhancement. Although carbon nanofibers are principally achievable from post-processing of electrospun precursor polymer nanofibers such as polyacrylonitrile (PAN) nanofibers, these fibers seem to have not been obtained in large quantity of continuous single yarns yet. Thus, extensive work both from the standpoint of nanofiber composite science (fabrication, characterization, modeling and simulation) and from industrial base (applications) viewpoint is necessary in the future [4].

1.2 The Need for Nanofibers

Electrospinning has been recognized as an efficient technique for the fabrication of polymer nano fibers. Various polymers have been successfully electrospun into ultra fine fibers in resent years mostly in solvent solution and some in melt form. Nanofibers are an exciting new class of material used for several value added applications such as medical, filtration, barrier, wipes, personal care, composite, garments, insulation, and energy storage.

Special properties of nanofibers like extremely high surface to weight ratio compare to conventional non woven's. Low density, large surface area to mass, high pore volume, and tight pore size make the nanofiber suitable for a wide range of applications [5].

CHAPTER II

ELECTROSPINNING AND NANOFIBERS

Electrospinning is the process using electrostatic forces to form a fine filament of the polymer solution.

2.1 OVERVIEW OF ELECTROSPINNING METHOD

Engineers have successfully created polymer fibers using mechanical methods for several decades using mechanical processes. Conventional mechanical fiber spinning techniques cannot produce fibers with diameters smaller than about 2 μm robustly. Although conventional methods of producing polymer fibers are capable of producing fibers with diameters in the μm range, many applications require nm range (6).

Production of synthetic filaments using electrostatic forces has been known for more than one hundred years. The process of spinning fibers with the help of electrostatic forces is known as electrospinning. It has been shown recently that electrospinning process is capable of producing fibers in the submicron range. In fiber science related literature, fibers with diameters below 100 nm are generally classified as nanofibers (1).

Recently a process called electrospinning has been developed. This process has produced fibers as small as 5 nm in diameter and is appropriately called nanofibers (6). Electrospinning process uses high voltage electric field to produce electrically charged jets from polymer solution or melts, which on drying by means of evaporation of the solvent produces nanofibers. The highly charged fibers are field directed towards the oppositively charged collector, which can be a flat surface or a rotating drum to collect the fibers (1).

Electrospinning is a technique for producing polymer fibers in the range of 10 μm to 10 nm by accelerating a charged polymer solution using a high electric field. These fibers due to their light weight and large surface area to volume ratio have potential applications in several fields such as "smart clothing" for military, filters, sensors, nanocomposites, nanoelectronic devices, wound dressing etc. In normal conventional spinning techniques, the fiber is subjected to a group of tensile, gravitational, aerodynamic, rheological and inertial forces [7].

In electrospinning, the spinning of fibers is achieved primarily by the tensile forces created in the axial direction of the flow of the polymer by the induced charges in the presence of an electric field [6].

2.2 History of Electrospinning

Electrospinning traces its roots back to electrostatic spray painting, which has been in operation for almost 100 years. In 1934, a process for the production of polymer filaments using electrostatic force was patented by Formhals. Formhals encountered a number of problems early in his work, but by 1940 he had not only overcome those initial problems, he had developed methods of producing composite fibers using multiple polymers and for producing fibers that were aligned parallel to one another. Although the fibers produced by Formhals were much larger than the nanofibers, his work set the stage for the production of these structures.

Taylor did a study of the polymer droplet at the end of the needle in an electrospinning setup in 1969. This study led to a better understanding of the process by which the polymer solution streams from the needle. In 1987, the experimental conditions and factors that cause highly conductive fluids exposed to increasing voltages to produce unstable streams was studied by Hayati et al. These conditions cause the fluid stream to whip around in different directions as it leaves the needle. The work of Doshi and Reneker explored how changing the concentration of the polymer solution and the voltage applied to the solution affected the formation of nanofibers.

Numerous other studies have been done to examine the effect of changing both the polymer solution and the experimental setup. Based on these studies it is clear that characteristics such as fiber diameter, fiber morphology and the amount of beading are dependent upon a large number of variables. These variables include solution concentration, viscosity, surface tension and conductivity and process variables, such as voltage, needle diameter, flow rate and needle-to-collector distance [3].

2.2.1 Electrospinning Theory and Process

Electrospinning is a unique approach using electrostatic forces to produce fine fibers. Electrostatic precipitators and pesticide sprayers are some of the well known applications that work similar to the electrospinning technique. Fiber production using electrostatic forces has invoked glare and attention due to its potential to form fine fibers. Electrospun fibers have small pore size and high surface area. There is also evidence of sizable static charges in electrospun fibers that could be effectively handled to produce three-dimensional structures.

Electrospinning is a process by which a polymer solution or melt can be spun into smaller diameter fibers using a high potential electric field. This generic description is appropriate as it covers a wide range of fibers with submicron diameters that are normally produced by electrospinning. Based on earlier research results, it is evident that the average diameter of electrospun fibers ranges from 100 nm - 500 nm. In textile and fiber science related scientific literature, fibers with diameters in the range 100 nm - 500 nm are generally referred to as nanofibers.

The advantages of electrospinning process are its technical simplicity and its easy adaptability. The apparatus used for electrospinning is simple in construction which consists of a high voltage electric source with positive or negative polarity, a syringe pump with capillaries or tubes to carry the solution from the syringe or pipette to the spinnerette and a conducting collector like aluminum. The collector can be made of any shape according to the requirements like flat plate, rotating drum, etc. The schematic of the eletctrospinning process is shown in Figure 2.1.

Polymer solution or the melt that has to be spun is forced through a syringe pump to form a pendant drop of the polymer at the tip of the capillary. High voltage potential is applied to the polymer solution inside the syringe through an immersed electrode thereby inducing free charges into the polymer solution. These charged ions move in response to the applied electric field towards the electrode of opposite polarity thereby transferring tensile forces to the polymer liquid. At the tip of the capillary, the pendant hemispherical polymer drop takes a cone like projection in the presence of an electric field. And, when the applied potential reaches a critical value required to overcome the surface tension of the liquid, a jet of liquid is ejected from the cone tip.

Most charge carriers in organic solvents and polymers have lower mobilities and hence the charge is expected to move through the liquid for larger distances only if given enough time. After the initiation from the cone, the jet undergoes a chaotic motion is field directed towards the oppositively charged collector, which collects the charged fibers. As the jet travels through the vacuum, the solvent spun straightly and it is left behind a dry fiber on the collecting device. For low viscosity solutions, the jet breaks up into droplets while for high viscosity solutions it travels to the collector as fiber jets [1].

2.3 Electrospinning Apparatus Setup

The electrospinning apparatus must contain a needle or spinneret, high voltage power supply, and a grounded collector. Figure 2.2 demonstrates the basic components needed to perform electrospinning as mentioned above. A syringe is filled with a polymer solution which is fed through a needle (or occasionally a spinneret) into an electric field usually through the use of a syringe pump or gravity. A syringe pump allows the solution to be introduced to the spinning system at a precisely controlled rate.

The polymer solution travels from the syringe into a metallic needle, which is connected to a high voltage power supply that is typically capable of producing between 1 to 30 kV. In order to create an electric field the system must contain, along with the charged needle, a grounded plate. This conductive plate completes a circuit and allows a strong electric field to be created between the needle and the plate. This grounded plate also serves as the collector for the completed nanofiber web that is fabricated during the electrospinning process [8].

2.3.1 Electrospinning Mechanism

Fibers are produced during electrospinning due to static electric forces that manipulate a polymer solution as it is carried through an electric field. The process begins as an electric field is generated by a high voltage power supply, between a conducting capillary (needle or spinneret) that holds a polymer solution and a grounded collector plate. The polymer solution is held in a droplet shape by surface tension and as the electric field moves from the high voltage supply to the needle and then to the solution, a charge is induced on the surface of the droplet.

An opposite charge (repulsion force) is also formed at this time that pulls the droplet towards the electric field. As the electric field increases, the charge on the droplet also increases and causes the spherical droplet to deform into a conical shape. This is known as the Taylor cone shown in Figure 2.3. When the force from of the electric field influences the repulsion force until it overcomes the surface tension, the charged solution is pulled into the electric field towards the ground plate.

As the solution, now a fluid filament is pulled through the electric field, internal and external charges cause the liquid jet to be whipped around within the field as it accelerates towards the grounded collector. This action simultaneously causes the solvent in the solution to evaporate and the polymer chains within the solution to stretch and slide past one another. This whipping motion allows the fibers found on the grounded collector to have diameters small enough to classify them as nanofibers [8].

2.3.2 Electrospinning Process Parameters

While the electrospinning setup and process itself may be relatively simple the variables involved in producing a nano-sized diameter, fiber mesh with relative uniformity are numerous. Both solution and machine parameters must be considered.

Solution parameters include polymer type, polymer concentration, and type of solvent, solvent concentration, viscosity, molecular weight of the polymer, conductivity and surface tension.Machine or process parameters include electric field strength, flow rate, distance from the capillary to the collector, shape and movement of the collector, room temperature, and humidity.

Solution viscosity is a particularly important parameter and is heavily influenced by polymer concentration. To produce fibers in any spinning mechanism a minimum amount of polymer chains must be present to allow for chain entanglement and fiber production. Increasing polymer concentration, which increases the number of polymer chains present in solution, also increases viscosity which can become too high to allow flow through a needle or spinneret and prevents the formation of the Taylor cone and subsequent fibers [8].

2.4. Nanofibers

Research and development of nanofiber products is very active over the world (1) fiber with diameter in nanometer range. Many types of polymers were processed into nanofibers of 50 to 1000 nanometers in diameter, several orders of magnitude smaller than conventional fiber spinning [10].

2.4.1 Background of Nanofibers

In recent years, the term nanotechnology has spread across the globe like worldwide. Millions of dollars in research grants and investments are being devoted to making proof less than 100 nanometers in size. Unlike many other aspects of the traditional textile industry in the United States which is said to be on death's doors, nanotechnologies generating quite a bit of interest [11].

The nonwoven industry generally considers nanofibers as having a diameter of less than one micron, although the National Science Foundation (NSF) defines nanofibers as having at least one dimension of 100 nanometer (nm) or less. The name derives from the nanometer, a scientific measurement unit representing a billionth of a meter, or three to four atoms wide [12].

When the diameters of polymer fiber materials are shrunk from micrometers (e.g.10 – 100 μm to sub-microns or nanometers (e.g.10 x10 $^{-3}$ – 100 x10 $^{-3}$ μm), A nanofiber is an elongated and threadlike structure with a diameter in the nanometer range. At this scale several amazing characteristics such as very large surface area to volume ratio (this ratio for a nanofiber can be as large as 10^{3} times of that of a microfiber), flexibility in surface functionalities, and superior mechanical performance (e.g. stiffness and tensile strength) compared with any other known form of the material. These outstanding properties make the polymer nanofibers to be optimal candidates for many important applications like filtration, protective clothing and biomedical applications .A large number of synthetic and fabrication methods have already been demonstrated for generating nanostructures in the form of fibers [4].

A number of processing techniques such as drawing, template synthesis, phase separation, self-assembly, electrospinning, etc. have been used to prepare polymer nanofibers in recent years.

Fibers with a diameter of between 100 nm-500 nm are generally classified as nanofibers (see Figure 2.4). These fibers can be made from a wide variety of materials ranging from metals to ceramics to polymers. What makes nanofibers of great interest is there extremely small size. With higher surface area to volume ratios and smaller spaces between individual fibers than larger fibers, nanofibers offer an opportunity for use in a wide variety of applications. Increased awareness of the current and the potential applications of nanofibers have in recent years accelerated the research and development of these structures.

The process takes relatively long period of time to transfer the solid polymer into the nano-porous foam. The self-assembly is process in which individual, pre-existing components organize themselves into desired patterns and functions. However, similarly to the phase separation the self-assembly is time-consuming in processing continuous polymer nanofibers. Thus, the electrospinning process seems to be the only method which can be further developed for mass production of one-by-one continuous nanofibers from various polymer [13].

2.4.2 Structure and Morphology of Polymeric Nanofibers

Nanofibers have attracted the attention of researches due its pronounced micro and nano structural characteristics that enable the development of sophisticated materials that have advanced applications. More importantly, high surface area, small pore sizes, and the possibility of producing three-dimensional structures have increased the interest in nanofibers. As theoretical studies on the electrospinning, process has been conducted by various groups for a while to understand the electrospinning process, there have been some simultaneous efforts to characterize the structure and morphologv of nanofibers as a function of process parameters and material characteristics.

The production of nanofibers by electrospinning process is influenced both by the electrostatic forces and the viscoelastic behavior of the polymer. Process parameters like solution feed rate, applied voltage, nozzle-collector distance, spinning environment and material properties like solution concentration, viscosity, surface tension, conductivity and solvent vapor pressure influence the structure and properties of electrospun nanofibers [1].

2.4.3 Properties of Nanofibers

The properties associated with nanofibers can be traced back to both process parameters and morphological characteristics. For example electrospun fibers have small pores that are a result of the evaporation of the solvent used during the electrospinning process and these pores affect mechanical properties of the fibers such as tensile strength and Young's modulus. Other studies have found that the physical properties of nanofibers tend to be somewhat inferior to that of their film and resin counterparts of a similar thickness. This is believed to be a result of lower crystallinity due to rapid evaporation of the solvent followed by rapid cooling, which occurs in the final stages of the electrospinning process [8].

2.4.3.1 Thermal Properties

There are a few published reports on the thermal properties of nanostructured materials. Thermal analysis has been carried out on a number of electrospun polymeric materials to understand the relationship between nanostructure and thermal properties. Zong *et al.* attributed the decrease in the T_g to the large surface to volume ratio of nanofibers with air as the plasticizer. The high evaporation rate followed by rapid solidification at the final stages of electrospinning is expected to be the reason for the low crystalinity.

The glass transition temperature T_g and the peak crystallization temperature (T_c) of the electrospun polyethylene terephthalate (PET) and polyethylene naphthalate (PEN) decreased significantly, while the heat of crystalline melting increased. The decrease in T_g and Tm, and the increase in the heat of melting were attributed to the increase in the segmental mobility. The melting temperature of the PIT and PEN electrospun fibers remained almost constant without any significant variations compared to that of regular fiber form. PEO nanofibers have shown a lower melting temperature and heat of fusion than the PEO powder, which is attributed to the poor crytallinity of the electrospun fibers.

Deitzel *et al.* inferred that PEO nanofibers retained the same crystal structure as PEO powders while there is a clear indication of reduced crystalline order in nanofibers. Thermal degradation of PET and PEN before and after electrospinning was analyzed by Kim and Lee using the TGA thermogram and they found that on eletrospinning the intrinsic viscosities of both PET and PEN reduced significantiy. The thermal degradation and hence the decrease in intrinsic viscosities (i.e., decrease of molecular weight) were postulated to be the reasons for the decrease in T_g and T_c caused by reduced entanglements [1].

2.4.3.2 Mechanical Properties

Electrospun fibers have nanostructured surface morphologies with tiny pores that influence the mechanical properties like tensile strength, Young's modulus, etc. Gibson *et al.* have found that there is no significant change in the Young's modulus of electrospun Pellethane thermoplastic elastomers. When compared with cast films, electrospun elastomers have shown a 40% reduction in the peak tensile strength and 60% reduction in elongation at maximum applied stress.

Nanofiber reinforced polymer composites have shown highly enhanced mechanical properties than the unfilled or carbon/glass fiber filled composites. Young's modulus of a nanofiber composite has been found to be ten fold greater than the pure Styrene-Butadiene rubber. As is evident, there is less information available on the mechanical properties of nanofibers and nanofiber composites. Research on the mechanical properties of nanofibers and its composites from a variety of polymers is essential for a greater understanding on the contributions of nanofiber to the mechanical and performance related characteristic of nanofiber composites [1].

2.5 Applications of Nanofibers

Nanomaterials have been attracting the attention of global materials research these days primarily due to their enhanced properties required for application in specific areas like catalysis, filtration, NEMS, nanocomposites, nanofibrous structures, tissue scaffolds, drug delivery systems, protective textiles, storage cells for hydrogen fuel cells, etc [2].

2.5.1 Electrical and Optical Application

Conductive nanofibers are expected to be used in the fabrication of tiny electronic devices or machines such as Schottky junctions, sensors and actuators. Due to the well-known fact that the rate of electrochemical reactions is proportional to the surface area of the electrode, conductive nanofibrous membranes are also quite suitable for using as porous electrode in developing high performance battery. Conductive (in terms of electrical, ionic and photoelectric) membranes also have potential for applications including electrostatic dissipation, corrosion protection, electromagnetic interference shielding, photovoltaic device, etc.

Waters et al reported to use electrospun nanofibers in the development of liquid crystal device of optical shutter which is switchable under an electric field between state in which it is substantially transparent to incident light and state in which it is substantially opaque. The main part of this liquid crystal device consisted of layer of nanofibers permeated with liquid crystal material, having thickness of only few tens microns. The layer was located between two electrodes, by means of which an electric field could be applied across the layer to vary the transmissivity of the liquid crystal/nanofiber composite. It is the fiber size used that determines the sensitivities of the refractive index differences between the liquid crystal material and the fibers, and consequently governs the transmissivity of the device.Obviously nanoscale polymer fibers are necessary in this kind of devices [14].

2.6 Advantages of Electrospun Nanofibers

The advantages of electrospun fibers are very appealing to a broad array of potential applications in many industry segments. The composites industry for one is especially interested in nanofibers technology because it now becomes possible to create products that are much smaller and lighter in weight, yet capable of performing at the same or enhanced mechanical standards. If the fibers can be collected individually and aligned to specific orientations, it is possible to increase the maximum volume fraction of fibers in a matrix thus increasing the strength of the material. The increased surface area/weight will also allow for better bonding with the matrix to help prevent failure by pullout of the fibers.

In addition to the composites industry, the filtration industry has already begun utilizing nanofibers and in some cases has generated commercially available products. Nano-fibrous mats can be made with varying fiber diameters based on several input parameters. With varying fiber diameters, the pore size of the mat can be controlled to a fairly high degree. As a result, nanofibrous mats can be designed to block out molecules of specific sizes. In addition to mechanical filtration as described above, nano-fibrous mats can be treated so that when molecules of specific design pass through, a chemical reaction takes place which neutralizes any potential hazards.

Similarly, nanofibrous mats are being explored as biomedical grafts and wound dressings. It has been found that cells can adhere and proliferate into the mats with a great deal of success. Also, because of the extremely small size of the nano-fibers, the potential exists for layering of different polymers with specific functionalities. Electrospinning techniques can be applied to nearly every polymer of sufficient molecular weight, including those which are FDA approved; therefore no issues on biocompatibility exist.

One of the greatest attributes of electrospinning and nanofibrous technology is that it is very much still in its infancy. Numerous ideas and concepts have been proposed or written about, but in many cases the theoretical expectations have yet to be realized. It has been shown that nearly every polymer imaginable can be electrospun either from solution or melt so there are no limitations in that regard. Today, the fibers are collected in the form of a mat of staple aligned fibers. Future developments and processing technologies must find a way to orient a continuous fiber for the technology to continue to advance in the right direction.

It has been shown to some degree that electrostatic attraction and repulsion can be used to control the path of the jet to some degree. With enhanced methods of doing so, it may be capable of directly producing woven or braided fabrics from the electrospinning station. While the process itself is basically waiting for the mechanical/processing mechanisms to catch up that are capable of maneuvering single fibers into specific configurations, much work still needs to be done to optimize the conditions for making a specific fiber diameter with a specific polymer. It is only after we can truly control the process, that we can use it to the best of its ability and capabilities [11].

2.7 Challenges in nanofibers

The process of making nanofibers is quite expensive compared to conventional fibers due to low production rate and high cost of technology. In addition the vapors emitting from electrospinning solution while forming the web need to be recovered or disposed of in an environmental friendly manner. This involves additional equipment and cost. The fineness of fiber and evaporated vapor also raises much concern over possible health hazard due to inhalation of fibers. Thus the challenges faced can be summarized as:

- Economics
- Health hazards
- Solvent vapor
- Packaging shipping handling

Because of its exceptional qualities there is an ongoing effort to strike a balance between the advantages and the cost [12].

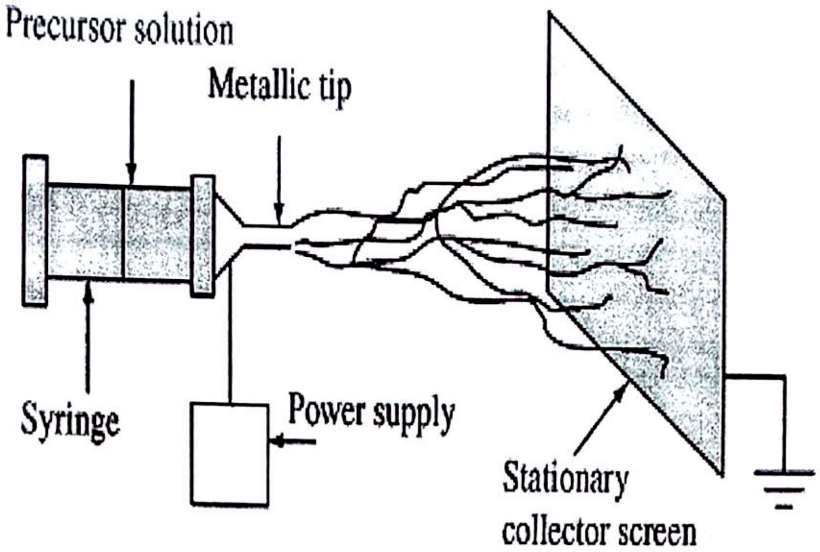

Figure 2.1: Schematic of the electrospinning setup

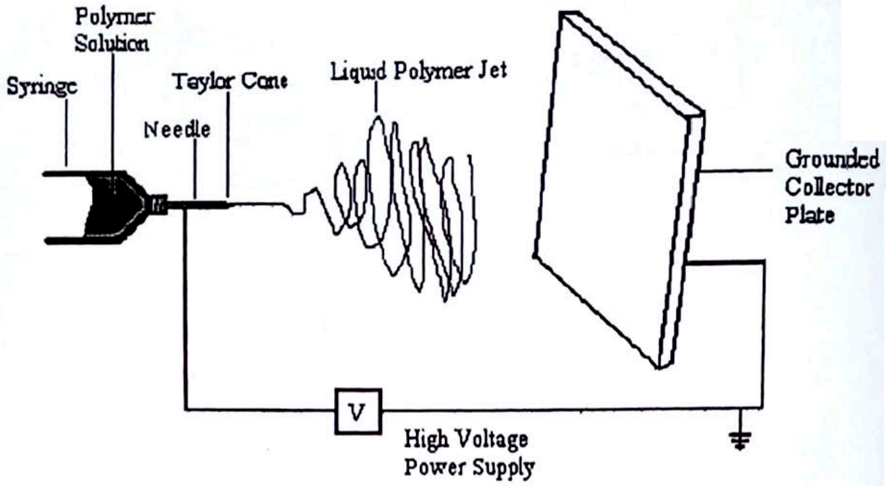

Figure 2.2 Basic components of electrospinning

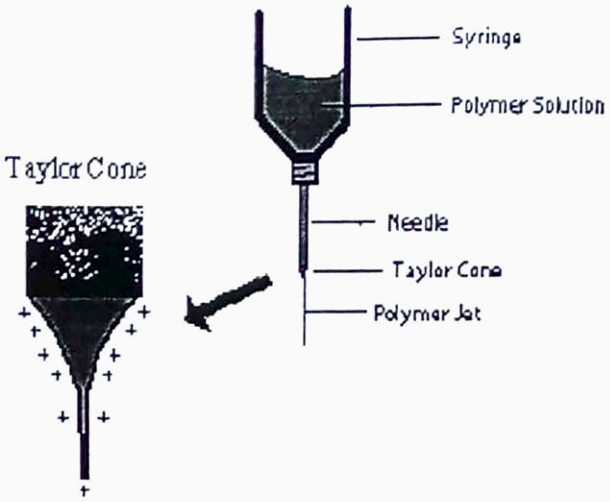

Figure 2.3 Taylor cone formation

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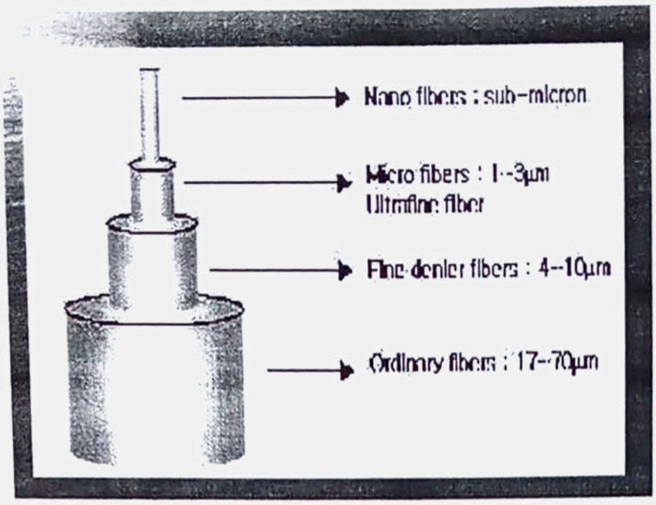


Figure 2.4 Comparison of fibers diameter

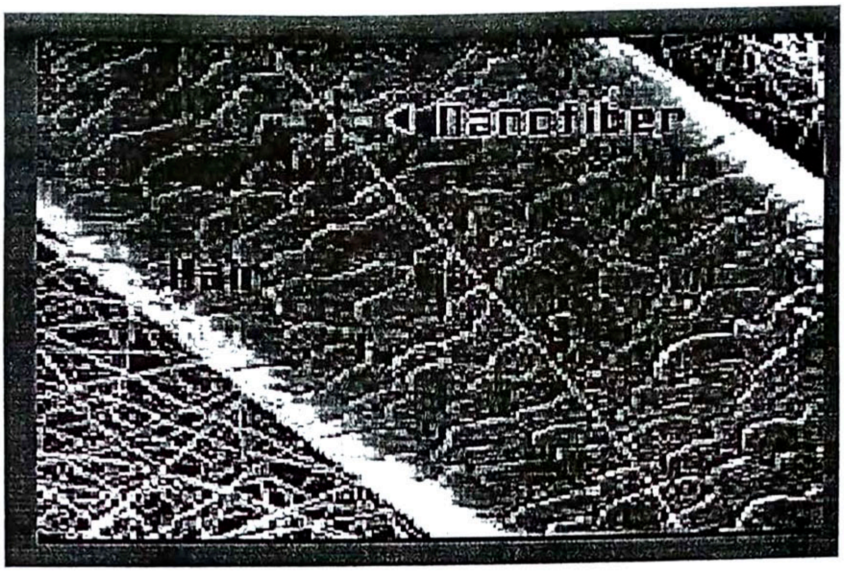


Figure 2.5 SEM image of nanofibers and human hair

CHAPTER III

FABRICATION AND CHARACTERIZATION TECHNIQUE

3.1 SOL-GEL Technique

The sol-gel process is a versatile solution process for making ceramic and glass materials. In general, the sol-gel process involves the transition of a system from a liquid "sol" (mostly colloidal) into a solid "gel" phase. Applying the sol-gel process, it is possible to fabricate ceramic or glass materials in a wide variety of forms: ultra-fine or spherical shaped powders, thin film coatings, ceramic fibers, microporous inorganic membranes, monolithic ceramics and glasses, or extremely porous aerogel materials [15].

The sol-gel process is a wet-chemical technique (Chemical Solution Deposition) for the fabrication of materials (typically a metal oxide) starting from a chemical solution that reacts to produce colloidal particles (sol). Typical precursors are metals alkoxides and metal chlorides, which undergo hydrolysis and polycondensation reactions to form a colloid, a system composed of solid particles (size ranging from 1nm to 1μm) dispersed and a solvent. The sol evolves then towards the formation of an organic network containing a liquid phase (gel).Formation of a metal oxide involves connecting the metal centers with oxo(M-O-M) or hydroxo(M-OH-M) bridges, therefore, generating metal-oxo or metal- hydroxo polymers in solution. The drying process serves to remove the liquid phase from the gel thus forming a porous materials, then a thermal treatment (firing) may be performed in order to favor further polycondensation and enhance mechanical properties.

The precursor sol can be either deposited on a substrate to form a film (e.g. by dip-coating or spin coating), cast into a suitable container with the desired shape. The sol –gel approach is interesting in that it is a cheap and low – temperature technique that allows for the fine control on the product's chemical composition, as even small quantities of dopants such as organic dyes and rare earth metals, can be introduced in the sol and end up of the final product finely dispersed. It can be used in ceramics manufacturing processes, as an investment casting materials, or as a means of producing very thin films of metal oxides for various purposes. Sol-gel derived materials have diverse applications in optics, electronics, emergency, space, (bio) sensors, medicine (e.g controlled drug release) and separation (e.g chromatography) temperatures, rapid cooling and subsequent vitrification of the glassy material. This procedure highly restricts choice of substances, which can be entrapped in the glass products. Basically only metal oxides and some inorganic salts can survive such drastic conditions avoiding thermal decomposition. Furthermore, the way in which conventional glass is produced makes thin films preparation extremely cumbersome and the only method of preparation of porous classical glasses requires etching or partial dissolving (e.g. Vycorâ glass). On the other hand glass and glassy materials possess several useful features for optical applications such as transparency, homogeneity, mechanical sturdiness, high refractive index etc.

An alternative approach to glass and glass-like materials is offered by the, so called, sol-gel technology. The process itself is known for more than a century, but it has gained a new importance in the last two decades after pioneering results of Dislich. He and other researchers improved the chemistry of the process so much that it is now possible to obtain samples in days (or even hours - in case of thin films) rather than months (or years) like in the case of the early samples.

The sol-gel technique is based on hydrolysis of liquid precursors and formation of colloidal sols. The precursors are usually organosilicates (e.g. TEOS - tetraethoxysilane) yielding silicate sol-gel materials. However, the method is not restricted to the silicon-compounds - for example compounds of zirconium, vanadium etc. can be used as precursors leading to materials possessing different physico-chemical properties. Furthermore, it is possible to obtain modified organosilicate precursors with direct Si-C bonds (which do not undergo hydrolysis) and possessing terminal functional groups (e.g. $-NH_2$, $-SH_2$ etc.). Such precursors, either pure or mixed with the conventional ones, yield inorganic-organic materials with mechanical (e.g. elasticity) and physico-chemical properties (e.g. wetability) modified by the organic components of the inorganic polymer network. The functional groups can be also used for covalent binding of various chemicals (including biomolecules) giving specifically modified glassy materials.

Another convenient feature of this technology is the fact that the sol-gel samples can be obtained as bulks, thin films and powders. It has to be noted that bulk sol-gel samples suffer very often from internal cracks, leading to their destruction. This effect is caused by evaporation of solvent molecules from the network of pores of the drying gels. The ensuing capillary pressure is high enough to cause the material collapse. However, for reasons only partially understood, sol-gel thin films are virtually immune from this destructive effect. Thus, for example sol-gel optodes based on such thin films possess all the attractive features of the sol-gel materials being, at the same time, virtually free from the most troublesome drawback of the method i.e. samples cracking.

The sol-gel technique is one of the fastest growing fields of contemporary chemistry. The main advantage of this process stems from the fact that it offers an alternative approach to conventional production of glasses, glass-like materials and ceramics of various properties and applications. The sol-gel technology enables production of doped glassy materials either as porous dry gels ("xerogels") or densified materials. Since the process starts from aqueous solutions of precursors it is possible to immobilize in glass-like materials various substances even as fragile as proteins (yielding bio-active glasses). Another attractive feature of this technology is the fact that sol-gel materials can be obtained as bulks, thin films (on various supports) and (nano) powders. Such matrices, activated by doping, impregnation or covalent bonding, yield materials which can be used as, among other possibilities, optical sensors, catalysts, medical materials (e.g. bone implants), active (e.g. "smart windows") and passive coatings (e.g. scratch-resistant or antireflective) or various optical materials (e.g. scintillators, powder lasers, amplifiers etc.).[3]

The starting materials used in the preparation of the "sol" are usually inorganic metal salts or metal organic compounds such as metal alkoxides. In a typical sol-gel process, the precursor is subjected to a series of hydrolysis and polymeration reactions to form a colloidal suspension, or a "sol". Further processing of the "sol" enables one to make ceramic materials in different forms. Thin films can be produced on a piece of substrate by spin-coating or dip-coating. When the "sol" is cast into a mold, a wet "gel" will form. With further drying and heat-treatment, the "gel" is converted into dense ceramic or glass articles. If the liquid in a wet "gel" is removed under a supercritical condition, a highly porous and extremely low density material called "aerogel" is obtained. As the viscosity of a "sol" is adjusted into a proper viscosity range, ceramic fibers can be drawn from the "sol". Ultra-fine and uniform ceramic powders are formed by precipitation, spray pyrolysis, or emulsion techniques [17].

A sol is a dispersion of the solid particles (~ 0.1-1 μm) in a liquid where only the Brownian motions suspend the particles. A gel is a state where both liquid and solid are dispersed in each other, which presents a solid network containing liquid components.

The sol-gel coating process usually consists of 4 steps:

(1) The desired colloidal particles once dispersed in a liquid to form a sol.

(2) The deposition of sol solution produces the coatings on the substrates by spraying, dipping or spinning.

(3) The particles in sol are polymerized through the removal of the stabilizing components and produce a gel in a state of a continuous network.

(4) The final heat treatments pyrolyze the remaining organic or inorganic components and form an amorphous or crystalline coating.

There are two distinct reactions in the sol-gel process: hydrolysis of the alcohol groups and condensation of the resulting hydroxyl groups. In the case of isomorphous γ-AlOOH precursor, it exists as the un-hydrolyzed species $[Al(OH_2)_6]^{3+}$ below pH_3,and can be hydrolyzed extensively with increasing pH. An overview of the sol-gel process is presented in a simple graphic work below in Figure 3.1 [18].

3.1.1 Advantages of sol-gel technique

Sol-gel technique has the following advantages;

- Can produce thin bond-coating to provide excellent adhesion between the metallic substrate and the top coat.
- Can produce thick coating to provide corrosion protection performance
- Can easily shape materials into complex geometries in a gel state.
- Can produce high purity products because the organo-metallic precursor of the desired ceramic oxides can be mixed, dissolved in a specified solvent and hydrolyzed into a sol, and subsequently a gel, the composition can be highly controllable.
- Can have low temperature sintering capability, usually 200-600°C.
- Can provide a simple, economic and effective method to produce high quality coatings.[4]

Sol-gel research grew to be so important that in the 1990s more than 50,000 papers were published worldwide on the process [18].

3.1.2 Applications

The applications for sol gel-derived products are numerous. E.G. Scientists have used it to produce the world's lightest materials and some of its toughest ceramics. One of the largest application areas is thin films, which can be produced on a piece of substrate by spin-coating or dip-coating. Other methods include spraying, electrophoresis, inkjet printing or roll coating. Optical coatings, protective and decorative coatings, and electro-optic components can be applied to glass, metal and other types of substrates with these methods.

Cast into a mold, and with further drying and heat-treatment, dense ceramic or glass articles with novel properties can be formed that cannot be created by any other method. Macroscopic optical elements and active optical components as well as large area hot mirrors, cold mirrors, lenses and beam splitters all with optimal geometry can be made quickly and at low cost via the sol-gel route. With the viscosity of a sol adjusted into a proper range, both optical and refractory ceramic fibers can be drawn which are used for fiber optic sensors and thermal insulation, respectively.

Ultra-fine and uniform ceramic powders can be formed by precipitation. These powders of single- and multicomponent compositions can be made in submicrometer particle size for dental and biomedical applications. Composite powders have been patented for use as agrochemicals and herbicides. Also powder abrasives, used in a variety of finishing operations, are made using a sol-gel type process.

One of the more important applications of sol-gel processing is to carry out zeolite synthesis. Other elements (metals, metal oxides) can be easily incorporated into the final product and the silicalite sol formed by this method is very stable.

Other products fabricated with this process include various ceramic membranes for microfiltration, ultrafiltration, nanofiltration, pervaporation and reverse osmosis.

If the liquid in a wet gel is removed under a supercritical condition, a highly porous and extremely low density material called aerogel is obtained. Drying the gel by means of low temperature treatments (25-100°C), it is possible to obtain porous solid matrices called xerogels.

Finally of historical note, a sol-gel process was developed in the 1950s for the production of radioactive powders of UO_2 and ThO_2 for nuclear fuels, without generation of large quantities of dust [15].

3.2 SCANNING ELECTRON MICROSCOPE

The first Scanning Electron Microscope (SEM) debuted in 1942 with the first commercial instruments appear around 1965. Its late development was due to the electronics involved in "scanning" the beam of electrons across the sample. It is a microscope that uses electrons rather than light to form an image. There are many advantages in using the SEM instead of light microscope.

The SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. Preparation of the samples is relatively easy since most SEMs require the sample to be conductive. The combination of higher magnification, larger depth of focus, greater resolution and ease of sample observation makes the SEM one of most heavily used instruments in research areas today.

Scanning electron microscopes (SEM) are patterned after Reflecting Light Microscopes and yield similar information:

Topography

The surface features of an object or "how it looks", its texture; detectable features limited to a few manometers.

Morphology

The shape, size and arrangement of the particles making up the object that are lying on the surface of the sample or have been exposed by grinding or chemical etching; detectable features limited to a few manometers.

Composition

The elements and compounds, the sample is composed of and their relative ratios, in areas ~1 micrometer in diameter.

Crystallographic Information

The arrangement of atoms in the specimen and their degree of order; only useful on single-crystal particles>20 micrometers,

1. The "Virtual source" at the top represents the electron gun, producing a stream of monochromatic electrons.
2. The stream is condensed b the first condenser lens (usually controlled by the "coarse probe current knob"). This lens is used to both form the beam and Limit the amount of current in the beam. It works in conjunction with the Condenser aperture to eliminate the high-angle electrons from the beam.
3. The beam is then constricted by the condenser aperture (usually not user selectable), eliminating some high-angle electrons.
4. The second condenser lens forms the electrons into a thin, tight, coherent beam and is usually controlled by the "fine probe current knob".
5. A user selectable objective aperture further eliminates high-angle electrons from the beam.
6. A set of coils then "scan" or "sweep" the beam in a grid fashion (like a television), dwelling on points for a period of time determined by the scan speed (usually in the microsecond range).
7. The final lens, the objective, focuses the scanning beam onto the part of the specimen desired.
8. When the beam strikes the sample (and dwells for a few microseconds) interactions occur inside the sample and are detected with various instruments.

9. Before the beam moves to its next dwell point these instruments count the number of interactions and display on a CRT whose intensity is determined by this number(the more relations the brighter the pixel).

10. This process is repeated until the grid scan is finished and then repeated, the entire pattern can be scanned 30 times per second.

3.2.1 Principle of SEM

As electron magnification microscope utilized an electron beam (e-beam) to produce a magnified image of the sample. There are three principle type of electron microscopes; scanning, transmission, and emission. In the scanning and transmission electron microscope, an electron beam incident on the sample produces an image, were as in the field-emission microscope the specimen it self is the source of electrons. A good discussion of the history of electron microscopy is given by cosslett. Scanning Electron Microscope (SEM) is similar to light microscopy, with the exception that electrons are used instead of photons. This has two main advantages: much larger magnifications are possible since electron wavelengths are much smaller than photon wavelengths and the depth of field is much larger.

3.2.2 Applications of SEM

The most common use of SEMs for semiconductor applications, include materials evaluation, failure analysis and quality control screening. Materials evaluations are obtained grain size, surface roughness, porosity, particle size distributions, material homogeneity and intermetallic distribution and diffusion. Failure analysis is described contamination location, mechanical damage assessment, electrostatic discharge effects and micro-crack location. Quality Control Screening is investigated “good” to “bad” sample comparison, film and coating thickness determination, dimension verification, gate width measurement and mil standard Screening [19].

The SEM is routinely used to generate high-resolution images of shapes of objects (SEI) and to show spatial variations in chemical compositions (usually EDS, also BSE and CL [add images here later]). This instrument is also widely used to identify phases based on qualitative chemical analysis and/or crystalline structure [add images here later]. Precise measurement of very small features and objects down to 50 nm in size is also accomplished using the SEM. Backescattered electron images can be used for rapid discrimination of phases in multiphase samples. SEMs equipped with diffracted backscattered electron detectors can be used to examine microfabric and crystallographic orientation in many materials.

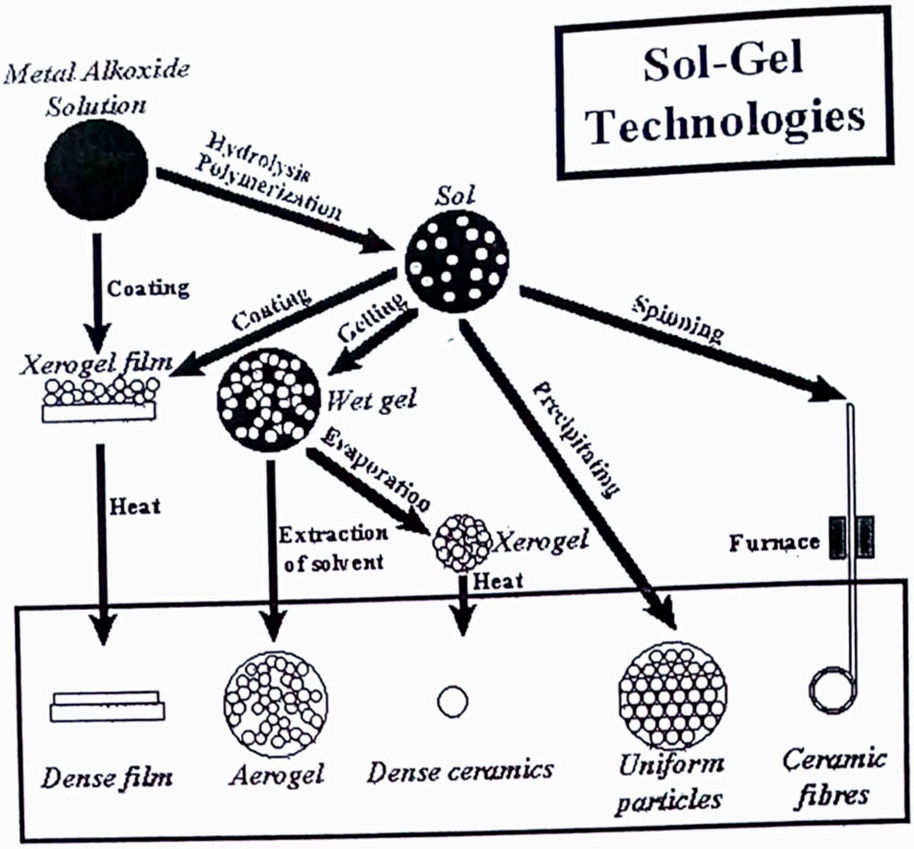


Figure 3.1 The schematic diagram of sol-gel technologies

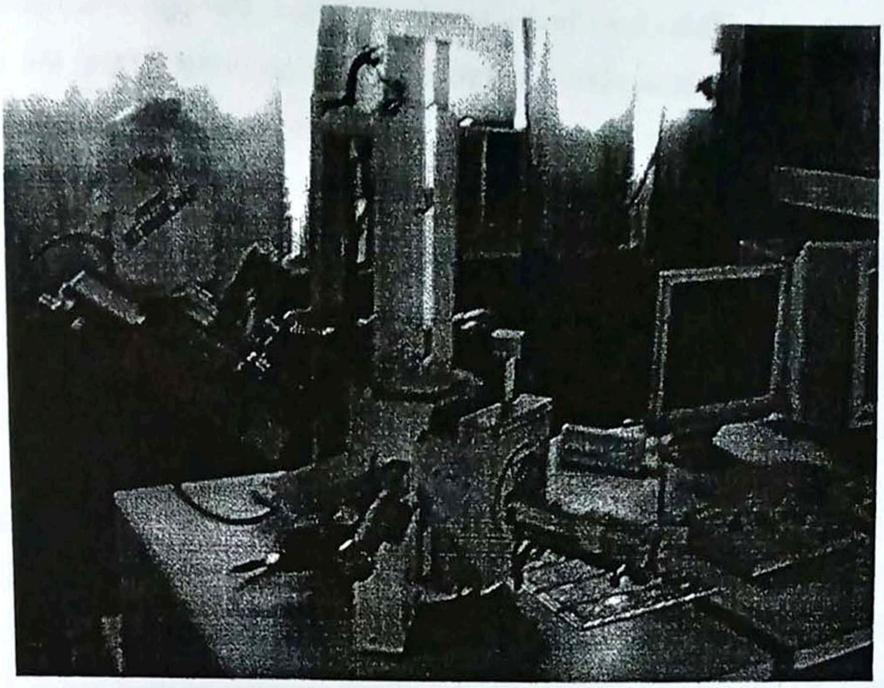


Figure 3.2 JEOL JSM -5610 Scanning Electron Microscope

CHAPTER IV

MATERIAL AND SETUP

4. 1 Materials Processing

Zinc acetate and polyvinyl alcohol was chosen as the polymer. This polymer was best suited for this project. In electrospinning setup as depicted in Figure 4.1, this has been setup modified through the progression of the experiment is to eliminate problems that occurred during the experiments. The electrospinning process takes place in a cylindrical shape of Plexiglas tube that has very limited exposure to elements exterior to the tube. This tube helps control the environment in which the electrospinning is taking place namely the unpredictable air currents in an uncontrolled environment that can dramatically alter nanofiber production. The tube was evacuated and polymer solution was ejected from the needle.

There are basically three components to fulfill the process: high voltage supplier, capillary tube with pipette or needle of small diameter, and a metal collecting screen. In the electrospinning process a high, voltage is used to create an electrically charged jet of polymer solution or melt out of the pipette. Before reaching the collecting screen, the solution jet evaporates or solidifies, and is collected as an interconnected web of small fibers. One electrode is placed into the spinning solution/melt and the other attached to the collector. The collector is simply grounded. The electric field is subjected to the end of the capillary tube that contains the solution fluid held by its surface tension. This induces a charge on the surface of the liquid. Mutual charge repulsion and the contraction of the surface charges to the counter electrode cause a force directly opposite to the surface tension.

As the intensity of the electric field is increased, the hemi- spherical surface of the fluid at the tip of the capillary tube elongates to form a conical shape known as the Taylor cone. When critical value is attained with which the repulsive electrostatic force overcomes the surface tension and the charged jet of the fluid is ejected from the tip of the Taylor cone. The discharged polymer solution jet undergoes an instability and elongation process, which allows the jet to become very long and thin.

Meanwhile, the solvent evaporates, leaving behind charged polymer fiber. Some polymers may emit unpleasant or even harmful smells, so the processes should be conducted within chambers having ventilation system. Furthermore, a DC voltage in the range of several to several tens of kVs is necessary to generate the electrospinning. One must be careful to avoid touching any of the charged jet while manipulation. Polymers, molten in high temperature, can also be made into nanofibers through electrospinning. Instead of a solution, the polymer melt is introduced into the capillary tube. However, different from the case of polymer solution, the electrospinning process for a polymer melt has to be performed in vacuum condition. Namely, the capillary tube, the traveling of the charged melt fluid jet, and the metal collecting screen must be encapsulated within a vacuum [13].

4.2 Material Background

4.2.1 Zinc acetate dihydrate

Zinc acetate is the chemical compound with the formula $Zn\ (CH_3COO)_2$ but more commonly refers to the dihydrate $Zn\ (CH_3COO)_2.2H_2O$ as shown in Figure 4.2(a). Both the hydrate and the anhydrous forms are colorless solids that are commonly used in chemical synthesis and as dietary supplements. The acetates group is capable of binding to metal ions in a variety of ways through its two oxygen atoms and several connectivities are observed for the various hydrates of zinc acetate. Anhydrous zinc acetate adopts a polymeric structure consisting of zinc coordinated to four oxygen atoms in a tetrahedral environment, each tetrahedron being connected to neighbors by the acetate groups.

Zinc acetate is used as a dietary supplement and in lozenges used to treat the common cold. Zinc acetate alone is thought be more effective at treating the common cold than zinc gluconate. Zinc acetate can also used to treat zinc deficiencies. As an oral daily supplement it is used to inhibit the body's absorption of copper as part of the treatment for Wilson's disease. Zinc acetate is also sold as an astringent in the form of an ointment, a topical lotion; or combined with an antibiotic for the topical treatment of acne. Industrial applications include wood preserving, manufacturing other zinc salts, polymers, manufacture of ethylene acetate, as a dye mordant, and analytical reagent [18].

4.2.2 Zinc Oxide

ZnO is widely used as a functional material with wide and band gap, large exciton binding energy, and excellent chemical and thermal stability [19]. As a wide band gap material, zinc oxide has received an increasing amount of attention due to its possible applications in ultraviolet (UV) lasers, light emitting devices [20]. ZnO is one of the hardest materials in II-VI compound semiconductors due to the higher melting point (1975°C) and larger cohesive energy. The constituent elements of zinc oxide are abundant and low cost. Also the material is non-toxic, which is an important consideration for environment. The cohesive energy of ZnO, is as large as 1.89 eV. This value should be compared with those of conventional semiconductors: GaAs (1.6eV); ZnSe(1.29eV) [21]. Among the II-VI compound semiconductors, ZnO has found use in both electrophotography as a photosensitive material and in paints and varnishes [22]. Zinc oxide is mainly used in sensors, solar cells and other electronic applications [23].

4.2.3 Polyvinyl Alcohol

Polyvinyl alcohol has excellent film forming, emulsifying, and adhesive properties. It is also resistant to oil, grease and solvent. It is odorless and nontoxic. It has high tensile strength and flexibility. However these properties are dependent on humidity, in other words, with higher humidity more water is absorbed. The water, which acts as a plasticiser, will then reduce its tensile strength, but increase it elongation and tear strength. PVA is fully degradable and is a quick dissolver. PVA has a melting point of 230°C and 180-190°C for the fully hydrolysed and partially hydrolysed grades. It decomposes rapidly above 200°C as it can undergo pyrolysis at high temperature [24]. Analar grade polyvinyl alcohol was shown in Figure 4.2(b).

4.3 Experimental

The local-made electrospinning apparatus contains a needle or spinneret, high voltage power supply, and a grounded collector. Horizontal experimental setup was chosen for electrospinning process. High voltage power supply, which is transferred from 21"TV fly pad (219x6M, Toshiba) indirectly. To obtain the capable of producing the high voltage in the range of 10kV~30kV, 60 of 10MΩ resistors are used in series connection. It is known by using high voltage probe that produces maximum voltage 27.32kV but the operating voltage is 25.19kV. A syringe holder and a collector are kept in the cylindrical shape of Plexiglas tube, length of 36.3cm and inside diameter is 8.45cm, 9 cm apart from each other. DC voltage generator of positive terminal is connected with hypodermic needle (0.55x25mm) and the circular shape of Al collector which is covered with Al foil is connected by negative terminal of Power Supply as system ground.

ZnO fibers were formed by calcinating the precursor PVA/Zinc acetate composite fibers and for the preparation of composite fiber, sol-gel process was used. In this study, zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$), distilled water and PVA(Polyvinyl alcohol) were used as raw materials for the preparation of PVA/Zinc acetate composite fiber. Firstly, Zinc acetate powder was weight by digital balance shown in Figure 4.2(c). This powder is dissolved in water and Zinc acetate solution was obtained after stirring for an hour. Weighed Polyvinyl alcohol as shown in Figure 4.2(d) was added in it by the equal ratio and it was stirred vigorously about 3 hours and highly concentrated zinc acetate solution was obtained after stirring for one hour at room temperature.. Then, a viscous gel of PVA/Zinc acetate composite was obtained. In this process, there are different molarities of gel such as 0.2 M, 0.3 M, 0.4 M and 0.5 M are used. The flow chart of the growth procedure for PVA/Zinc acetate composite was illustrated in Figure 4.3.

Table 4.1 Concentration of composite

Sr No	Molarity (M)	Zinc acetate (g)	PVA (g)	Water (ml)
1.	0.2	43.87	43.87	1000
2.	0.3	65.81	65.81	1000
3.	0.4	87.75	87.75	1000
4.	0.5	109.69	109.69	1000

4.3.1 Sample preparation for Fibers

Before setting the vacuum glass-ambient, the experimental setup was prepared. PVA/Zinc acetate precursor solution about 20 cc was put into the syringe. The projectile of colloidal solution and target aluminium foil was apart 9 cm. after that the glass tube was pumped out until the expected value of the atm pressure was about 0.1 mm Hg by pumping motor. In the electronspinning process, a high voltage was applied to create an electrically charged jet of colloidal solution which solidified to leave a fiber. One electrode was placed into the spinning solution and the other attached to a colloidal solution. This induced a charge on the surface of the liquid. In this way, a charged jet of liquid was ejected from the tip of the capillary tube. The ejected liquid lay itself randomly on a grounded colleting target aluminium foil. The resultant Al-foil was examined with microscope. The comparison of original plane of Al-foil and the electrospun surface of Al-foil is shown in Fig 4.20. The resultants Al-foil with different molarities were calcined at 500°C for 1 h each respectively. The surface morphology of each PVA/Zinc oxide coated Al-foils of before and after calcination were examined by using JEOL JSM -5610 Scanning Electron Microscope shown in Figure 3.2.

Table 4.2 Typical range of operating parameters used for electrospinning experiments with PVA/Zinc Acetate ultrafine fiber

Syringe Capacity	20 cc
Electrode Spacing	9 cm
Capillary Diameter	0.55 mm
High Voltage Power Supply (DC)	25.19 kV
PVA/Zinc Acetate Concentration	0.2 M, 0.3 M, 0.4 M, 0.5 M
Running Time	1 h
Cooling Time	10 h
Annealing Temperature	500°C
Annealing Time	1 h

(See Figures 4.1 to 4.21 for experimental details)

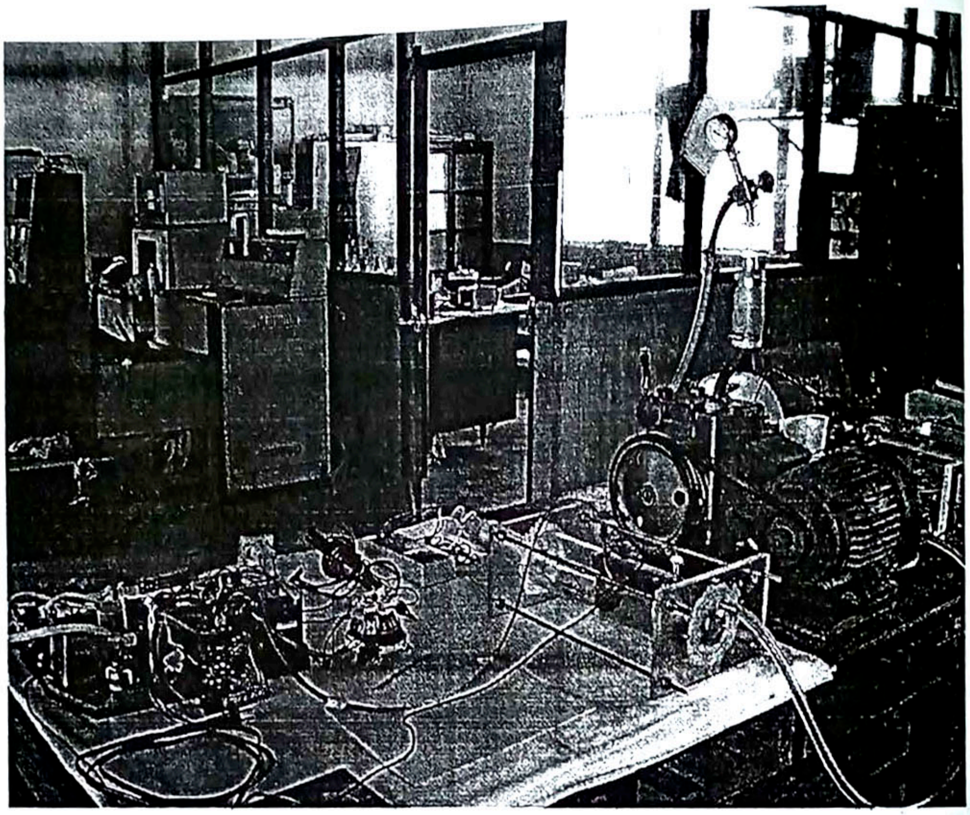


Figure 4.1 Experimental setup for electrospinning system

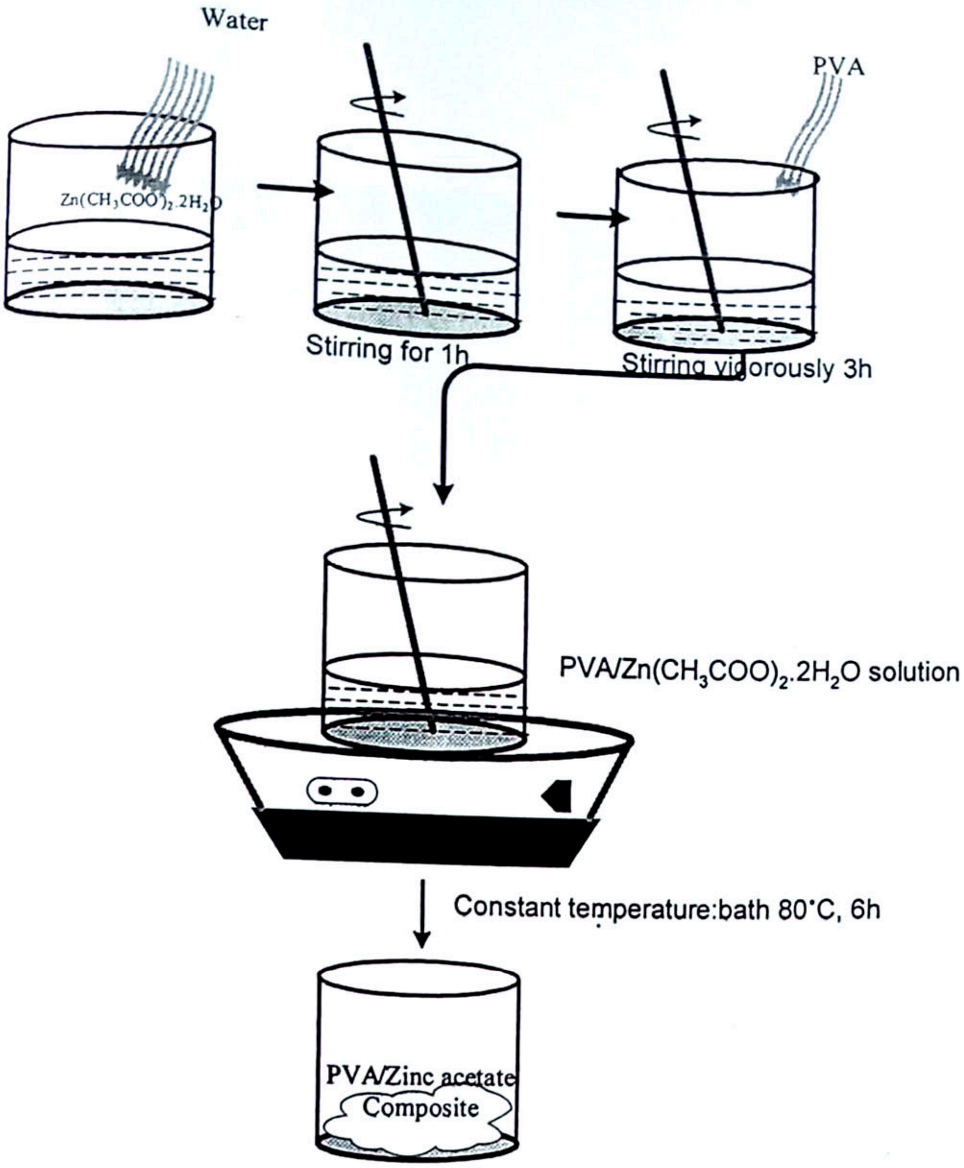


Figure 4.2 The flow chart of the growth procedure for PVA/Zinc acetate composite

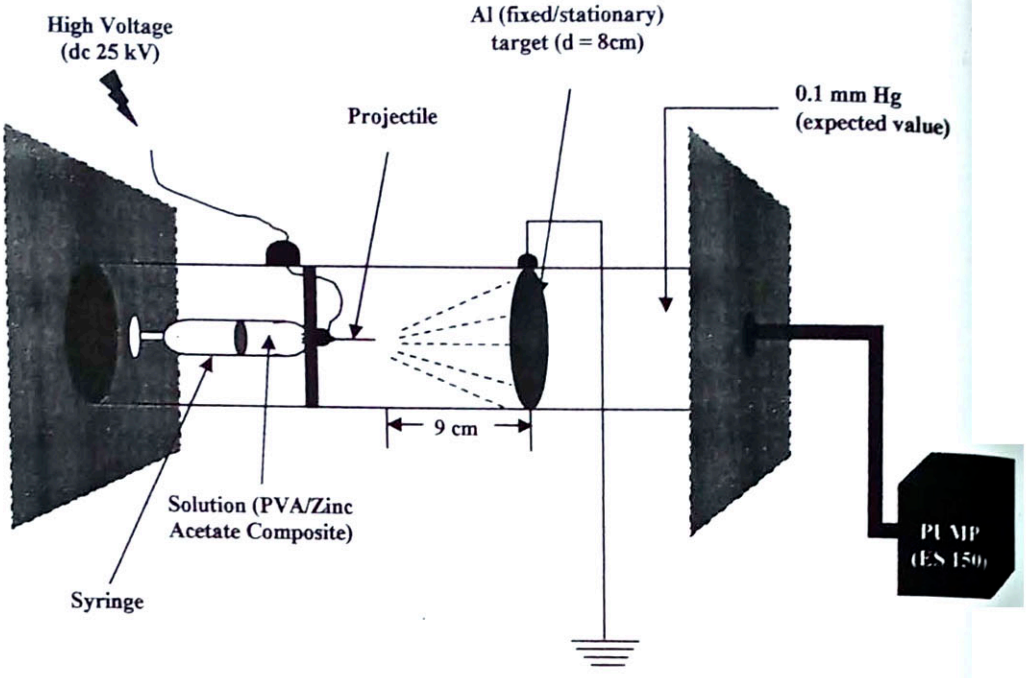
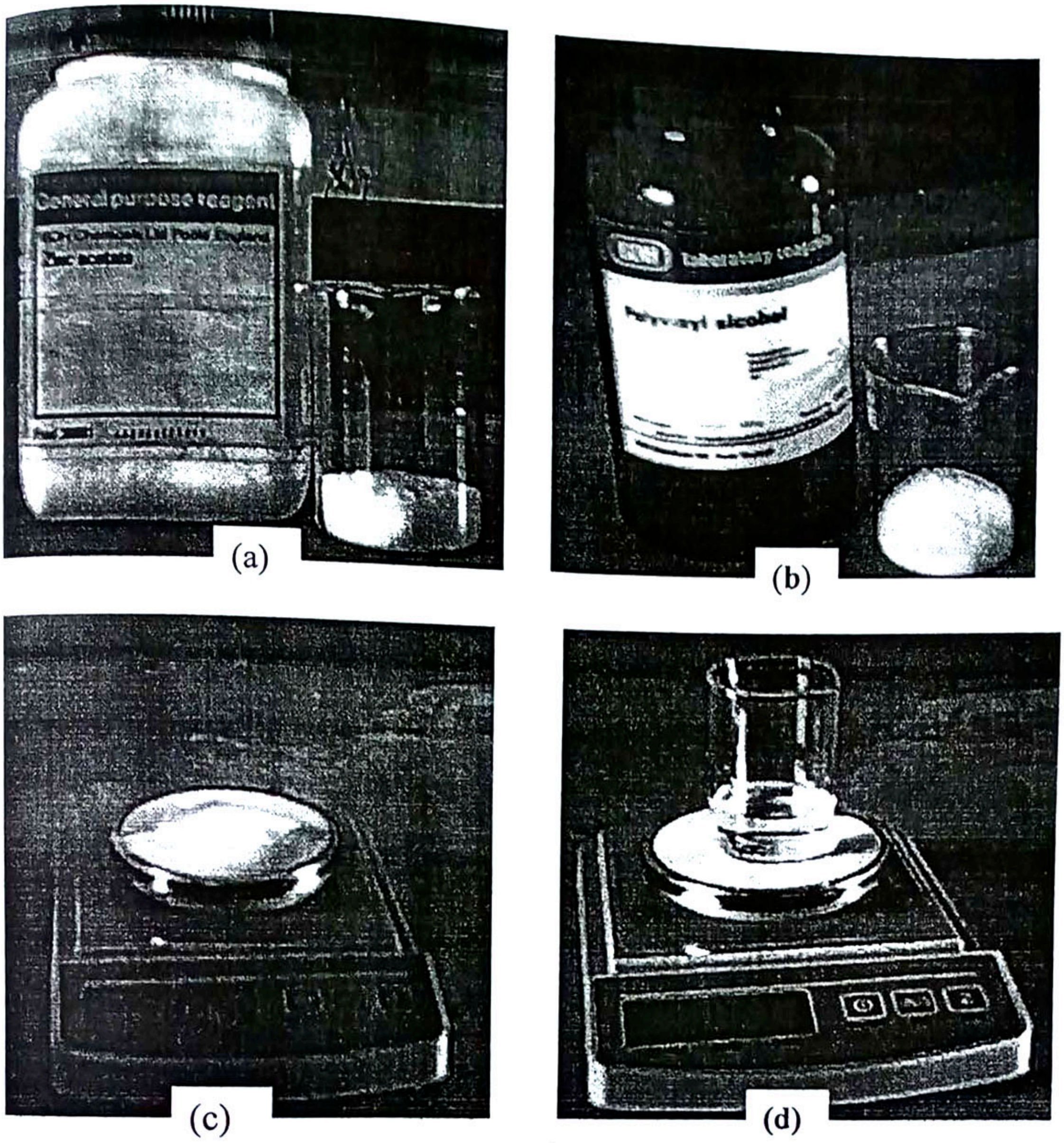


Figure 4.3 Experimental setup for electrospinning process



(a) (b) (c) (d)

Figure. 4.4 This figure shows (a) Zinc acetate and (b) Polyvinyl alcohol, (c) Digital balance (d) distilled water and PVA

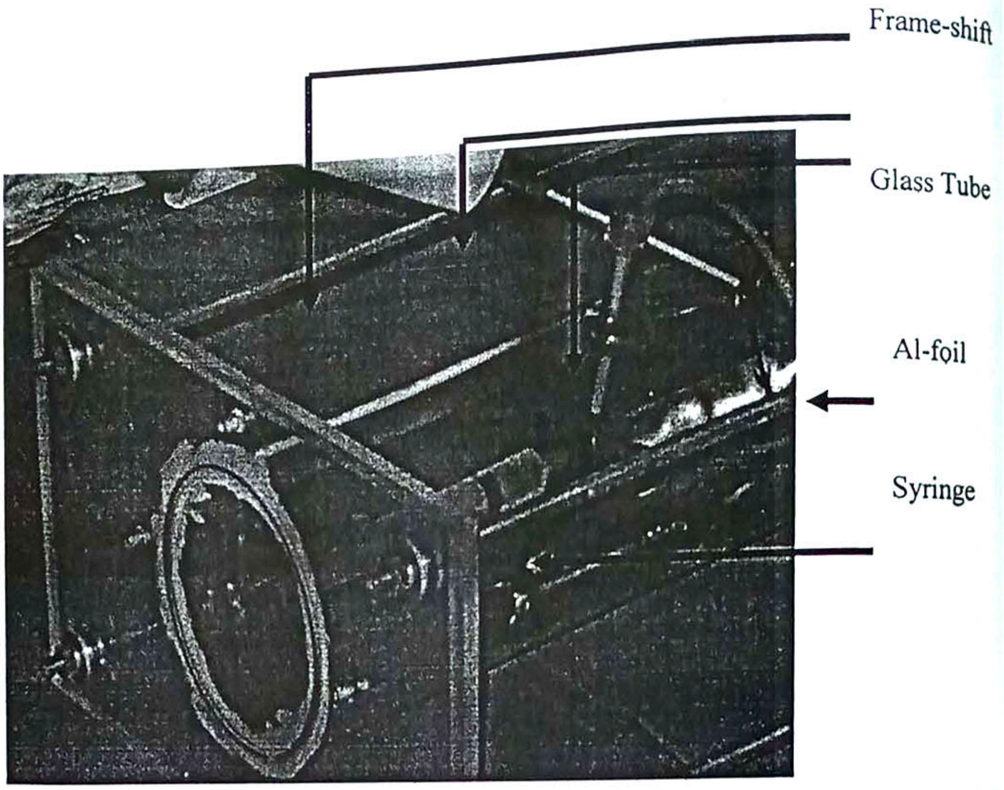


Figure 4.5 Testing the ambient vacuum condition

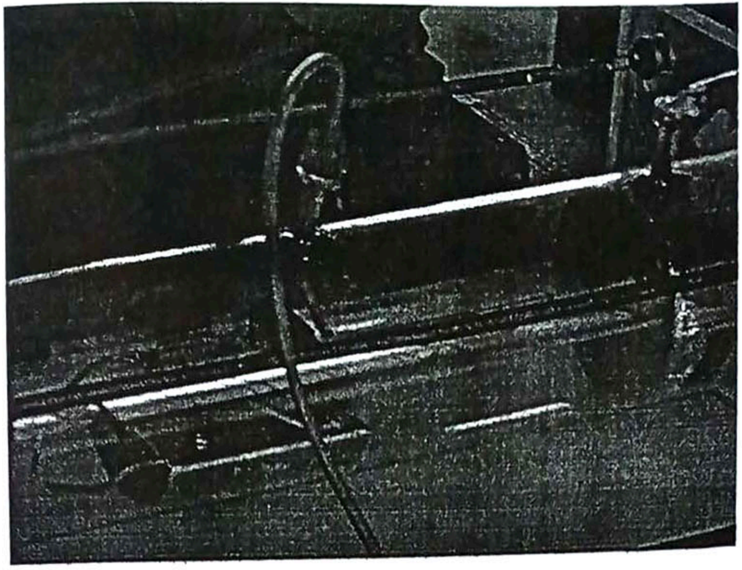


Figure 4.6 Plexiglas tube of length 26.3cm and inside diameter 8.45cm. It is evacuated approximately 0.1mm Hg to eject the solution from the spinneret.

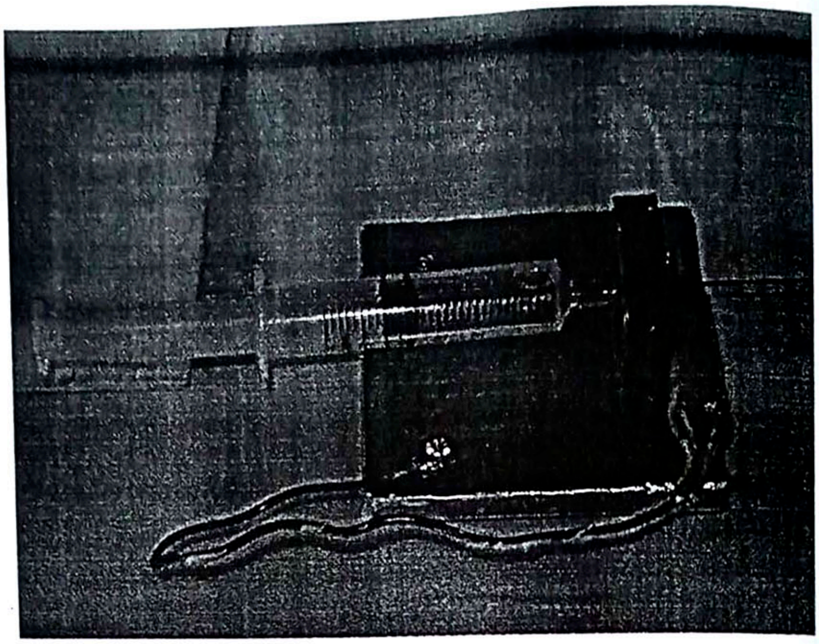


Figure 4.7 Syringe with polymer solution

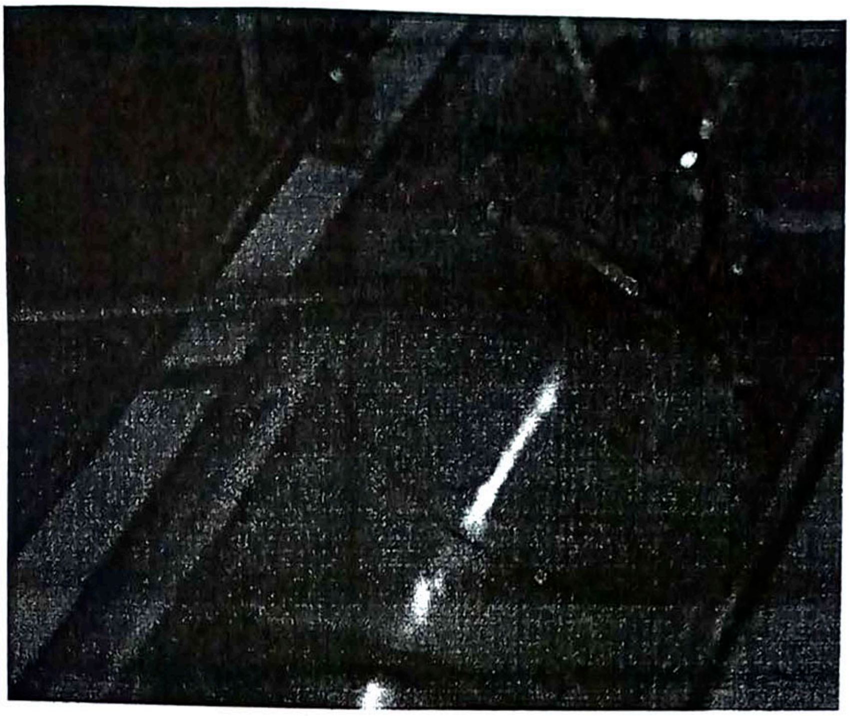


Figure 4.8 Collector covered with Al foil (stationary target)

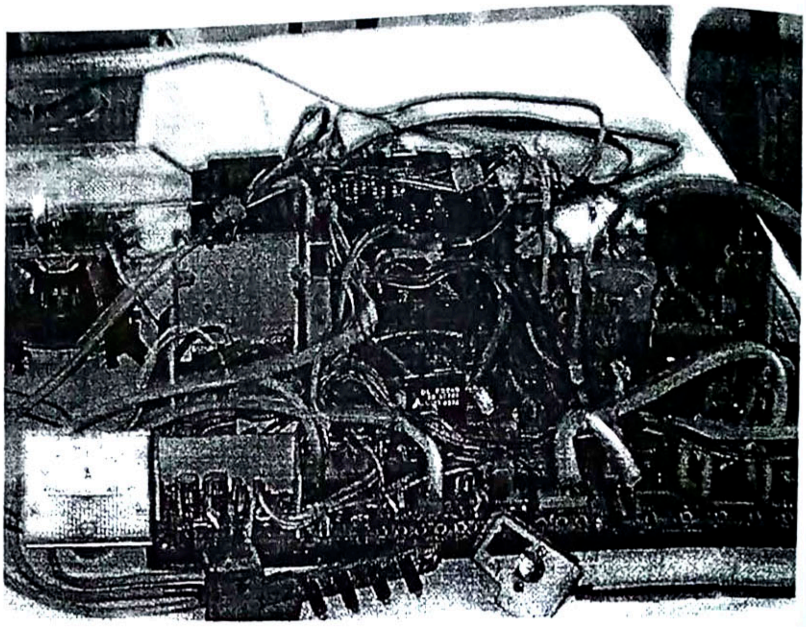


Figure 4.9 21" TV fly pad, Toshiba, for voltage supply

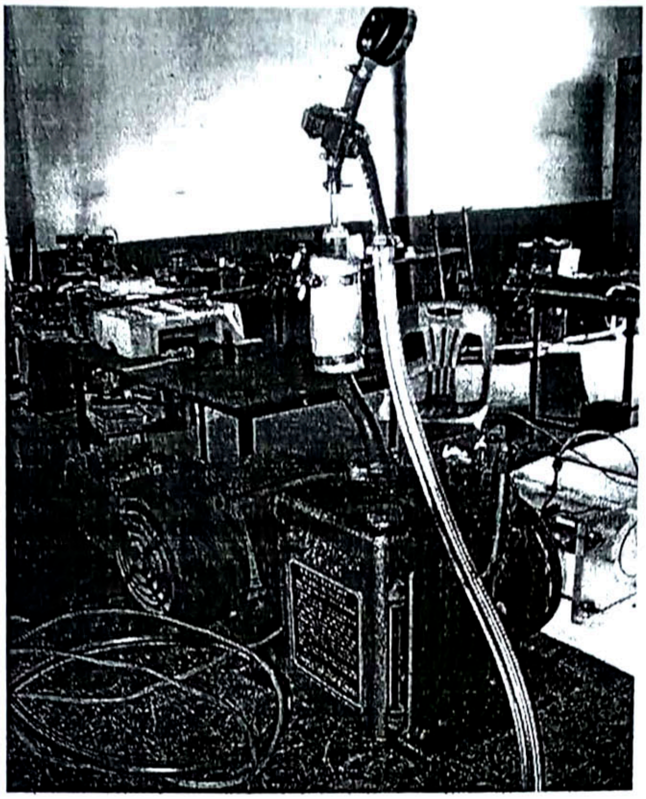


Figure 4.10 Vacuum Pump

Characteristics of vacuum pump
0.75 kW 4 pole (Rating cont.)
EL 150 model
Capacitor 300μF
Model EC-FB
Bearing 6204-6203
50 Hz
230V
6.7 A
1430 rpm

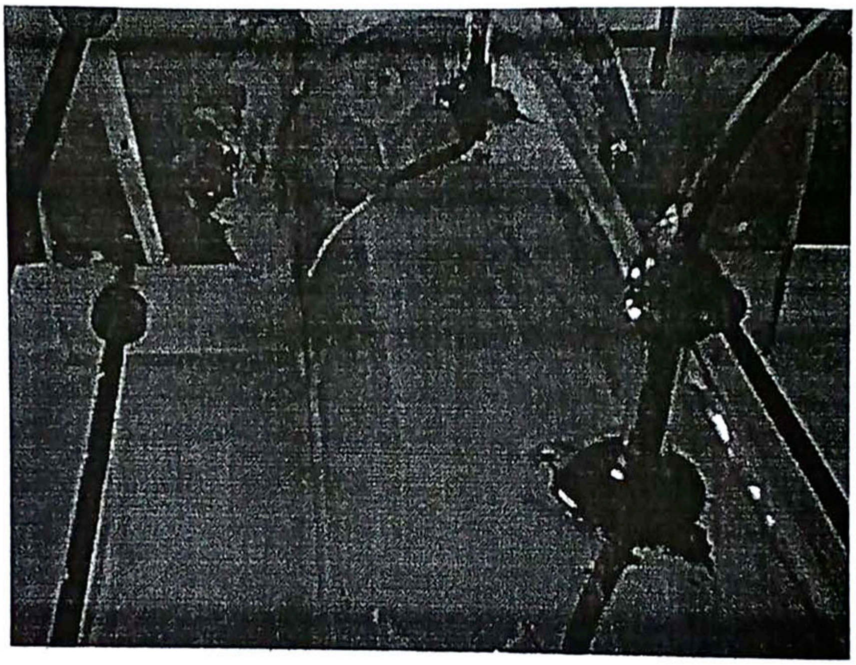


Figure 4.11 Polymer solution being ejected when high voltage is applied

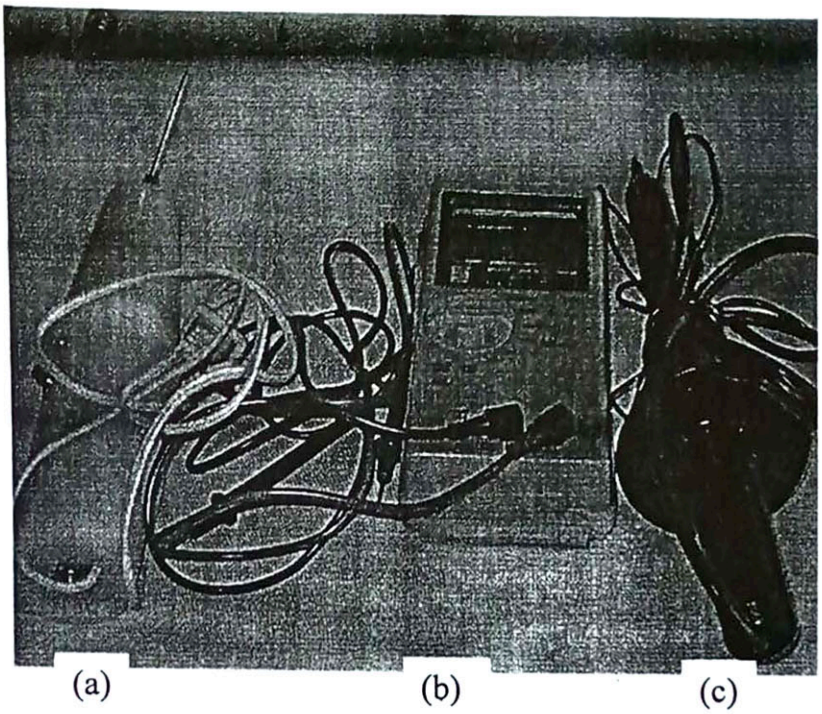


Figure 4.12 Equipment used for detecting vacuum and high voltage

- (a) Vacuum tester
- (b) Digital multimeter
- (c) High voltage probe

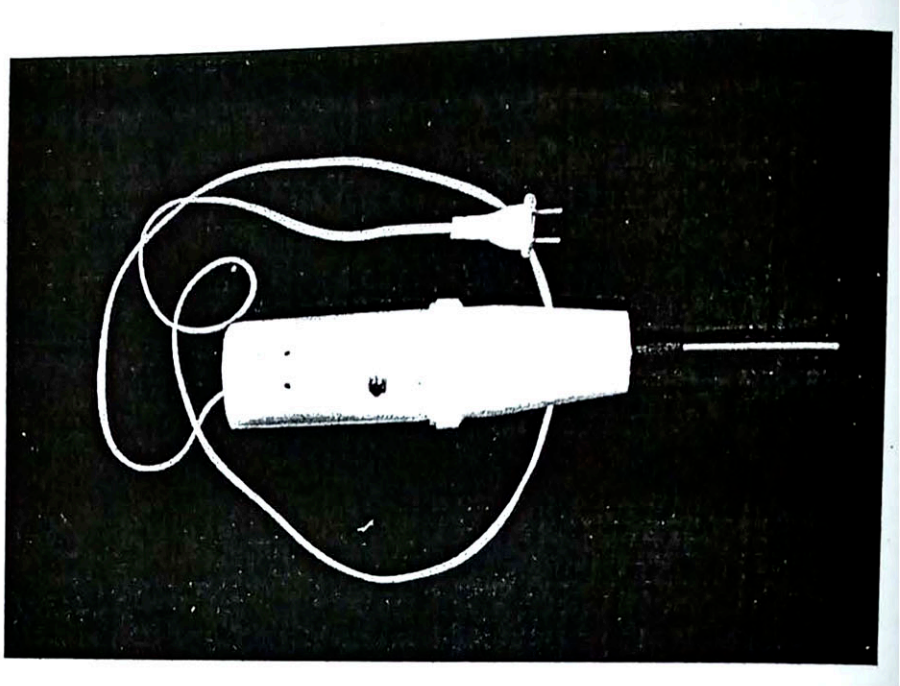


Figure 4.13 Vacuum tester

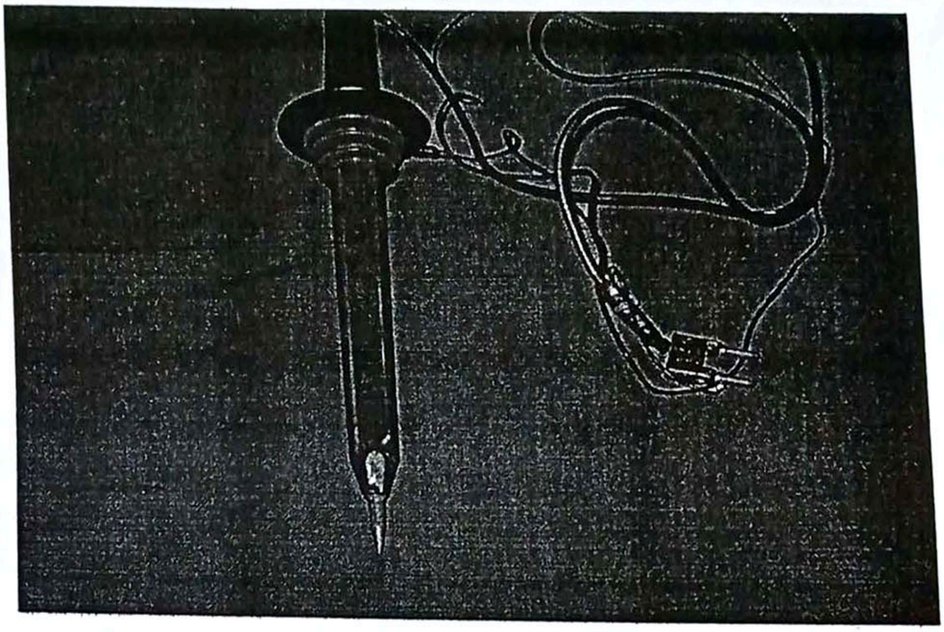


Figure 4.14 High voltage probe

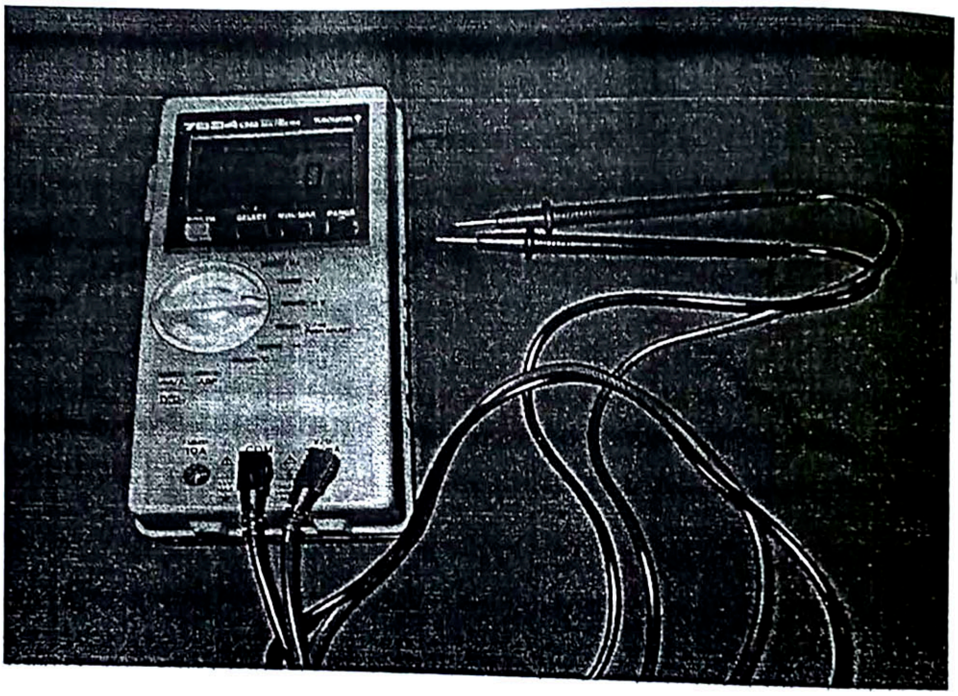


Figure 4.15 Digital multimeter (Modal 7534-02, YOKOGAWA)

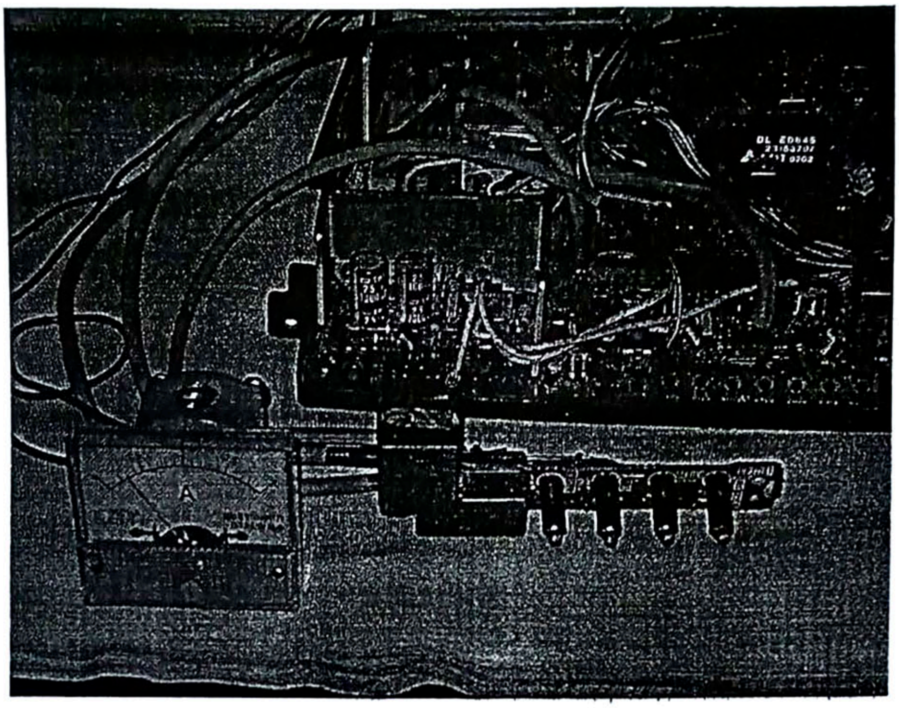


Figure 4.16 Fly pad, Ammeter

Figure 4.17 Detecting system with digital voltmeter

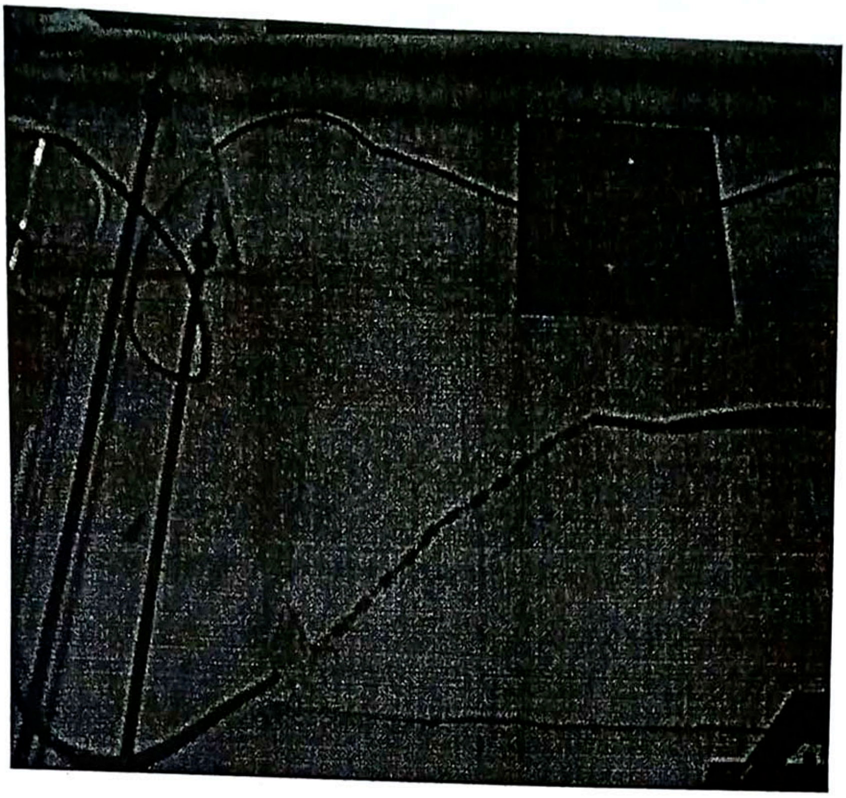


Figure 4.18 Resistors package

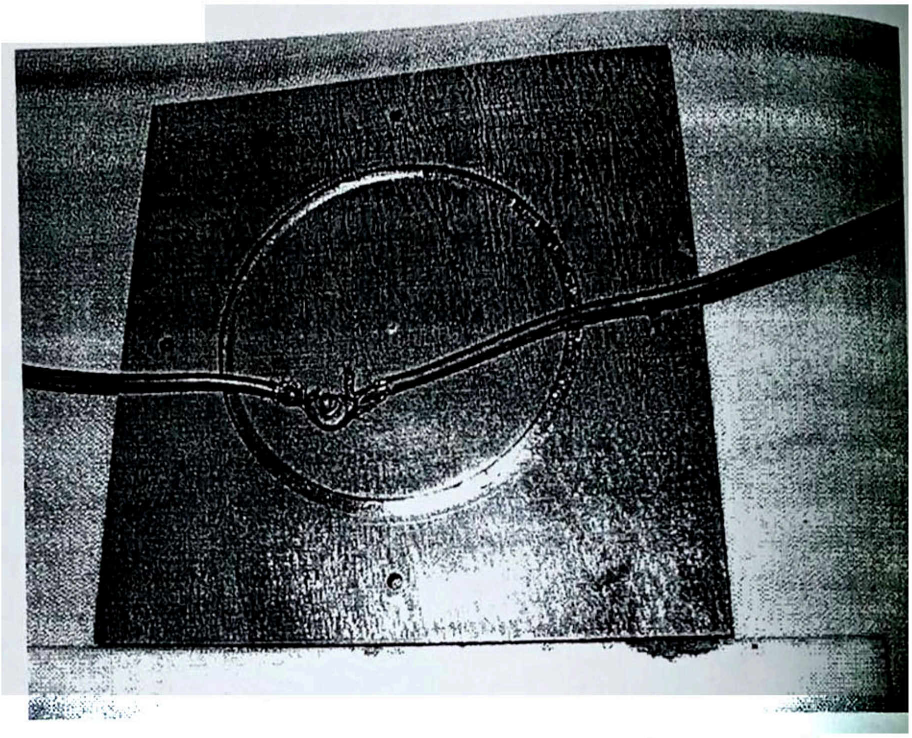


Figure 4.19 Al plate for grounding the system

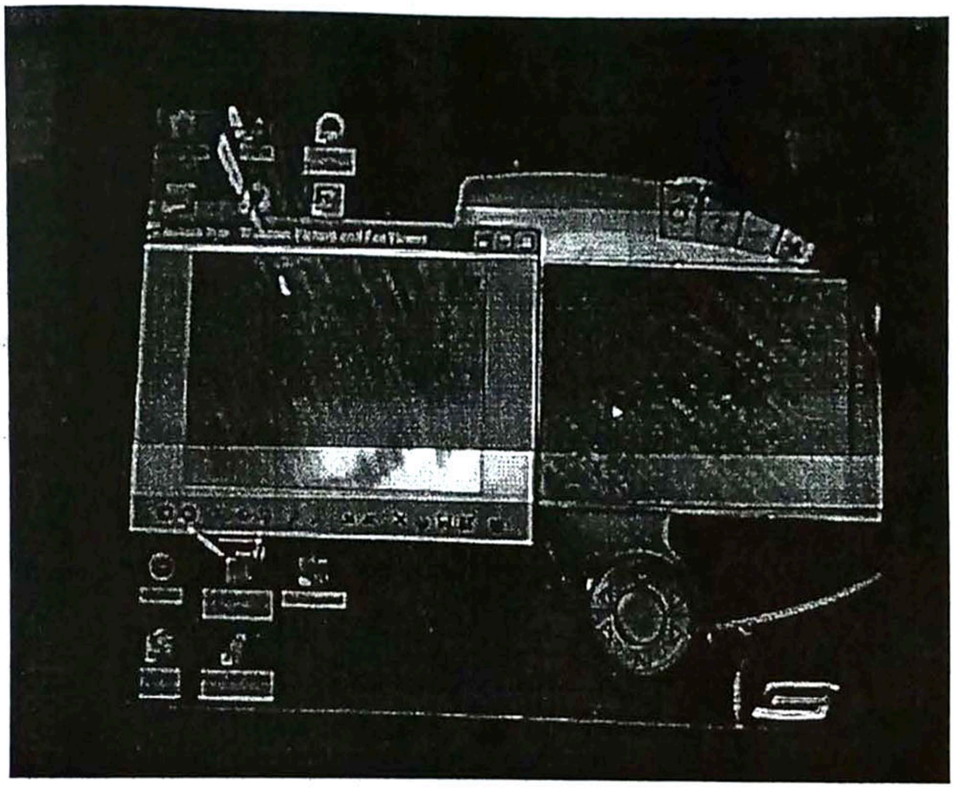


Figure 4.20 A comparison of Al surface and PVA/Zinc acetate composite fiber.

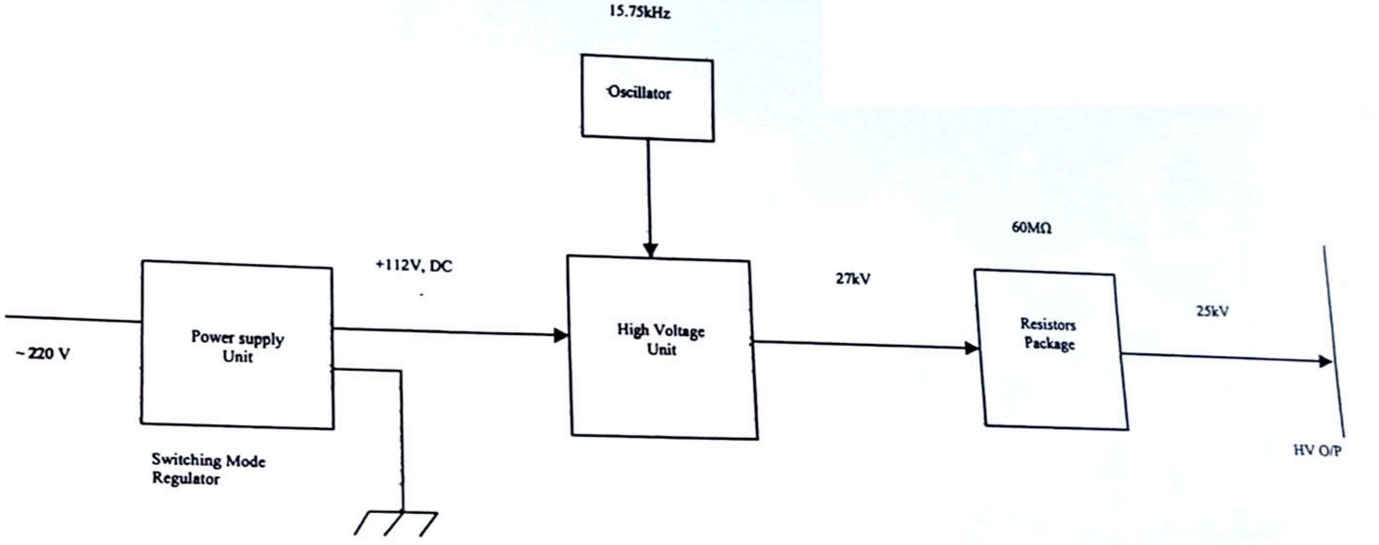


Figure 4.21 Schematic diagram of High Voltage Power Supply

CHAPTER V

RESULTS AND DISCUSSION

5.1 SEM Analysis of PVA/Zinc acetate Composite Fibers

The PVA/Zinc acetate composite fiber was this formed on Al-foil (0.5x0.5) cm^2 and SEM was employed to characterize these fibers. The set of SEM images for PVA/Zinc acetate composite fiber was recorded at Figure 4.1 (a ~ d). Figure 4.1(a) showed the SEM picture of PVA/Zinc acetate composite fiber with 0.2M. AS it was seen in Figure 4.1(a), it was obvious that sub-micro fibers were appeared by splitting of bicomponent fibers. The shape of this fibers was segmented pie structure. Bicomponent fibers were split with the help of high forces of air or water jets. Eight fibers were significantly formed. Figure 4.1(b) gives the SEM plot of PVA/Zinc acetate composite fiber with 0.3 M. Different lengths of fibers were produced. The fibers orientation was randomized. The fiber used in this electrospinning technique looked islands-in-a-sea. Number of filament of a pack in single islands could not divided/counted. The fiber diameter was approximately equal to 1.87 μm. The SEM plot of PVA/Zinc acetate composite fiber was given as Figure 4.1(c). Non-uniform fiber distribution was observed. Fiber length was also different. Film surface was smooth, low density; high pore volume and tight pore size were formed. The fiber diameter was 2.12 μm. Figure 4.1(d) described the SEM micrograph of PVA/Zinc acetate composite fiber. Non- uniformed fiber length was obviously formed. Some fibers were separated by pores and some was in continuity. The fiber diameter was seemed to be 1.49 μm.

5.2 SEM Analysis of PVA/ZnO Fibers

Pure ZnO (or) PVA/ZnO fiber was appeared by calcination at temperature of 80°C for 6 h. The set of SEM images of PVA/ZnO fibers with different molarities was shown in Figure 4.2 (a ~ d). In the epitaxial film with 0.2 M, crystalline was highly oriented, normally vertical and parallel with each fiber.

It was crack –free and that in microstructure. The fiber diameter was estimated to be 2.95 µm. The fiber distribution was non-uniform and little amount of pore was observed on this micrograph. Eight fibers were significantly formed. The mean pore size was examined to be 1.77 µm. Figure 4.2(b) showed the SEM picture of PVA/ZnO fibers with 0.3 M. Non-uniform fiber distribution was clearly observed. The mid-zone of film was relatively dense. The film morphology looked like a mat. It was non-cracked and flat. Figure 4.2(c) give the SEM micrograph of PVA/ZnO fibers with 0.4 M As described at figure, the fibers were formed by splitting of component fibers. The fiber orientation was formed right. The fiber length was examined to be different. The fiber diameter was about 1.82 µm. Figure 4.2(d) described the SEM plot of PVA/ZnO fibers with 0.5 M. Non-uniform fiber distribution was clearly formed in this picture. The fiber length was also different. The fiber diameter was 1.26 µm.

Table 5.1 Dependence of Molarity on diameter of PVA/Zinc acetate composite

		Before Calcination	After Calcination
SrNo.	Molarity (M)	Diameter (µm)	Diameter (µm)
1.	0.2	2.90	2.96
2.	0.3	1.87	2.80
3.	0.4	2.12	1.82
4.	0.5	1.49	1.26

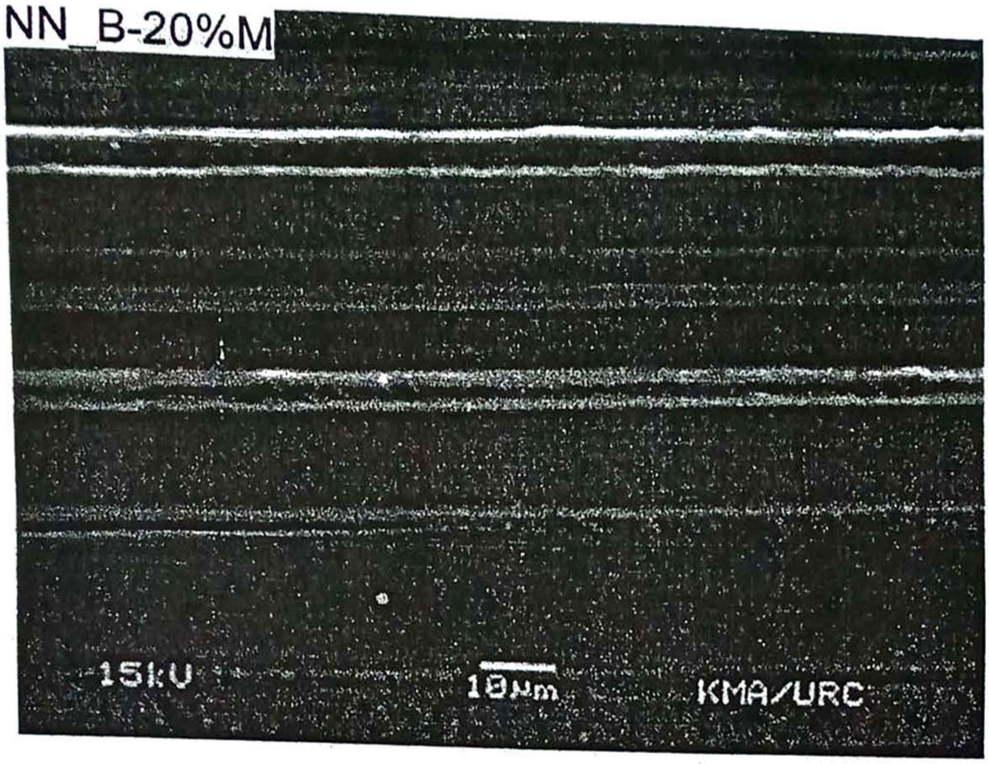


Figure 5.1(a) Continuous as-spun nanofibers deposited on Al-foil of PVA/Zinc acetate composite, 0.2 M.

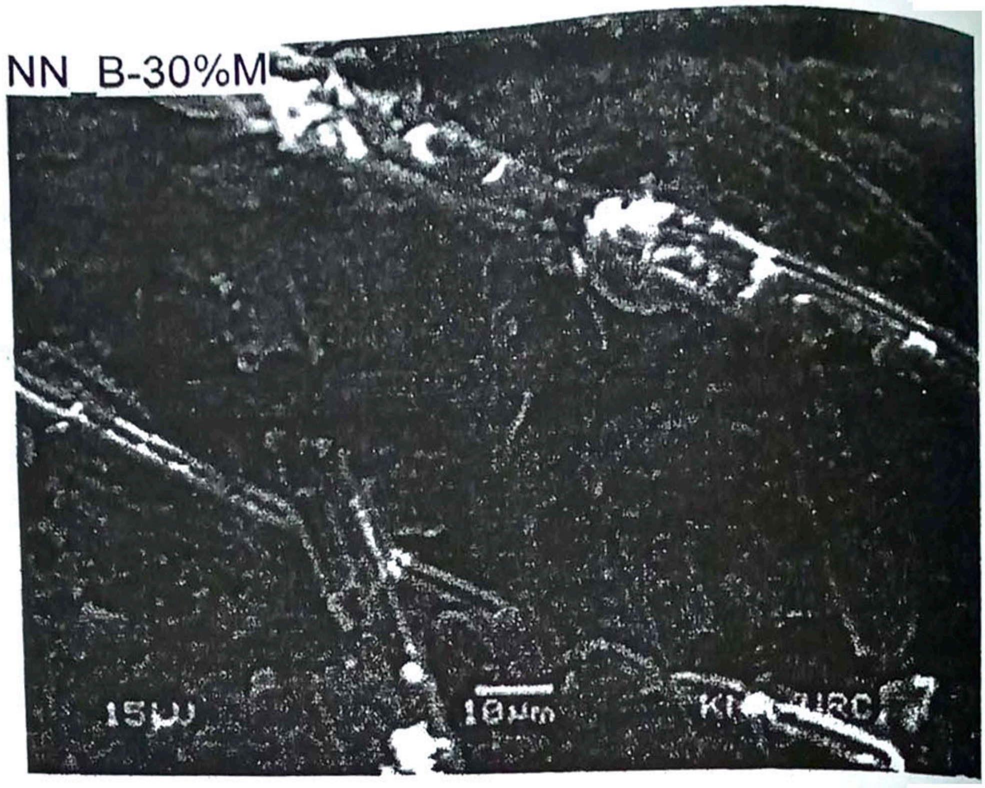


Figure 5.1(b) SEM image (magnification = 10 000) of polymer solution 0.3 M

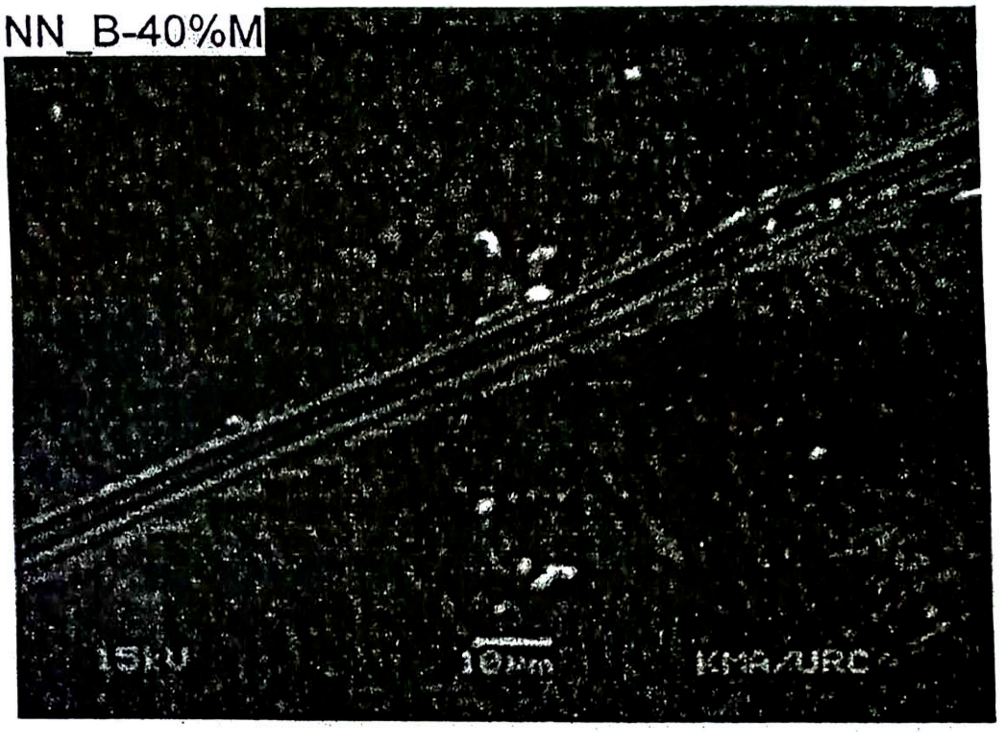


Figure 5.1(c) Typical SEM image of PVA/Zinc acetate composite, 0.4 M

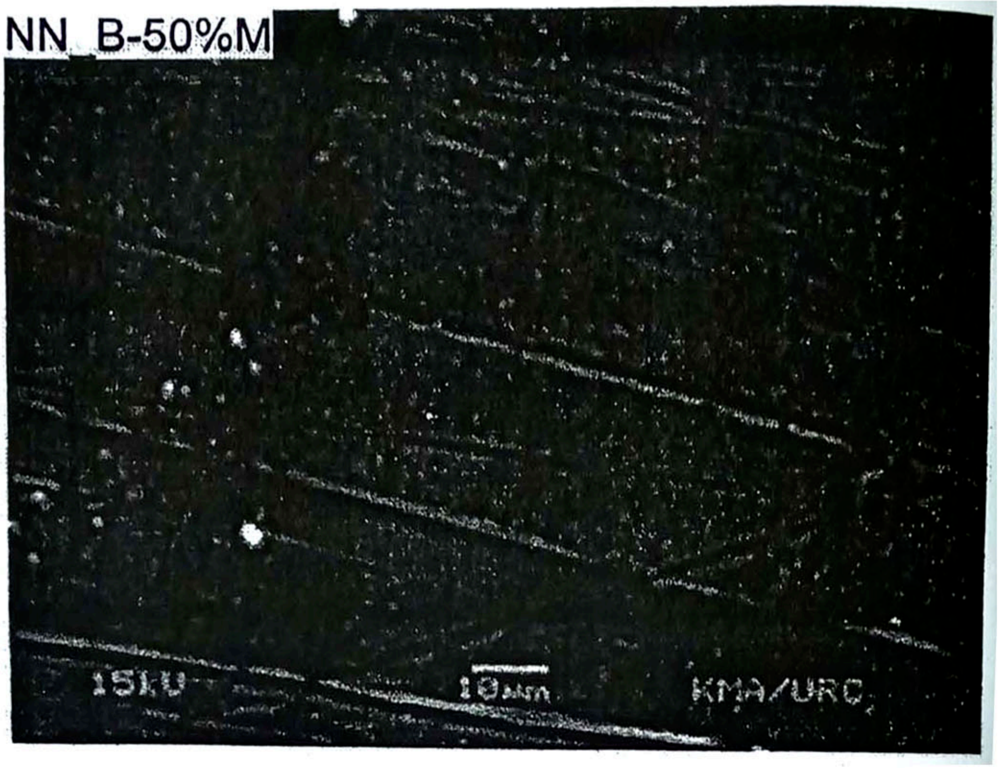


Figure 5.1(d) SEM micro graph of 0.5 M Zinc acetate fiber

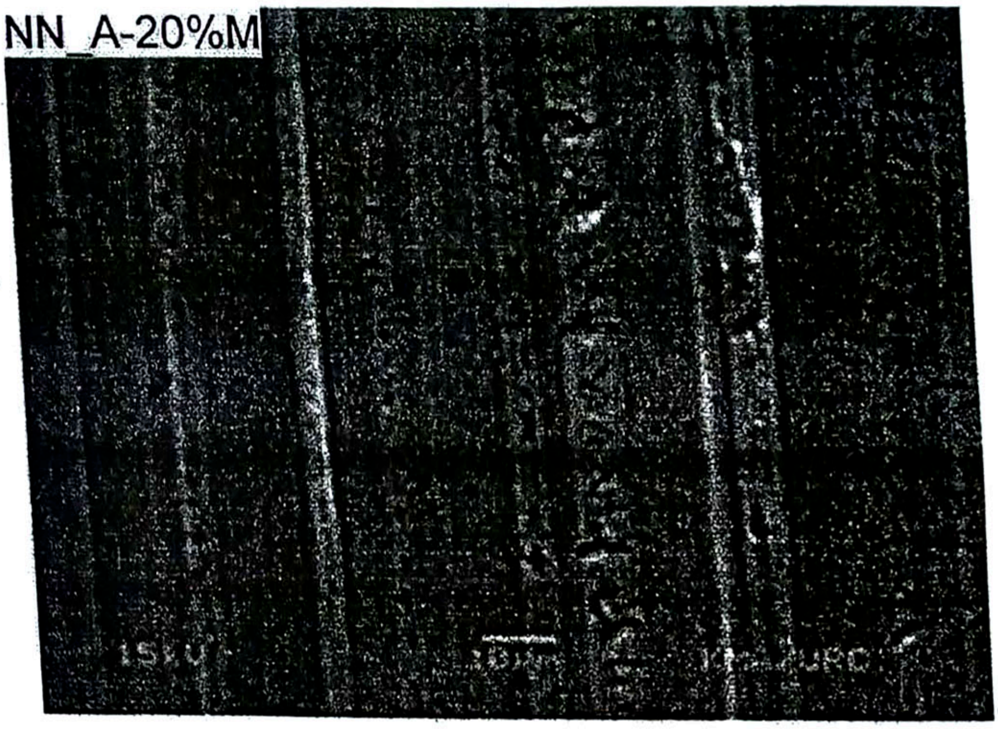


Figure 5.2(a) Aligned electrospun ultrafine fibers of 0.2 M

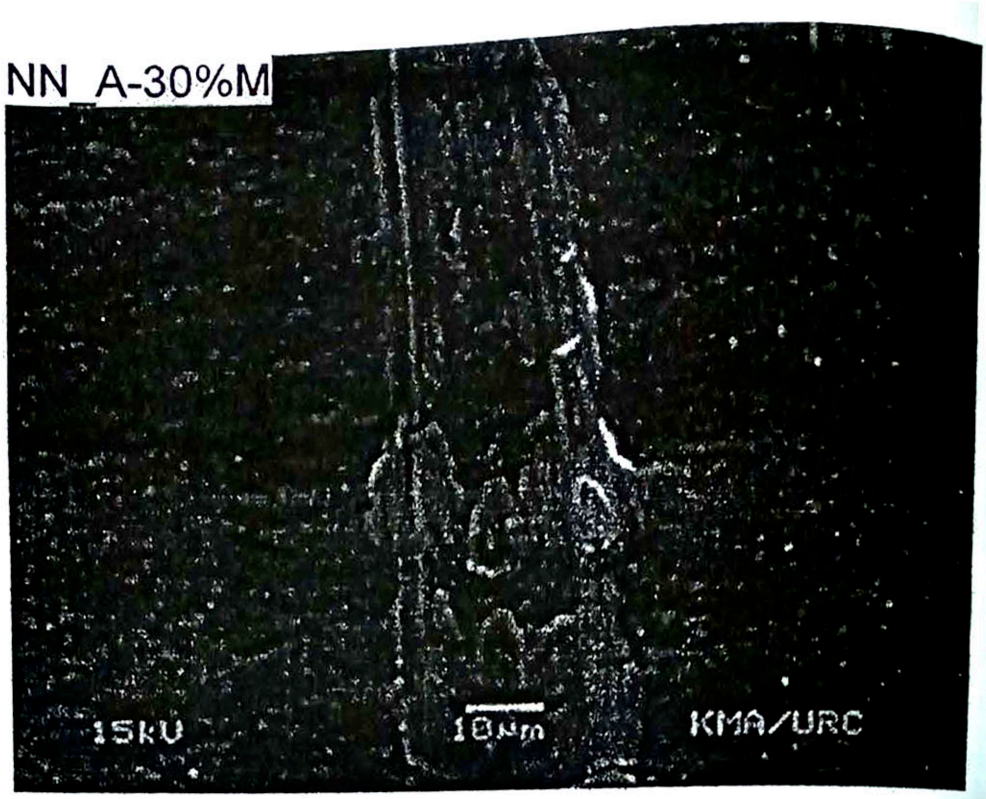


Figure 5.2(b) SEM image of PVA/ZnO fiber electrospun of 0.3 M at annealing temperature 500 °C for 1 h

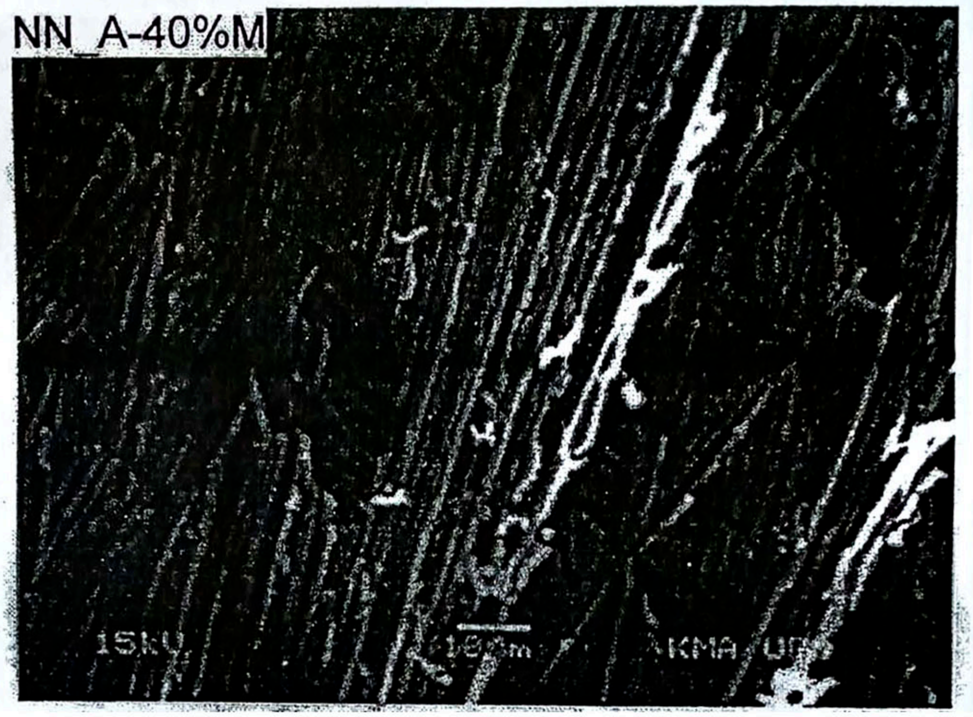


Figure 5.2(c) Surface morphology of PVA/ZnO fiber with concentration 0.4 M

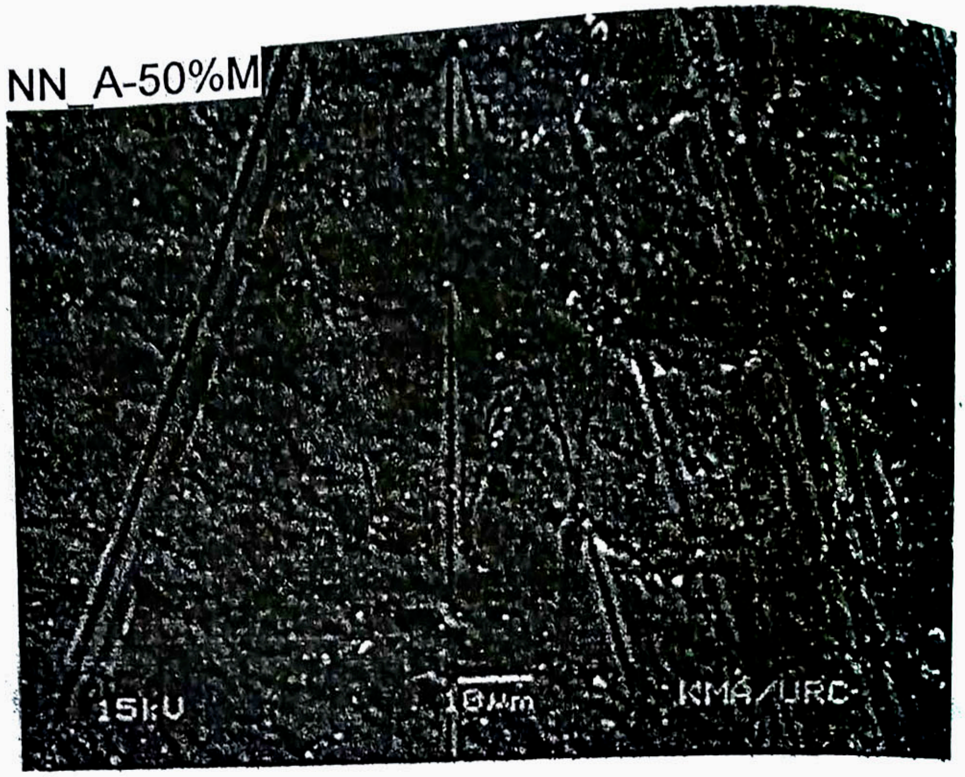


Figure 5.2(d) SEM micrograph of electrospun fiber

CHAPTER VI

CONCLUSION

The micron fibers have been prepared by the following sequential steps;

(1) Preparation of a solution with suitable inorganic precursor

(2) Mixing inorganic solution with a polymer template to get the solution for electrospinning with appropriate viscosity

(3) Electrospinning of the solution to obtain inorganic/ organic composite fibers

(4) Calcination of the as prepared composite fibers to yield pure metal oxide fibers.

The electrospinning process took place in cylindrical shape of Plexiglas tube that had very limited exposure to elements exterior to the tube. This tube helped control the environment in which the electrospinning was taking place namely the unpredictable air converts in an uncontrolled environment that could dramatically alter fiber production. The inside of the tube also took vacuum condition that was ejected from the needle during the experiments. Our apparatus count three compact components: high voltage supplier, capillary tube with pipette or needle of small diameter and a grounded Al foil. In this process, a high voltage was needed to create an electrically charged jet of polymer solution. Before reaching the collecting screen, the solution jet evaporated or solidified and was collected as an interconnected web of small fibers. From the SEM results, it was concluded that all fibers before and after calcinations were said to be "submicron fibers". The SEM images for both PVA/Zinc acetate composite fiber (before calcinations) and PVA/ZnO fiber (after calcinations) were not remarkably different in micro structures (see Table 5.1). The smallest value of fiber diameter was found to be 1.26µm for corresponding to 0.5 M.

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