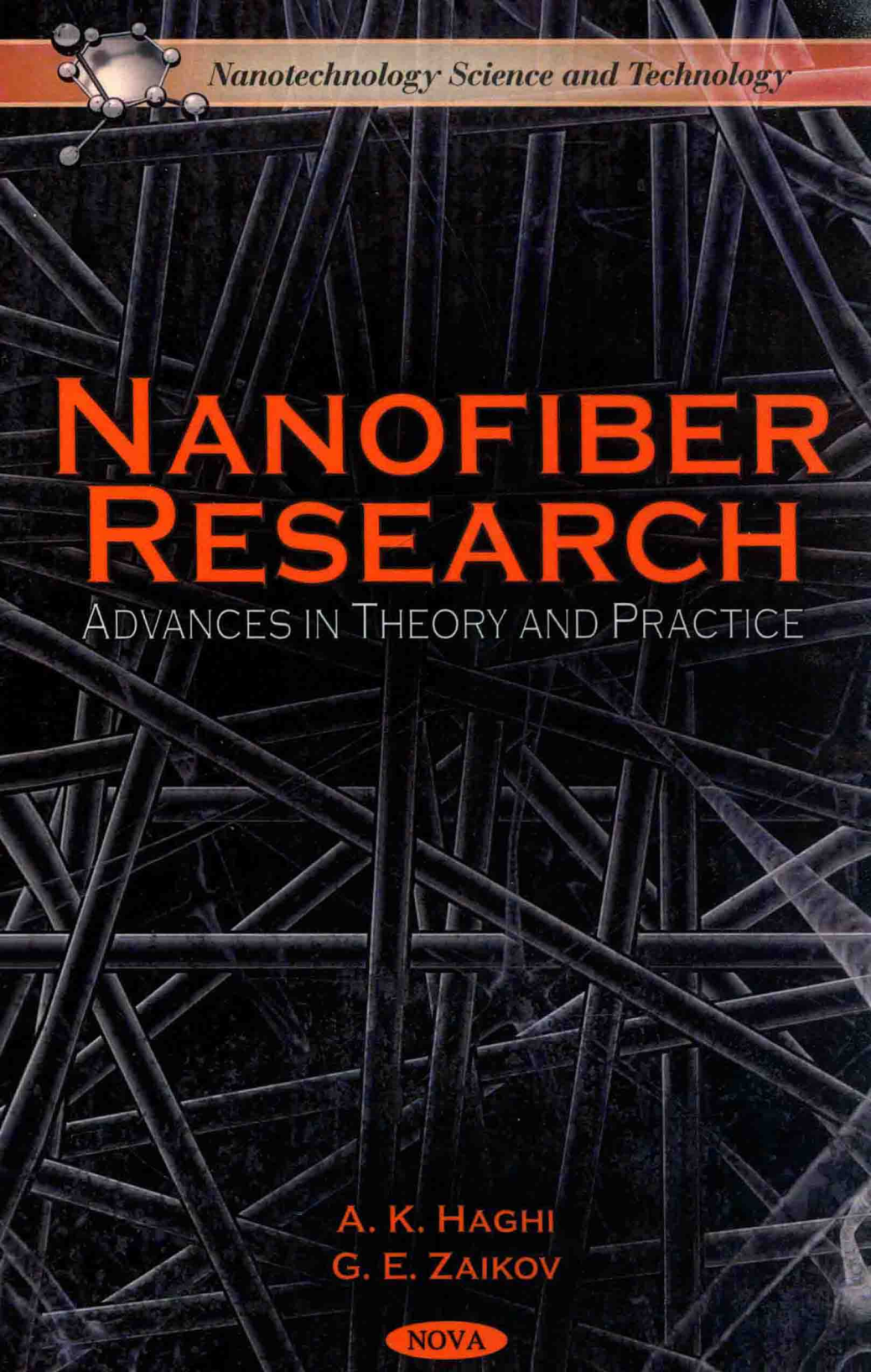
Nanotechnology Science and Technology
NANOFIBER RESEARCH
ADVANCES IN THEORY AND PRACTICE
A. K. HAGHI
G. E. ZAIKOV
NOVA

NANOTECHNOLOGY SCIENCE AND TECHNOLOGY

NANOFIBER RESEARCH: ADVANCES IN THEORY AND PRACTICE

A. [illegible]HACHU
AND
G. E. ZAIKOV

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PREFACE

Nanotechnology is revolutionizing the world of materials. The research and development of nanofibers has gained much prominence in recent years due to the heightened awareness of its potential applications in the medical, engineering and defense fields. Among the most successful methods for producing nanofibers is the electrospinning process. Electrospinning introduces a new level of versatility and broader range of materials into the micro/nanofiber range. An old technology, electrospinning has been rediscovered, refined, and expanded into non-textile applications. Electrospinning has the unique ability to produce ultrathin fibers from a rich variety of materials that include polymers, inorganic or organic compounds and blends. With the enormous increase of research interest in electrospun nanofibers, there is a strong need for a comprehensive review of electro spinning in a systematic fashion. With the emergence of nanotechnology, researchers become more interested in studying the unique properties of nanoscale materials. Electrospinning, an electrostatic fiber fabrication technique has evinced more interest and attention in recent years due to its versatility and potential for applications in diverse fields. The notable applications include in tissue engineering, biosensors, filtration, wound dressings, drug delivery, and enzyme immobilization. The nanoscale fibers are generated by the application of strong electric field on polymer solution or melt. The non-wovens nanofibrous mats produced by this technique mimics extracellular matrix components closely as compared to the conventional techniques. The sub-micron range spun fibers produced by this process, offer various advantages like high surface area to volume ratio, tunable porosity and the ability to manipulate nanofiber composition in order to get desired properties and function. Over the years, more than 200 polymers have been

electrospun for various applications and the number is still increasing gradually with time.

Electrospinning is a highly versatile method to process solutions or melts, mainly of polymers, into continuous fibers with diameters ranging from a few micrometers to a few nanometers. This technique is applicable to virtually every soluble or fusible polymer. The polymers can be chemically modified and can also be tailored with additives ranging from simple carbon-black particles to complex species such as enzymes, viruses, and bacteria. Electro spinning appears to be straightforward, but is a rather intricate process that depends on a multitude of molecular, process, and technical parameters. The method provides access to entirely new materials, which may have complex chemical structures. Electrospinning is not only a focus of intense academic investigation; the technique is already being applied in many technological areas.

This book presents some fascinating phenomena associated with the remarkable features of nanofibers in electrospinning processes and new progress in applications of electrospun nanofibers.

This new book offers an overview of structure–property relationships, synthesis and purification, and potential applications of electrospun nanofibers. The collection of topics in this book aims to reflect the diversity of recent advancesin *electrospun nanofibers* with a broad perspective which may be useful for scientists as well as for graduate students and engineers.

CONTENTS

Chapter 1

SYSTEMATIC PARAMETER STUDY FOR NANO FIBER FABRICATION VIA ELECTROSPINNING PROCESS

ABSTRACT

The precise control of fiber diameter during electrospinning is very crucial for many applications. A systematic and quantitative study on the effects of processing variables enables us to control the properties of electrospun nanofibers. In this contribution, response surface methodology (RSM) was employed to quantitatively investigate the simultaneous effects of four of the most important parameters, namely solution concentration (C), spinning distance (d), applied voltage (V) and volume flow rate (Q) on mean fiber diameter (MFD) as well as standard deviation of fiber diameter (StdFD) in electrospinning of polyvinyl alcohol (PVA) nanofibers.

Keywords: Electrospinning, Nanofibers, Fiber diameter, Processing variables, Response surface methodology

INTRODUCTION

Electrospinning is a novel and efficient method by which fibers with diameters in nanometer scale entitled as nanofibers, can be achieved. In electrospinning process, a strong electric field is applied on a droplet of polymer solution (or melt) held by its surface tension at the tip of a syringe's

needle (or a capillary tube). As a result, the pendent drop will become highly electrified and the induced charges are distributed over its surface. Increasing the intensity of electric field, the surface of the liquid drop will be distorted to a conical shape known as the Taylor cone [1]. Once the electric field strength exceeds a threshold value, the repulsive electric force dominates the surface tension of the liquid and a stable jet emerges from the cone tip. The charged jet is then accelerated toward the target and rapidly thins and dries as a result of elongation and solvent evaporation. As the jet diameter decreases, the surface charge density increases and the resulting high repulsive forces split the jet to smaller jets. This phenomenon may take place several times leading to many small jets. Ultimately, solidification is carried out and fibers are deposited on the surface of the collector as a randomly oriented nonwoven mat [2]-[5]. Figure 1 shows a schematic illustration of electrospinning setup.

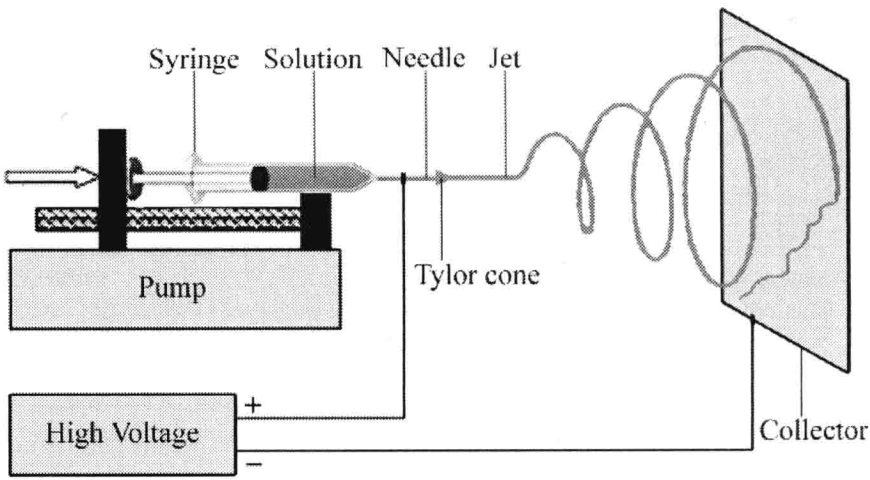


Figure 1. Electrospinning setup [6].

Featuring various outstanding properties such as very small fiber diameters, large surface area per mass ratio [3], high porosity along with small pore sizes [7], flexibility, and superior mechanical properties[8], electrospun nanofiber mats have found numerous applications in biomedical (tissue engineering[9]-[11], drug delivery[12], [13], and wound dressing [14], [15]), protective clothing [7], filtration[16], reinforcement in composite materials [8], [17], and micro-electronics (battery [18], supercapacitors [19], transistors [20], sensors[21], and display devices [22]).

Morphology of electrospun nanofibers such as fiber diameter, depend on many parameters which are mainly divided into three categories: solution properties (solution viscosity, solution concentration, polymer molecular weight, and surface tension), processing conditions (applied voltage, volume flow rate, spinning distance, and needle diameter), and ambient conditions (temperature, humidity, and atmosphere pressure) [23].

As mentioned earlier, electrospun nanofibers have numerous applications some of which have been commercialized. Most of these applications require nanofibers with desired properties suggesting the importance of the process control. This end may not be achieved unless having a comprehensive outlook of the process and quantitative study of the effects of governing parameters which makes the control of the process possible. In addition, qualitative description of the experimental observations are not adequate to derive general conclusions and either the equations governing behavior of the system must be found or appropriate empirical models need be presented. In Ziabicki's words, "in the language of science 'to explain' means to put forward a quantitative model which is consistent with all the known date and capable of predicting new fact" [24]. Employing a model to express the influence of electrospinning parameters will help us obtain a simple and systematic way for presenting the effects of variablesthereby enabling the control of the process. Furthermore, it allows us to predict the results under new combination of parameters. Hence, without conducting any experiments, one can easily estimate features of the product in unknown conditions. That's to say, a model tells us to what extent the output of a system will change if one or more parameters increased or decreased. This is very helpful and leads to a detailed understanding of the process and the effects of parameters.

Despite the surge in attention to the electrospinning process, a few investigations have addressed the quantitative study of the effects of the parameters which has hindered the control of the process. Changing the behavior of materials in nano-scale, presence of electric field, branching of the jet, random orientation of fibers, etc. made the analysis of the process extremely complex and difficult that to date there has been no reliable theory capable of describing the phenomenon. Furthermore, the development of an empirical model has also been impeded due to the lack of systematic and characterized experimentations with appropriate designs. Adding to the difficulty is the number of parameters involving in the electrospinning process and the interactions between them which made it almost impossible to investigate the simultaneous effects of all variables.

Affecting the characteristics of the final product such as physical, mechanical and electrical properties, fiber diameter is one of the most important structural features in electrospun nanofiber mats. Podgorski et al. [25] indicated that filters made of fibers with smaller diameters have higher filtration efficiencies. This was also proved by the work of Qin et al. [16]. Ding et al. [26] reported that sensitivity of sensors increase with decreasing the mean fiber diameter – due to the higher surface area. In the study on designing polymer batteries consisting of electrospun PVdF fibrous electrolyte by Kim et al. [27], it was demonstrated that lower mean fiber diameter results in a higher electrolyte uptake thereby increased ionic conductivity of the mat. Moroni et al. [28] found fiber diameters of electrospun PEOT/PBT scaffolds influencing on cell seeding, attachment, and proliferation. They also studied the release of dye incorporated in electrospun scaffolds and observed that with increasing fiber diameter, the cumulative release of the dye (methylene blue) decreased. Carbonization and activation conditions as well as the structure and properties of the ultimate carbon fibers are also affected by the diameters of the precursor PAN nanofibers[29]. Consequently, precise control of the electrospun fiber diameter is very crucial.

Sukigara et al. [30] employed response surface methodology (RSM) to model mean fiber diameter of electrospun regenerated Bombyx mori silk with electric field and concentration at two spinning distances. They applied a full factorial experimental design at three levels of each parameter leading to nine treatments of factors and used a quadratic polynomial to establish a relationship between mean fiber diameter and the variables. Increasing the concentration at constant electric field resulted in an increase in mean fiber diameter. Different impacts for the electric field were observed depending on solution concentration. Trend of the effects of the two parameters on mean fiber diameter varied with changing the spinning distance which suggests the presence of interaction and coupling between the parameters.

Gu et al. [31] and Gu et al. [32] also exploited the RSM for quantitative study of PAN and PDLA respectively. The only difference observed in the procedure was the use of four levels of concentration in the case of PAN. They included the standard deviation of fiber diameter in their investigations by which they were able to provide additional information regarding the morphology of electrospun nanofibers and its variations at different conditions. Furthermore, they analyzed the significance of the factors in the models in order to understand the level of influence of each parameter. In the case of PAN, voltage as well as its interaction with concentration had no significant effects on both mean and standard deviation of fiber diameter.

Hence, they eliminated the terms corresponding to these factors thereby obtained simplified quadratic models according to which mean and standard deviation of fiber diameter increased with polymer concentration. On the contrary, both voltage and its interaction with concentration were found to be significant in the case of PDLA. However, the effect of polymer concentration was more pronounced. Increasing voltage at constant concentration favored thinner fiber formation which gained momentum with increasing concentration. Fibers with more uniform diameters (less standard deviation) were obtained at higher applied voltage or concentration.

In the most recent investigation in this field, Yördem et al. [33] utilized RSM to correlate mean and coefficient of variation (CV) of electrospun PAN nanofibers to solution concentration and applied voltage at three different spinning distances. They employed a face-centered central composite design (FCCD) along with a full factorial design at two levels resulting in 13 treatments at each spinning distance. A cubic polynomial was then used to fit the data in each case. As with previous studies, fiber diameter was very sensitive to changes in solution concentration. Voltage effect was more significant at higher concentrations demonstrating the interaction between parameters. Despite high reported R^2 values, the presented models seemed to be inefficient and uncertain. Some terms in the models had very high p-values. For instance, in modeling the mean fiber diameter, p-value as high as 0.975 was calculated for cubic concentration term at spinning distance of 16 cm, where half of the terms had p-values more than 0.8. This results in low R^2_{pred} values which were not reported in their study and after calculating by us were found to be almost zero in many cases suggesting the poor prediction ability of their models.

As it was mentioned by the previous authors, there are some interactions between electrospinning parameters. In the past studies, however, they only investigated the simultaneous effects of two variables; therefore they were unable to thoroughly capture the interactions which exist between the parameters. For instance, Sukigara et al. [30] and Yördem et al. [33] both agreed that spinning distance has a significant influence on fiber diameter and that this effect varies when solution concentration and/or applied voltage altered. However, they could not describe their findings in terms of quantitative relationships. Hence, the presented models suffer from lack of comprehensiveness. In addition, in every research where modeling of a process is targeted, the obtained models need to be evaluated with a set of test data which were not used in establishing the relationships. Otherwise, the

effectiveness of the models will not be guaranteed and there will always be an uncertainty in the prediction of the models in new conditions. Hence, it is possible for a model very efficient in describing experimental data, to present unsatisfactory prediction results. In none of the previous works, however, the presented models were evaluated with a series of test data. Therefore, their models may not generalize well to new data and their prediction ability is obscure.

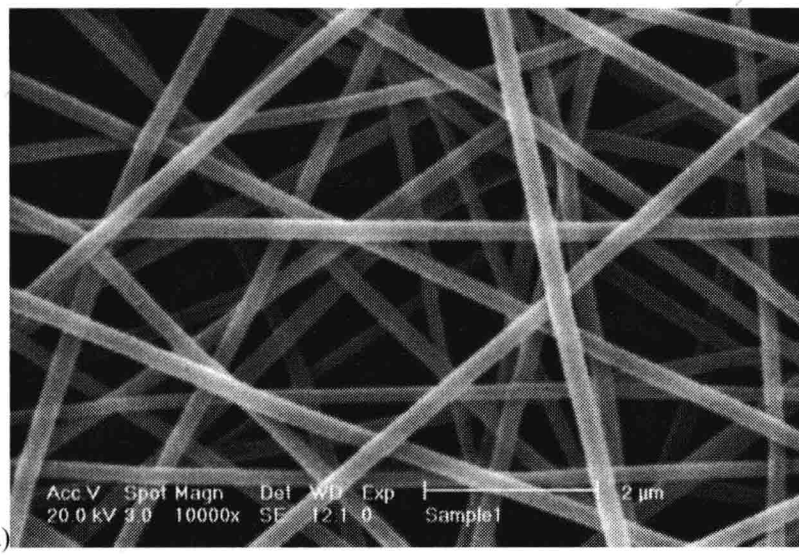
In this contribution for the first time, the simultaneous effects of four electrospinning parameters (solution concentration,spinning distance, applied voltage, and volume flow rate) on mean and standard deviation of polyvinyl alcohol (PVA) fiber diameter were systematically investigated. PVA, the largest volume synthetic water-soluble polymer produced in the world, is commercially manufactured by the hydrolysis of polyvinyl acetate. The excellent chemical resistance and physical properties of PVA along with non-toxicity and biodegradability have led to its broad industrial applications such as textile sizing, adhesive, paper coating, fibers, and polymerization stabilizers[34], [35]. Several patents reported process for production of ultrahigh tensile strength PVA fibers comparable to Kevlar® [36]-[38]. PVA has found many applications in biomedical uses as well due to its biocompatibility[39]. For instance, PVA hydrogels were used in regenerating articular cartilages [40], [41], artificial pancreas[42], and drug delivery systems [43], [44]. More recently, PVA nanofibers were electrospun and used as a protein delivery system [45], retardation of enzyme release [45] and wound dressing [46]. The objective of this paper is to use RSM to establish quantitative relationships between electrospinning parameters and mean and standard deviation of fiber diameter as well as to evaluate the effectiveness of the empirical models with a set of test data.

EXPERIMENTAL

Solution Preparation and Electrospinning

PVA with molecular weight of 72000 *g/mol* and degree of hydrolysis of >98% was obtained from Merck and used as received. Distilled water as solvent was added to a predetermined amount of PVA powder to obtain 20 *ml* of solution with desired concentration. The solution was prepared at 80°C and gently stirred for 30 min to expedite the dissolution. After the PVA had

completely dissolved, the solution was transferred to a 5 *ml* syringe and became ready to electrospin. The experiments were carried out on a horizontal electrospinning setup shown schematically in Figure 1. The syringe containing PVA solution was placed on a syringe pump (New Era NE-100) used to dispense the solution at a controlled rate. A high voltage DC power supply (Gamma High Voltage ES-30) was used to generate the electric field needed for electrospinning. The positive electrode of the high voltage supply was attached to the syringe needle via an alligator clip and the grounding electrode was connected to a flat collector wrapped with aluminum foil where electrospun nanofibers were accumulated to form a nonwoven mat. The electrospinning was carried out at room temperature. Subsequently, the aluminum foil was removed from the collector. A small piece of mat was placed on the sample holder and gold sputter-coated (Bal-Tec). Thereafter, the morphology of electrospun PVA fibers was observed by an environmental scanning electron microscope (SEM, Phillips XL-30) under magnification of 10000X. For each specimen, fiber diameter distribution was determined from the SEM micrograph based on 100 measurements of random fibers. A typical SEM micrograph of electrospun nanofiber mat and its corresponding diameter distribution are shown in Figure 2.



(a)

Figure 2. (Continued).

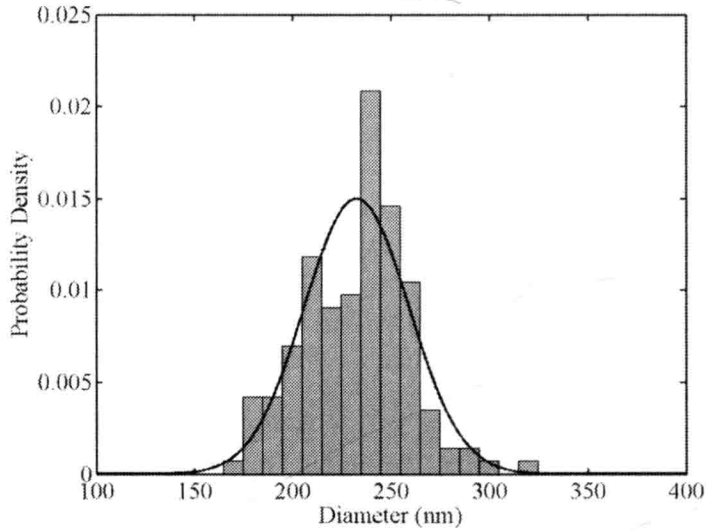


Figure 2. (a) a typical SEM micrograph of electrospun nanofiber mat, (b) its corresponding diameter distribution.

Choice of Parameters and Range

As it was mentioned earlier in this paper, the number of variables which have the potential to alter the electrospinning process is numerous. Hence, investigating all of them in the framework of one single research would almost be impossible. However, some of these parameters can be held constant during experimentation. For instance, performing the experiments in a controlled environmental condition, which is concerned in this study, the ambient parameters (i.e. temperature, air pressure, and humidity) are kept unchanged. Solution viscosity is affected by polymer molecular weight, solution concentration, and temperature. For a particular polymer (constant molecular weight) at a fixed temperature, solution concentration would be the only factor influencing the viscosity. In this circumstance, the effect of viscosity could be determined by the solution concentration. Therefore, there would be no need for viscosity to be considered as a separate parameter.

In this regard, solution concentration (C), spinning distance (d), applied voltage (V), and volume flow rate (Q) were selected to be the most influential parameters in electrospinning of PVA nanofibers as for the purpose of this study. The next step is to choose the region of interest – that is the ranges over

which these factors are varied. Process knowledge, which is a combination of practical experience and theoretical understanding, is required to fulfill this step. The aim is here to find an appropriate range for each parameter where dry, bead-free, stable, and continuous fibers without breaking up to droplets are obtained. This goal could be achieved by conducting a set of preliminary experiments while having the previous works in mind along with utilizing the reported relationships.

The relationship between intrinsic viscosity ($[\eta]$) and molecular weight (M) is given by the well-known Mark-Houwink-Sakurada equation as follows:

$$[\eta] = KM^{a} \tag{1}$$

where K and a are constants for a particular polymer-solvent pair at a given temperature[47]. For the PVA with molecular weight in the range of 69000 $g/mol<M<690000$ g/mol in water at room temperature, K=6.51 and a=0.628 were found by Tacx et al. [48]. Using these constants in the equation, the intrinsic viscosity for PVA in this study (molecular weight of 72000 g/mol) were calculated to be $[\eta]$=0.73.

Polymer chain entanglements in a solution can be expressed in terms of Berry number (B), which is a dimensionless parameter and defined as the product of intrinsic viscosity and polymer concentration ($B=[\eta]C$) [49]. At each molecular weight, there is a minimum concentration at which the polymer solution cannot be electrospun. Koski et al. [50] observed that $B>5$ is required to form stabilized fibrous structures in electrospinning of PVA. On the other hand, they reported the formation of flat fibers at $B>9$. Therefore, the appropriate range in this case could be found within $5<B<9$ domain which is equivalent to $6.8\%<C<12.3\%$ in terms of concentration of PVA. Furthermore, Koski et al. [50] observed that beaded fibers were electrospun at low solution concentration. Hence, it was thought that the domain $8\%\leq C\leq 12\%$ would warrant the formation of stabilized bead-free fibers with circular cross-sections. This domain was later justified by forming some preliminary experiments.

As for determining the appropriate range of applied voltage, referring to previous works, it was observed that the changes of voltage lay between 5 kV to 25 kV depending on experimental conditions; voltages above 25 kV were rarely used. Afterwards, a series of experiments were carried out to obtain the desired voltage domain. At $V<10$ kV, the voltage was too low to spin fibers and $10kV\leq V<15$ kV resulted in formation of fibers and droplets; in addition,