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Effect of Fiber Diameter and Web Porosity on Breathability of Nanofiber Mats at Various Test Conditions

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Effect of Fiber Diameter and Web Porosity on Breathability of Nanofiber Mats at Various Test Conditions

by

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Thesis

Presented to the Faculty of the Graduate School of

The University of Texas at Austin

in Partial Fulfillment

of the Requirements

for the Degree of

Master of Science in Textile and Apparel Technology

The University of Texas at Austin

May 2014

Acknowledgements

Firstly, I want to express my gratitude to my supervisor, Dr. Mourad Krifa, for his kind and patient instruction over the progress of this thesis. The thesis would not be completed without his advice. I would also like to thank Dr. Bugao Xu for being the reader of my thesis. Special thanks to my lab mate Hao Wu, who provided help and guidance in many aspects of this thesis. My sincere thanks also go to all the faculty and staff in the School of Human Ecology who offered their generous help to me. Last but not least, I want to thank my friends and family for their encouragement and unconditional support throughout my life.

Abstract

Effect of Fiber Diameter and Web Porosity on Breathability of Nanofiber Mats at Various Test Conditions

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Barrier fabrics laminated with nanofiber membranes are used in protective textiles due to their ability to achieve high breathability or water vapor transmission rate (WVTR) while maintaining required barrier properties. The objective of this thesis is to investigate the factors impacting nanofiber membrane breathability. To achieve this objective, the effect of test conditions on breathability, and the relationship between fiber diameter, web porosity and breathability were explored. Nanofiber membranes were solution-spun by electrospinning from 15wt% and 20wt% PA6 solution concentrations, and by forcespinning from 20wt% and 25wt% concentrations. Three web area densities were made from each spinning method and solution combination: 5GSM, 10GSM and 15GSM. In order to investigate the impact of measurement conditions, breathability of all samples was measured by upright cup method (ASTM E96B) at two relative humidity levels (20% and 50%), and three air flow velocity levels (300fpm, 500fpm and 700fpm).

The results showed that WVTR of all samples increased significantly when decreasing humidity or increasing air flow velocity. Webs with a lower density (5GSM or

10GSM) had higher changes of WVTR than those with a higher density (10GSM or 15GSM). These results indicate an interaction between the ambient conditions and the nanoweb structure, whereby conditions that are more conducive to water vapor transmission, such as 20%RH and 700fpm, are more discriminant between membranes.

Both electropspun and forcespun membranes processed from the lower concentration solutions (15wt%, and 20wt%, respectively) exhibited smaller fiber diameters and smaller mean pore size. Overall, WVTR values varied with membrane thickness, and with solution concentration following a similar pattern as porosity. These effects were more accentuated for the forcespun samples, which had considerably larger pores (2811-5230nm) than the electrospun counterparts (163-298nm).

Furthermore, samples forcespun by 20wt% solution were found to have clearly higher WVTR (1587-2194g/m^2/24h at 700fpm) than electrospun samples (1526-1614g/m^2/24h at 700fpm). This can be explained by the significant difference of pore size between electrospun and forcespun webs. It was concluded that breathability of forcespun samples, particularly those low density ones, could be effectively adjusted by solution concentration and is more sensitive to change of test conditions than that of electrospun webs.

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Chapter I: Introduction

1.1 Motivation

Increasing attention has been given to the production of fabrics with high water vapor transmission at low cost. Water vapor transmission, or breathability, is the ability of fabrics to allow transfer of moisture by diffusion and it shows how quickly moisture passes through a fabric (Mukhopadhyay & Vinay Kumar, 2008). Breathability is of great importance to maintain thermal comfort of human body under various environments. However, it remains a challenge to achieve high water vapor transmission for fabrics used in protective textiles as they usually sacrifice breathability for barrier properties. To help provide a solution to this challenge, this thesis aims to investigate the use of nanofibers in breathable fabrics and the ways to control breathability values under various environments and nanofiber spinning conditions. Two nanofiber spinning methods were adopted in this thesis: conventional electrospinning and newly developed forcespinning.

One of the most widely used breathability measurement method is the cup method based on ASTM-E96. Although the standard method suggests a range of testing conditions such as temperature, relative humidity and air flow velocity, results reported in practice do not always conform to these suggestions. Often, breathability results used to publicize brands of breathable fabrics do not even mention measurement conditions. As a result, breathability values sometimes varied significantly among research from different scholars and other sources due to inconsistent test conditions. Without the understanding of the effect of test conditions on breathability values, data obtained cannot be compared and analyzed effectively. In addition to test conditions, nanofiber spinning parameters also play an important role in controlling breathability values. To optimize the water vapor transmission value, fiber diameter and web porosity were also investigated. Therefore, another objective of this research is to study the effect of test conditions on WVTR and the relationship among fiber diameter, web porosity and breathability.

1.2 Background

1.2.1 Literature Review: breathable barrier fabrics

1.2.1.1 Water Vapor Transmission/Diffusion Process

Comfort is a state in which there is a balance between heat produced and heat lost. This balance allows human body not to feel too warm or too cold in various environments. In order to achieve sufficient comfort, fabrics, particularly those used as protective textiles, must be able to provide thermal balance that can maintain a stable microclimate around the skin regardless of ambient environment and physical activity (Das, Das, Kothari, Fanguiero, & Araújo, 2008). Water vapor permeability of fabrics plays a critical role in maintaining the thermal balance. A higher water vapor permeability provides better cooling for human body in the production and evaporation of sweat (Gibson, 1993). During the perspiration process, water liquid is released from skin and evaporated to form water vapor (Haghi, 2004). The water vapor is removed from the body by either convection or through the fabric and the heat is taken away together with the vapor. If a fabric is considered to have low water vapor transmission at a given situation, water vapor will be prevented from moving through the fabric and condensation takes place thereafter. This moisture build-up disrupts thermal balance and causes discomfort (Zhang, Watanabe, Kim, Tokura, & Gong, 2001).

The vapour pressure gradient is the precondition for water vapour transmission to take place. Water vapour transmission is governed by Fick's Law (Incropera, Lavine, & DeWitt, 2011) in which the relationship between water vapour flux and gradient concentration is explained.

$$J_{ax} = -D_{AB}\frac{dC_A}{dx}$$

Where J_{ax} is the water vapour transmission rate; dC_A/dx is the concentration gradient; D_{AB} is the diffusion coefficient or mass diffusivity of substance A (water vapor) diffusing through substance B (porous material). The mass diffusivity of a certain liquid at the same atmospheric conditions relies on the nature of porous media, particularly porosity. Therefore, porosity of the media fabrics determines their water vapour transmission (B. Das, Das, Kothari, Fanguiero, & Araujo, 2007).

1.2.1.2 Conventional waterproof and breathable fabrics

Conventional waterproof and breathable textiles are mainly comprised of coated, densely woven and laminated fabrics using micron-sized fibers. Technology development of coating and lamination has made it possible to manufacture conventional breathable barrier fabrics (Jeong & An, 2002). There have been lab works on different laminated polymer membranes and new coating technologies in order to improve the quality of previous products (Lomax, 1990; Painter, 1996; Van Roey, 1992). However, barrier properties and breathability are having a negative relationship and it is difficult to make a fabric with micron-sized fibers both protective and breathable while maintaining a reasonable price. For example, polyurethane rezin coated fabric has been long known as a waterproof material but it fails to provide thermal comfort due to insufficient breathability and air permeability.

One of the most famous conventional barrier fabric is Gortex®, which was first introduced to the public in 1969 and was first issued a patent in 1976 (Gore, 1976). Figure 1 shows how Gortex® fabrics work to maintain waterproofness and breathability at the same time (Sunshine, 2013). There is an outer layer on the face made by fibers like nylon or polyester that can provide abrasion resistance to the garments. DWR (Durable Water Repellent) is applied on this layer to keep the fabric from becoming saturated so that water can bead up and roll off the fabric. However, DWR is not the source of waterproofness and the function comes from the membrane. The membrane below the outer layer is made of micro-porous expanded polytetrafluoroethylene (ePTFE). Expanded PTFE is made by heating and stretching PTFE sheet so that the material is more porous. The pores are too small for water droplets to enter but are large enough to allow transfer of water vapor or perspiration. According to the information from the website of Gore-tex®, it claims that the pores are 20,000 times smaller than a water droplet and 700 times larger than a water vapor molecule (Gortex). There is an optional insulation layer below the membrane serving to protect the membrane from contaminants such as oil and sweat. The soft lining layer can be a separate layer or connected with the upper ones to form different construction leading to different properties. For example, Gore-tex® garments can have 2-layer construction and 3-layer construction based on the relative position between lining and upper layers

Gore-tex® products, however, also have problems such as high price and insufficient breathability (Iriyama, Yasuda, Cho, & Yasuda, 1990). To meet this gap, researchers started to adopt nanomaterials to achieve the goal with low price and high breathability. With the soring development of nanofiber fabrication technology, breathable materials made by nanofibers can be cheaper than gore-tex. In addition, nanofiber membrane also has the potential to achieve micro-porosity and it may be better than ePTFE via choosing proper parameters in nanofiber fabrication.

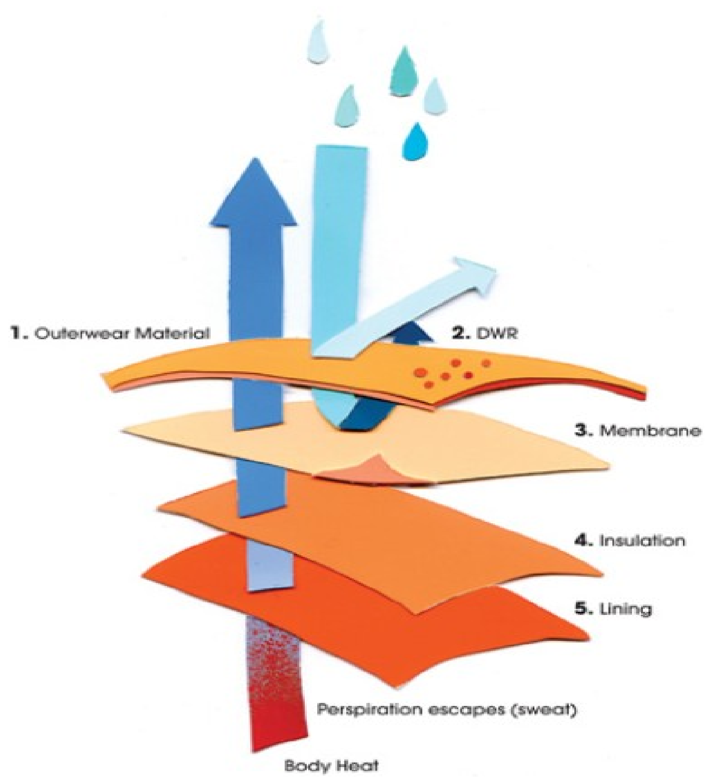


Figure 1 Mechanism of moisture transfer in Gortex® fabrics (Sunshine, 2013)

1.2.1.3 Nanofiber membrane laminated barrier textiles

In order to achieve higher protective properties against harmful substances such as water and chemicals, protective textiles tend to have lower breathability (Bagherzadeh et al., 2012). Schreuder-Gibson et al. (Schreuder-Gibson et al., 2002) found that a protective layer made with nanofiber mats may enhance aerosol protection without significant decrease of water vapor transmission. In addition, directly depositing nanofiber mats on garments can solve seam-sealing problems, thus reducing the manufacturing cost (Gibson, Schreuder-Gibson, & Rivin, 2001). Bagherzadeh et al. (Bagherzadeh et al., 2012) compared comfort properties among Gortex® fabric, multi-layered electrospun nanofiber mats equipped fabric (MENMEF) and a control group of identical woven fabric substrates without nanofiber mats. The nanofiber mats were prepared by electrospinning of polyacrylonitrile (PAN) dissolved in N, *N*-dimethylformamide (DMF). The concentration of PAN in DMF and the electrospinning time were adjusted to optimize the function of MENMEF. Air permeability, water vapor transmission and water repellency were measured respectively. It was found that increasing electrospinning time, from 60min, 90min to 180min, and the concentration of the polymer solution, from 10%, 14%, 16% to 18%, could result in higher waterproofness (800-1000 $g/m^2/24h$), lower air permeability and slight changes of breathability for MENMEF. It was concluded that the multilayered fabrics with nanofiber membranes, compared with the PTFE coated Gortex fabric, exhibit higher water vapor transmission, higher windproof properties and poorer but acceptable water repellency (Bagherzadeh et al., 2012). Different application could be achieved by varying electrospinning time (area density) and polymer concentration. Specifically, 1.5h time and 16% concentration were suggested as the best parameters to make breathable and windproof nanofiber multi-layered fabric.

Nanofiber membranes electrospun with other materials have also been proven to be able to have sufficient water vapor transmission for barrier materials. Lee et al. (Lee & Obendorf, 2007) explored the use of polyurethane nanofibers in protective textiles aiming to prevent liquid penetration while maintaining thermal comfort via suitable water vapor transmission and air permeability. Electrospun polyurethane nanofibers were layered on nonwoven substrates. Water vapor transmission was measured based on ASTM-E96 standard using a vapometer. In addition, the effect of web area density was evaluated via pore size distribution of the layered material, which was measured by Capillary Flow Porometer (PMI, Inc.). It was found that the barrier performance was largely improved by the use of nanofiber membrane regardless of its web area density. However, with the increase of web area density from $1g/m^2$ to $2g/m^2$, water vapor transmission remains almost unchanged around $480g/m^2/24h$ and air permeability significantly drops to a number less than half of its original value. This suggests again that breathability will not be compromised for protective textiles using nanofiber layered materials. The authors claimed that the air permeability of the layered fabric, although reduced dramatically with the increase of web density, is acceptable due to the fact that an air permeability value $100cm^3/s/cm^2$ for the layered fabric is still larger than most of the current protective textiles in use. Therefore, it was concluded that thermal comfort can be achieved.

Another interesting aspect about the above mentioned reference (Lee & Obendorf, 2007) is its exploration of pore size distribution for layered fabrics with different web area density. Pore size was significantly reduced as the web area density increases. This means pore size can be controlled by web density and different thermal comfort properties can be achieved by suitable choice of nanofiber web density. Fiber diameter and fiber mass is closely related with the pore size distribution of nanofiber mats. Li et al. (Li, Frey, & Joo, 2006) explored the influence of fiber mass and fiber diameter on Polylactic acid (PLA) nanofiber membrane. It was found that pore size was decreased and pore size distribution was shifted towards lower diameter values with increasing membrane mass. In addition, decreasing fiber diameter leads to dramatically lower pore size for materials with constant mass. This is because larger fiber diameter leads to the formation of larger pores.

Gorji et al. (Gorji, Jeddi, & Gharehaghaji, 2012) investigated the use of polyurethane nanofibers in protective textiles by exploring the effect of electrospinning duration, i.e. web density. Water vapor permeability was measured based on ASTM E96 standard. It was found that, with the increase of electrospinning duration, web density, tensile strength and hydrostatic pressure all increased. On the other hand, water vapor permeability remains almost unchanged ranging from 39-41 $g/m^2/24h$. In addition, the author also pointed out that the mass of the PU nanofiber mats is much lower than conventional PTFE membrane, which could be a potential advantage in sportswear application. Kang et al. (Kang, Park, Kim, & Kang, 2007) examined the difference between electrospun PU web/fabric (ESF) and PU resin coated fabrics (RCF) in terms of waterproofness and breathability properties. WVT was measured by the desiccant cup method in ASTM E96. Test conditions were set as 40±2°C and 90±5%RH. They found that the WVT value of ESF is greater than 250 $g/h/m^2$, a value that can be regarded as high level of WVT for waterproof fabrics, and it is significantly higher than that of RCF, which range from 13.45 to 64.40 $g/h/m^2$. As far as water resistance is concerned, ESF is only 36.5 cm H_2O, a value that stands for low level of water resistance, and it is significantly lower than RCF. However, water resistance of ESF can be improved by fiber/pore size and web thickness. In addition, ESF has a lower weight than RCF at the same thickness because it has a lot of pores and an open structure.

Hae Wook et al. (Hae Wook, Chung Hee, & Seung Eun, 2011) examined the difference between electrospun polyurethane nanofiber laminate and PTFE-coated clothes in terms of thermal comfort properties. The water vapor transmission was measured by cup method with desiccant based on ASTM E-96 standard. Especially notable was that the author chose to adjust the temperature and relative humidity to investigate the effect of test conditions on breathability of nanofiber web laminates. As shown in table 1 below, water vapor transmission of all samples increased with the rise of temperature and humidity. However, the gap of water vapor transmission between PU nanowebs and PTFE laminates widens significantly at higher temperature and humidity. Therefore, it was concluded that nanoweb laminate is more effective at high temperature and high humidity gradient between the inner and outer layer of the clothing than PTFE laminate in terms of water vapor transmission. This can be another advantage of nanofiber-used barrier materials compared with the conventional ones.

Table 1 Water Vapor Transmission ($g/m^2/24h$) of samples under different temperature and relative humidity (Hae Wook et al., 2011)

	32°C			36°C		
	30%	50%	80%	30%	50%	80%
Nanoweb laminate	996-1026	1958-1979	3684-3742	1224-1269	2527-2573	4475-4496
PTFE laminate	479	880	1981	604	1122	2513

Yoon et al. (Yoon & Lee, 2011)investigated the difference between fabrics with layered structure based on electrospun nanofiber webs and traditional waterproof breathable fabrics, in terms of breathability and barrier performance. They found that the lamination process and nanofiber web uniformity are of great importance for enhanced barrier performance. Specifically, different barrier performance and breathability level can be achieved by controlling layer structure and substrate fabrics. The WVT was tested by desiccant cup method at 38 ±0.5°C and 90±2%RH according to ISO 2528 standard. The results showed that WVT value for densely woven fabrics was 5500 $g/m^2/24h$ whereas the value for nanofiber layered fabrics ranged between 2899 and 4300 $g/m^2/24h$ and the value for PU coated fabrics was only 250 $g/m^2/24h$.

1.2.2 Nanofibers

With high surface area and porosity, nanofibers have applications in many fields, such as tissue engineering (Yoshimoto, Shin, Terai, & Vacanti, 2003), drug delivery (Katti, Robinson, Ko, & Laurencin, 2004), biosensors (Liu et al., 2008), filtration (Gopal et al., 2006), energy storage (Ji, Lin, Medford, & Zhang, 2009), and protective textiles (Schreuder-Gibson et al., 2002). To achieve nano-level diameter, researchers have developed different methods and nanofibers were successfully produced from a broad range of polymers. In this thesis, electrospinning and forcespinning will be discussed as two methods to produce nylon 6 nanofibers.

1.2.2.1 Electrospinning

The most popular method to make nanofibers is electrospinning. Electrospinning has gained tremendous attention in recent years due to its capability of producing polymer fibers with diameters ranging from 3nm to greater than 5μm (Subbiah, Bhat, Tock, Parameswaran, & Ramkumar, 2005). The electrospinning set-up is simple and it is shown in figure 2. The apparatus comprises a high voltage source, a syringe with a needle charged by the voltage source, a syringe pump and a grounded collector. A strong electric field can be generated between the charged needle and grounded collector. The polymer solution or melt is filled into the syringe and the syringe pump pushes the liquid at a certain pump rate. The solution or melt is charged and is stretched by the electric force to form a jet during the electrospinning process. The jet is separated to many nanofibers strands with a certain amount of distance away from the needle. The nanofibers are deposited on the grounded collector. As a result, nanofiber mats can be collected from the surface of the collector.

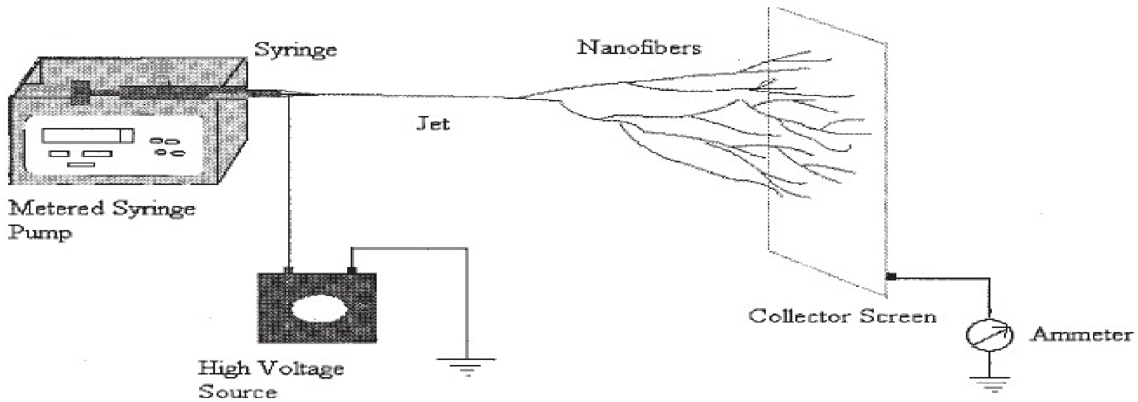


Figure 2 Schematic of electrospinning process (Subbiah et al., 2005)

Morphology of electrospun nanofibers can be affected by a number of parameters. They can be divided into three major categories: solution (solution concentration, etc.), process (voltage, etc.) and ambiant conditions such as temperature and humidity (Doshi & Reneker, 1995).

Although nanofibers can be successfully spun, it remains a problem that the productivity is very low for regular electrospinning with only one needle (Nayak, Padhye, Kyratzis, Truong, & Arnold, 2012). To solve this problem, some scholars (Yang, Jia, Li, Hou, & Guan) proposed to adopt multiple needles in the spinneret or use a non-needle spinneret to get higher productivity. However, with more needles used, needle blocking problems become more frequent and larger space is required for the placement of needles. Needleless electrospinning was also explored as it significantly increased the productivity (Niu, Lin, & Wang, 2009; Yarin & Zussman, 2004). Nevertheless, needleless electrospinning process takes a very high voltage to be initiated and the productivity increased with the applied voltage, leading to high energy consumption. Needleless electrospinning has been available commercially from Nanospider by Elmarco Inc. and is successfully used at high-throughput industrial scale.

1.2.2.2 Forcespinning

Though widely used in the past few decades (Nayak et al., 2012), electrospinning has disadvantages including low nanofiber productivity, high voltage power requirement and limited type of solvents caused by dielectric factor. To solve these problems, a new technology called forcespinning was first developed in 2009 (Lozano & Sarkar, 2009) and has been commercialized by Fiberio Inc.

With the high speed of the rotating spinneret, forcespinning applies centrifugal force to stretch polymer melts or solutions through orifices at the end of the spinneret to form nanofibers. Due to the lack of electric field, forcespinning makes it feasible to spin conductive and nonconductive polymer melts and solution into nanofibers, thus broadening the range of spinnable polymers (McEachin & Lozano, 2012).

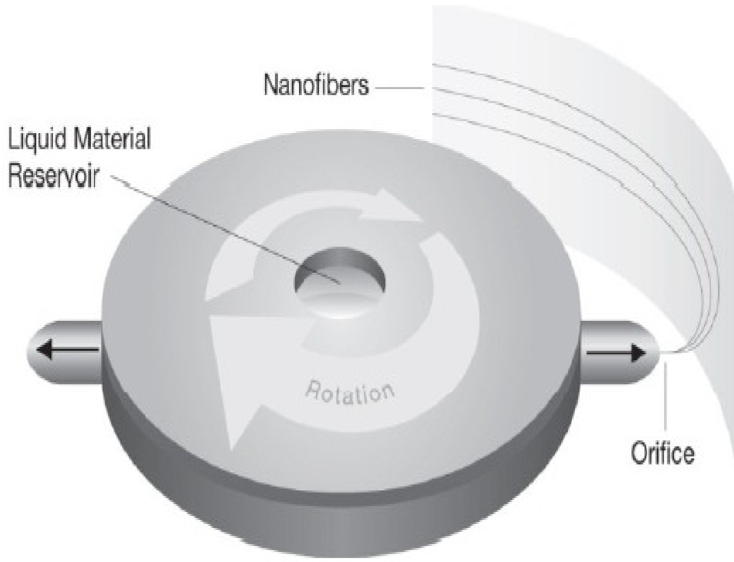


Figure 3 Schematic of forcespinning process (Fiberio)

So far, many polymers have been successfully spun into nanofibers that have desirable fiber diameter and morphology. These include polyamide (Vivekanandhan, Schreiber, Mohanty, & Misra, 2014), polyethylene oxide (Padron et al., 2012), polypropylene (Bharath Raghavan, Soto, & Lozano, 2013), polyvinylidene fluoride (Vazquez, Vasquez, & Lozano, 2012), polytetrafluoroethylene (Rane, Altecor, Bell, & Lozano), polylactic acid (Patlan, 2012), polycaprolactone (McEachin & Lozano, 2012) and so on.

1.3 Introduction to Breathability Measurement

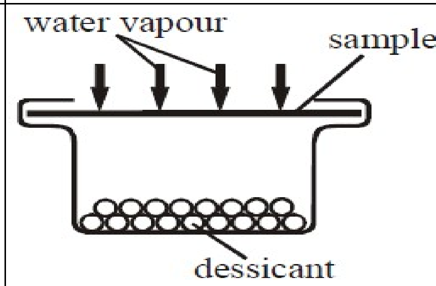
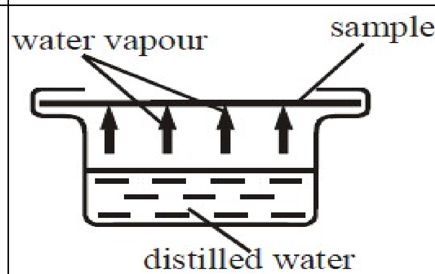
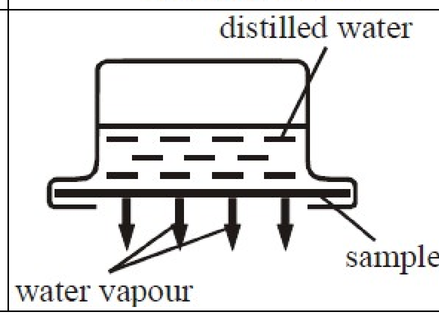
1.3.1 Major Testing Methods

1.3.1.1Cup/Gravimetric method

There are some standard methods available for measuring the breathability or water vapor transmission rate of a fabric: ASTM E96, BS7209, JIS L1099, ISO15496, ISO 2528 and ISO 11092. Among all of these methods, ASTM E96 is most widely used. ASTM E96 test method is also called the "cup method" as the test is performed by sealing a fabric specimen over the open mouth of a test cup that has either desiccant or water under controlled conditions (ASTM-E96/E96M, 2012).

Table 2 is a summary of different types of cup methods (Arabuli, Vlasenko, Havelka, & Kus, 2010). As demonstrated in table 2, cup methods can be divided into desiccant method and water method. In the desiccant method, desiccants such as calcium chloride are placed inside the test cup and the quantity of the water vapor absorbed by the desiccant is quantified by weighing the cup at different times. As for the water method, distilled water is filled into the test cup and the quantity of water vapor evaporated through the test specimen is quantified similarly. Based on the position of test cup, water method can be further classified as upright method and inverted water method. Inverted water method allows direct contact between test material and distilled water, eliminating the effect of air resistance to water vapor transmission. However, this method only applies to hydrophobic material as absorption-desorption of water liquid also affects the weight difference.

Table 2 Different Types of Cup Methods (Arabuli et al., 2010)

Method	Summary	Diagram
Desiccant	Vapor moves from the environment to the inside of the cup filled with desiccant	
Water	Vapor moves from the environment to the inside of the cup filled with water	
Inverted Water	Similar to the water method, but the cup is inverted so that the fabric is in contact with water	

The test unit is periodically weighted and the relationship between weight change and the time can be plotted. The slope of the plotted curve is the vapor transmission rate. Water vapor transmission rate (WVTR) can be calculated using

$$\text{WVTR} = \frac{G}{t * A} = \frac{G}{t} \times \frac{1}{A}$$

where G is the weight change, t is the time during which G occurred and A is the area of the cup mouth.

1.3.1.2 Sweating Hot Plate Method

ASTM F1868 and ISO 11092 introduce a standard testing method using a sweating hot plate (ASTM-F1868, 2012; ISO-11092, 1993). The sweating hot plate can simulate both thermal and moisture transfer from the human body to the environment through garments. Therefore, it can measure both breathability and thermal resistance. Figure 4 is a schematic diagram of the apparatus (Huang, 2006). The apparatus contains a water reservoir (water supply unit), measuring unit and temperature controller. The device will drive heat to transfer upward through the fabric to the environment. To measure breathability or water vapor transmission rate, distilled water is fed to the surface of the plate from the water reservoir. If no water is supplied, the device measures the thermal resistance. The sweating hot plate method is costly due to its high instrument price, high energy cost and large amount of textile needed to run the test.

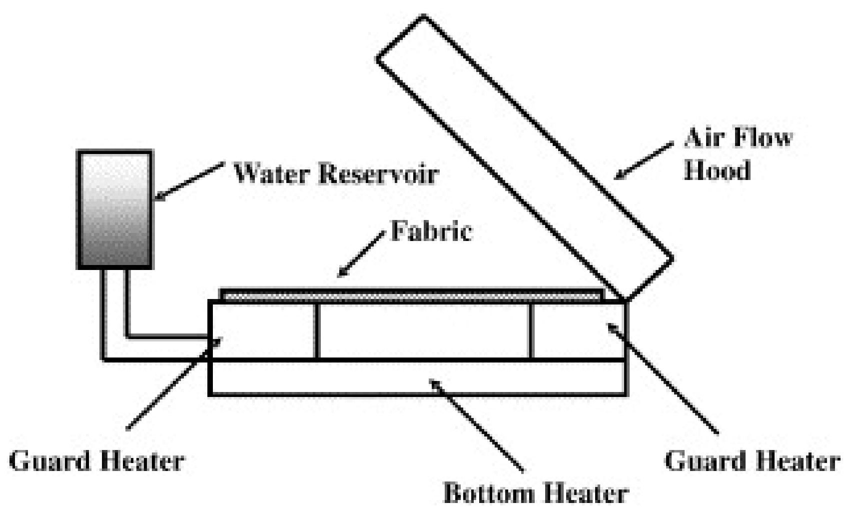


Figure 4 Schematic diagram of sweating hot plate (Huang, 2006)

Huang et al. (Huang & Qian, 2008) pointed out that cup methods can be used for quality control whereas hot plate method is more of being used in simulation of real working experience as it can monitor body temperature. Among cup methods, upward cup method is the cheapest and most convenient one while providing equally effective results as long as the cup is in relatively drier conditions (Huang & Qian, 2008). Therefore, upward cup method was used in this research to compare breathability among different membranes.

1.3.2 Test Conditions

Different test standards/procedures tend to have different test conditions. Table 3 is a summary of the test conditions for different procedures in cup methods (ASTM-E96/E96M, 2012). As shown in the table, temperature has 3 values and relative humidity has 2 values both inside and outside cup. This indicates conditions may differ even within the same standard.

Table 3 Test Conditions for Different Standard Procedures (Arabuli et al., 2010)

Procedure	Method	Temperature, ℃	Relative humidity, %	
			inside cup	outside cup
A	Desiccant	23	0	50
B	Water	23	100	50
BW	Inverted Water	23	100	50
C	Desiccant	32.2	0	50
D	Water	32.2	100	50
E	Desiccant	37.8	0	90

Water vapor transmission data collected by researchers are sometimes very different even when the same method is used. The disparity of breathability value comes from different test conditions such as temperature, humidity and air velocity within the same method. The compliance with the conditions of the upright cup method is not consistent in the literature. For example, Nanpadensky et al. (Napadensky & Elabd, 2004) examined the breathability of sulfonated poly(styrene-isobutylene-styrene) using upright cup method with conditions different from the stipulated ones. The humidity outside the cup was just 10% and the air velocity was not mentioned. The reported results ranged from 2000-5000 $g/m^2/24h$, which is significantly different from some of the WVTR data obtained by upright cup method as shown in 1.2.1.3. These differences might cause inaccuracy when it comes to understanding and comparison of data collected from different conditions. To avoid this problem, the effect of test conditions was investigated in thesis. Humidity and air flow velocity were selected to examine how test condition affects water vapor transmission of nylon 6 nanofiber membranes in the upright cup method.

1.4 Research Problem and Goal

Conventional barrier fabrics cannot maintain desired breathability and protective level simultaneously, economically and persistently. As a porous material with low pore size that can provide good barrier properties, nanofibrous membranes allow direct passage of air and the air carries moisture in the form of vapor. Therefore, nanofiber membrane laminated barrier fabrics are widely regarded as a potential solution to the problem.

It is important to accurately measure the breathability values. The breathability data in the aforementioned references are significantly different due to the fact that they may be based on different standard methods or identical method but with various regulated testing conditions. These differences, on one hand, create a barrier when comparing data from different researchers. On the other hand, they may hinder the ability to predict performance in real environments. Therefore, the first objective of this research was to investigate the impact of test conditions on WVTR measured using the cup method.

All of the past research about the use of nanofibers in barrier materials was done by electrospinning. However, electrospinning cannot meet the increasing need of amount and types of nanofibers. In addition, the relationship between breathability and nanofiber membrane structural characteristics has not been elucidated. Therefore, the second major objective of this research is to explore the use of forcespinning as an alternative high production method, and to investigate the relationship among fiber diameter, membrane porosity and breathability.

Chapter II: Material and Methods

2.1 Sample Preparation

In this thesis, nylon 6/PA6/polycaprolactam is selected as the polymer to be spun into nanofibers. Solvent spinning is used for both electrospinning and forcespinning as it generates nanofibers with lower diameter. Medium viscosity nylon 6 pellets (Aegis® H95ZI) were purchased from Honeywell Corporation. Formic acid (concentration>88%) was purchased from Sigma-Aldrich Chemical Corporation. The PA6 was dissolved in formic acid. The solution was mixed for more than 24 hours at room temperature with magnetic stirrer until the solute was fully dissolved. To prevent solvent loss during the mixing process, the beakers that contained solutions were sealed by parafilms. Once the mixing was complete, the prepared solution was set to stand for 1h at room temperature to determine if the solution was stable.

According to Raghavan et al. (B. Raghavan, Ner, Peno, Gomez, & Lozano, 2011), the favourable solution concentration for forcespun nylon 6 nanofibers ranges from 20% to 25%. Although the concentration of electrospun nylon 6 solutions could range from 10wt% to 30wt%, the concentration of 15wt% to 20wt% are favourable to producing membranes large enough to be used for breathability testing. In this thesis, 15% and 20% concentration were selected for electrospun nanofiber membranes whereas 20% and 25% concentration were selected for forcespun ones. The membrane density was controlled by varying spinning duration. Web density of 5GSM, 10GSM and15 GSM was chosen to be spun for both electrospinning and forcespinning process.

2.2.1 Electrospinning

The electrospinning set-up in our lab is shown as in figure 5 below. A high voltage supply (Gamma High Voltage Research, ES100P-10W/DAM) was used as a power supply and the voltage was fixed at 25 kV. A syringe pump (Harvard Apparatus) was used to feed polymer solution at a rate of 4ul/min and the pump was connected with an 18 Gauge needle (Harvard Apparatus). A piece of grounded aluminum foil was used as a collector. The tip-to-collector distance was set to 12cm. The electrospun nylon 6 nonwoven mats were removed from the foil carefully by peeling.

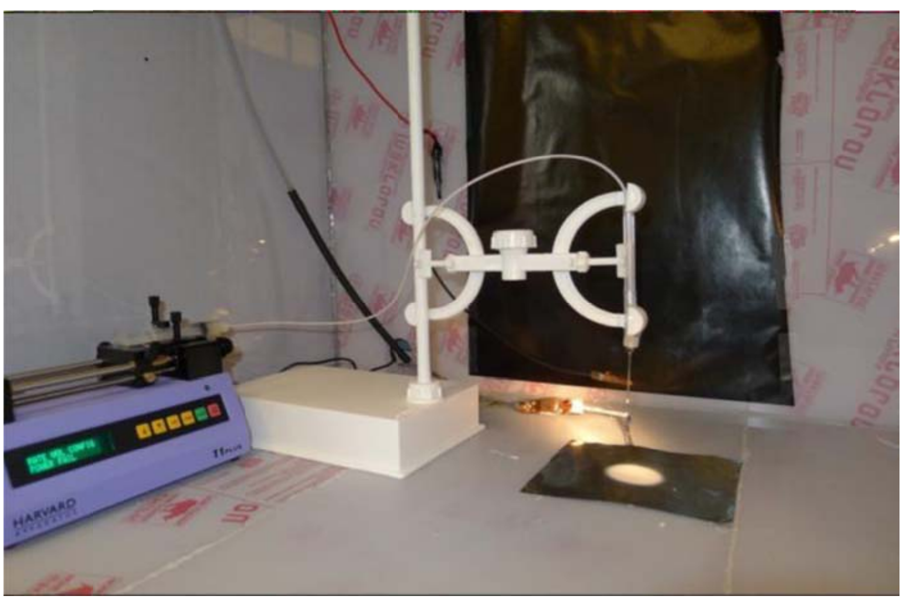


Figure 5 Lab-built electrospinning set-up

Polymer solutions with 15% and 20% concentration were prepared to be electrospun. All of the electrospinning parameters were maintained at constant value except the electrospinning duration. The duration time was adjusted to produce nanofiber membranes with 5GSM, 10GSM and 15GSM.

2.1.2 Forcespinning

The forcespinning apparatus (Cyclone L-1000M/D, Fiberio Technology Corp.) in our lab is shown as in figure below. The spinneret was connected to two 30 gauge ½ inch regular needles (Exelint International, Corp.). Syringes were used to inject polymer solutions to the spinneret. A nonwoven fabric was placed on a fan as the substrate, and the fan was used to draw fibers towards the substrate. The power of the fan can be adjusted as a percentage of capacity. To ensure membrane stability and sufficient drawing force at the same time, the fan was turned on at a 60% power percentage. The fan was placed closely to an aluminum plate where 3 bars were taken away from the plate to make room for fiber deposition. Nanofiber mats were carefully removed from the substrate and collected for further use of testing.

Figure 6 Forcespinning apparatus

Solution concentration, spinneret rotation speed and needle gauges are the most important parameters for forcespinning. Hammami et al. (Hammami, Krifa, & Harzallah, 2014) forcespun nylon 6 nanofibers and examined the effect and interaction of the aforementioned three parameters on fiber diameter. It was found that solution concentration played a dominant role in determining nanofiber diameter compared to the other two parameters. Therefore, spinneret rotation speed and needle gauge were kept constant in this thesis whereas solution concentration varied between 20% and 25%. According to tests conducted by Raghaban et al. (B. Raghavan et al., 2011) and preliminary tests in our lab, the optimal rotation speed for nylon 6 forcespinning is at 6000-7000rpm and the optimal needle size is at 27-30 gauge. In this research, the rotation speed was set at 7000rpm and the needle size was fixed at 30 gauge.

2.2 Characterization

2.2.1 Solution Viscosity

To quantify the exact viscosity of nylon 6 polymer solutions, all of the three solutions were measured by a cone-plate rheometer (Brookfield Corp.).

2.2.2 Fiber Analysis

Morphology of the collected nylon 6 nanofibers was examined by Scanning Electron Microscopy (SEM, Hitachi S-5500). All samples were sputter coated with gold prior to SEM analysis. Fiber diameter was measured by image software called Image J (NIH, http://rsbweb.nih.gov/ij/) based on images obtained from SEM analysis. As many as 100 fibers were selected for each sample on different positions. Nanofiber diameter of each sample was estimated by statistics from those fibers.

2.2.3 Pore Size Distribution

Nanofiber nonwoven webs are generally brittle and are sensitive to pressure in the characterization process. As a result, the measuring technique should assure that the pore structure is not distorted. Capillary Flow Porometry was used in this experiment because the test pressure is very low such that the influence of the pressure can be neglected (Jena & Gupta, 2005). Galwick (Porous Materials, Inc.) was used as the wetting agent for porosity measurement and its surface tension is 15.9 dynes/cm. Membranes were prepared to be cut in circles for measurement.

The pore size distribution can be calculated by the software based on the equation below. The equation indicates the relationship between the differential pressure, P, required to force wetting liquid out at a certain location and the diameter of the pore, D, at the location. In the equation, θ stands for the contact angle of mercury and γ represents the surface tension of mercury.

$$P = \frac{4\gamma cos\theta}{D}$$

2.3 Breathability

2.3.1 Material

Nylon 6 nanofiber membranes produced from electropsinning and forcespinning methods were used in breathability measurement under different test conditions. The web density of the membranes differs from 5GSM, 10GSM and 15GSM. For each density, electrospun samples were prepared from 15wt% and 20wt% solution concentration, and forcespun samples were prepared from those of 20wt% and 25wt%. As a result, there are 12 kinds of samples to be spun based on spinning methods, web density and solution concentration. The upright cup method with distilled water was used for breathability test in this thesis. The membranes were placed and sealed between two rubber rings at the mouth of the cups. The diameter of the cups is 3 inch and the nanofiber membranes were cut into circular pieces with 3 inch diameter so that they can match the cups. The standard test conditions and procedures are based on ASTM E96/E96M-12 (ASTM-

E96/E96M, 2012). The cups were all placed in a chamber that can keep temperature, humidity and air flow velocity around constant values. The weight loss of every cup was measured periodically and the breathability values were calculated based on data measured for 50 hours.

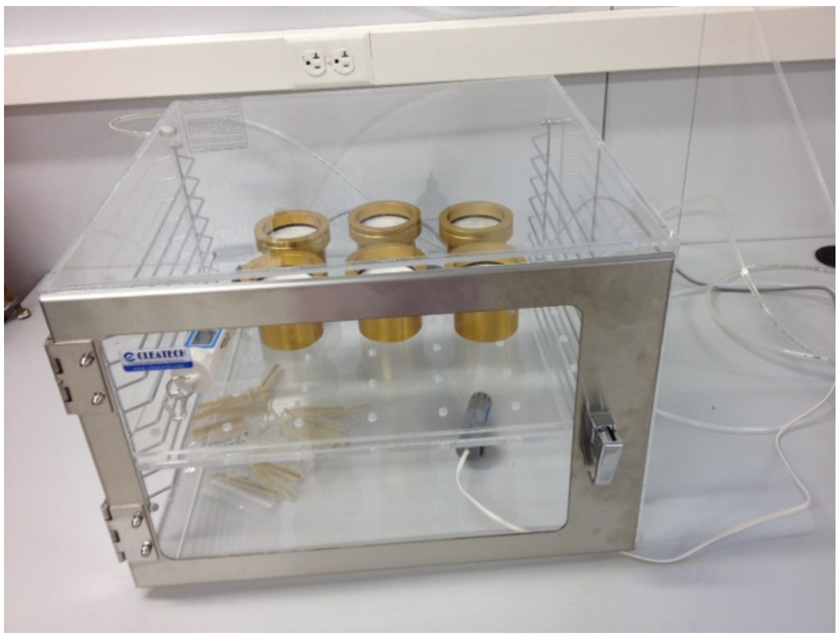


Figure 7 Breathability measurement chamber and cups placed within

2.3.2 Breathability Test under Different Relative Humidity

In addition to 50% relative humidity stipulated in upright cup method in ASTM E96, 20% was also selected to be another RH for measurements of all nanofiber membrane samples. The humidity error was controlled within 3% for 50% and 20% RH. Temperature was set to be 23°C and air flow velocity was kept at a low value, less than 60fpm, in the chamber. Breathability values tested under 20% and 50% RH were compared.

2.3.3 Breathability Test under Different Air Flow Velocity

In order to generate different air flow velocity, three positions in the chamber were chosen for the placement of cups. The three positions were in a horizontal line that is closest to the air source of the chamber. Air flow velocity for the three positions is 700 fpm, 500 fpm and 300 fpm. The velocity error was controlled within 30fpm for all three levels of velocity. Breathability values tested under different air flow velocity were compared. In order to save time, the period was shortened from 50 hours to 24 hours in this part.

Chapter III: Results and Discussion

3.1 Breathability at Different Test Conditions

3.1.1 Breathability Test under Different Relative Humidity

WVTR of samples electrospun from 20wt% nylon solution changes with the change of relative humidity. As shown in figure 8, WVTR of the three samples with different web density all significantly increased and nearly doubled as humidity decreased from 50% to 20%. In addition to humidity, WVTR also rose with the decrease of web density regardless of humidity value, but the influence of web density was significantly less than that of humidity. At 50% humidity, the breathability difference between membranes with different density was not clear although it still indicates that lower density leads to higher breathability. However, the gap of water vapor transmission was found to be enlarged as humidity reduced from 50% to 20%. For example, the gap between membranes with 5GSM and 15 GSM at 50% humidity was 19.0 $g/m^2/24h$ whereas the number at 20% humidity was 104.1 $g/m^2/24h$. This indicates web density tends to have a larger effect at lower humidity levels.

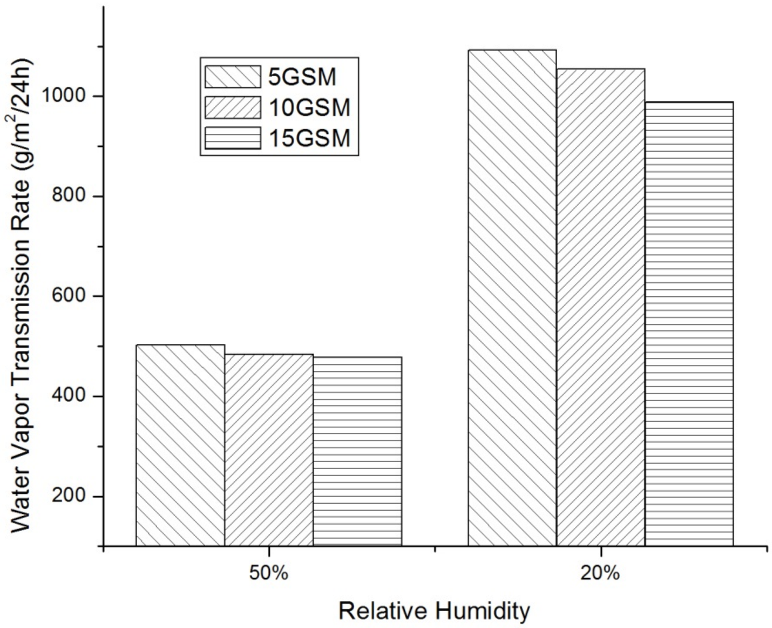


Figure 8 Water vapor transmission rates at two humidity levels for nanofiber membranes electrospun from 20wt% solution

The relationship between WVTR and humidity for samples forcepsun from 20wt% nylon solution was plotted as shown in figure 9. Like electrospun samples, WVTR of forcespun ones also increased dramatically after changing humidity from 50% to 20%, and gap between membranes with different web density increased with reduced humidity. The breathability values at 50% humidity were close to those of electrospun samples, but those at 20% humidity were larger than the latter. This indicates that humidity has a larger effect on WVTR of forcespun samples than that of electrospun ones. Details about the structure of electrospun and forcespun webs will be discussed in the next chapter.

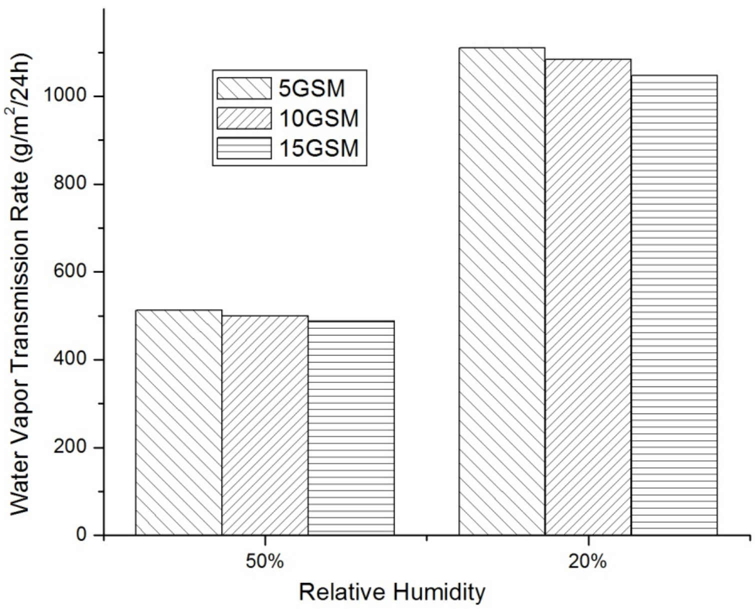


Figure 9 Water vapor transmission rates at two humidity levels for nanofiber membranes forcespun from 20wt% nylon solution

3.1.2 Breathability Test under Different Air Flow Velocity

As shown in figure 10, it is clear that air flow velocity has a significant effect on WVTR of electrospun nanofiber webs as the WVTR values are much higher than those in figure 8 and figure 9. The WVTR values did not increase notably with the air flow velocity increasing from 300fpm to 500fpm regardless of web density. However, the WVTR values proceeded to increase significantly when increasing the wind velocity from 500fpm to 700 fpm. This indicates that the relationship between air flow velocity and WVTR is not linear. Plotted in figure 10 was a exponential relationship where WVTR values increased sharply between 500fpm and 700fpm. Density played a role in this process and membranes with less density tend to increase more in WVTR. As a result, the gap of WVTR at 700 fpm is notably wider than that at 300 fpm or 500rpm between webs with density of 5GSM, 10GSM and 15GSM.

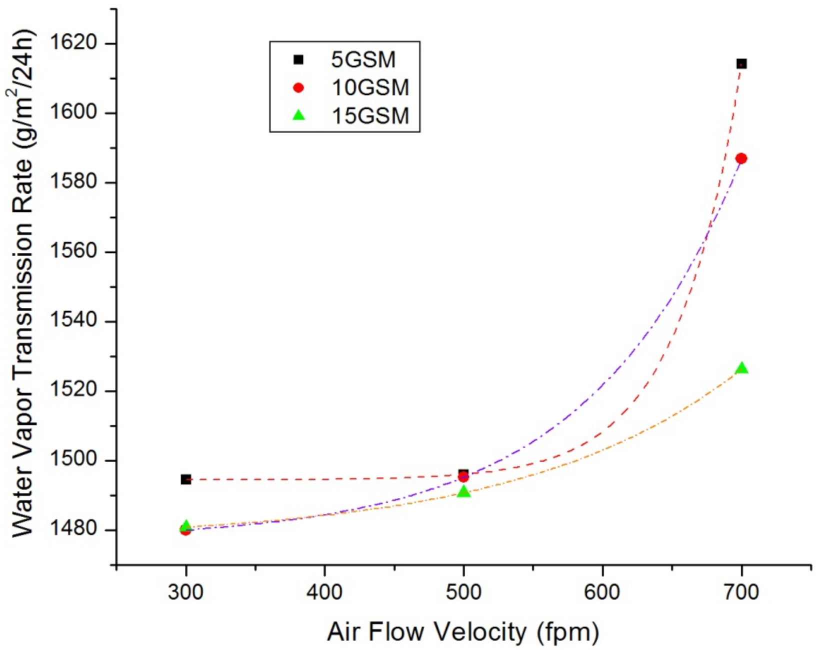


Figure 10 Water vapor transmission rates at three velocity levels for nanofiber membranes electrospun from 20wt% solution

As demonstrated in figure 11, air flow velocity also has a dramatic effect on WVTR of forcespun nanofiber webs. Similar to electrospun ones, the WVTR values slowly increased from 300fpm to 500fpm and went on to rise significantly at 700fpm. Especially noteworthy was that air flow velocity has a greater effect on the WVTR of forcespun nanofiber webs than that of electrospun ones because, for example, the WVTR of 5GSM and 10GSM samples are both higher than 2000 $g/m^2/24h$ whereas the counterparts of electrospun ones are only around 1600 $g/m^2/24h$ as shown in figure 10. This is expected to be caused by the structure difference of membranes produced from the two spinning methods.

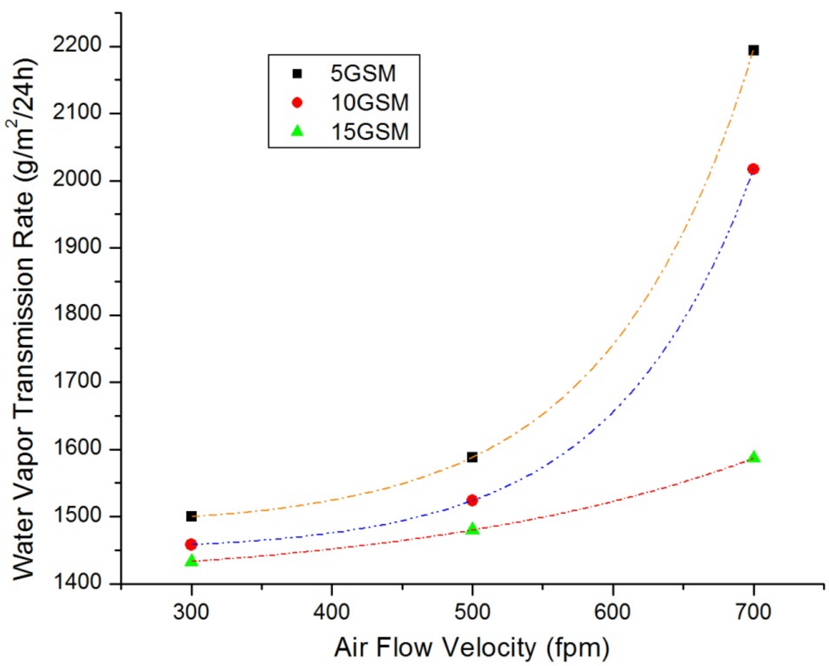


Figure 11 Water vapor transmission rates at three velocity levels for nanofiber membranes forcespun from 20wt% solution

3.1.3 Summary

The effect of relative humidity and air flow velocity on breathability of electrospun and forcespun nanofiber webs was examined in 3.1. All of the nanofibers tested in this part were from 20wt% solution concentration in order to compare the effect of spinning methods on WVTR. The relative humidity was set to have two levels: 20% and 50%. The air flow velocity was chosen to be 300fpm, 500fpm and 700fpm. It was found that the differences of WVTR values of all tested samples at 50%RH, 300fpm and 500fpm were limited. However, WVTR values rise with the decrease of humidity and increase in air flow velocity. More importantly, the difference of breathability between samples with different density (5GSM, 10GSM and 15GSM) increased significantly with surrounding environment changing from 50%RH to 20RH% and from 300fpm or 500fpm to 700fpm. In addition, the WVTR of forcespun samples was found to respond more actively when exposed to low humidity and high air flow velocity than that of electrospun ones.

The results in 3.1 indicate that WVTR can be changed by manipulation of test conditions (humidity and air flow velocity), nanofiber web density and spinning methods. In addition, the interaction observed indicates that the measurement method allows better disctimination between different samples under some specific conditions. It is expected that web density and spinning methods change the structure of the nanofiber webs and thus affect WVTR. In order to understand the structure change, fiber morphology and pore size of the nanofiber webs will be examined. Solution concentration was adjusted to control fiber diameter.

3.2 Relationship among Fiber Diameter, Porosity and Breathability

3.2.1 Solution Viscosity

Figure 12 shows the relationship between solution viscosity and polymer solution concentration. Solution viscosity was found to be higher as solution concentration increases. Moreover, the two parameters appear to be in an exponential relationship as researchers found before (Thomas & Thomas, 1960; Wang & Dong, 2009). In order to spin nanofiber membranes with sufficient area for breathability measurement, the viscosity could not be too high or too low. In electrospinning, concentration less than 15wt% or more than 20wt% was either non-spinnable or results in membranes that are too small to be used. In forcespinning, concentration less than 20wt% or more than 25wt% had the same problem like that in electrospinning. The reason for these problems is that viscosity is closely related to spinnability. When the solution viscosity or concentration is too low, chain overlapping is not enough to form nanofibers (Kroschwitz, 1990), resulting in droplets sprayed out of the needle. When the solution viscosity or concentration is too high, it takes very high voltage or spinneret speed to generate membranes large enough to be peeled. Solution concentration is the most important factor in both electrospinning and forcespinning process (Hammami et al., 2014; Ryu, Kim, Lee, Park, & Lee, 2003) and it is of great importance to test the viscosity beforehand so that good fiber coverage on the collector can be achieved.

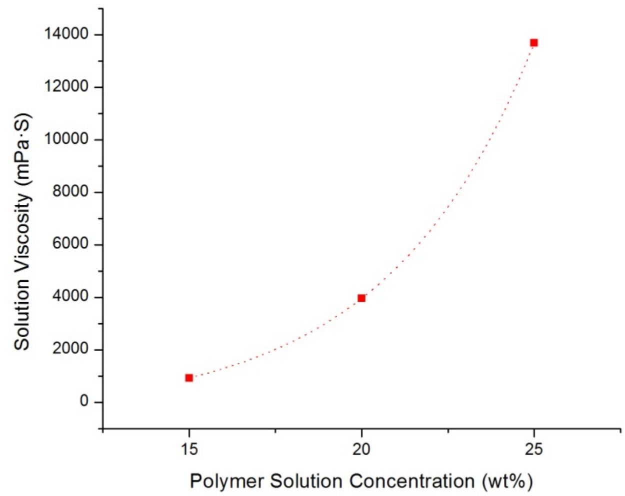


Figure 12 Relationship between solution viscosity and polymer solution concentration of the three prepared nylon 6/formic acid solution

3.2.2 Fiber Analysis

Images of selected electrospun and forcespun nanofiber mats were presented in figure 13. The nanofibers were randomly distributed within the web. As shown in table 4, figure 14 and figure 15, fiber diameter increased with higher polymer concentration for both spinning methods. In addition, forcespun nanofibers have significantly larger diameter than those electrospun ones at the same concentration. As indicated by the standard deviation column in table 4, nanofibers tend to have broader distribution of fiber diameter if made by forcespinning method or higher concentration, which agrees with what figure 14 illustrates. In electrospun samples from 15wt% solution, fiber diameter ranges from 50-300 nm and 90% of the fibers lied in the region of 100-200 nm. In contrast, electrospun fibers from 20wt% solution had diameter from 100-600 nm and most of them were from 200-300nm. The distribution was even broader for forcespun nanofibers from either 20wt% or 25wt% as they ranged from 200 nm to more than 1000nm. This difference may result from mechanisms of the two methods in which electrospinning relies on electric force and forcespinning depends on centrifugal force.

Table 4 Diameter of nanofibers made by different concentration and spinning methods

Sample	Average Diameter (nm)	Standard Deviation (nm)
15%-Electrospinning	135.8	±29.9
20%-Electrospinning	265.5	±76.2
20%-Forcespinning	468.4	±148
25%-Forcespinning	585	±243.9

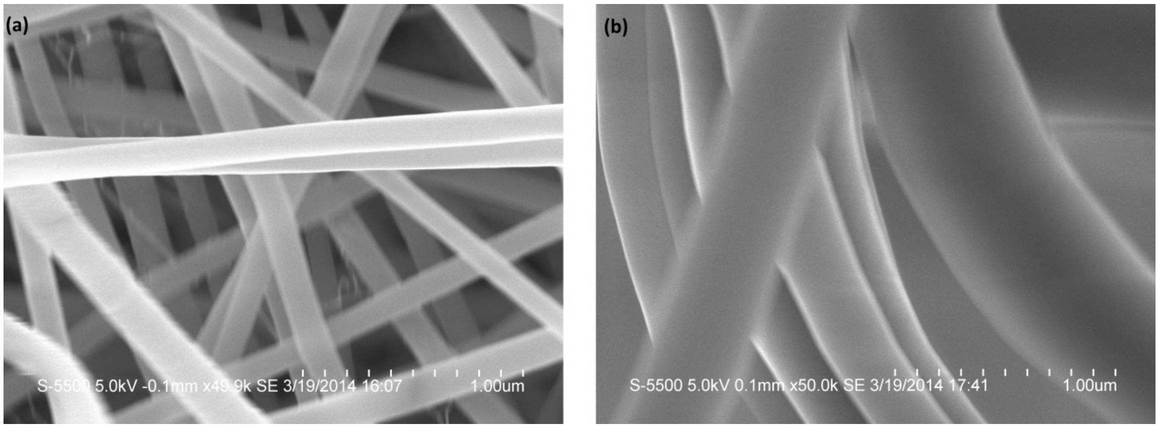


Figure 13 SEM images of nanoweb samples (a) electrospun from 15wt% solution and (b) forcespun from 20wt%

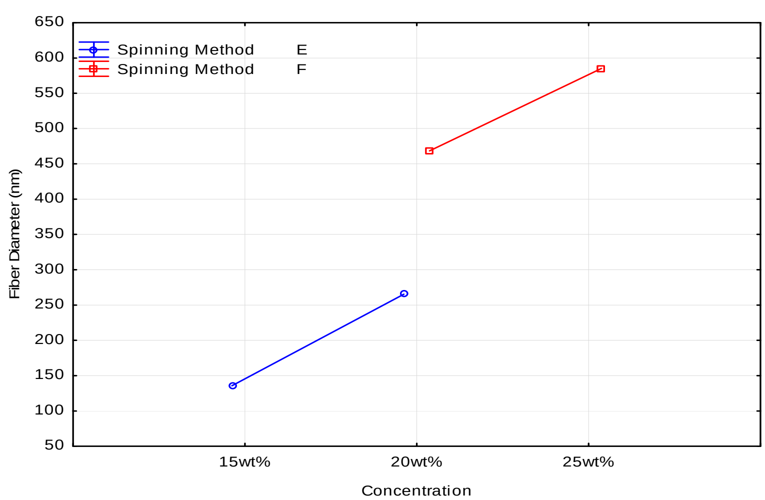


Figure 14: Fiber diameter variation with spinning method and solution concentration

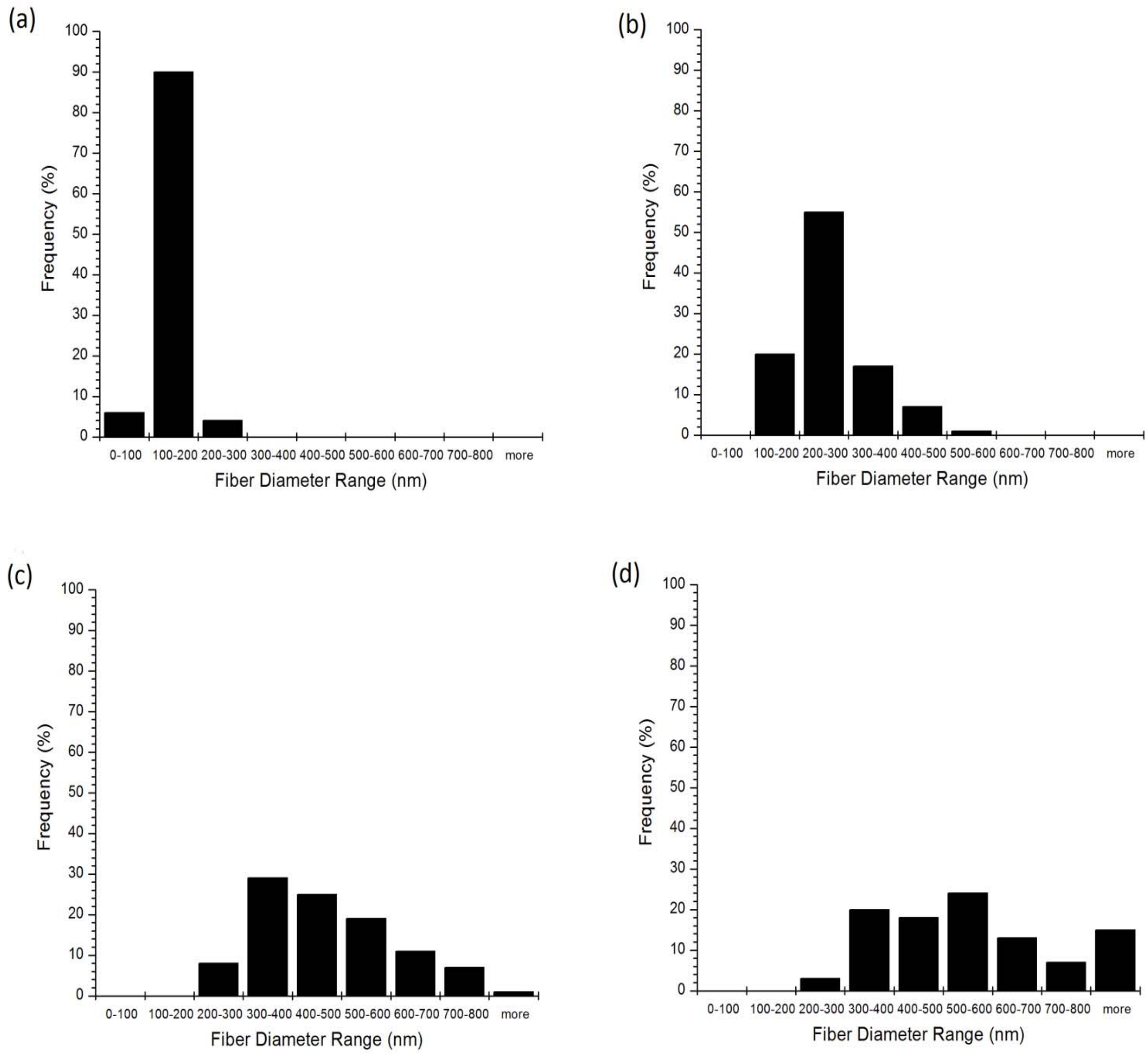


Figure 15 Distribution of fiber diameter range of electrospun and forcespun nanofiber mats at different polymer concentration. Details of the four charts are: (a) Electrospun-15wt%, (b) Electrospun-20wt%, (c) Forcespun-20wt% and (d) Forcespun-25wt%.

3.2.3 Pore Size Distribution

Pore size of all prepared nanofiber samples were listed in table 5 and pore size distribution were demonstrated in figure 16. As presented in table 5, pore size was found to fall down with the increase of web density regardless of spinning methods and solution concentration. This can be explained by increased thickness and layers leading to smaller interfiber space. On the other hand, polymer solution concentration also makes a difference in pore size of nanofiber webs. As can be seen in table 5, electropsun nanofiber webs with 20wt% solution concentration tend to have larger pore size than those with 15wt% concentration. Likewise, pore size of the forcespun samples with 25wt% concentration is larger than that with 20wt% concentration. Due to the fact that increasing polymer concentration results in rising fiber diameter, the reason of the pore size difference can be explained by widening interfiber space caused by higher fiber diameter. In addition, spinning method has a significant effect on pore size of nanofiber webs. Forcespun webs can have pore size more than 30 times larger than that of electrospun ones as noted by 5067nm mean flow pore diameter in a forcespun web compared to that of 163nm in an electrospun one. This huge disparity results partially from the difference of fiber diameter between electrospun and forcespun nanofibers discussed in 3.2.2, and partially from the fiber formation mechanisms between these two spinning methods. It is possible that different fiber elongation and collection systems lead to completely different fiber coverage and interfiber structure. A combination of pore size distribution in figure 17 also provides a straightforward view on the different of pore size for nanofiber webs generated by the two spinning methods.

Table 5 Pore size of electrospun and forcespun nanofibers at 3 levels of concentration and web density

Spinning Method	Concentration	Density	Mean Flow Pore Diameter	Standard Deviation
Electrospinning	15wt%	5GSM	201nm	±67nm
Electrospinning	15wt%	10GSM	164nm	±69nm
Electrospinning	15wt%	15GSM	163nm	±65nm
Electrospinning	20wt%	5GSM	298nm	±182nm
Electrospinning	20wt%	10GSM	237nm	±239nm
Electrospinning	20wt%	15GSM	231nm	±158nm
Forcespinning	20wt%	5GSM	3693nm	±3897nm
Forcespinning	20wt%	10GSM	3102nm	±1348nm
Forcespinning	20wt%	15GSM	2811nm	±2601nm
Forcespinning	25wt%	5GSM	5230nm	±3134nm
Forcespinning	25wt%	10GSM	5067nm	±4039nm
Forcespinning	25wt%	15GSM	4471nm	±3899nm

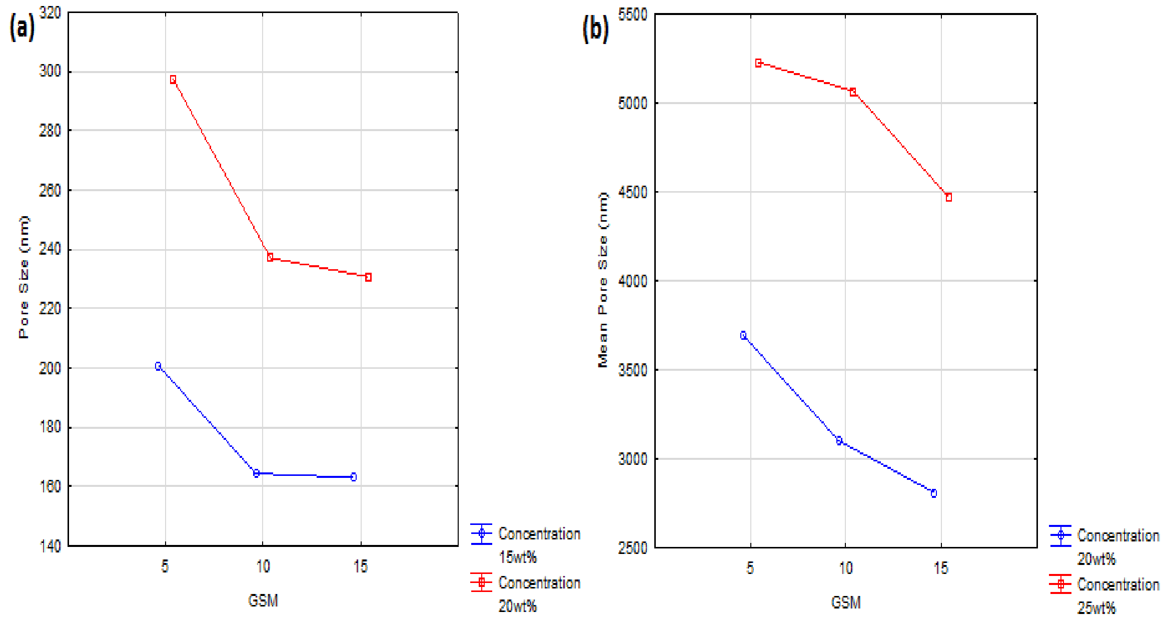


Figure 16 Mean pore size distribution of electrospun and forcespun nanofiber webs

Another characteristic obtained in table 5 is the standard deviation (STD) of all nanofiber membranes. It is generally true that pore size of samples with the same spinning method and solution concentration tend to have similar standard deviation, although exception like forcespinning-20wt%-10GSM existed. It is clear that pore size of forcespun samples have significantly higher standard deviation than that of electrospun ones, which can be also seen in figure 17 where pore size distribution of forcepsun samples are broader than that of electrospun ones.

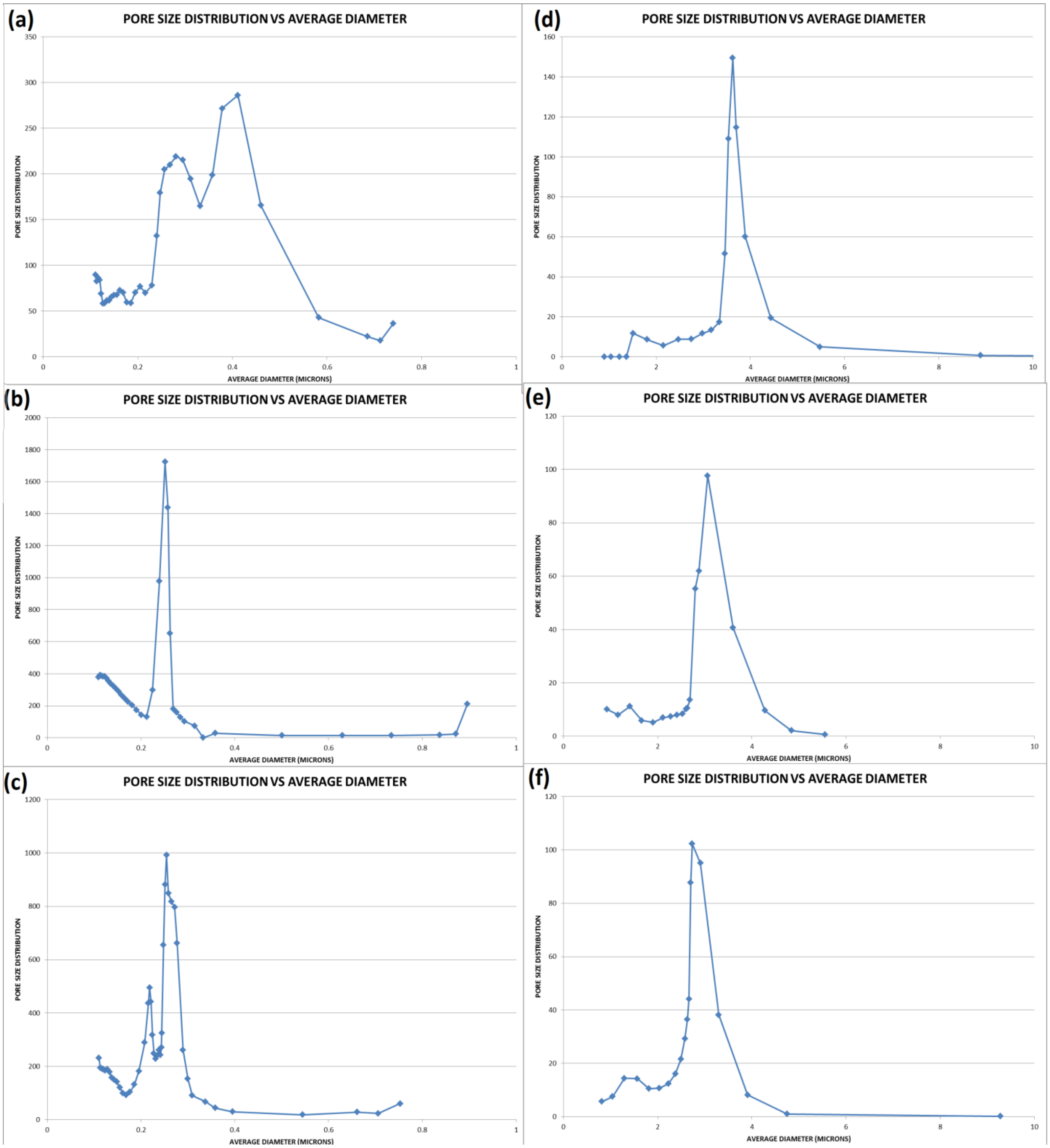


Figure 17 Pore Size Distribution of Nanofiber Membranes: (a)Electrospun-20wt%-5GSM, (b) Electrospun-20wt%-10GSM, (c)Electrospun-20wt%-15GSM, (d)Forcespun-20wt%-5GSM, (e) Forcespun-20wt%-10GSM and (f) Forcespun-20wt%-15GSM.

3.2.4 Effect of fiber diameter and web porosity on breathability

In section 3.1, we discussed the effect of test conditions on breathability of the nanofiber webs under the interaction of web density and spinning methods. The results indicated that web density and spinning methods had influence on the web structure, which resulted in WVTR changes among different samples. This can be explained by the pore size distribution in figure 17. It is clear that the pore size of forcespun nanofiber webs is significantly higher than that of electrospun ones. For example, the mean pore size of the 5GSM forcespun web from 20wt% solution concentration is 3693nm whereas the counterpart of the 5GSM electrospun web from 20wt% concentration is only 298nm. Such difference leads to what was found in section 3.1 in which WVTR of the 5GSM and 10GSM forcespun membranes at 20%RH or 700fpm is significantly higher than that of the electrospun counterpart at the same conditions. However, especially notable was that the WVTR of 15GSM forcespun nanofiber web did not differ that much compared to that of the 15GSM electrospun one at high humidity and air flow velocity despite the fact that pore size of the former is significantly higher than the latter. This exception might be explained by the increased thickness of the web. Based on Darcy's law, fabric thickness is inversely related with flow rate and thus large fabric thickness leads to low water vapor transmission. Such effect of fabric thickness on WVTR was found to be correct in a study about cotton fabrics (S. Das & Kothari, 2012) where thinner cotton fabrics were found to have higher WVTR than that of the thicker ones even though porosity was similar for the two type of fabrics. It is possible that the effect of thickness on WVTR for nanofiber webs with more than 15GSM density outweighs the effect of porosity. As a result, porosity plays a major role in 5GSM and 10GSM electrospun and forcespun webs, whereas its effect is less apparent with thicker nanofiber webs.

As discussed in 3.2.2, fiber diameter differs among different solution concentration and spinning methods. As a potential factor to control pore size and WVTR of nanofiber webs, fiber diameter was manipulated in this thesis. It has been shown in table 4 that higher concentration and forcespinning produce larger fiber diameter. The effect of spinning methods on WVTR of the nanofiber webs has been discussed in 3.1. To better understand the effect of solution concentration on web breathability, 15wt% and 20wt% concentration was used in electrospinning, whereas 20wt% and 25wt% was chosen for forcespinning.

Plotted in figure 18 is the variation of WVTR of electrospun samples under the effect of the interaction between solution concentration and membrane thickness, at different levels of air flow velocity. Part (a) of figure 18 depicts results obtained at 50% relative humidity and less than 60fpm air velocity, whereas part (b) and (c) show results obtained at 300fpm and 700fpm air velocity with 20%RH. As can be seen in the figure, there was no difference between 15wt% and 20wt% WVTR at 50% RH and at low air flow velocity. The WVTR difference between concentrations appears to be more sizable for the test conducted at 300fpm air velocity (b), however, the actual effect size is just 54.6 g/m^2/24h, which cannot be regarded as a clear difference compared to forcespun sample results, which will be introduced next in figure 19. The similar WVTR values may be explained by the limited difference of pore size between samples electrospun from 15wt% and 20wt% concentration. As shown in table 5, pore size of all electrospun samples ranged from 163 to 298nm, whereas the range for forcespun ones were 2811 to 5230 nm. Such a small gap of pore size is possibly unable to provide a clear WVTR gap for the samples.

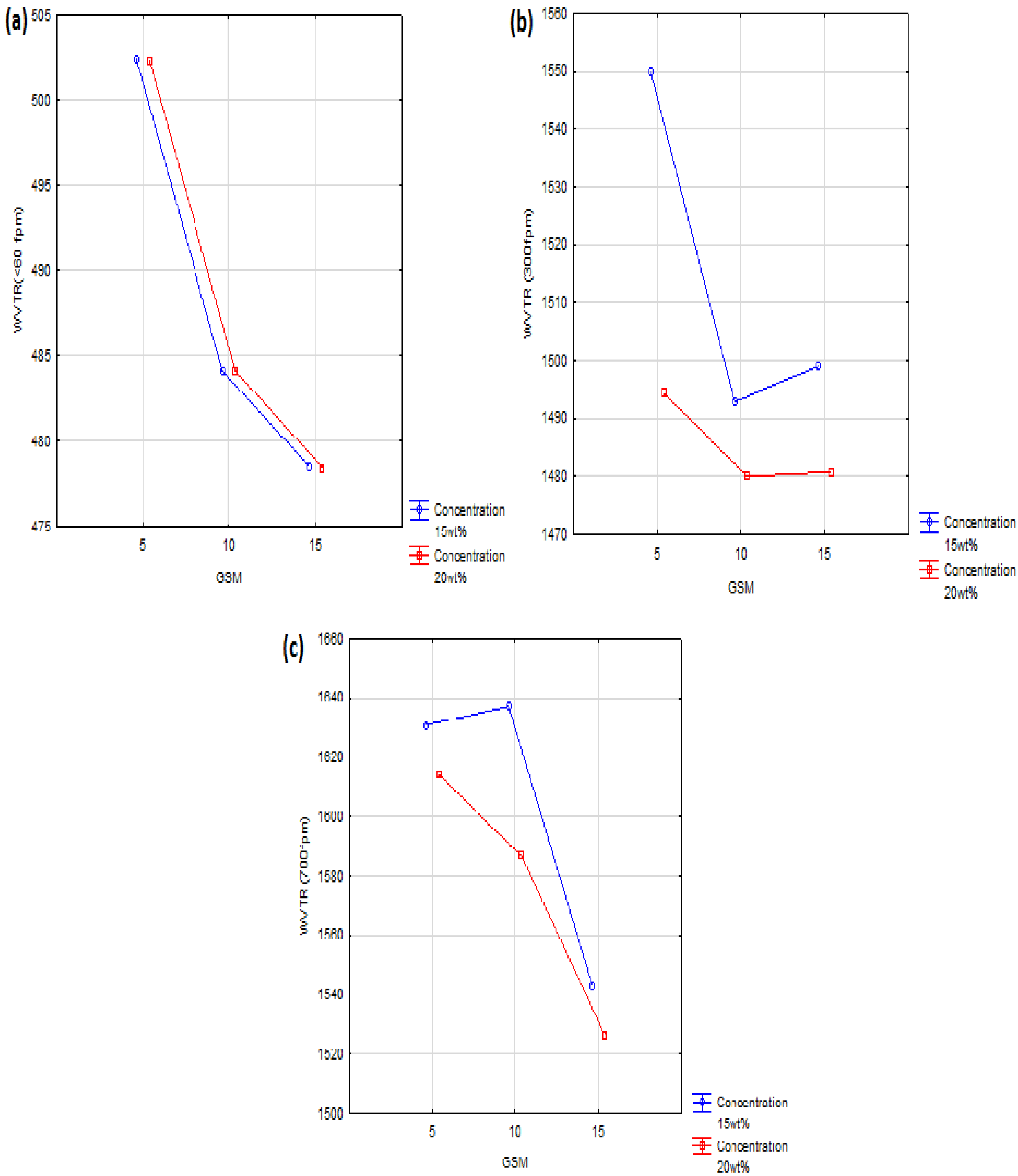


Figure 18 Comparison of WVTR of nanofiber webs electrospun with 15wt% and 20wt% concentration at different air flow velocity: (a) <60fpm, (b) 300fpm and (c) 700fpm

Presented in figure 19 is the comparison of WVTR of forcespun samples between concentrations*web thickness combinations. Similar to electrospun samples, the WVTR of forcepsun nanowebs at 50%RH and less than 60fpm air velocity did not show clear difference between concentrations. However, the results were significantly different when the air flow velocity became 300fpm and 700fpm. Particularly for 5GSM samples at 700fpm, WVTR of the 20wt% one is 2194 $g/m^2/24h$ whereas that of the 25wt% one is 3498 $g/m^2/24h$. It can be found from table 5 that pore size of forcepsun nanowebs ranged from 2811 to 5230 nm, which is significantly higher than the range (163 to 298nm) observed in electrospun samples. With the air flow favoring water vapor circulation at the cup mouth, it is possible that air flow velocity has larger influence on WVT for low density webs as they have larger pore size and smaller thickness. However, exception point exists in part (b) of the figure where WVTR of the 20wt% -10GSM-sample is slightly larger than that of the 25wt% -10GSM-sample, although the 5GSM and 15GSM sample still matches the expected order.

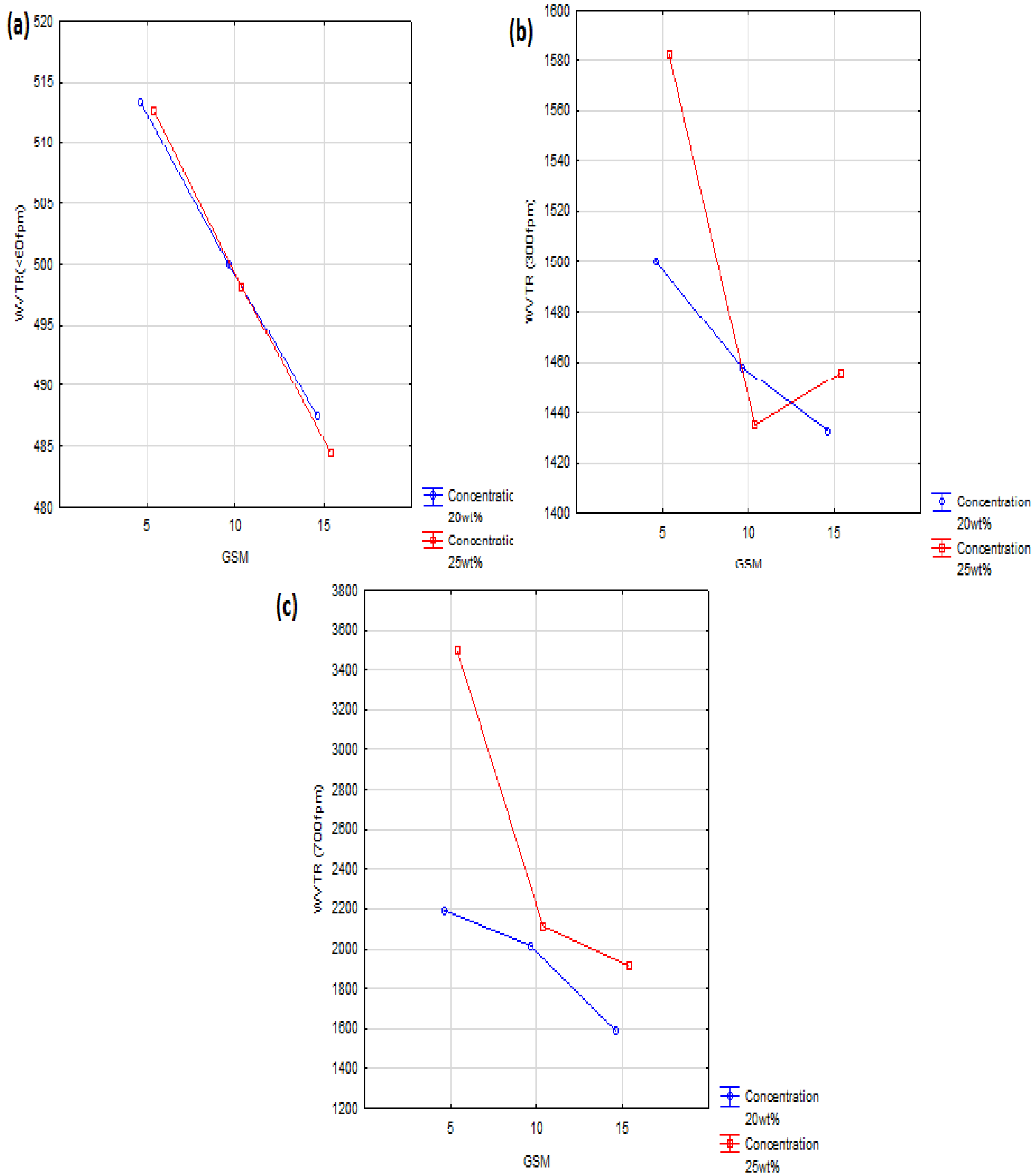


Figure 19 Comparison of WVTR of nanofiber webs forcespun with 20wt% and 25wt% concentration at different air flow velocity: (a) <60fpm, (b) 300fpm and (c) 700fpm

3.2.5 Summary

Fiber diameter and pore size were measured. It was found that nanofiber webs produced by forcespinning and higher solution concentration tend to have higher fiber diameter and larger pore size. As a result, forcespun samples have significantly higher WVTR than electrospun ones at low humidity and high air flow velocity. As the variation of pore size is not large, electrospun samples with 15wt% and 20wt% concentration did not exhibit clear difference in terms of WVTR. With the large variability of pore size, forcespun samples from 20wt% and 25wt% concentration have different WVTR at high air flow velocity.

Chapter Ⅳ: Conclusion

In order to better understand the use of nanofiber membranes in breathable barrier materials, two problems have been raised and discussed in this thesis: breathability at different test conditions, and the relationship among fiber diameter, porosity and breathability. To address the two problems, nanofiber webs were made by solution spinning from nylon 6/formic acid solution. The nanofiber webs were prepared to have three density levels: 5GSM, 10GSM and 15GSM. As an alternative spinning method, forcepspinning was used together with the familiar electrospinning as the ways to produce nanowebs. Three concentration of the solution were prepared for nanofiber fabrication, among which 15wt% and 20wt% were used for electrospinning, and 20wt% and 25% were used for forcespinning.

In the first part of the thesis, the effect of ambient relative humidity and air flow velocity on breathability of nanofiber webs was examined. There were two levels of relative humidity (20%RH and 50%RH), and three levels of air flow velocity (300fpm, 500fpm and 700fpm). The results showed that all nanofiber webs, regardless of density, spinning concentration and spinning methods, had similar WVTR when measured at 50%RH and low air flow. On the other hand, WVTR levels not only increased when decreasing ambient humidity and increasing air flow velocity, they also exhibited more sizable variations with spinning method, web density, and solution concentration. Indeed, nanofiber webs with lower density tend to have larger WVTR increase than those with higher density when the conditions change. In addition, forcespun samples presented higher WVTR changes under varied conditions than that of electrospun ones.

In the second part of the thesis, fiber diameter and pore size of all samples were measured to explore their relationship with breathability. The results indicated that higher fiber diameter and larger pore size can be achieved for nanofiber membranes by using forcespinning and higher solution concentration. The significantly higher pore size for forcepsun samples is the reason for its overall higher WVTR. In terms of the WVTR values at different concentrations, electrospun samples did not show sizable differences, whereas forcespun samples had significant differences, especially under high air flow velocity. This is caused by much wider difference of pore size between the 20wt% and 25wt% forcepsun webs, and by higher influence of air velocity over humidity on WVTR. In addition, the influence of porosity on WVTR tends to be weaker with the rise of web density. As a result, the effect of thickness surpasses that of porosity on WVTR at high density levels, i.e. 15GSM webs, such that forcepsun samples have similar WVTR compared to those of electrospun under the same conditions.

For future work, additional effort should be given to the measurement of thickness of nanofiber webs to understand the interaction between thickness and porosity on WVTR. In addition, temperature as a test condition should also be studied to explore a better combination of factors on optimization of breathability for barrier materials.

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