EFFECT OF PROCESSING CONDITIONS ON THE STRUCTURE, AND PROPERTIES OF MELT BLOWN POLYLACTIC ACID (PLA) NONWOVENS

by

HOMEIRA AZARI

(Under the Direction of Gajanan Bhat)

ABSTRACT

In this research, the influence of process conditions on the properties of polylactic acid (PLA) nonwoven fabrics by melt blowing are described. A commercially available PLA being developed for melt blowing application was processed under various conditions and with a processing aid using a melt blowing pilot line. Produced nonwoven samples were studied by scanning electron microscope (SEM), capillary flow porometer, absorbency and air permeability testing system. In addition, the physical and mechanical properties of nonwoven fabrics were determined. The results are discussed in terms of changes in the structure and properties of the meltblown nonwoven fabrics due to changes in the forming process. The fiber diameter changes explain the observed changes in the physical and mechanical properties of the nonwoven fabrics obtained under different process conditions.

INDEX WORDS: Nonwoven fabrics, meltblown technology, polylactide acid (PLA), and fiber diameter

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HOMEIRA AZARI

Bachelor of Engineering, University of Guilan, Iran, 2014

A Thesis Submitted to the Graduate Faculty of The University of Georgia in Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE

ATHENS, GEORGIA

2018

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HOMEIRA AZARI

Major Professor:	Gajanan Bhat
Committee:	Suraj Sharma
	Hitesh Handa

Electronic Version Approved:

Suzanne Barbour
Dean of the Graduate School
The University of Georgia
August 2018

DEDICATION

This thesis is dedicated to my parents, for their forever love and support. My sister, brother, supportive friends, and teachers for always believing in me, inspiring me, and encouraging me to reach higher in order to achieve my goals.

ACKNOWLEDGMENTS

I would like to thank my advisor Dr. Gajanan S. Bhat who gave me an opportunity to work under his guidance. Without his support and encouragement, this work would not have been possible. Special thanks go to thank my committee members: Dr. Suraj Sharma, and Dr. Hitesh Handa for their valuable advice and encouragement.

I would also thank my family for their understanding, patience, and encouragement during my life and education.

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CHAPTER 1

INTRODUCTION

With a steady increase in growth of disposable nonwoven products in both commercial and domestic sectors, their disposability is becoming a major issue of concern than ever before, and the nonwoven industry is spending its resources on finding polymers and fibers which are biodegradable under composting or landfilling conditions.

As a matter of fact, among all nonwoven producing methods, modified meltblown process is a unique approach to produce submicron fibers. Fibers can be produced at rates many orders of magnitude higher than that possible from electrospinning at the industrial scale. Moreover, handling many different polymers as well as blends of polymers is another advantage of meltblown technology[1].

In recent years, polylactic acid (PLA) has attracted a great deal of attention because of its compostability and bioabsorbability properties[2,3]. PLA is a thermoplastic polymer that is a fermentation product of renewable sources such as corn dextrose, potatoes, and biomass waste, that is shown to be biodegradable and melt processable at temperatures below its thermal degradation[2,4]. So, from an industrial point of view, it is a promising alternative to petroleum-based polymers and a solution to reduce the amount of solid waste caused by disposable nonwoven products.

PLA as a novel polymer to the area of nonwovens holds certain unique characteristics, and it showed acceptable processability in melt blowing web with good hand but low strength and breaking elongation. In addition, produced PLA webs are very brittle with low shelf life. Therefore, more researches should be done to evaluate the effect of different parameters on producing melt blown PLA nonwovens[5].

The present study focused on the influence of different process conditions such as air pressure, melt throughput, and presence of zinc stearate as a plasticizer and mold release agent on the structure of the PLA fibers produced by the melt-blowing procedure. The microstructure of the obtained webs was analyzed, that is, mean fiber and pore diameter and distribution, air permeability and water absorbency. Additionally, the influence of the fiber diameter on the mechanical properties of the fabrics was investigated. All of the studied nonwoven fabrics were produced using a melt blown pilot line. Their structures and properties were investigated using a scanning electron microscope (SEM), capillary flow porometer, absorbency, air permeability, and tensile test.

1.1 Statement of Problems

- Demonstrate the feasibility of producing meltblown nonwoven products with desired properties from a sustainable polymer to help resolve disposable waste issues

1.2 Objectives of Study

- To utilize renewable and potentially more sustainable sources of raw materials (polymers produced from cornstarch instead of crude oil)
- To investigate the processability of biodegradable Ingeo polymer into microfibers
- To determine the correlation between the process variables and structure and properties of the webs

1.3 Hypotheses

- Nonwoven webs can be produced with micro- and submicron-fibers using polylactic acid in the meltblown process
- Meltblown process variables (polymer throughput and process air) affect the properties of produced nonwovens webs
- Plasticizers affect the properties of polylactic acid meltblown nonwovens by reducing the melting viscosity

1.4 Limitations

- The only effect of zinc stearate as a plasticizer and mold release agent at three different percentage will be studied
- Effect of die and air temperature and die to collector distance were not studied
- Only the effect of two different screw speeds and air pressures were studied in this research

CHAPTER 2

LITERATURE REVIEW

A broad review of the existing literature was conducted to be familiar with the areas of nonwoven textiles and web forming methods, especially melt-blown process, the raw material for melt-blown nonwovens as well as polylactic acid polymers (PLA), the effect of additives on melt blown processing, application of meltblown nonwoven webs, and on other topics related to this research. After a brief review of the nonwoven processes, products and markets, a more extensive review of the melt blown process and PLA polymers are reported in the following sections.

2.1 Nonwovens

2.1.1 Nonwovens Background

The first approach to produce nonwoven materials was most likely the processing of animal hair by felting which is a mechanical action using water, heat and alternatively chemicals[6]. In the 19th century, the rapid development of new non-traditional production methods for producing fabrics occurred during and after the second world war to meet the increasing demand for inexpensive textile materials[7]. Progress in chemistry and polymer science allowed the development of fabric production methods without the necessity of first producing and processing yarns which made the production of nonwovens more effective and less expensive compared to previous methods[6,8]. Nowadays, nonwovens include a wide variety of technologies and products. These products possess various structures and, properties, depending on the raw materials and production methods used making them suitable for diverse end-uses[9].

The definition of nonwovens most commonly used nowadays is that by the Association of Nonwoven Fabrics Industry (INDA), which defines the nonwovens as a sheet, web, or batt of natural or human-made fibers or filaments, excluding paper, that have not been converted into yarns, and that are bonded to each other by adding an adhesive, chemical, mechanical interlocking, or thermal bonding[9,10].

Production of nonwoven textiles is fast and straightforward due to forming of fabrics directly from fibers and bypassing the step of converting fibers to yarn[11,12], and therefore, the process is inexpensive, and production rates are higher[8]. The relative production speeds of various fabric formation technologies are compared in Table 2.1.

Table 2.1. Relative Production Rate of Various Fabric Formation Methods[8].

Technology	**Relative Production Rate (m/min)**
Weaving	1-6
Knitting	3-16
Nonwovens – web forming:	
• Carding	120-400
• Spunbond	200-2000
• Wet-laid	2300
Nonwovens – bonding:	
• Stitchbonding	40
• Needling	30-500
• Calendaring	2000
• Hot air bonding	5000

Nonwovens are one of the fastest-growing sections of the textile industry, and the production of nonwovens amounts to approximately 20% of the total production of textiles, and the percentage grows year by year[13]. The latest estimates, in 2013, put the global nonwovens production at over 1,500,000 tons in North America, over 2,000,000 tons in China, and around 2,500,000 tons in Europe[14]. According to nonwovens industry magazine, based on rising demand in nonwoven industry, 7% average year-to-year increase, will affect the global nonwovens market to be worth $50.8 billion in 2020, up from a value of $37.4 billion in 2015[15].

2.1.2 Applications of Nonwovens

Non-woven materials are entering a continuously broadening field of applications with new products appearing almost daily[7]. To list and classify all of them would not be possible and is not within the scope of this thesis. However, some of the most common applications of nonwoven materials are listed in Table 2.2.

Table 2.2. Most Common Applications of Nonwoven Materials[1,7,14,16].

Application areas	**Examples**
Abrasives	Coated discs, pads, fabric
Apparel	Interlinings, inner and outer accessories, etc.
Coated fabrics	Automotive, furniture, upholstery, shoes, luggage, wall covering, rug backing, tentage, etc.
Filters	Milk, chemical, air, water, oil, blood, etc.
Laminated plastics	Low and high pressure excluding glass
Sanitary and medical	Hospital and doctor supplies, diapers, bandages, etc. (For instance polypropylene nonwoven fabrics have the properties of high durability, excellent biocompatibility, low toxicity, liquid absorbing and antibacterial activity, which lead to accelerated wound healing)
Tapes and ribbons	Decorative and industrial

Wiping cloths	Dust, polishing, shining, mopping (Wet wipes are well known commercial consumer products which are available in many forms. They are available in individual, sealed packets which typically contain a single premoistened wipe and are useful for away-from-home cleaning needs. Although wet wipes frequently are based on cellulosic nonwoven sheets such as tissues, wet wipes which include melt-blown nonwoven webs are known)
Miscellaneous household	Towels, napkins, drapes, shades, covers, pads, etc.
Miscellaneous small items	Casket lining, permanent waving, bookbinding, etc.

As summarized in Table 2.2, nonwoven materials are used in numerous applications ranging from baby diapers to high-performance industrial textiles. Some of the essential areas where nonwovens are treated as a primary alternative for traditional textiles are in geotextiles, materials for building, thermal and sound insulating materials, hygienic and healthcare textiles and automotive industries[15,17].

In addition, nanofiber nonwovens applications for ballistic and chemical/biological protection, filtration and biomedical applications are actively being investigated, and nanofiber nonwoven technology is under development for future army lightweight protective clothing systems[10,18].

Figure 2.1. Application of Nonwovens in Various Areas[7].

2.1.3 Nonwoven Processes

Various systems of nonwovens classification have been developed, based mainly on production methods and bonding processes as shown in Figure 2.2 and Table 2.3. The methods differ from each other in productivity and fiber orientation, and properties of resulting fiber layers. Since this research focusses on polymer laid nonwovens, only meltblown spunlaid fabric formation will be discussed in detail here.

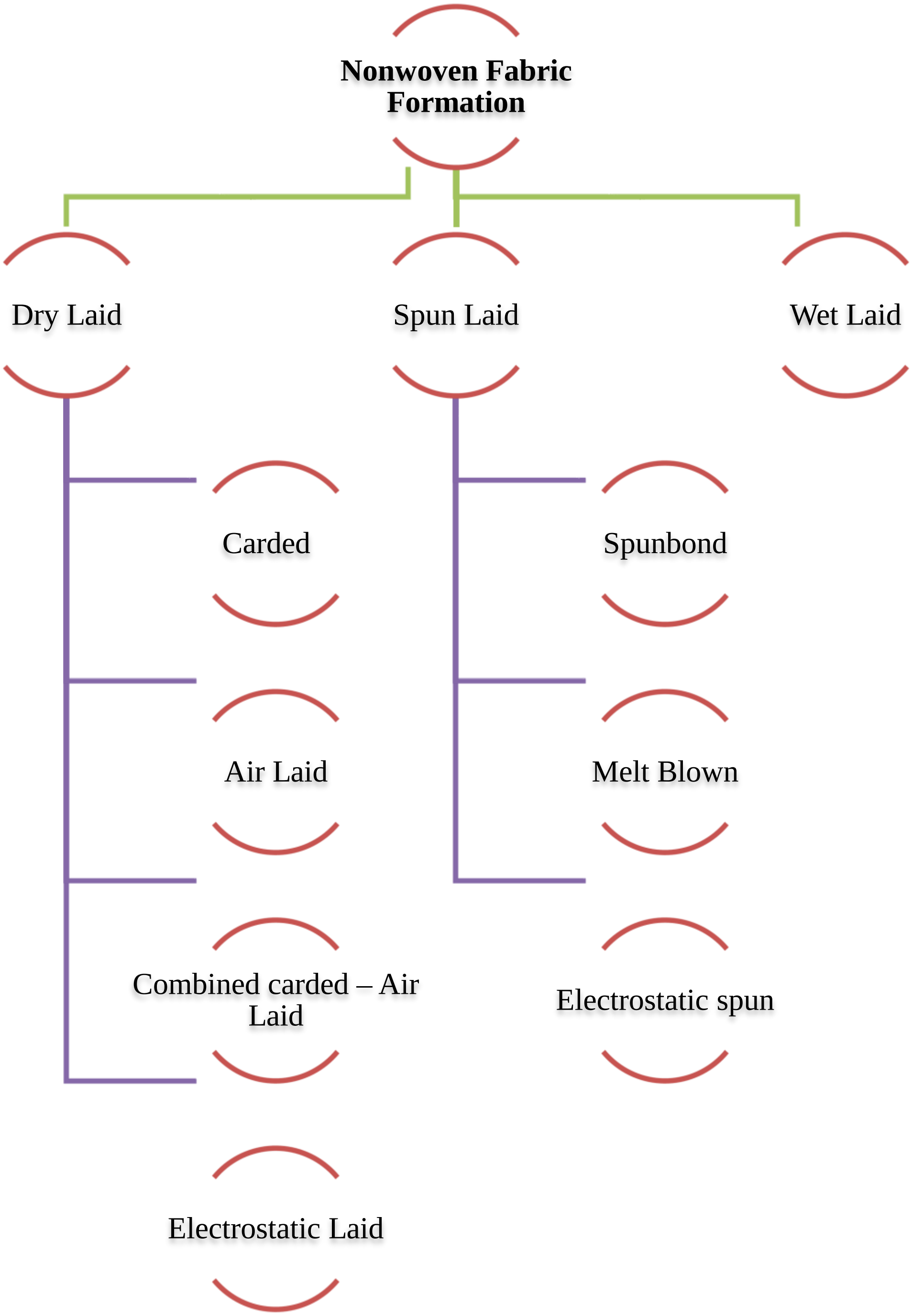


Figure 2.2. Nonwoven Fabric Formation Methods[8,12].

Table 2.3. Nonwoven Bonding Processes[15,17].

Bonding Processes		
Physical Process		Chemical Process
Mechanical Process	Thermal Process	• Impregnation • Spraying • Printing • Foaming
• Needling • Looping • Entangling	• Hot air • Calendering • Welding	

The primary spunlaid processes were developed in the late 1950s, and now turnkey lines are being offered by a number of nonwoven machinery manufactures. A direct conversion of a polymer into the fiber layers is the general feature of spunlaid methods[19]. Spunlaid produces the majority of nonwovens today, and according to Nonwovens Industry Magazine, spunlaid will remain the leading web forming process as it is accounting for 48.7% of all nonwovens consumed in 2015 and since 2010, has had the highest growth rate of any process, with an annual growth rate of 8.5% during 2010-2015[20,21].

2.1.4 Meltblown Process

The melt-blown process, commercially introduced in the late 1970s[8], allows the production of extremely fine fibers[19]. Meltblown fabrics possess unique characteristics of high coverage with low pore size, which are very well suited for products with highly effective and efficient filtration and barrier properties[1,22].

The melt-blowing process as shown in Figure 2.3, consists of the following integrated operations[16,19,23]:

- Polymer melting, transport, and filtration of the polymer melt
- Polymer extrusion and filament forming using hot air
- Forming web on the surface of a wire screen collector, drum or belt

- There is no separate bonding required, and fibers are entangled and held together simultaneously during the web consolidation.

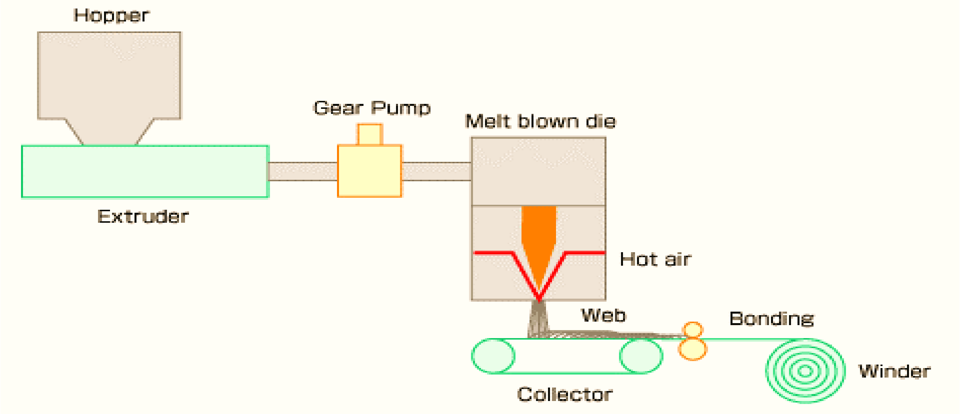


Figure 2.3. Melt-blowing Process[24].

Generally, any thermoplastic polymer can be processed by melt-blowing[24]. Polypropylene, polyester, polyethylene, and polyamide are the most common polymers used to produce melt blown fabrics for large-scale commercial applications[7,24].

The polymer pellets or granules are fed into the hopper and then the extruder. As the polymer moves through the extruder, it melts due to heat and friction. The polymer melt is conveyed to the metering gear pump which ensures a consistent flow and required process pressure of molten polymer into the die assembly. The polymer melt is filtered in the screen pack which is placed at the output end of the extruder as well as in the die block assembly before the spinneret[8,23,24].

A special die assembly is used in the melt-blowing process (Figure 2.4). The polymer melt goes directly to the nosepiece of the die and passes through the spinning orifices leading to the edge of the nosepiece. Orifices have diameters of 0.2-0.4 mm and are spaced at 1-4 per millimeter apart on the nose-tip edge[19,25]. In a linear die, there are more than ten holes/cm. The air manifolds supply the high-velocity hot air through slots from the top and bottom sides of the nosepiece. After the molten polymer is extruded from the die holes, high-velocity hot-air streams weaken the polymer streams to form microfibers[1,8]. As the hot-air stream containing the microfibers progresses towards the collector screen, it draws a significant amount of surrounding air that cools and solidifies the fibers. Simultaneously the fibers are partially drawn and entangled[19,26].

The solidified fibers are settled incidentally onto the collecting screen to form the web. The fibers in the web are adhered together by a combination of entanglement and cohesive sticking. This cohesive sticking depends on the level of fiber solidification[25]. Self-bonding due to fiber entanglement and cohesive sticking ensures sufficient cohesion of the melt-blown webs in many applications[1,26]. Additional calender bonding may be required in some cases.

2.1.5 Process Variables in Melt blowing

The most critical on-line variables of the melt-blowing process are as below[8,24]:

- Polymer melt temperature
- Air temperature
- Polymer throughput rate (screw speed)
- Air throughput rate (airflow pressure)
- Mass ratio of air: polymer
- Die-to-collector distance (DCD)

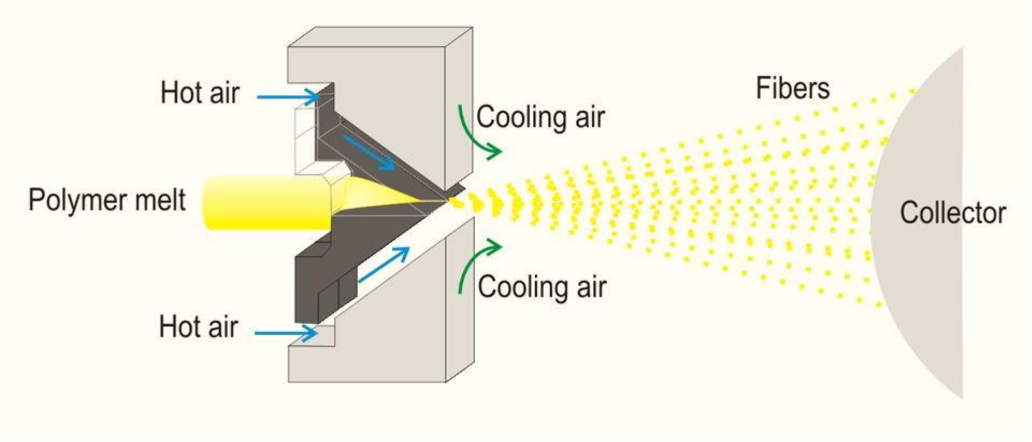


Figure 2.4. Melt-blowing Die Assembly.

The polymer melt viscosity and the quantity of high-velocity hot air control the final fiber diameter and fiber entanglements[27]. The polymer/die and air temperatures in conjunction with air flow rate affect the appearance and tactile hand of fabrics and fabric uniformity[28,29]. The hot air temperature is especially beneficial for the drawing process. The die-to-collector distance generally affects fiber-to-fiber thermal bonding as well as web structure and thickness. For the same basis weight, with increasing DCD, webs become loftier and thicker[29,30].

Commonly, air permeability and mean flow pore size of nonwoven webs are correlated with each other while other parameters also affect this correlation. Mean pore size and air permeability of meltblown nonwovens decrease with airflow but increase with DCD[30,31].

The diameters of fibers are generally smaller with[26,30]

- Lower viscosity of the polymer melt (higher MFR, higher temperature)
- Higher air temperature

- Higher ratio of air: polymer (higher air throughput rate and lower polymer throughput rate)

2.1.6 Raw Material for Melt-Blown Nonwovens

Many factors affect the selection of raw materials for nonwovens, including process efficiency and product performance. With melt blown nonwovens, the choice of material is closely connected with the requirements to be met by the final products[7]. In addition, the process parameters also correlate with filament draw or film draw affecting the product performance.

Melt blown nonwovens are made from thermoplastic polymers such as polypropylene (PP) and polyester (PET). To a small extent, other polyolefins such as high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE) as well as a variety of polyamides (PA), mainly PA 6 and PA 6.6 are used. Lately, several new polymers, as well as engineering plastics, have been successfully melt blown for especially applications[7,32].

Polypropylene is the extensively used polymer for melt blown nonwovens due to its properties such as hydrophobicity, sterilizability, and its low polymer density. After PP, PET is the second most important polymer to make melt blown nonwovens. As compared with PP, PET is suitable for a variety of uses that require higher thermal resistance and low shrinkage. As compared with PP and PET, the polyamides PA 6 and 6.6 are of minor importance. PA used to be processed to a more significant extent to make melt blown nonwovens for applications in the field of packing materials. Melt blown nonwovens from HDPE and LLDPE show great softness, which is taken advantage of to make cover stock nonwovens for hygiene uses[33,34].

Here are some of the most critical parameters for using PP, the most commonly used raw material in the melt blown nonwoven webs[32]:

- Melt index MFI: 100-1600 g/10 min
- Polydispersity $\frac{M_W}{M_N}$: 3.5-7 unit to measure mole weight distribution
- Atactic share: ≤2.5%

2.1.7 Applications of Melt-Blown Webs

The main applications of melt-blown webs are in filtration, thermal insulation, oil absorption, industrial wipes, battery separators, surgical face masks, adhesives, diaper cover stocks, and respirators[26]. In several instances such as diaper cover stocks and other hygiene products, melt blown fabrics are part of the composite SMS (spunbond-meltblown-spunbond) fabrics.

The development of nonwovens for hygiene products is characterized by rising quality demands on the products and increased growth in volume. The main groups of hygiene products are baby diapers and training pants, incontinence products and feminine hygiene. Hygiene products also include wet wipes and swabs[9,22].

The field of filtration is tremendously diversified. There are more than 1000 different applications characterized by different profiles and conditions and consequently requiring different filter materials. One of the most important segments of filter materials is meltblown nonwovens. Due to their variability and their economical manufacture they can easily be adapted to nearly all kinds of filtration products[1,22].

Whereas in the past, the aforementioned nonwoven products were manufactured for multiple uses, especially in the diaper and filtration sectors, in the last few decades they have evolved into single-use or “disposable” products[19].

Figure 2.5. Applications of Melt-Blown Nonwoven Webs.

2.1.8 Challenges of Melt Blown Products

As the world moves forward, the amount of municipal solid waste (MSW), one of the most important by-products of an urban lifestyle, is growing even faster than the rate of urbanization[35]. In 2000, 2.9 billion urban residents generated about 0.64 kg of MSW per person per day (0.68 billion tons per year). This report estimates that by 2025, this will increase to 4.3 billion urban residents generating about 1.42 kg/capita/day of municipal solid waste (2.2 billion tons per year), thus proper MSW management is crucial for urban public health. Meanwhile, the sustainability of landfills is also of concern as increasing volumes of MSW consume finite landfill space[35–37].

The most common raw materials that are currently in use in industry for melt blown products are petrochemical polymers that are largely resistant to biological attack because microorganisms do not have an enzyme capable of the degradation of these polymers. Hence, they are not biologically degradable and compostable[28,32]. Also, as the most usage of meltblown nonwoven webs are in single-use or "disposable" products, melt blown disposable products waste form a significant part of municipal solid waste and causes increasing environmental concerns.

Moreover, recycling is viewed as the primary mechanism to reduce the environmental and waste management issues associated with the use of disposable products. However, melt blown disposable materials may not be eligible for recycling or reuse because of the mixed level of contamination in the materials after the use of products[26,38].

As a result, in recent years, the development of biodegradable materials from renewable natural resources (e.g., cornstarch) has received increasing attention, and significant progress has been made to produce biodegradable materials with similar functionality to that of the petrochemical synthetic polymers. It is anticipated that, as the materials are from renewable resources and biodegradable they would contribute to sustainable development, and if properly managed would reduce their environmental impact upon disposal[39,40].

The objectives in the development of biodegradable materials for melt blown products are:

(1) To utilize renewable and potentially more sustainable sources of raw materials (cornstarch instead of crude oil)

(2) To facilitate waste management approaches to reduce landfill

(3) To produce greener and more eco-friendly products

2.2 Polylactic Acid (PLA)

2.2.1 Polylactic Acid (PLA) Background

Due to the increasing environmental concerns and the shortage of fossil resources (as demonstrated by the approaching of peak oil for example), the ability to manufacture products from sustainable resources which are fully compostable at the end of their productive life is drawing attention. Therefore, the use of starch resources in many applications has experienced considerable development in the past two decades[37,41].

Polylactide or poly(lactic acid) (PLA) as one of the most essential environment-friendly bio-based, resorbable, and biodegradable (under industrial composting conditions) thermoplastic polymer with the best availability as well as the most attractive cost structure and the extensive application is the front-runner in emerging markets[3,42].

2.2.2 Production of PLA

The production of the polylactic acid from lactic acid, an organic compound with the formula of $CH_3CHCOOH$, is comparatively simple. PLA can be manufactured by different polymerization routes, which are schematically described in Figure 2.6, directly from its basic building block lactic acid, that is obtained by fermentation of sugars from 100% renewable carbohydrate sources such as corn starch, cassava roots, chips or starch, sugarcane, or tapioca[3,43].

In addition, PLA requires 25% - 55% less energy to produce than petroleum-based polymers, and this can be further reduced to less than 10% in the future. Lower energy use makes PLA production potentially advantageous concerning cost as well[3,39].

As it is shown in Figure 2.6, PLA of high molecular weight is most commonly made by ring-opening polymerization (ROP) of the ring-formed dimer, dilactide (lactide; 3,6-dimethyl-1,4-dioxane-2,5-dione), which is made by depolymerization of the polycondensed lactic acid (LA; 2-hydroxypropanoic acid). This route is a two-step reaction that usually involves additional purification steps. Direct dehydration condensation reaction is often known for the preparation of a low molecular weight PLA and therefore is not satisfactory for many applications. If the lactic acid is polycondensated in the presence of difunctional monomers (e.g., diols or diacids), the resulting prepolymer will have the same end groups in both chains ends; that is, the prepolymer is a telechelic macromer[40,44].

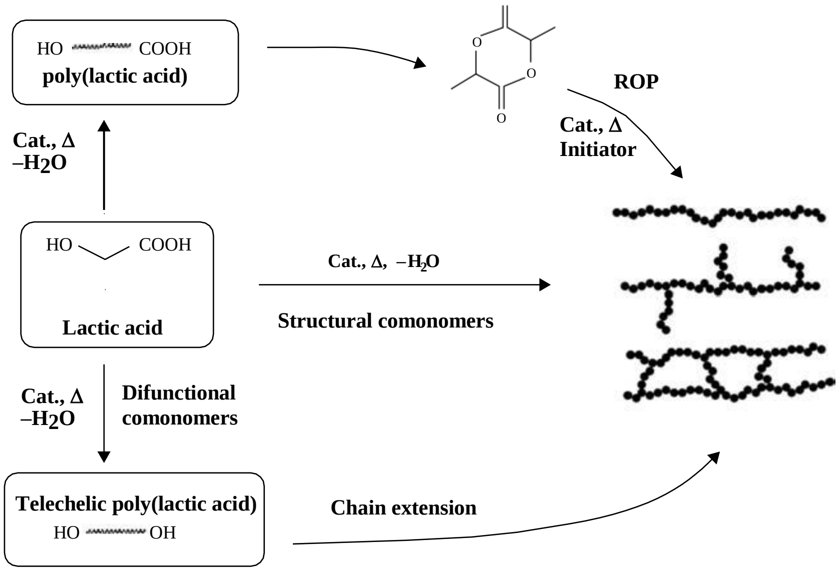


Figure 2.6. Manufacturing Routs for Lactic Acid-based Polymers[42].

The constitutional unit (i.e., chemical structure or molecular structure) of PLA is shown in Figure 2.7. PLA is a chiral polymer containing asymmetric carbon atoms with a helical conformation[3,42].

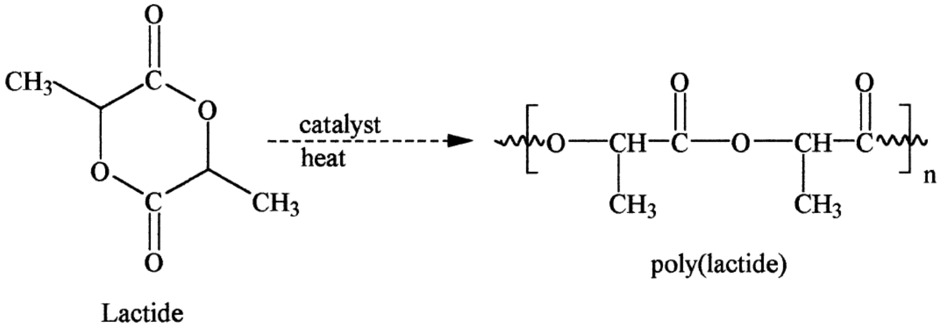


Figure 2.7. Synthesis of Poly(lactide) (PLA)[42].

2.2.3 Applications of PLA

Since PLA is compostable and derived from sustainable sources, it has been viewed as a bright material to reduce the societal solid waste disposal problem and also its low toxicity, along with its environmentally benign characteristics, has made PLA an ideal material for food packaging and other consumer products[42,45].

Moreover, PLA as a thermoplastic material has rigidity and clarity similar to polystyrene (PS) or poly(ethylene terephthalate) (PET) and end uses of PLA are in rigid packaging, flexible film packaging, cold drink cups, cutlery, apparel and staple fiber, bottles, injection molded products, extrusion coating, and so on[41].

Indeed PLA has better thermal processability compared to other biopolymers such as poly(hydroxyl alkanoates) (PHAs), poly(ethyele glycol) (PEG) and poly(αcaprolactone) (PCL), following standard melt processes such as injection moulding, film blowing or melt spinning. Furthermore, PLA is known as the only melt-processable fiber from annually renewable natural resources[41,44].

Several researchers have studied the physical and structural properties of PLA fibers and confirmed that this polymer has significant economic potential as a textile fiber as the controlled crimp, smooth surface, mechanical properties and low moisture regain of PLA fibers are broadly similar to that of many other thermoplastic fibers, especially that of conventional PET[17,42].

2.2.4 Thermal and Mechanical Properties of PLA Fibers

PLA is a stiff polymer at room temperature. The glass transition temperature (Tg) and melting temperature (Tm) of PLA are typically between 55–65℃ and 160–170℃ respectively. Figure 2.8 indicates the DSC scans for PLA and PET. It can be seen that PLA exhibits a melting temperature (endothermic peak) of approximately 166℃ while melting temperature of PET is around 254℃. This low melting point compared to that of PET causes limitations in some of the downstream processing technologies, but the primary concern is for the consumer after-care of garments. Garment pressing and ironing temperatures have to be lower than that of the favorite fibers of cotton and PET, and despite the appropriate care labeling instructions being used, it is a fact that consumers often disregard these. However, the thermosetting capability of the fiber provides fabric stability as well as low shrinkage through repeated washings for garments[42,46].

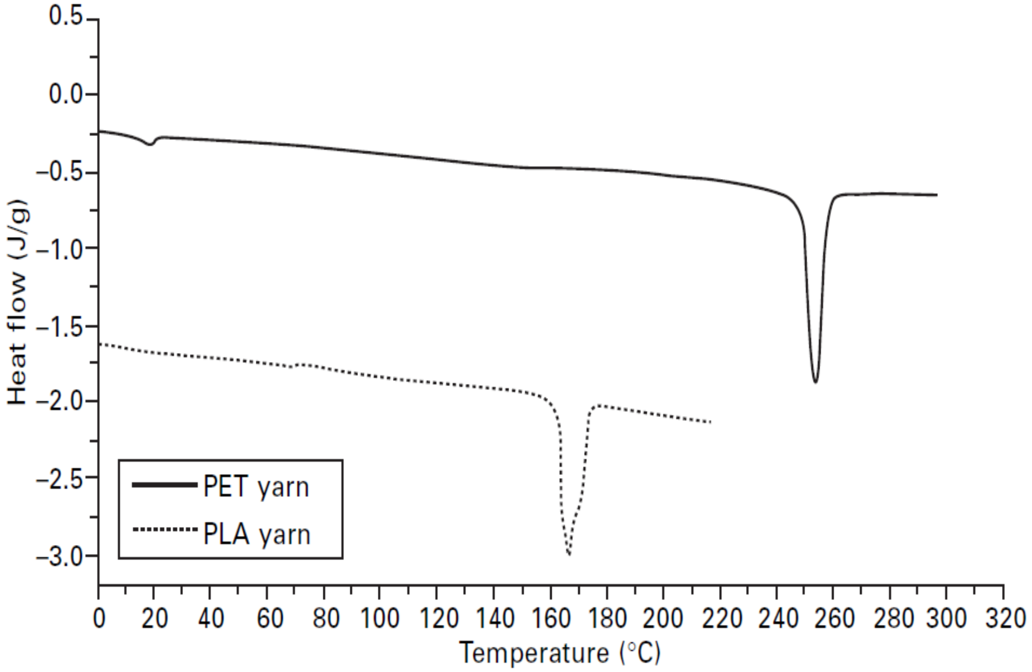


Figure 2.8. DSC Scans of PET and PLA[42].

The tensile properties of PLA fiber as used in staple form for textile processing are shown in Figure 2.9. PLA fibers are very different from those of high tenacity polyester and more akin to wool with relatively low final tenacity and high fiber extension when stressed. However, the yield point of PLA fibers, which fibers (and spun yarns) stretch very easily once past this point, is relatively low, the initial modulus (at 2% extension) is comparable to that of many other textile fibers. High elongation along with relatively high work of rupture gives PLA yarns and fabrics a satisfactory performance in commercial use. The elastic recovery of PLA fibers at 2% and 5% strain is 99.2% ±0.75 and 92.6%±1.60% respectively which is higher than for most other fibers and provides excellent shape retention and crease resistance for these fibers[3,42].

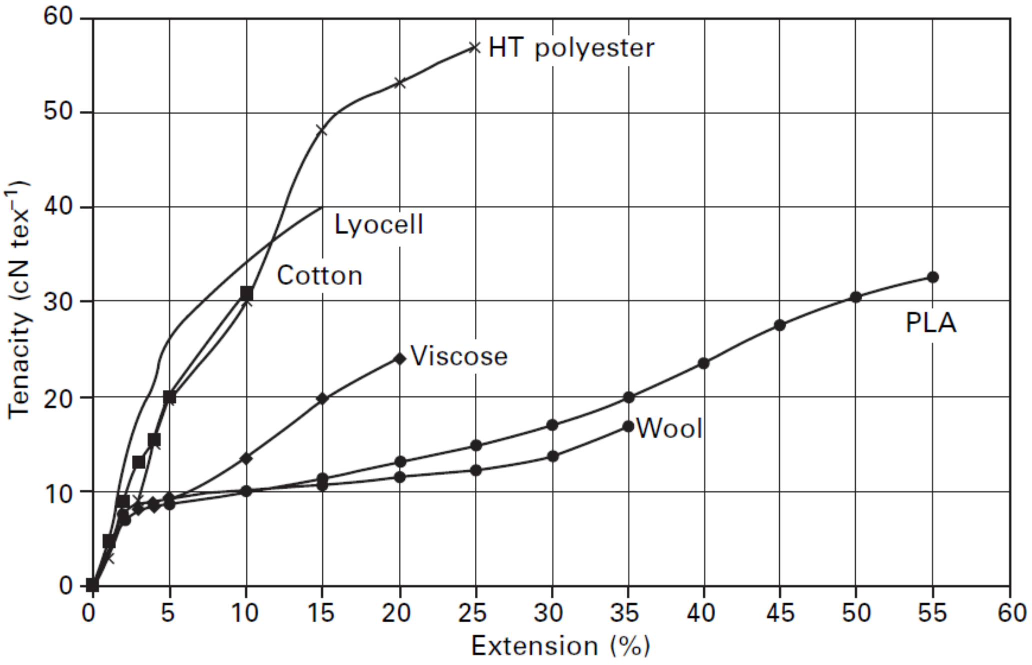


Figure 2.9. Tenacity-extension Curves for PLA and Other Common Textiles Fiber (20°C and 65% RH)[3].

In conclusion, PLA processes and products are comparable to that of PET in many of the downstream processing technologies since in all of the manufacturing stages of the supply chain, the existing machinery can be used and there is no need for any specialized capital investment when processing PLA. Also, the ease of melt processing, coupled with the unique property spectrum, performance benefits, and renewable resource origin, has led to PLA fibers finding increasing acceptance across a variety of commercial sectors.

Table 2.4. Fiber Properties of Various Fibers[46].

Fiber Property	**Nylon 6**	**PET**	**PLA**	**Rayon**
Tg (°C)	90	125	55-60	-
Tm (°C)	215	255	130-175	None
Tenacity (g/d)	5.5	2.4-7.0	2.0-6.0	2.5
Moisture Regain (%)	4.1	0.2-0.4	0.4-0.6	11
Elastic Recover (5% strain)	89	65	93	32

2.2.5 PLA Nonwovens

Nonwoven products are a major application segment offering great potential from the unique benefits of PLA. Outside of the fiberfill products, the major markets are in spunlaid, industrial and household wipes, hygiene, and filtration areas[12,47].

Typical polyester spun bond lines can be used to produce spun bond PLA products in a variety of fabric weights, and once again the ability to replace petroleum-based fibers with enhanced performance with a natural-based fiber has strong consumer appeal. Further, PLA is used to produce dry-laid and wet-laid nonwovens via spunlaces, thermal bonding, and needle punching[42,46,48].

The first studies about the PLA meltblown process were done in 2001 and found that PLA is processable over a wide range of temperatures and processing parameters are significant to the structure and properties of webs.[5,28,49]

Keeping this in focus that under the correct conditions of temperature and humidity, PLA fabrics are entirely compostable and can return naturally to the soil releasing carbon dioxide and water. However, fabrics under normal storage conditions and use are durable enough to meet the various market and supply chain requirements[50,51].

2.3 Zinc Stearate

Zinc stearate is a "zinc soap" that is widely used industrially with a chemical formula of $C_{36}H_{70}O_4Zn$ (as shown in Fig 2.10) and molar mass of 632.33 $g{\cdot}mol^{-1}$. In this context, soap is used in its conventional sense, a metal "salt" of a fatty acid[52,53]. A few characteristics of zinc stearate are mentioned in Table 2.4.

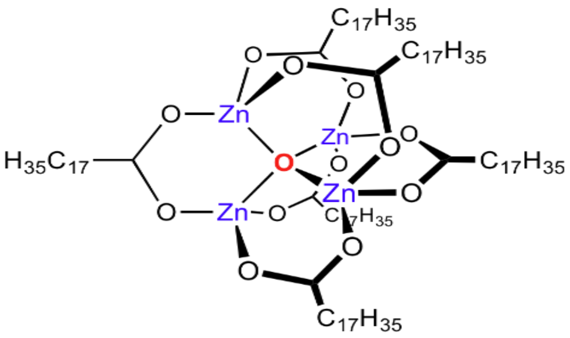


Figure 2.10. Chemical Formula of Zinc Stearate[54].

Table 2.5. Characteristics of Zinc Stearate[54].

Properties	
Appearance	soft, white powder
Odor	slight, characteristic
Density	1.095 g/cm^3, solid
Melting point	120 to 130 °C (248 to 266 °F; 393 to 403 K)
Boiling point	Decomposes
Solubility in water, alcohol, and ether	Insoluble
Solubility in benzene	slightly soluble

Zinc stearate works as a plasticizer in thermal processing at temperatures higher than that of its melting point, 128°C[55]. Plasticizers are typically small molecules that can be added to polymers during their thermal processing. They push the polymer molecules slightly further apart, space them out from each other, increase the free volume, weakening the forces between them and making the material softer and more flexible by lowering the glass transition temperature. Therefore, plasticizers enhance processibility and improve the properties of final products[56]. When used as a plasticizer zinc stearate increase the plasticity, processibility and reduce glass transition temperature[55,57].

Because plasticizers can form bonding interactions with starch-based polymers and weaken the interaction of starch molecules, they facilitate movement among starch molecules and increase output in extruded applications[41,58].

Additionally, zinc stearate, a white solid with hydrophobic effects, is one of the most powerful mold release agents among all metal soaps[52,54], which dissolves in hot polymer and acts as a release agent by coming out of solution during the extrusion process to the surface between polymer melt and tool[59,60]. When Zinc stearate dissolves in the melt, it can reduce melt viscosity and enhances the flowability of the system, thereby improving surface detail[55,57]. The amount of reduction in melt viscosity of polymers is quite complicated and depends on a number of parameters, such as processing history, polymer type and the presence of other additives[59,60]. The melt viscosity of starch-based polymers decreases typically with the addition of mold release agents at a constant temperature; it also decreases with increasing temperature at the same weight of mold release agents [39–41].

Zinc stearate has low surface energy and a high contact angle that provide the critical barrier between polymer melt and tool. Without such a barrier in place, the polymer melt would become fused to the tool, resulting in difficult clean-up and dramatic loss in production efficiency. In this way, zinc stearate exhibits its "non-stick" properties[52,59,61]. Furthermore, the zinc stearate dry powder mold release does not interfere with post-finishing operations; parts can be painted, stenciled, hot stamped, glued, plated, or otherwise decorated[52,62].

Applications of zinc stearate are mostly in the plastics and rubber industry, where it is widely used as a plasticizer and releasing agent for the production of many kinds of objects such as rubber, polyurethane, polyester processing system and powder metallurgy[52,54].

There are presently around 300 plasticizers manufactured. Of these, about 100 are of commercial importance. A list of some common commodity and specialty plasticizers can be found in Table 2.6. Plasticizer performance depends on the chemical properties of molecular volume, chain length or molecular weight and linearity. In general, the higher molecular weight gives superior performance[63].

Among the comparable plasticizers, zinc stearate possesses good plasticizing efficiency and viscosity due to its high molar mass (632.33 g·mol^{-1}), that coupled with a competitive price, make it attractive to the plastics and rubber industry[57,63].

Table 2.6. Common Commodity and Specialty Plasticizers[56,63].

Plasticizers	**Carbon Chain**	**Molecular Weight**	**Vapor Pressure (Pa)**	**Specific Gravity (25°/25°C)**	**Viscosity (mPa.s@25°C)**
Dinormalhexyl phthalate (DnHP)	16	335	400	1.008	30
Diisoheptyl phthalate (DIHP)	7	362	280	0.983	30
Diheptyl phthalate (DnHP)	17	362	253	0.983	30
Di(2-ethylhexyl) phthalate (DEHP)	8	391	173	0.982	58
Diheptylnonyl phthalate (DnHNP)	17, 19	398	147	0.978	49
Dinormaloctyldecyl phthalate (DNODP)	16, 18, 110	401	80	0.965	34
Diheptylnonylundecyl phthalate (DnHNUP)	17, 19, 111	414	107	0.969	41
Diisononyl phthalate (DINP)	9	418	67	0.970	72

Dinonyl phthalate (DNP)	9	418	57	0.971	80
Dinormalnonyl phthalate (DnNP)	19	418	43	0.967	39
Diisodecyl phthalate (DIDP)	10	447	47	0.964	88
Dinormalnonyldecylundecyl phthalate (DnNDUP)	19, 110, 111	450	40	0.958	48
Dinonylundecyl phthalate (DnNUP)	19, 111	458	40	0.954	50
Diundecyl phthalate (DUP)	111	475	80	0.952	54
Diisoundecyldodecyl phthalate (DUDP)	11, 12	502	20	0.955	185
Ditridecyl phthalate (DTDP)	13	530	11	09.51	160
Di(2-ethylhexyl) teraphthalate (DOTP)	8	391	160	0.981	63
Butylbenzyl phthalate (BBP)	4, 7	312	253	1.119	42
Diheptylnonyl adipate (DnHNA)	17, 19	370	440	0.920	12
Di(2-ethylhexyl) adipate (DEHA)	8	370	307	0.924	14
Diisononyl adipate (DINA)	9	398	227	0.924	2
Diisodecyl adipate (DIDA)	10	426	77	0.916	25
Triheptylnonyl trimellitate (TnHNTM)	17, 19	530	16	0.984	105
Tri(2-ethylhexyl) trimellitate (TOTM)	8	530	21	0.987	220
Triisononyl trimellitate (TINTM)	9	589	13	0.975	315
Di(2-ethylhexyl) sebacate (DOS)	8	426	131	0.911	25
Di(2-ethylhexyl) azelate (DOZ)	8	412	147	0.914	15

2.4 Summary

It is obvious from all the earlier work that nonwovens is a growing area and thee will continue to be increasing volume of disposable nonwoven-based products. In this context, it makes perfect sense to develop nonwovens from biodegradable/compostable polymers. PLA is one such polymer that is bio-based, from renewable sources, biodegradable, and at the same time stable for all the relevant applications with desired properties. Also, lately PLA prices have been coming down, and it is likely to become a commodity plastic. That is why it is the most attractive polymer to evaluate for nonwoven products.

Although PLA has been available for the past two decades, meltblown grade PLAs have been produced, more for experimental research only in the recent past. That is why this study is relevant. Earlier efforts to melt blow PLA that was available at that time did not result in fine fiber webs, and currently available PLA resins are likely to produce finer fibers close to 2microns or less in average fiber diameter. Use of some plasticizers have been known to help processing polymers, and of the many available plasticizers, zinc stearate was determined to be one promising candidate with stability during the processing conditions for PLA and with no known adverse effects. That is why zinc stearate was selected for this study to evaluate its effect on processing and to determine whether using such a plasticizer can help achieve finer fibers. This study is highly relevant and timely, with possible commercial success, if positive results are observed, in terms of processability and melt blown nonwoven properties.

CHAPTER 3

MATERIALS AND METHODS

PLA resin is a relatively new material for the meltblown process. The process parameters have a significant effect on the structure of the PLA meltblown webs and thus on the performance[5]. So, the parameters should be designed carefully in order to produce products with high-performance properties.

3.1 Materials

PLA used in this study was Inego^{TM} biopolymer 6252D with a relative viscosity of 2.5, supplied by NatureWorks LLC (Minnetonka, MN). PLA is a hygroscopic thermoplastic material and ready to absorb moisture from the atmosphere. The presence of even small amounts of moisture would hydrolyze PLA in its melt phase, and seriously affect the normal melt spinning process. As a result, PLA should be thoroughly dried just prior to its melt processing. PLA pellets were dried at 80ºC for five hours under vacuum to remove moisture.

Zinc Stearate ^{TM} used in this study was purchased from American International Chemical LLC (Framingham, MA).

3.2 Melt Blowing of PLA Nonwovens

The processing was performed with the aid of zinc stearate as an additive. Prior to introducing PLA, the system was purged appropriately to prevent foreign polymer contamination and associated spinning problems. Extrusion of the PLA was performed using a twin-screw extruder (UTNRL, Knoxville, TN) under N_2 gas flow in order to prevent thermo-oxidative degradation of the polymer during processing. Melt blowing was conducted on a 15.24 cm (6 in.) line using Exxon dies with ten holes per centimeter in the process. Nonwoven samples were collected on a rotating drum with collector speed of 15 m/min. Samples were produced without process aid and by varying amounts of process aid such as 0.1, 0.3 and 0.5 percent by weight. Airflows varying between 55 and 83 kPa, and different screw speeds of 10 and 16 rpm were used. A summary of the varied processing parameters is presented in Table 3.1. In brief, PLA meltblown webs were produced as follows: drying of PLA chips → melt extruding → filtration → gear pumping → spinning → hot air drawing → cooling → collector → winding.

The melt spinning process takes place at the temperature of 230°C considering PLA meltblown webs exhibited reasonable mechanical properties with uniform fiber distribution and without any crystal particles[5,25]. Hot air temperature, an essential parameter in the meltblown process, is usually 30-50℃ higher than the spinning temperature[47], which is determined by the structure of the meltblown spinning die and in this research, the set hot air temperatures were 265℃, and the process parameters are summarized in Table 3.2. These parameters were chosen to produce webs with optimal quality based on previous experience.

The structural properties (fiber diameter, porosity, air permeability and water absorbency), mechanical properties (modulus and tensile strength), physical properties (basis weight, thickness, and shrinkage) and thermal properties of the meltblown PLA nonwovens were determined by selecting random sections along the centerline of nonwoven mats avoiding edges of the samples.

Figure 3.1. Meltblown Pilot Line Equipment and Produced Webs

Table 3.1. Melt Blowing Process -Varied Parameters

Low air pressure (55 kPa)				**High air pressure (83 kPa)**				**Low air pressure (55 kPa)**	
Screw Speed (16 rpm)								Screw Speed (rpm)	
Zinc Stearate (%)				Zinc Stearate (%)					
No Additive	0.1	0.3	0.5	No Additive	0.1	0.3	0.5	10	16
L_0	**L_1**	**L_2**	**L_3**	**H_0**	**H_1**	**H_2**	**H_3**	**S_1**	**S_2**

Table 3.2. Melt-blowing Process - Fixed Parameters

Process Parameter	**Unit**	**Value**	
Die Temperature	°C	~230	
Extruder Temperature	°C	Zone 1	~160
		Zone 2	~200
Connector Temperature	°C	~215	
Air Temperature	°C	265	
Collector Speed	m/min	~15	
DCD	cm	30	

3.3 Nonwovens' Characterization

3.3.1 Fiber Diameter Measurements

Before fiber size analysis, the PLA nonwoven samples were mounted on aluminum studs using carbon tape and coated for 30 s with gold in an argon environment at 20 milliamps. A Leo1525 scanning electron microscope (SEM) equipped with Zeiss SmartSEM software was used to collect images of each nonwoven for fiber diameter measurements. Four areas from each meltblown nonwoven were sampled to acquire more than 100 fiber diameter measurements for each nonwoven. ImageJ version 1.45s (Wayne Rasband National Institute of Health, USA) was used to obtain measurements of fiber diameter from the SEM images. JMP Pro Version 13.2 (University of Georgia, GA) was used to determine the mean fiber diameter and distribution for each web.

3.3.2 Basis Weight

The weight of the meltblown nonwoven webs, expressed as gram per square meter, were determined by cutting test pieces of 10 cm x 10 cm in dimension using special sample cutter and an average of 5 measurements is reported by weighing them using a Mettler AE 240 microbalance.

3.3.3 Pore Size Determination

Pore sizes and mean flow pore diameters for each PLA nonwoven were determined using a Capillary Flow Porometer, Model CFP-100-AEX (Porous Materials, Ithaca, NY) according to ASTM F316 − 03 (2011) method. Galwick with a surface tension of 16 dynes/cm was used as a wetting agent. Wet Up/Dry Up, no wait at dry test type was followed where the pressure remained in between 0-27579 Pa. Samples from three different areas of the nonwoven web were selected and tested for porosity. Data analysis was performed using JMP software.

3.3.4 Tensile Testing

Tensile testing was performed according to ASTM D5035-06 to determine the tensile modulus and strength of PLA nonwovens in the machine direction (MD). Samples for testing were 15.2 cm by 2.54 cm. Five samples in the MD were used to determine these properties. An Instron Tensile Testing machine equipped with a 450 kg load cell was used to conduct the tests at a crosshead speed of 1.52 cm/min. Each PLA nonwoven sample started with an initial gauge length of 7.6 cm and was tested until failure.

3.3.5 Thickness

Thickness of the webs was measured using ProGage Thickness Tester (Made by Thwing-Albert Instrument Company) according to ASTM D 5729-95 with test specimen size of 100 cm^2. Average of 5 measurements is reported here.

3.3.6 Differential Scanning Calorimetry

The differential scanning calorimetry (DSC) was conducted using a Mettler Toledo Star System DSC 822e according to ASTM D3418-08. This technique was used to follow the melting behavior of PLA nonwovens as a function of processing parameters. A 5–10 mg sample was obtained from each meltblown nonwoven web, placed in an aluminum DSC pan, and heated from 50 to 250℃ at 10℃/min. The sample was allowed to equilibrate at 250℃ for 2 min before being cooled back to room temperature at 10℃/min. All DSC experiments were conducted using a N2 environment at 200 cc/min.

3.3.7 Air Permeability

Air permeability was measured according to ASTM D73796 with area specimen of 38 cm^2 and under the constant pressure of 125 Pa. TEXTEST FX3330 air permeability tester was used, and an average of six measurements is recorded for each sample.

3.3.8 Water absorbency properties

Water absorbency properties (to deionized water) of all the samples were evaluated using an ATS-600 Absorbency Testing System. All Samples were cut from the webs into 2-inch x 2 inches and placed on the table oriented in the same direction. Time Tests were run for 300 seconds, to ensure that absorption had tapered off, and the differential fluid head was set approximately at 3 mm.

3.3.9 Thermal Gravimetric Analysis

Thermogravimetric analysis (TGA) was performed on zinc stearate white powder under the flow of N2 gas (60 cc/min) on a Mettler Toledo Star System TGA (Athens, GA). Samples were heated from 50 to 600℃ at a rate of 10℃/min.

3.4 Normalization of Data

Air permeability test data were analyzed based on basis weight. Results are reported for 100 GSM. Normalizing data were done to eliminate the unwanted effects of basis weight on air permeability and produce a smooth pattern where the proper changes can be seen. This will allow better comparison of results for various samples.

3.5 Statistical Analysis

Fiber diameter distribution, normal quantile plot and summary statistics of PLA nonwoven webs were generated using data analysis software JMP Pro Version 13.2 (University of Georgia, GA) and results are reported.

Normal quantile plot is used to visualize the extent to which the variable is normally distributed. The empirical cumulative probability for each value is computed as follows:

$$\frac{r_i}{N+1}$$

Where N is the number of non-excluded observations, and ri is the rank of the ith observation. The normal quantile values are computed as follows:

$$\Phi^{-1}\left(\frac{r_i}{N+1}\right)$$

Where Φ is the cumulative probability distribution function for the normal distribution.

CHAPTER 4

RESULTS AND DISCUSSION

The results are separated into four sections. The thermal, physical (weight, thickness, and shrinkage), structural (fiber diameter, porosity, absorbency and air permeability), and mechanical (modulus and tensile strength) properties of the meltblown PLA nonwovens.

4.1 Thermal Properties

4.1.1 Thermal Properties of PLA Resin and Zinc Stearate Powder

As the first step to understand the properties of the materials used, we investigated the thermal stability of pristine PLA by differential scanning calorimetry (DSC) under a nitrogen atmosphere as is shown in Figure 4.1. It was observed that the onset and endset melting temperature (T_m) of PLA are 167.3 ºC and 178 ºC respectively, which are lower than all the temperatures used in the melt blowing process. However, PLA resins should not be processed at temperatures above 300°C due to excessive thermal degradation. In this study, no degradation was expected or detected in meltblown nonwovens since all the temperature used were below 265℃.

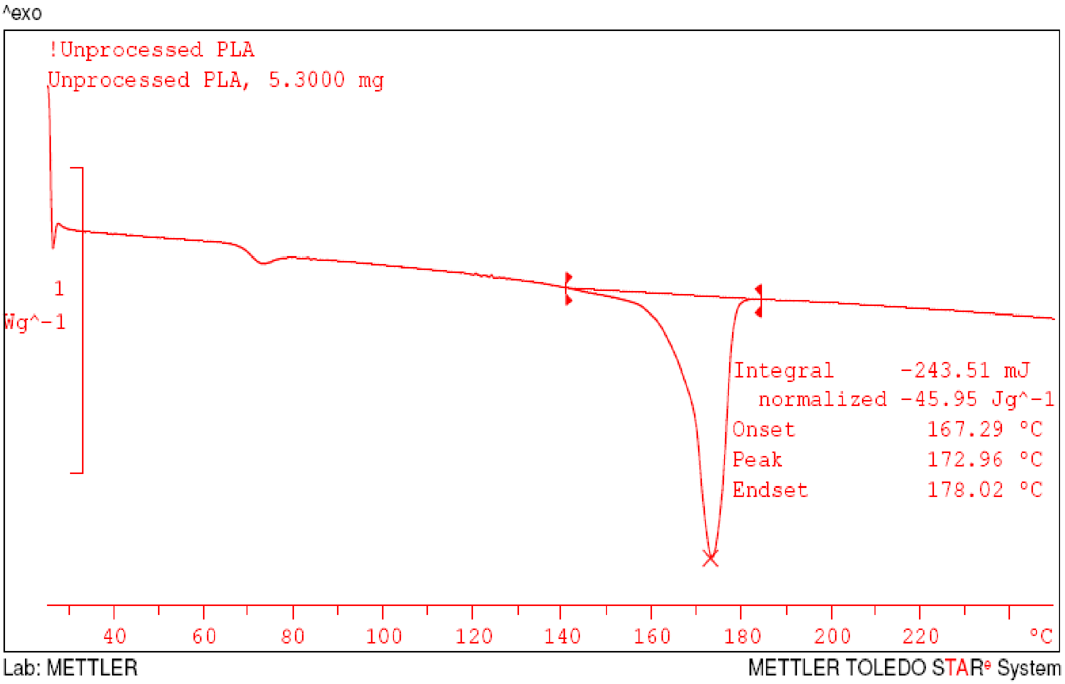


Figure 4.1. The DSC Thermogram for the As-received PLA.

Similarly, the thermal stability of zinc stearate powder was measured by DCS and TGA under a nitrogen atmosphere as shown in Figure 4.2 and 4.3 respectively. The Peak melting temperature of zinc stearate was observed to be 125°C. This temperature is less than all the temperatures used in the melt blown process. This low peak melting temperature causes the zinc stearate powder mix evenly through the melting procedure.

The degradation process for zinc stearate begins at approximately 300°C. No degradation was observed in meltblown nonwovens since the die temperature, and air temperature in this study were 230°C and 265°C respectively.

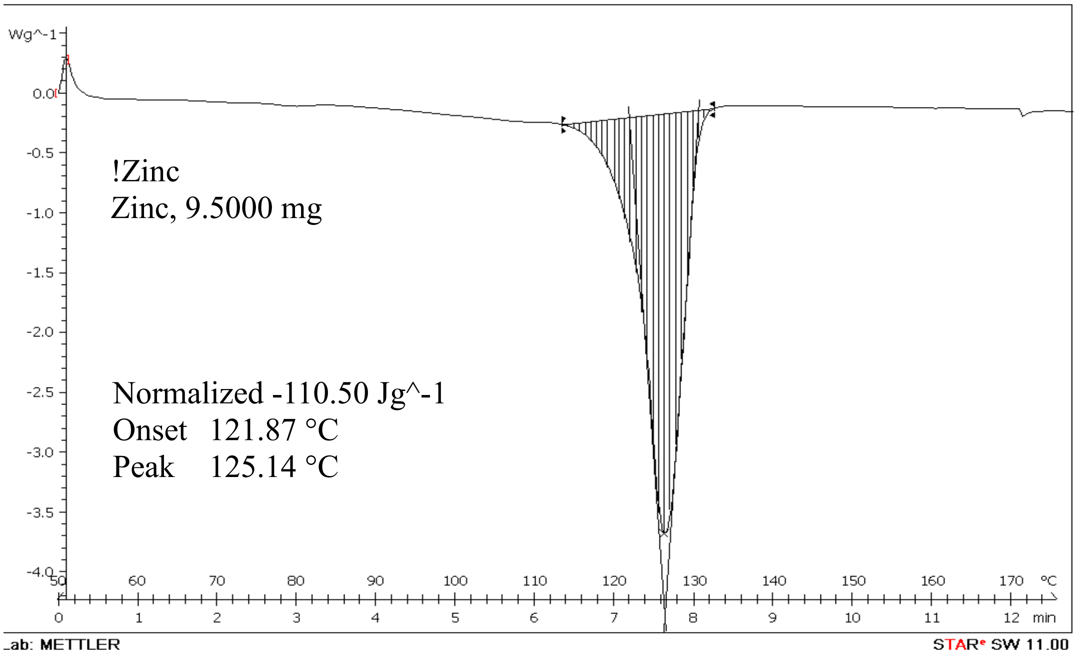


Figure 4.2. The DSC Thermogram for Zinc Stearate.

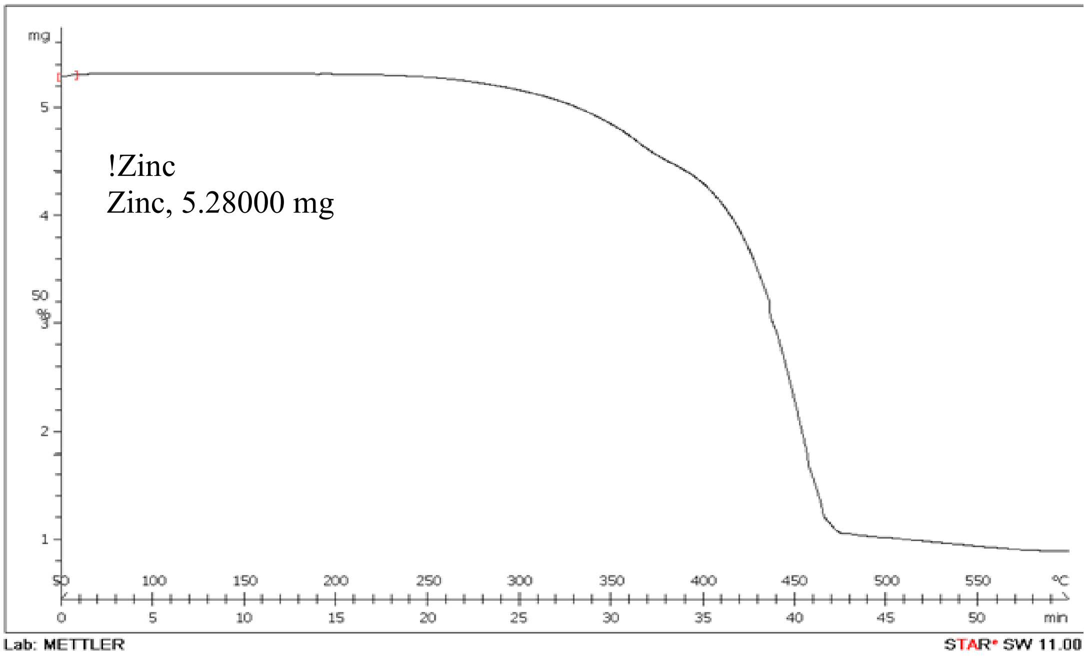


Figure 4.3. The TGA Thermogram for Zinc Stearate.

Since higher loading of zinc stearate provides a greater extent of plasticization and enhances the flowability of the system, the DSC analysis for mixtures of NatureWorks 6252D PLA with different percentage of zinc stearate powder was done (Figure 4.4). The melting peak temperatures for the PLA are observed at 171°C, 170.8°C and 169.7°C with 0.1%, 0.3%, and 0.5% zinc stearate powder respectively. This indicates that the addition of zinc stearate reduces the melting peak temperature of PLA from 172°C to a slightly lower value but not a significant reduction. Moreover, based on experience and literature review there is no advantage of using greater percentage of zinc stearate. Please refer to Appendix A for additional info.

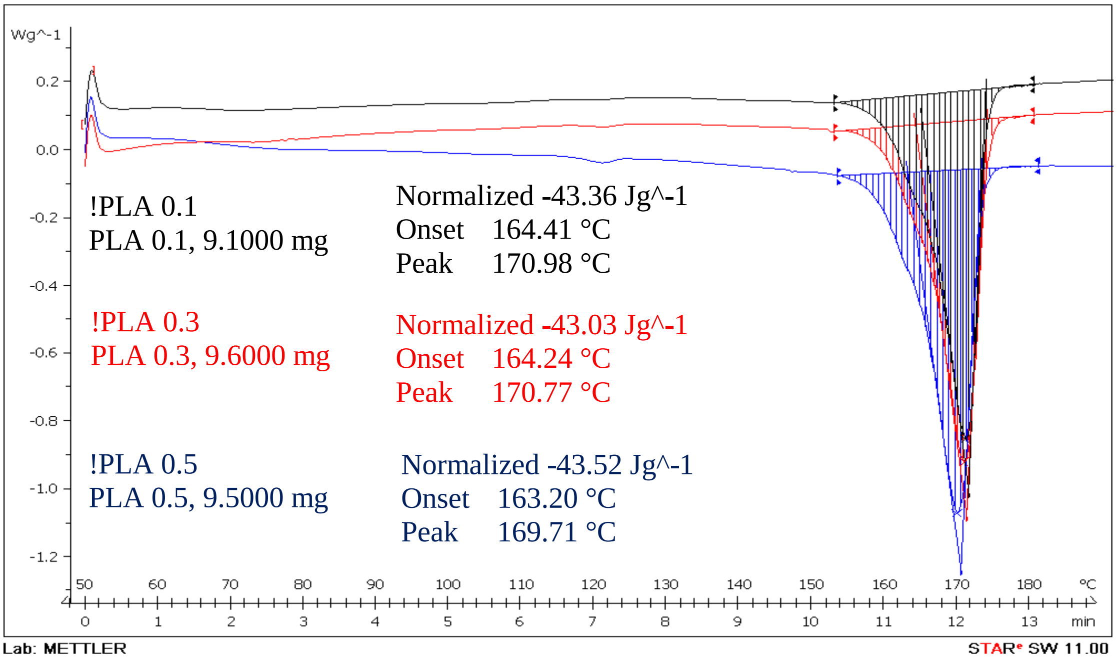


Figure 4.4. The DSC Thermogram for PLA with Zinc Stearate.

4.1.2 Thermal Properties of PLA Melt blown Nonwovens

DSC analysis of samples produced at low and high air pressure with varying percentage of zinc stearate was done at a heating rate of 10°C/min. A nitrogen flow was maintained throughout the test. The glass transition temperature (Tg), the cold crystallization temperature (Tcc), crystallinity percentage, and the melting temperature (Tm) were determined. Summary of results is shown in Table 4.1. Results were calculated based on the heat of fusion of 93 J/g for PLA.

Zinc stearate shifted glass transition and melting temperature of produced webs to slightly lower temperature when compared with neat PLA webs as it is shown in Figure 4.5 for samples produced at 55 kPa and Figure 4.6 for samples produced at 83kPa.

The addition of zinc stearate as a plasticizer and mold release agent enhanced the segmental molecular mobility of PLA, so the Tg slightly depressed and also resulted in the depression of the melting point. This Tg reduction enables crystallization to start at an earlier temperature upon heating while the percentage of crystallinity is almost same for all the samples.

Table 4.1. Summary of Thermal properties of PLA nonwoven webs

Sample ID	**L0**	**L1**	**L2**	**L3**	**H0**	**H1**	**H2**	**H3**
Tg (°C)	64.9	64.6	63.4	63	62.5	62.4	62.6	61.6
Tcc (°C)	99.5	99.5	98.1	97.8	98.1	98	96	96
Tm (°C)	169.6	168.9	168.7	168.3	167.6	167.6	166.8	166.6
Cold crystallinity (%)	20.9	21.1	21.2	20.7	20.6	20.6	21.2	20.5

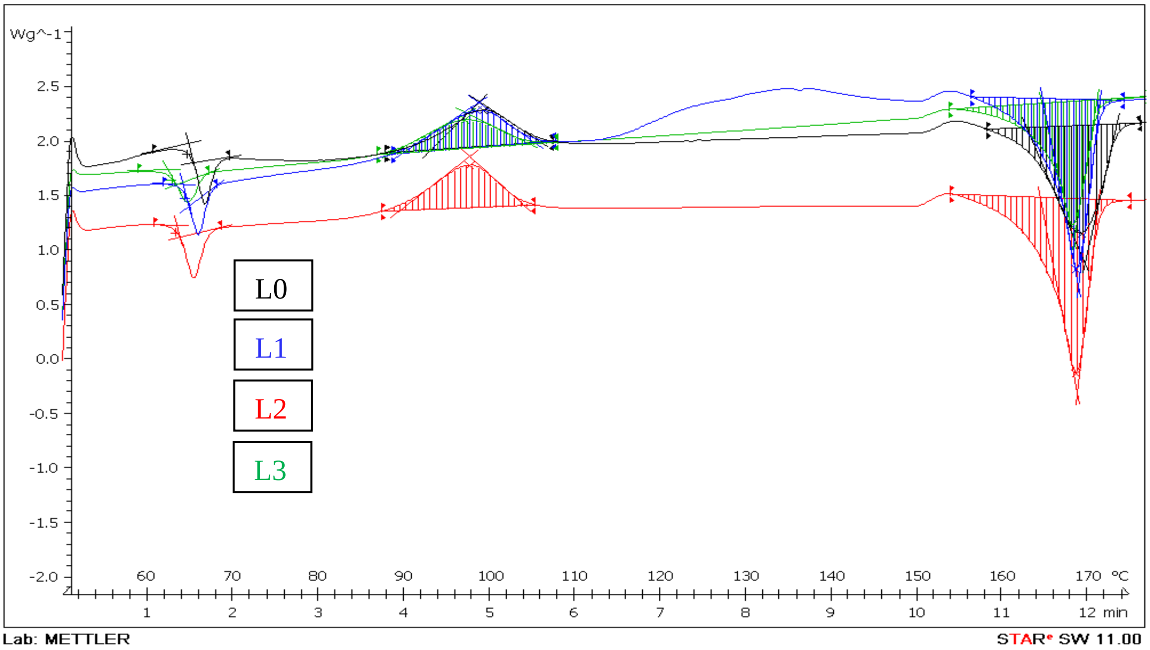


Figure 4.5. The DSC Thermogram for PLA with Zinc Stearate.

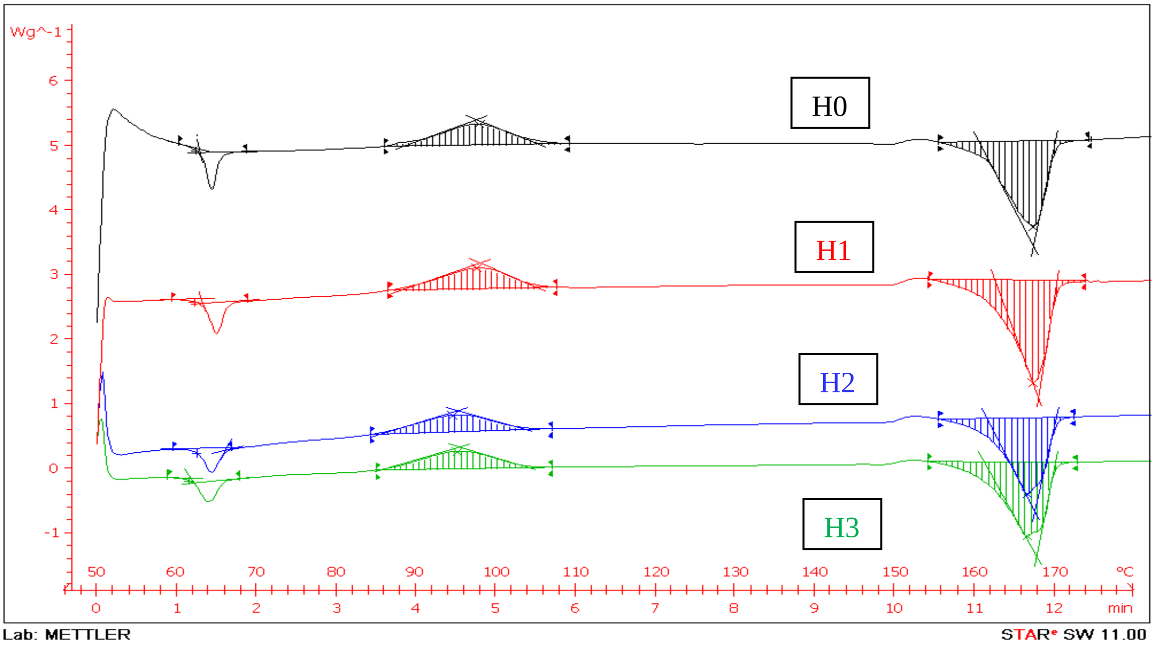


Figure 4.6. The DSC Thermogram for PLA with Zinc Stearate.

4.2 Physical Properties of PLA Melt blown Nonwovens

Weight and thickness of nonwoven webs play a significant role on their properties. To make a better comparison of results for various samples, normalization of data was done based on basis weight and thickness. Whereas the target weight was 35gsm, because of the process interactions, the actual weight of the samples varies slightly, and that has been observed. The thickness of the webs is an effect of fiber diameter and web consolidation and will have an impact on barrier properties. Average shrinkage of almost all of the sample was observed to be around 40% as it is listed in Table 4.2.

Table 4.2. Summary of Physical Properties of Meltblown Nonwoven Webs.

Sample ID	Ave. Basis Weight (GSM)	Ave. Thickness (mm)	Ave. Shrinkage (%)
L0	29.6±0.5	0.32	45
L1	38.1±0.2	0.25	48±0.5
L2	48.8±0.4	0.41	41±0.1
L3	49.3±0.6	0.38	38±0.6
H0	35.9±0.5	0.30	39±0.2
H1	41.8±0.1	0.26	42±0.6
H2	46.9±0.6	0.38	38±0.3
H3	36.4±0.3	0.31	34±0.5
S1	16.7±0.2	0.27	39±0.1
S2	29.6±0.4	0.32	45±0.3

4.3 Structural Properties of PLA Melt blown Nonwovens

Generally, mean fiber diameter and distribution determine the properties of nonwoven webs and the diameters of fibers is usually smaller with [26,30]

- Lower viscosity of the polymer melt (higher MFR, higher temperature)
- Higher air temperature

- Higher ratio of air: polymer (higher air throughput rate and lower polymer throughput rate)

4.3.1 Fiber Diameter with Change in Air Pressures and Percentage of Zinc Stearate

The fiber diameters in the regular melt blowing process are in the range of 3-5 microns. However, to achieve better performance, fibers with smaller diameters are preferred, and one of the challenges in the nonwoven industry is to manufacture nonwovens with smaller fiber diameters[23,30]. Figure 4.7 shows SEM images of meltblown PLA nonwoven fabrics for samples L0-L3 and H0-H3, respectively.

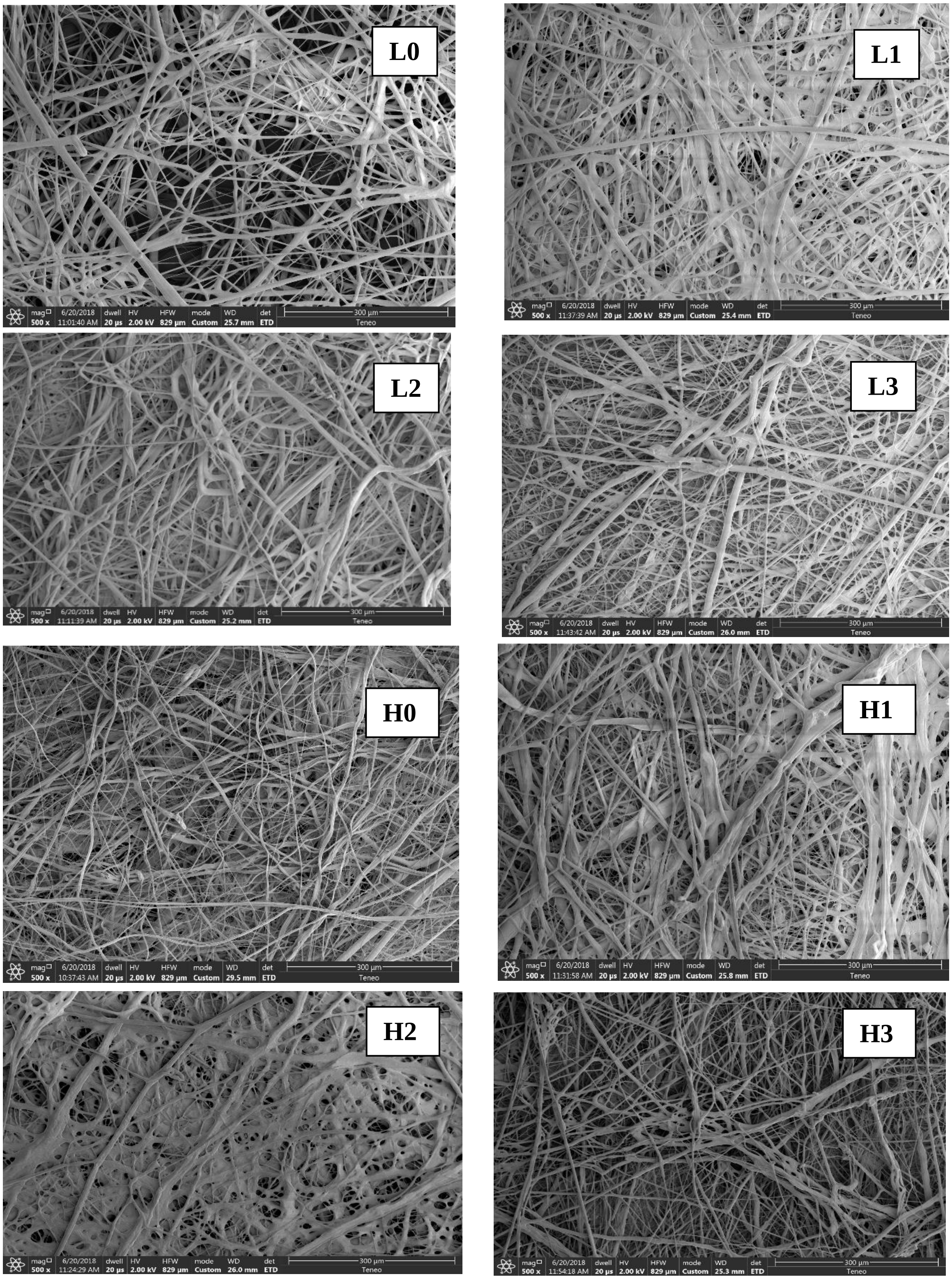


Figure 4.7. SEM Images of Samples (L0 to L3) and (H0 to H3).

The mean fiber diameter of PLA nonwoven webs produced at the low and high air pressures in the presence of zinc stearate are presented in Figure 4.8 and 4.9 respectively. The low pressure samples were reduced down to as much as 13% of their original 2.3 µm diameter with the presence of additives. Fiber diameter reduction can be attributed to the effect of zinc stearate on cooling efficiency and flow modification, which enhances the flowability of the melt by pushing the polymer molecules slightly further apart, weakening the forces between them and making the material softer and more flexible and thereby resulting in a reduction of apparent viscosity. The increase in the quantity of zinc stearate from 0.1% to 0.3%, however, doesn’t change the fiber diameter significantly. On the contrary, high-pressure samples showed an increase by as much as 12% of their original 1.6 µm diameter in the presence of the additive. The cause of this behavior is not well understood. It is clear, however, is that in high air pressure there is more turbulences cause to increase the variability, and with that being said, in high air pressure there is no advantage of using process aid.

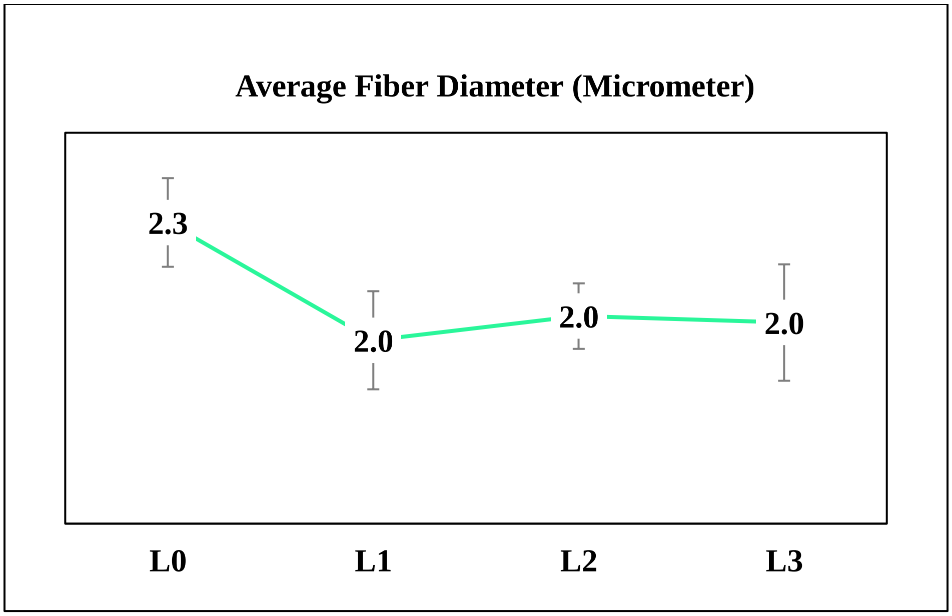


Figure 4.8. Average Fiber Diameter of the Samples at 55 kPa and Varying Percentages of Zinc Stearate.

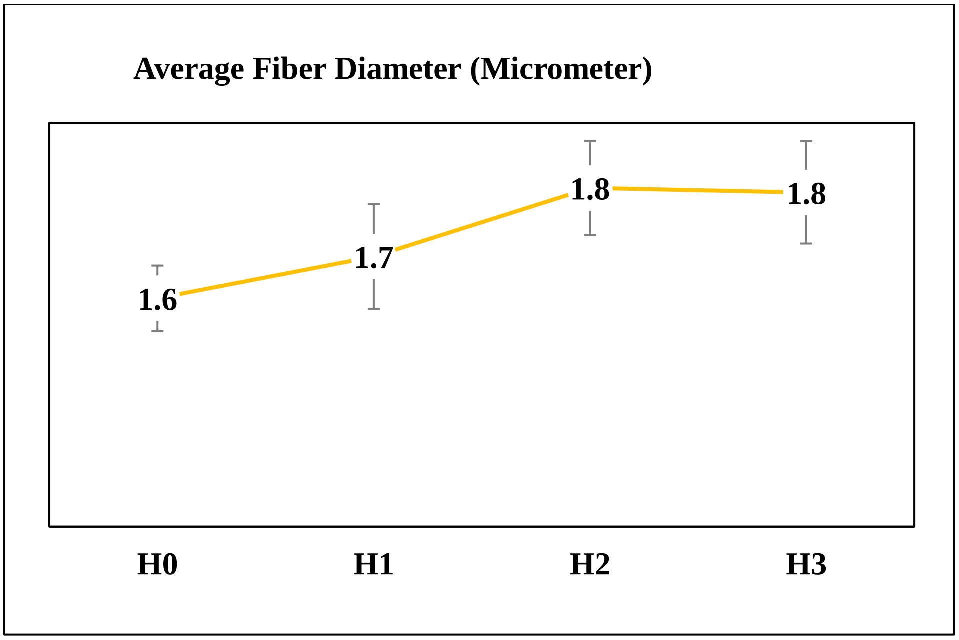


Figure 4.9. Average Fiber Diameter of the Samples at 83 kPa and Varying Percentages of Zinc Stearate.

The dependence of fiber diameter on air pressure can be seen from the data in figure 4.10. It is observed that the average fiber diameter is smaller in samples produced at high air pressure (83kPa). This is consistent with all the earlier observations. During the meltblown process, the air pressure dominates many other processing variables affecting the fiber attenuation. The reason is that the speed of the air increase fiber speed significantly, and thereby the drag force increase.

What is more important is that melt blown webs with average fiber diameters less than 2 microns could be produced at low air pressure and this is a definite advantage as the majority of melt blown cost comes from providing high-pressure hot air and producing fine fibers by running the line at low air pressure reduce the cost of processing.

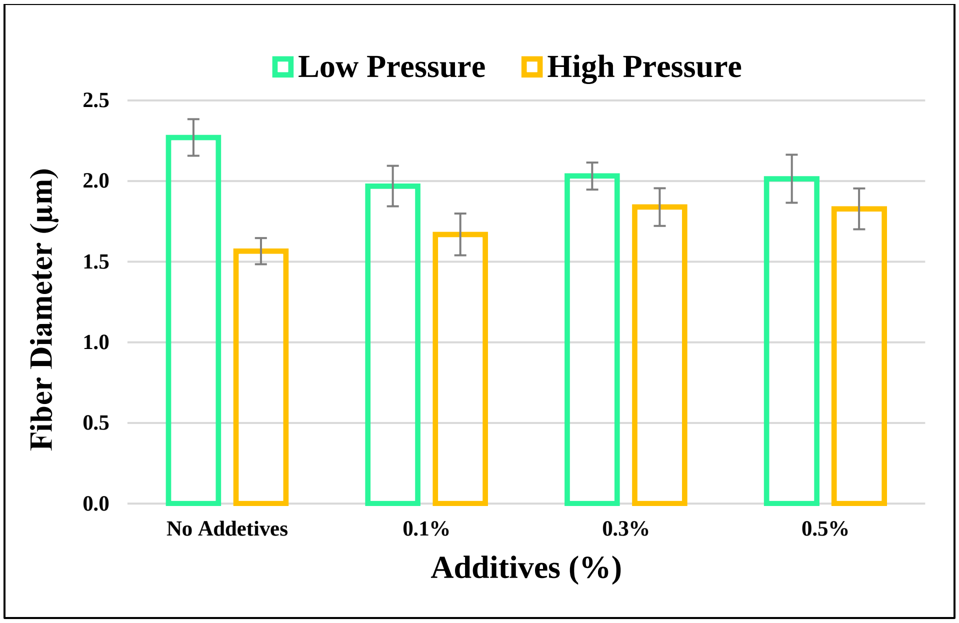
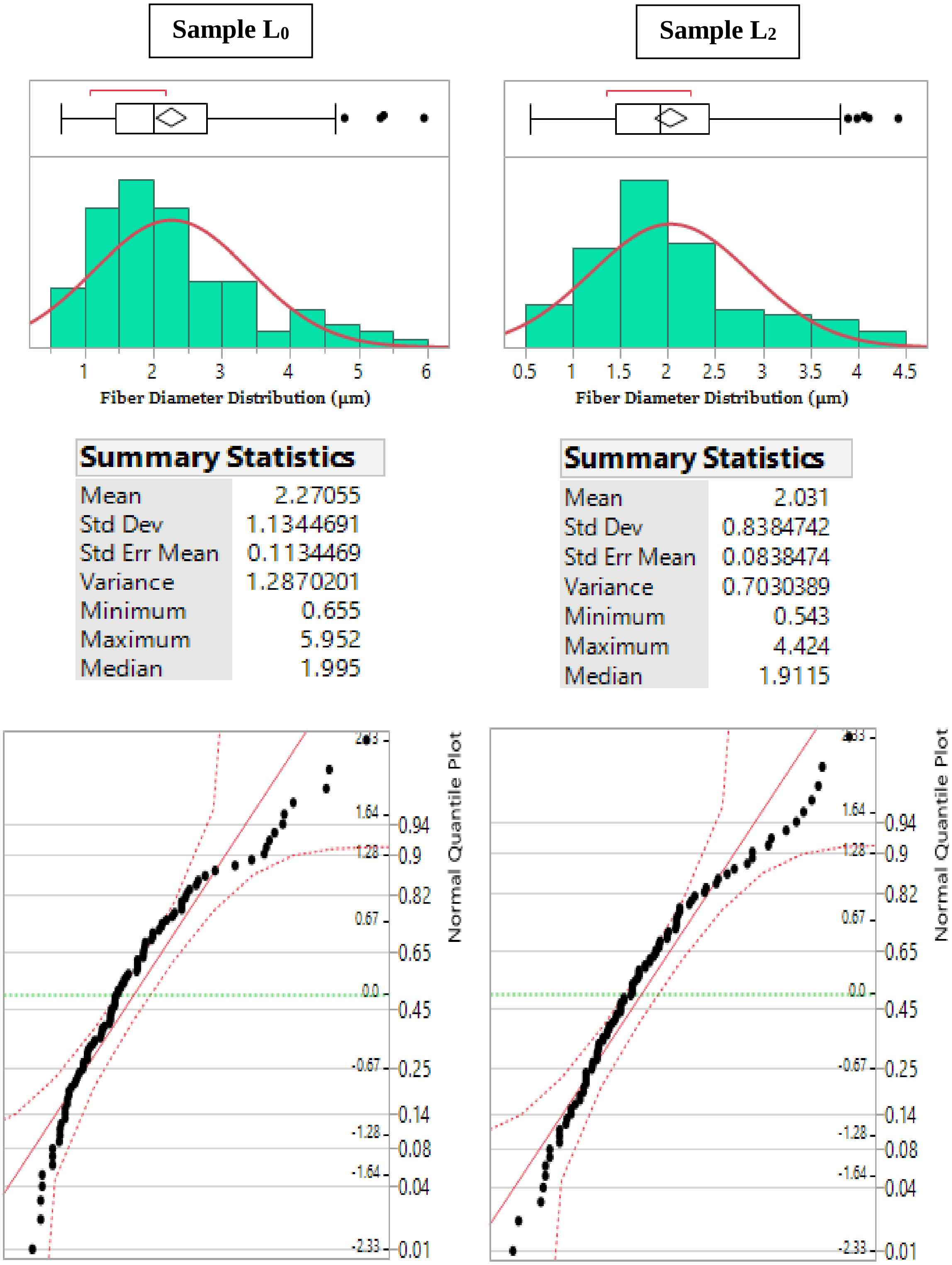


Figure 4.10. Average Fiber Diameter of the Samples at Various Air Pressure Levels.

4.3.2 Fiber Diameter Distribution with Change in Air Pressures and Percentage of Zinc Stearate

Measurement and the control of the fiber diameter distribution are also important because it will likely have some effect on the finished web properties of nonwovens[30].

Fiber diameter histogram for samples produced from PLA and PLA with 0.3% zinc stearate at a constant air pressure of 55 kPa are shown in Figure 4.11. It is observed that the fiber diameter distribution of the samples is slightly more symmetric with the addition of zinc stearate. It is reasonable to explain that the distribution of diameter is influenced by fiber contact and entanglement that is encountered in the presence of zinc stearate. Moreover, the peak diameter for samples with no additives is between 1 and 2.5 µm whereas the peak diameter for samples with 0.3% zinc stearate is between 1 and 2 µm. Distribution became narrower with 0.3% of zinc stearate, from (0-6 µm) to (0.5-4.5 µm). Normal quantile plot uses to visualize the extent to which the variable is normally distributed. If a variable is normally distributed, the normal quantile plot approximates a diagonal straight line. Samples with zinc stearate showed slightly better following of straight line and consequently more normally distributed. Data for additional samples with varying percentages of zinc stearate are provided in Appendix B.



Sample L_0

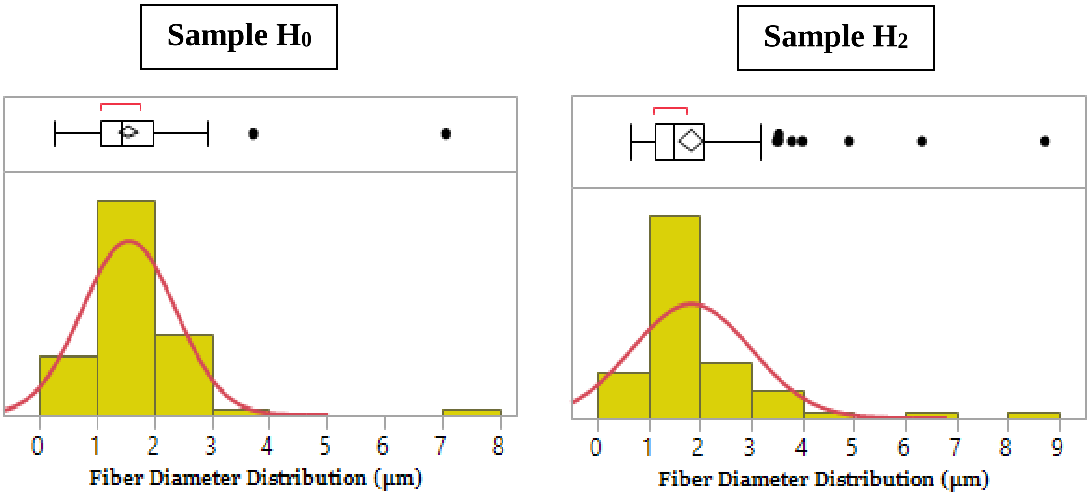
Summary Statistics	
Mean	2.27055
Std Dev	1.1344691
Std Err Mean	0.1134469
Variance	1.2870201
Minimum	0.655
Maximum	5.952
Median	1.995

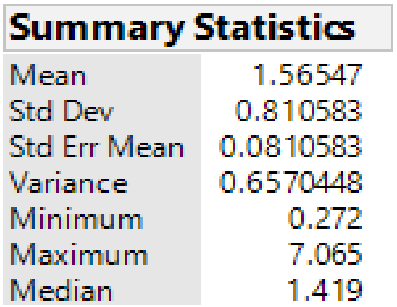
Sample L_2

Summary Statistics	
Mean	2.031
Std Dev	0.8384742
Std Err Mean	0.0838474
Variance	0.7030389
Minimum	0.543
Maximum	4.424
Median	1.9115

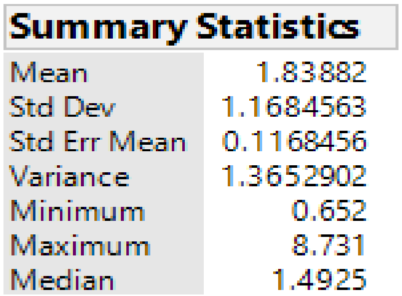
Figure 4.11. Fiber Diameter Distribution and Normal Quantile Plot of Samples L0 and L2.

Fiber diameter histogram for samples produced without and with 0.3% zinc stearate at a constant air pressure of 83kPa are shown in Figure 4.12. It is observed that the fiber diameter distribution of the samples does not vary significantly with the addition of zinc stearate. Additionally, the peak diameter for both samples (with and without zinc stearate) is between 1 and 2 µm. There is not much different in the range of distribution and normal quantile plot. In high air pressure, there is more turbulence cause to increase the variability and wider fiber diameter distribution. In this way, under high air pressure, there is no advantage of using process aid. Data for additional samples with varying percentages of zinc stearate are provided in Appendix B.





Summary Statistics	
Mean	1.56547
Std Dev	0.810583
Std Err Mean	0.0810583
Variance	0.6570448
Minimum	0.272
Maximum	7.065
Median	1.419



Summary Statistics	
Mean	1.83882
Std Dev	1.1684563
Std Err Mean	0.1168456
Variance	1.3652902
Minimum	0.652
Maximum	8.731
Median	1.4925

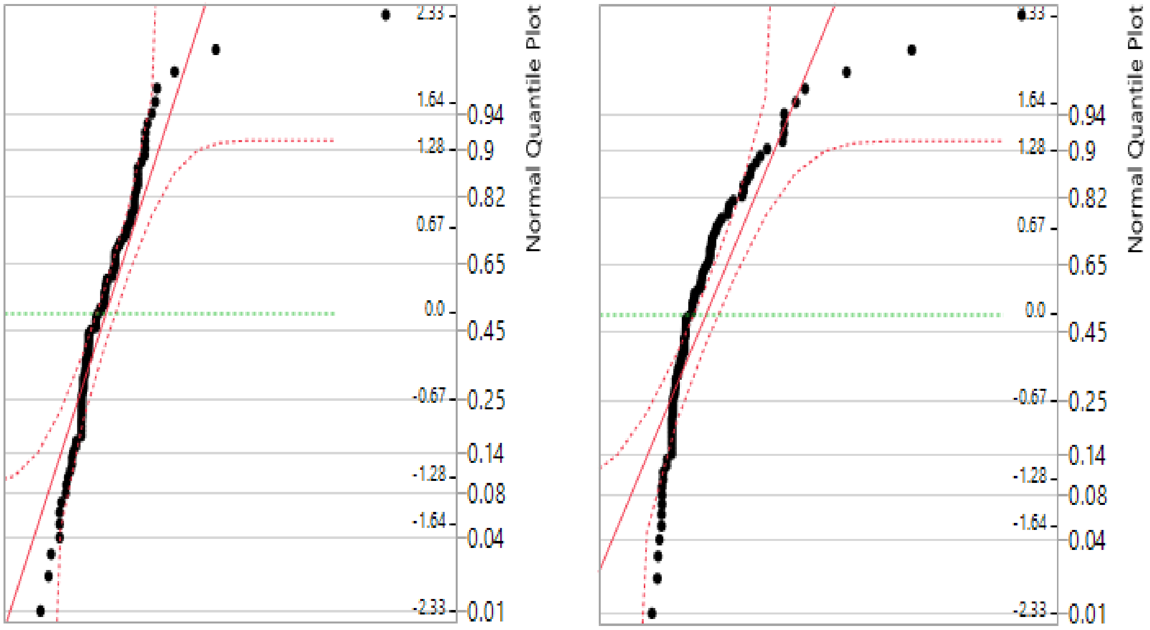


Figure 4.12. Fiber Diameter Distribution and Normal Quantile Plot of Samples H0 and H2.

4.3.3 Fiber Diameter with Change in Throughput

Lower polymer throughput rate cause to have lower mean fiber diameter. Fibers with diameter of almost 1 µm with several submicron fibers can be produced by decreasing the polymer throughput with the screw speed of 10 rpm (Figure 4.13).

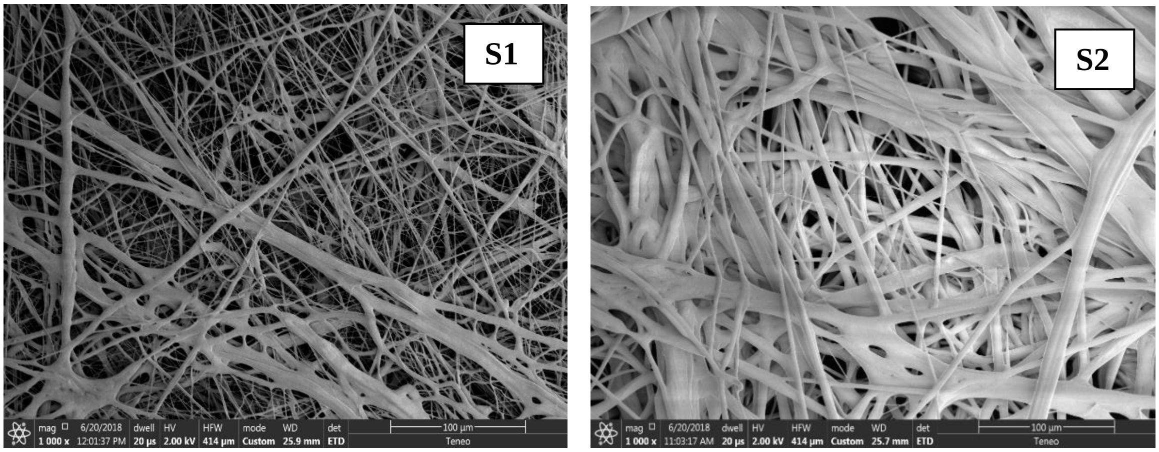


Figure 4.13. SEM Images of Samples S1 and S2.

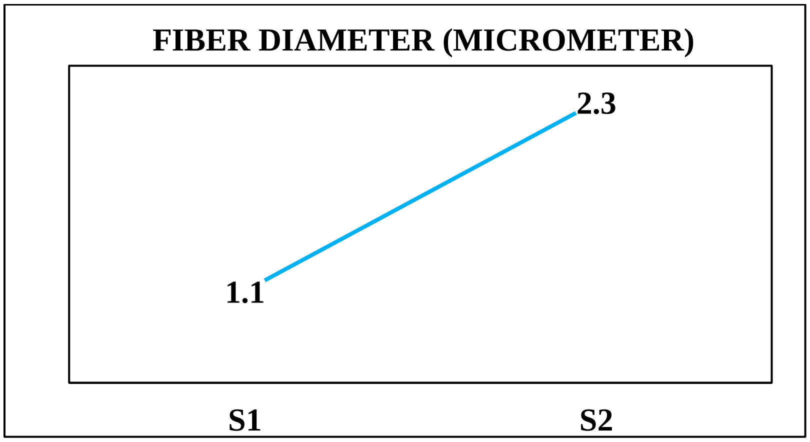
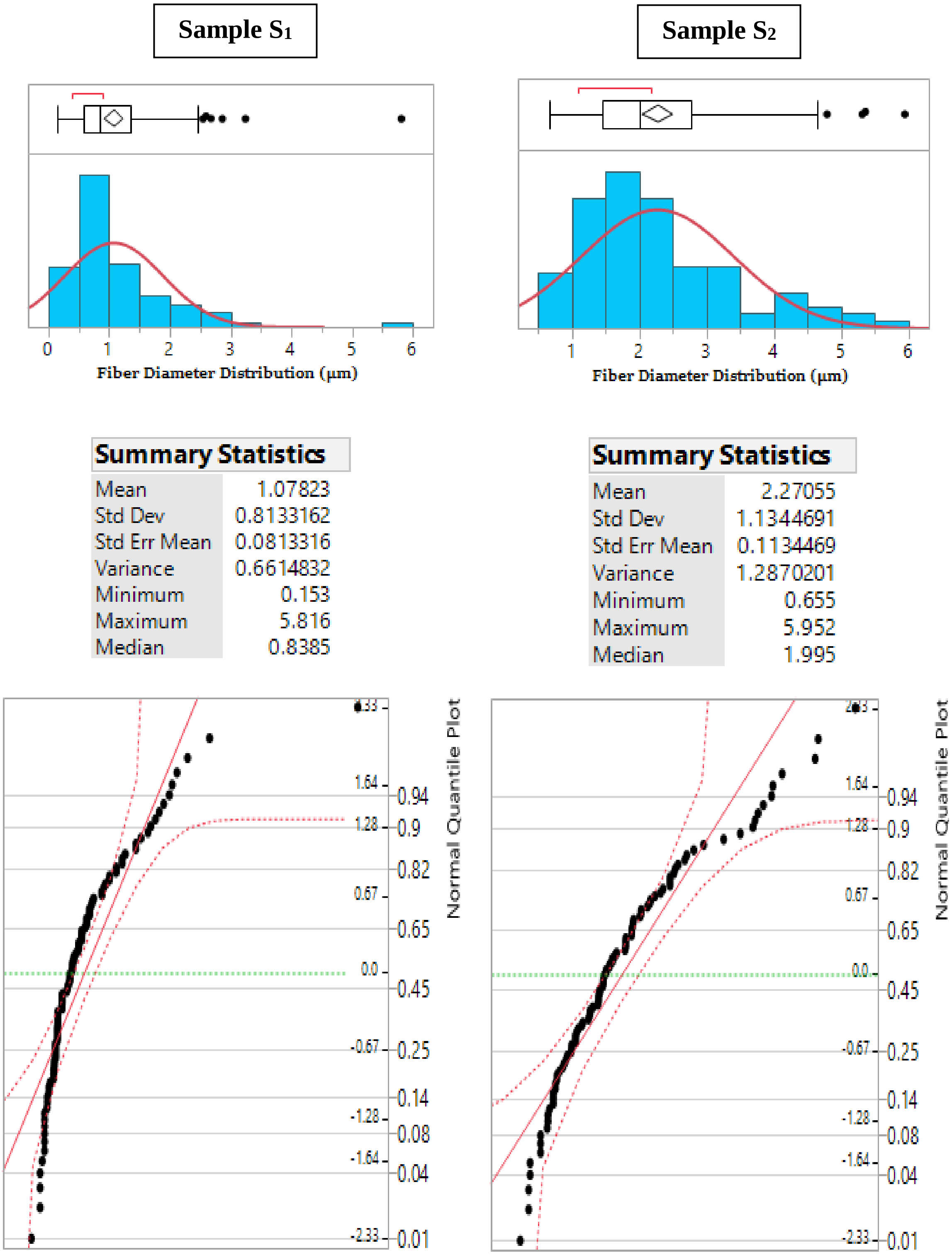


Figure 4.14. Average Fiber Diameter of the Samples at 55 kPa and Varying Screw Speed.

4.3.4 Fiber Diameter Distribution with Change in Throughput

The fiber diameter histogram indicates that with low polymer throughput, nanofibers can be produced with a narrow distribution between 0-3 µm. As it can be seen in normal quantile plot, fiber diameters of the sample produced with low polymer throughput are more normally distributed.



Sample S_1

Sample S_2

Summary Statistics

Mean	1.07823
Std Dev	0.8133162
Std Err Mean	0.0813316
Variance	0.6614832
Minimum	0.153
Maximum	5.816
Median	0.8385

Summary Statistics

Mean	2.27055
Std Dev	1.1344691
Std Err Mean	0.1134469
Variance	1.2870201
Minimum	0.655
Maximum	5.952
Median	1.995

Figure 4.15. Fiber Diameter Distribution and Normal Quantile Plot of Samples S1 & S2.

4.3.5 Mean Flow Pore Diameter and Range with Change in Air Pressures and Percentage of Zinc Stearate

The porous structure of nonwoven webs plays a key role in improving the performance in many applications including filtration, wound dressing, membrane separation and scaffolds for tissue engineering [31]. So, the porous and porosity structure of the webs was studied using capillary flow porometer.

The mean pore sizes of PLA nonwovens using different percentages of additives at low and high air pressure are presented in Figure 4.16 and Figure 4.17 respectively. It is observed that the mean flow pore diameter of the PLA nonwovens decreases significantly in the presence of zinc stearate regardless of the applied air pressure. In case of low air pressure (55 kPa), the flow pore diameter decreased by almost 60% when the percentage of zinc stearate was increased by 0.5%. In case of high air pressure (83 kPa), the flow pore diameter decreased by almost 50% when the percentage of zinc stearate was increased by 0.5%. Fiber diameter, as well as packing of the fibers and fiber entanglements, affect the mean pore diameter and distribution. The best possible explanation for the reduction of pore diameter and distribution is due to some sticky parts that have been created in the presence of zinc stearate (it can be observed from SEM pictures) and cause to have better packing and entanglements.

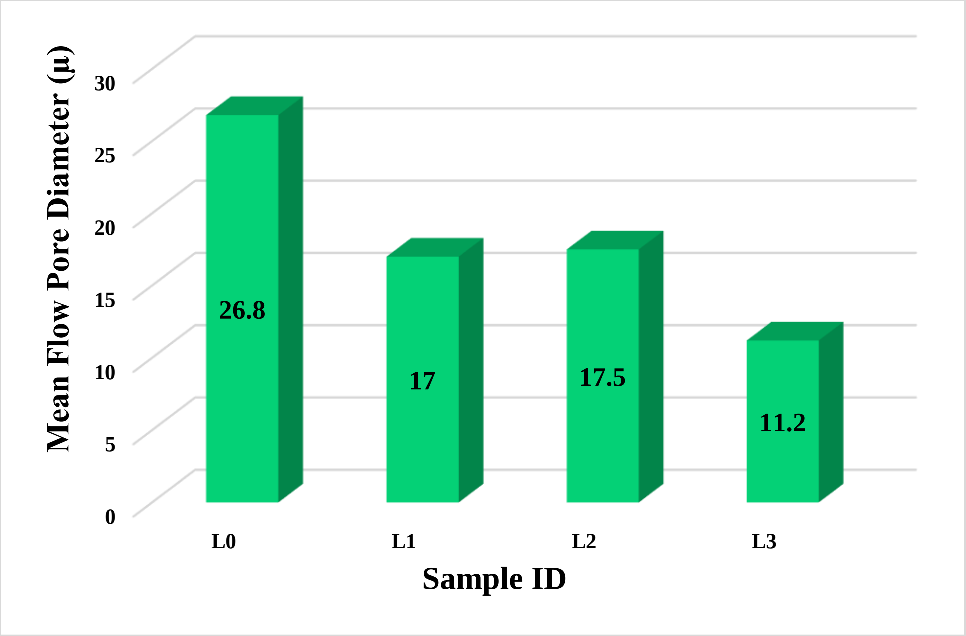


Figure 4.16. Average Mean Flow Pore Diameter of the Samples at 55 kPa and Varying Percentages of Zinc Stearate.

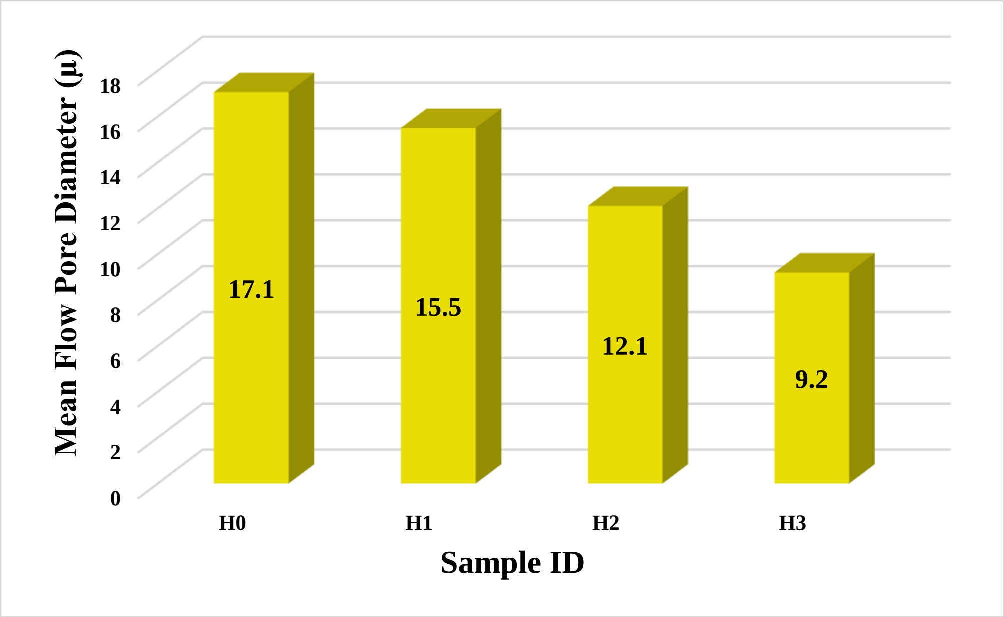


Figure 4.17. Average Mean Flow Pore Diameter of the Samples at 83 kPa and Varying Percentages of Zinc Stearate.

4.3.6 Mean Flow Pore Diameter and Range with Change in Throughput

Mean flow pore diameter of nonwoven PLA is almost 30% less when the throughput is one third. This can be explained by the effect of fiber diameter. (Figure 4.18)

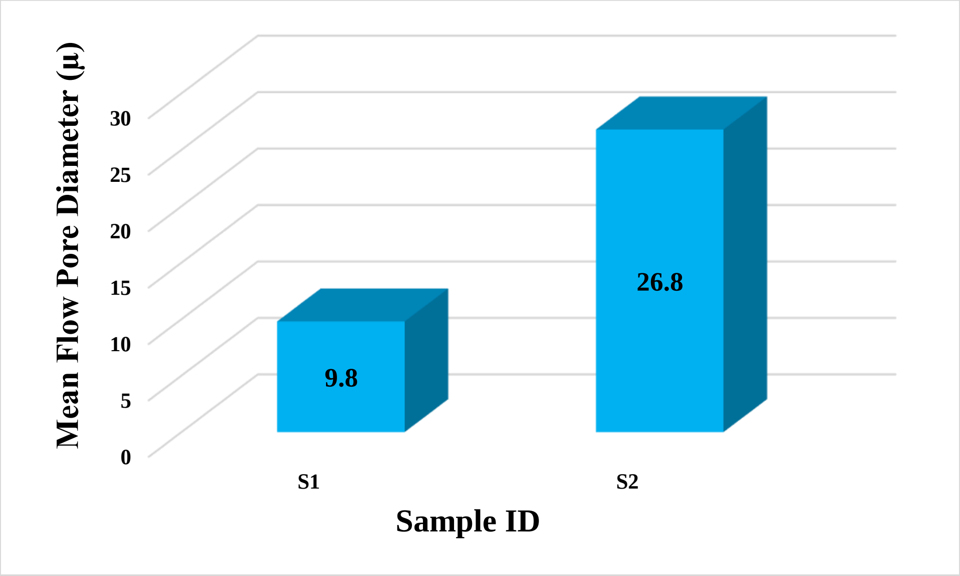


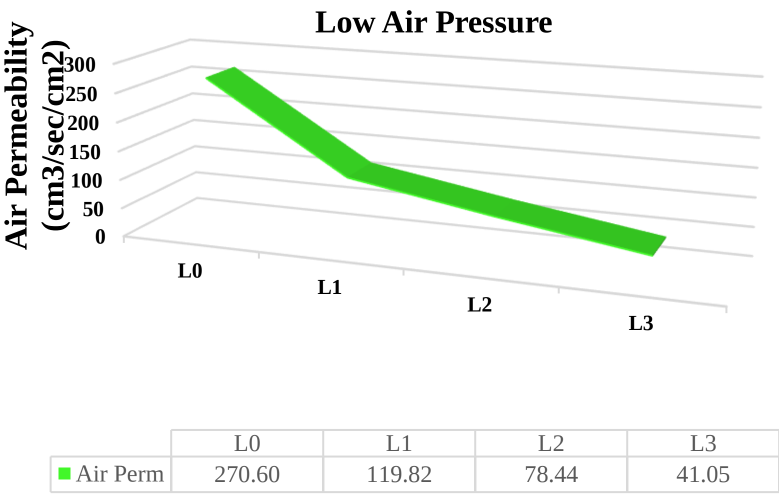
Figure 4.18. Average Fiber Diameter of the Samples at 55 kPa and Varying Throughput.

Table 4.3. Summary of Mean Flow Pore Diameter and Pore Diameter Range

Sample ID	**Mean Flow Pore Diameter (μ)**	**Pore Diameter Range (μ)**
L0	26.8	(5.6 - 55.1)
L1	17	(4.5 - 30.9)
L2	17.5	(3.7 - 32.5)
L3	11.2	(2.4 - 17.7)
H0	17.1	(3.9 - 32.8)
H1	15.5	(3.7 - 23.6)
H2	12.1	(2.7 - 21)
H3	9.2	(2.4 - 18)
S1	9.8	(3.2 - 14)
S2	26.8	(5.6 - 55.1)

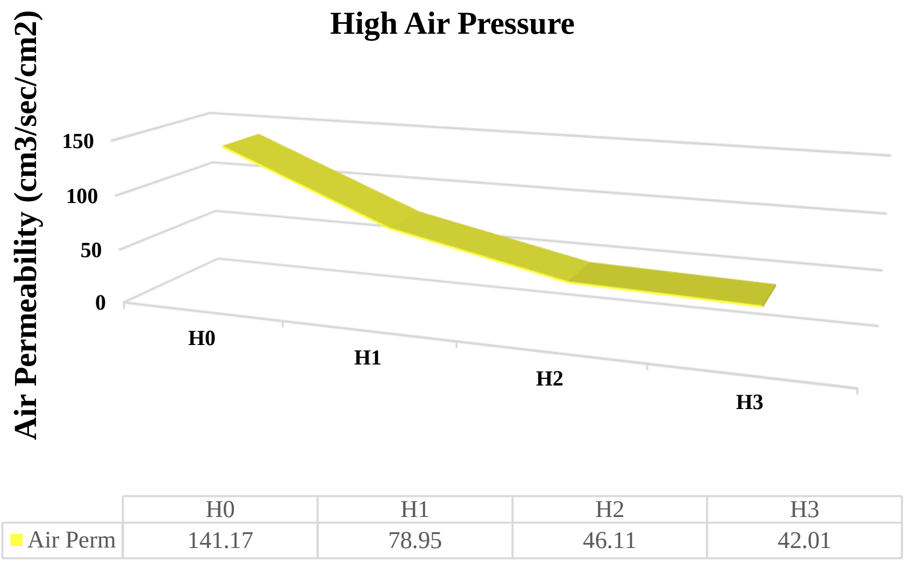
4.3.7 Air Permeability with Change in Air Pressures and Percentage of Zinc Stearate

Lower porosity generally gives lower air permeability. Air permeability is affected by fiber diameter, packing, entanglements, roping, and bundling of the fibers. The air permeability of the PLA nonwoven decreases significantly at both low and high air pressure conditions by adding zinc stearate. At low air pressure (55kPa), the decrease in air permeability is due to a combination of both better packing and smaller fiber diameter in the presence of zinc stearate. While, the decrease in air permeability in the presence of zinc stearate for high air pressure (83kPa) samples can be explained by better packing, entanglement and sticking of the fibers that cause blockages as it can be observed from SEM pictures. Additionally, more roping and bundling of the fibers can block the effective force and change the air permeability.



	L0	L1	L2	L3
🟩 Air Perm	270.60	119.82	78.44	41.05

Figure 4.19. Air Permeability of Webs at 55 kPa with Different Percentage of Zinc Stearate.

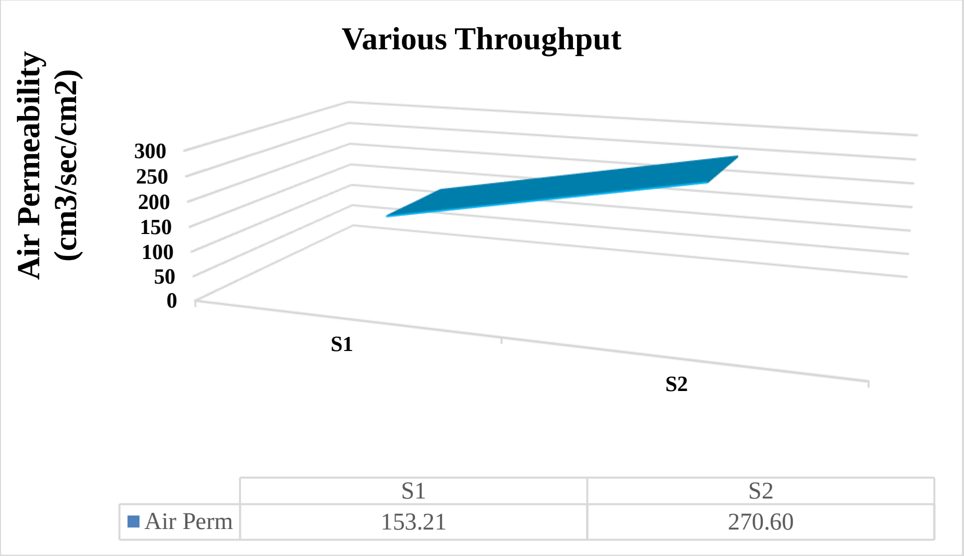


	H0	H1	H2	H3
🟨 Air Perm	141.17	78.95	46.11	42.01

Figure 4.20. Air Permeability of Webs at 83 kPa with Different Percentage of Zinc Stearate.

4.3.8 Air Permeability with Change in Throughput

The air permeability of the PLA nonwoven samples increased significantly when the throughput is increased. This trend can be explained with the reasons mentioned above.



	S1	S2
■ Air Perm	153.21	270.60

Figure 4.21. Air Permeability of Webs at 55 kPa and Varying Throughput.

4.3.9 Water Absorbency

PLA nonwoven samples have low water acsorbtion regardless of the process variables. This can be observed from the absorption rates in Table 4.3.

Table 4.4. Summary of Water Absorbency Properties of Nonwoven Webs

Sample ID	Maximum Absorption (grams/gram)	Absorption Rate (grams/sec)
L_0	0.568	0.2369
L_1	0.409	0.2366
L_2	0.404	0.0374
L_3	1.045	1.2237
H_0	0.656	0.0002
H_1	0.379	0.1867
H_2	0.31	0.0002
H_3	1.116	0.9732
S_1	3.43	0.5368
S_2	0.568	0.2369

4.4 Mechanical Properties of PLA Melt blown Nonwovens

Nonwoven webs strength is related to individual fiber strength, average fiber length and fiber entanglement.

4.4.1 Young’s Modulus and Tensile Strength with Change in Air Pressures and Percentage of Zinc Stearate

Young’s modulus and tensile strength of PLA nonwoven samples exhibit an increasing trend at low and high air pressures and also when the percentage of zinc stearate is increased in the samples. This increase can be explained by better entanglement and packing of the fibers. Samples produce in high air pressure showed better strength probably due to lower fiber diameter and better packing.

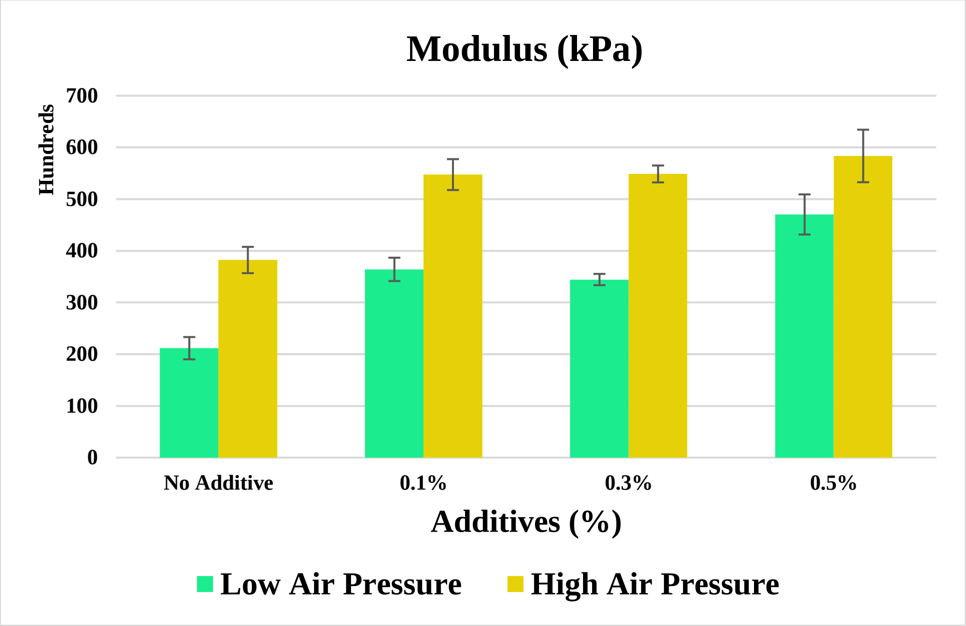


Figure 4.22. Modulus of the Samples at Various Air Pressure Levels and Percentages of Zinc Stearate.

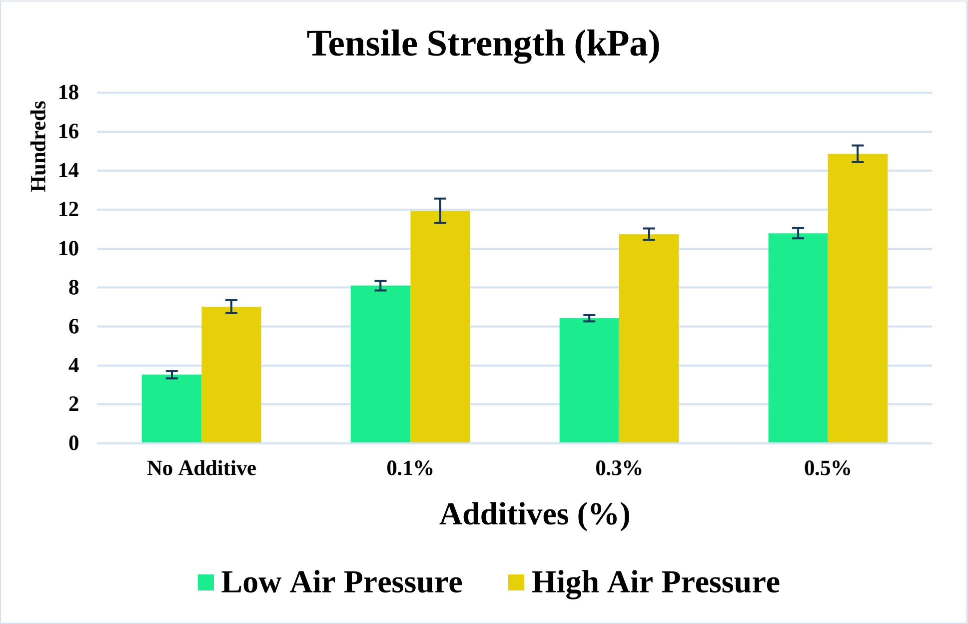


Figure 4.23. Tensile Strength of the Samples at Various Air Pressure Levels and Percentages of Zinc Stearate.

4.4.2 Young’s Modulus and Tensile Strength with Change in Throughput

Young’s modulus of PLA nonwoven samples is increased when the throughput is increased, but the tensile strength of PLA nonwoven samples is decreased when the throughput is increased. Samples produced at lower throughput due to smaller fiber diameter showed higher strength. However, lower modulus could be explained by higher strain.

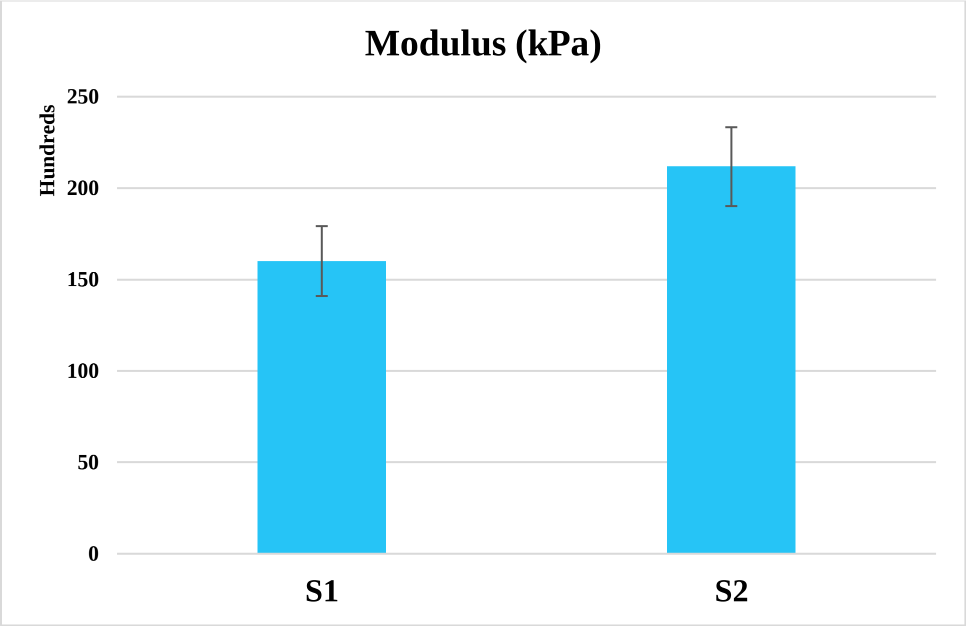


Figure 4.24. Modulus of the Samples at 55 kPa and Varying Throughput.

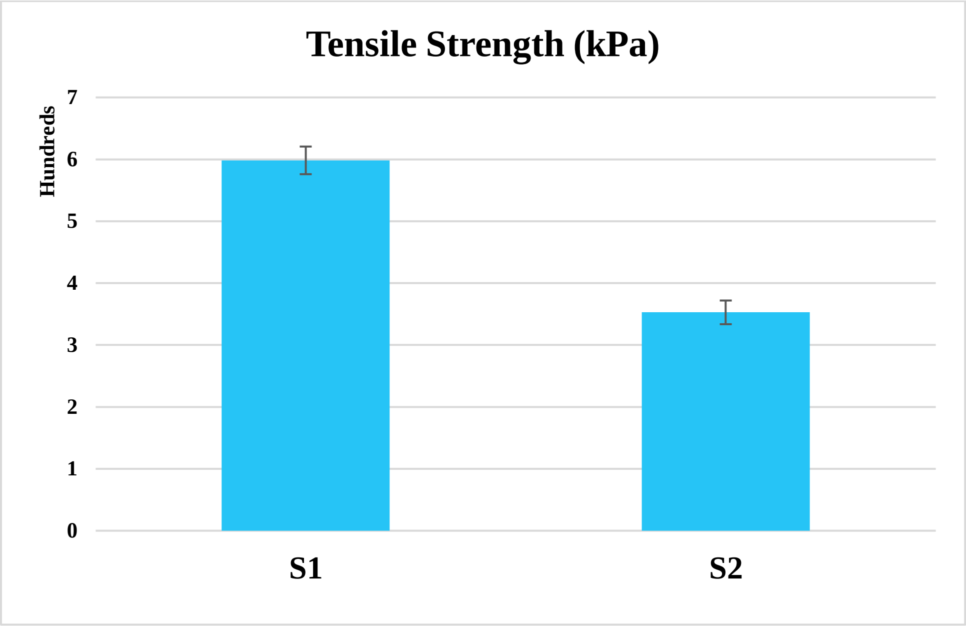


Figure 4.25. Tensile Strength of the Samples at 55 kPa and Varying Throughput.

CHAPTER 5

SUMMARY AND FUTURE WORKS

Summary

PLA nonwoven webs have been successfully produced under different processing conditions using a melt blowing pilot line. A detailed analysis of the influence of the processing conditions on the microstructures of PLA fibers showed the importance of an additive, as well as process air pressure and throughput rate on fiber diameter and diameter distribution. Results indicate that a decrease in fiber diameter and diameter distribution can be achieved by the addition of zinc stearate at low processing air pressures. This can be of benefit considering the fact that most of the melt blown process cost comes from high-temperature, high-pressure process air.

At higher process air pressures, fiber diameters were relatively smaller in all the cases, and the effect of the additive was not consistent. With lower throughput, submicron fibers can be produced with good properties. Fiber diameter is one of the most important features of the meltblown web, like that of any other nonwoven, and all the other performance properties depend on the fiber diameter. Properties such as air permeability and tensile properties also changed with process conditions, and they followed the expected trend based on the changes in fiber diameter. In addition to fiber diameter, web consolidation also affects the structure and properties of the melt blown nonwovens. SEM photographs and porosity measurements are helpful in understanding the overall effect of fiber diameter and web consolidation to help understand the changes in performance properties of the melt blown webs.

Recommendation for future works

- Additional changes in throughput for achieving submicron fibers
- Evaluate the filtration efficiency of the webs
- Determine melt viscosity of PLA with zinc stearate at different temperatures
- Evaluate the effect of other additives to reduce shrinkage
- Evaluate the effect of other plasticizers

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APPENDICES

APPENDIX A

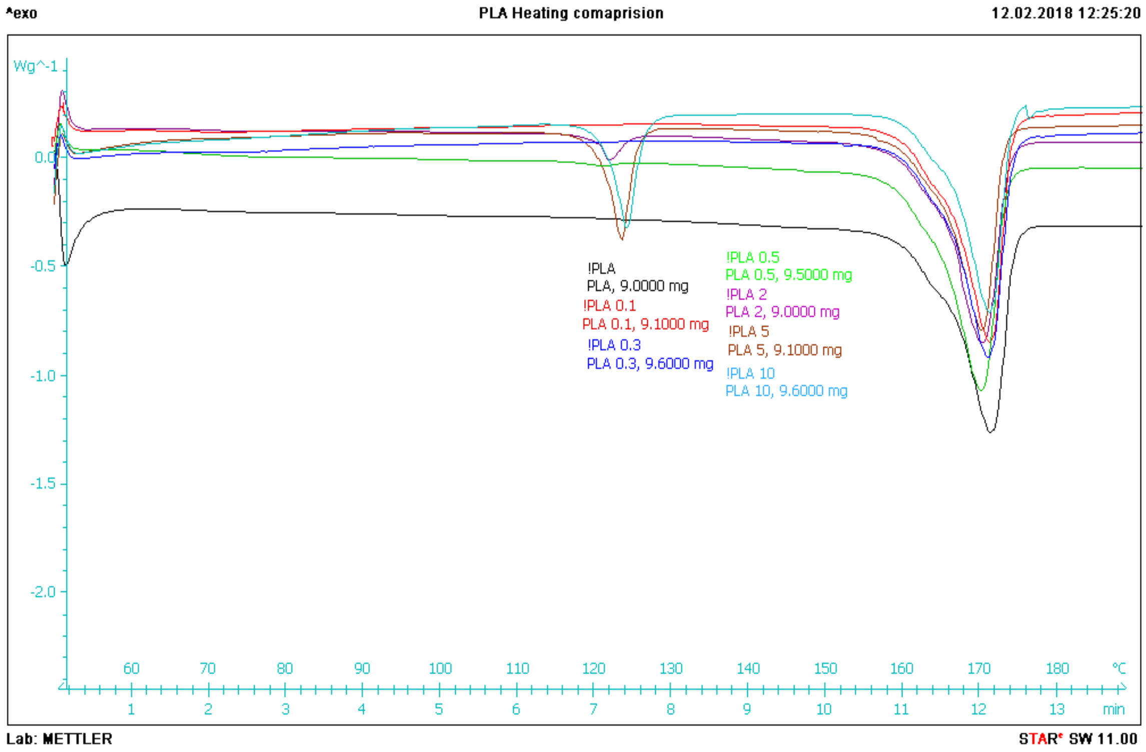


Figure A.1. The DSC Thermogram for PLA with Zinc Stearate.

APPENDIX B

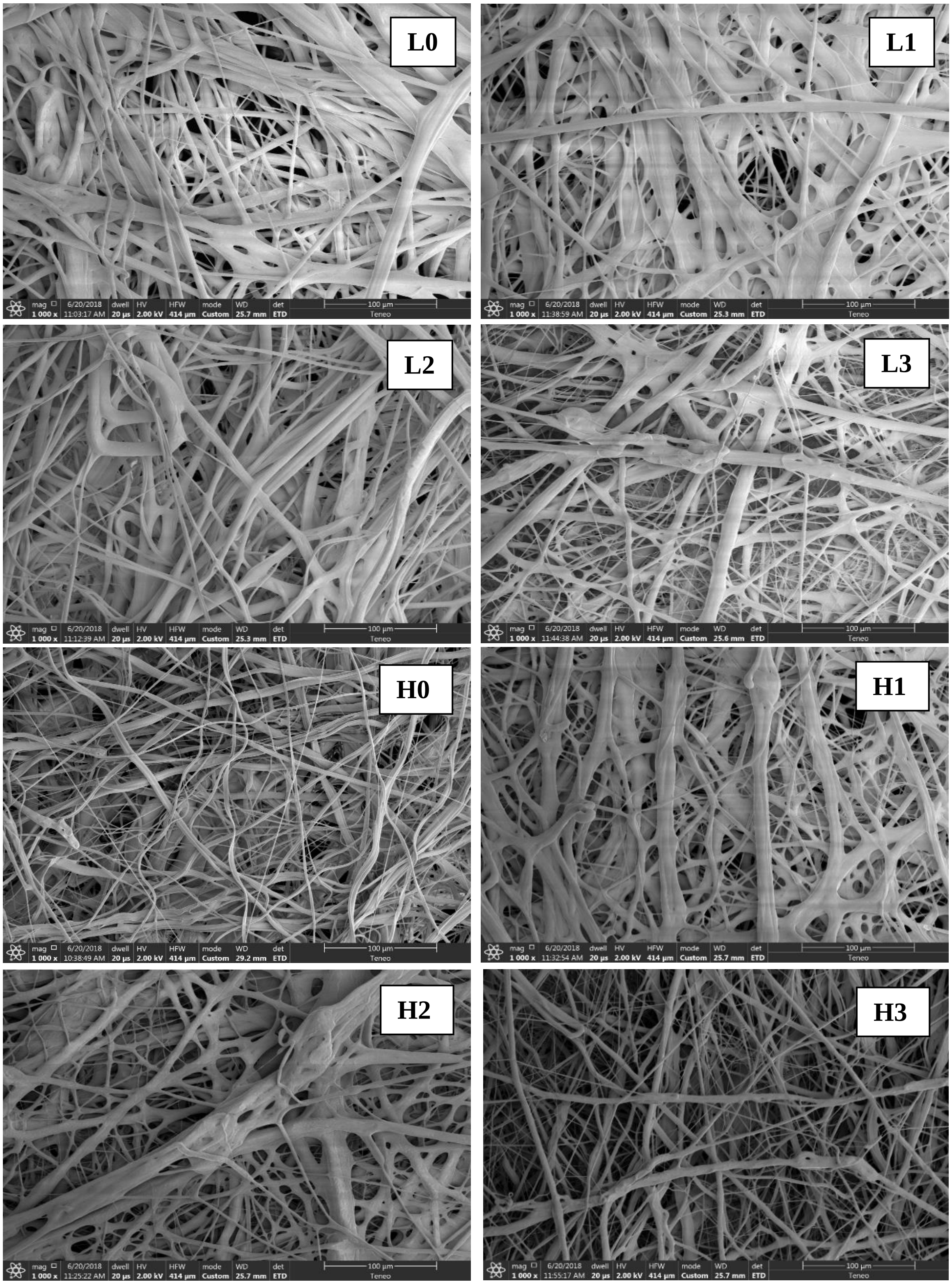
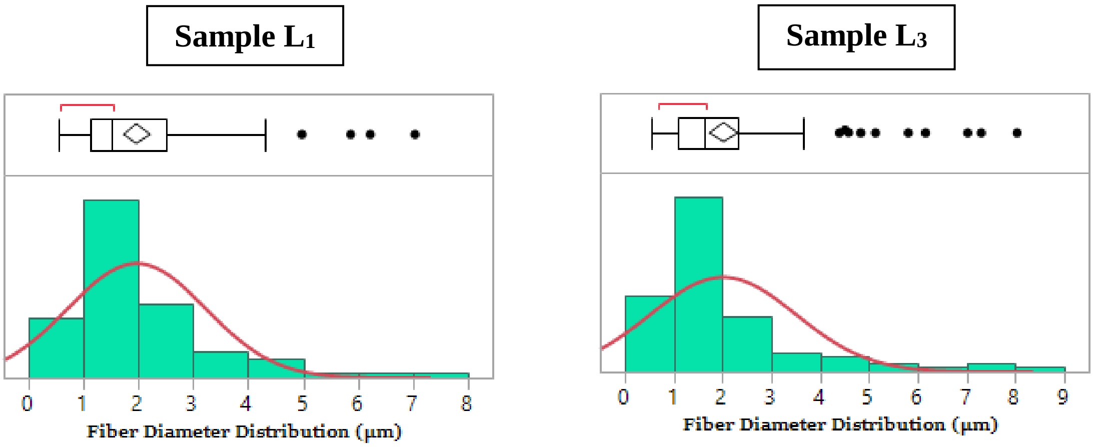


Figure B.1 SEM Images of Samples (L0 to L3) and (H0 to H3)



Summary Statistics	
Mean	1.96919
Std Dev	1.2549778
Std Err Mean	0.1254978
Variance	1.5749693
Minimum	0.537
Maximum	7.037
Median	1.523

Summary Statistics	
Mean	2.01452
Std Dev	1.4893267
Std Err Mean	0.1489327
Variance	2.2180939
Minimum	0.54
Maximum	8.036
Median	1.625

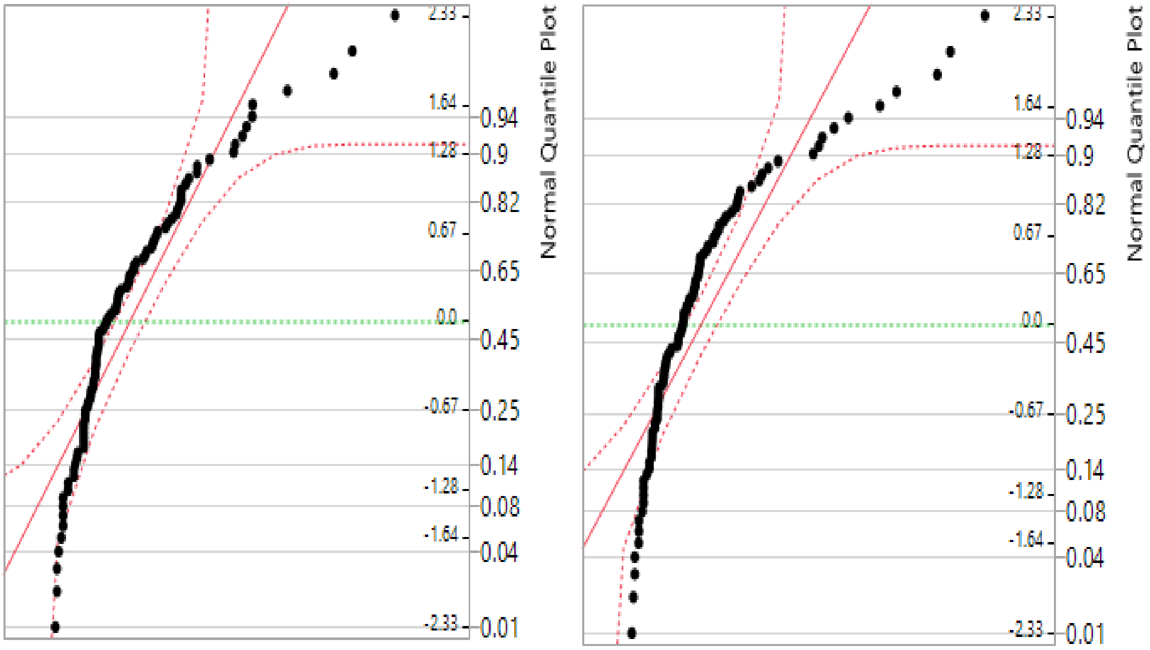
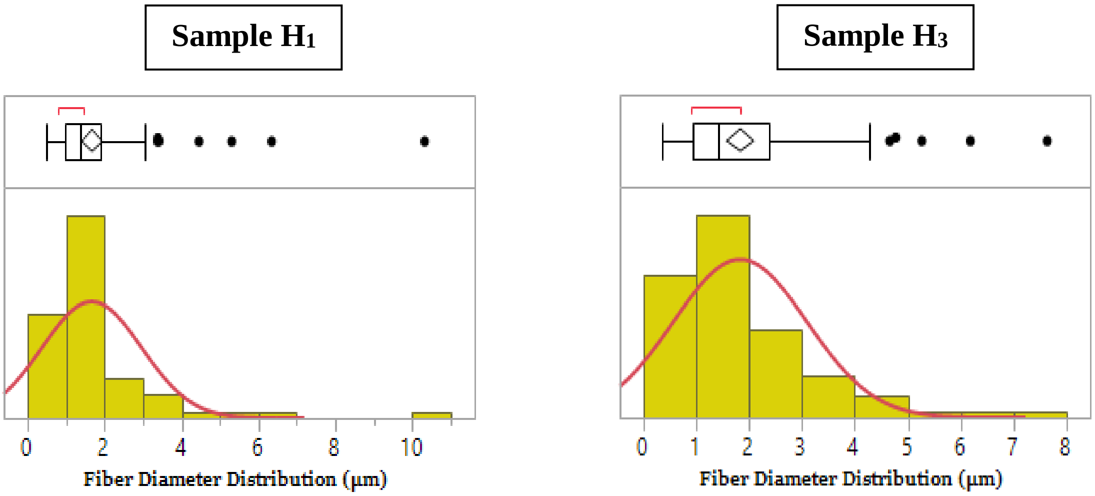
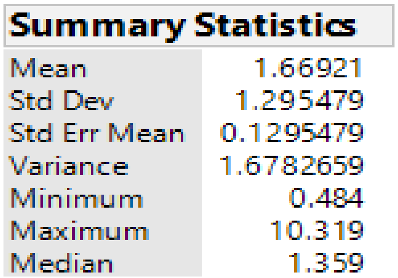


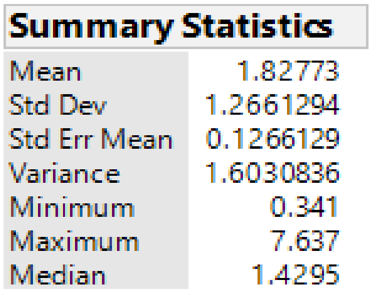
Figure B.2. Fiber Diameter Distribution and Normal Quantile Plot of Samples L1 and L3.





Summary Statistics

Mean	1.66921
Std Dev	1.295479
Std Err Mean	0.1295479
Variance	1.6782659
Minimum	0.484
Maximum	10.319
Median	1.359



Summary Statistics

Mean	1.82773
Std Dev	1.2661294
Std Err Mean	0.1266129
Variance	1.6030836
Minimum	0.341
Maximum	7.637
Median	1.4295

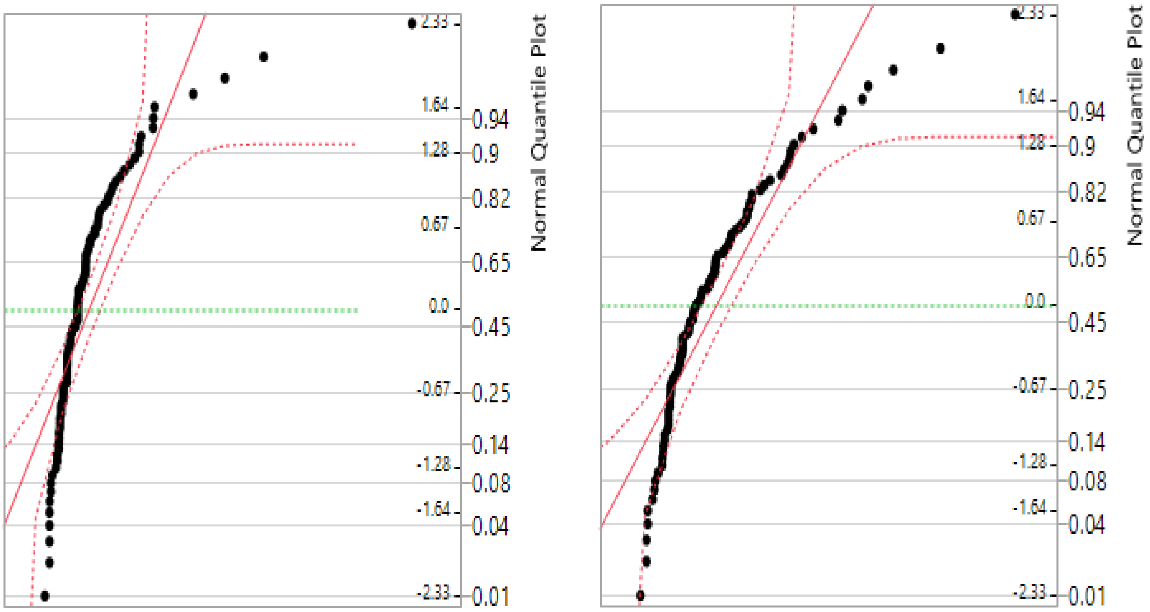


Figure B.3. Fiber Diameter Distribution and Normal Quantile Plot of Samples H1 and H3.

APPENDIX C

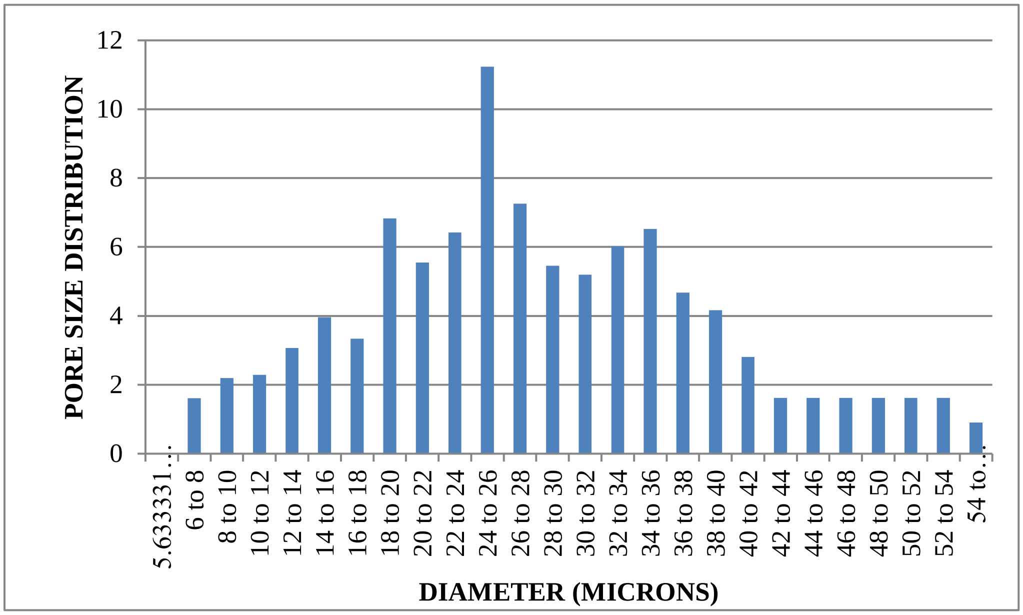


Figure C.1. Pore Distribution vs. Diameter for Sample L0

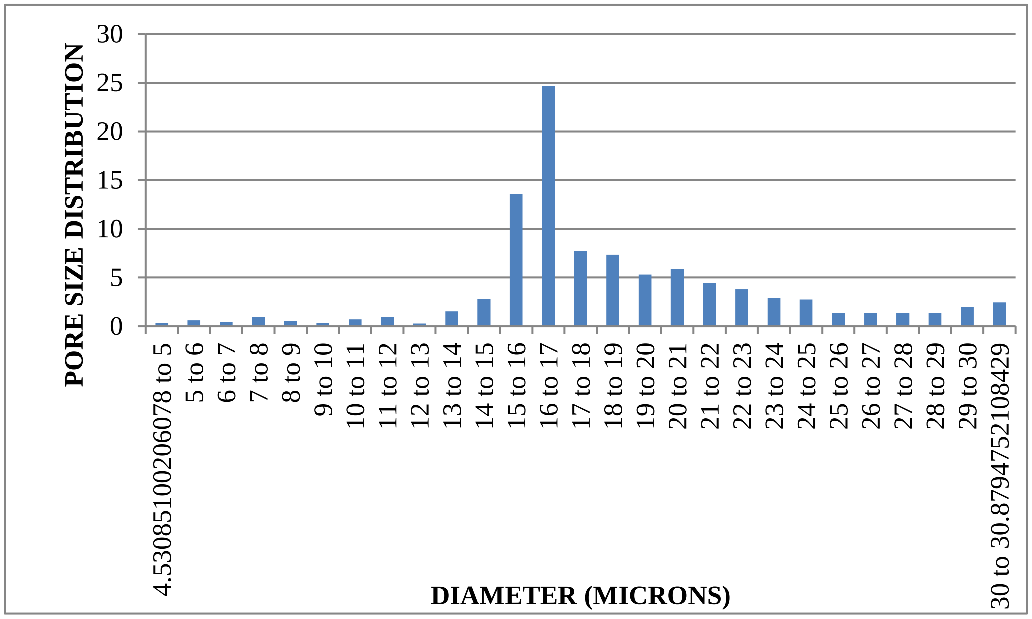


Figure C.2. Pore Distribution vs. Diameter for Sample L1

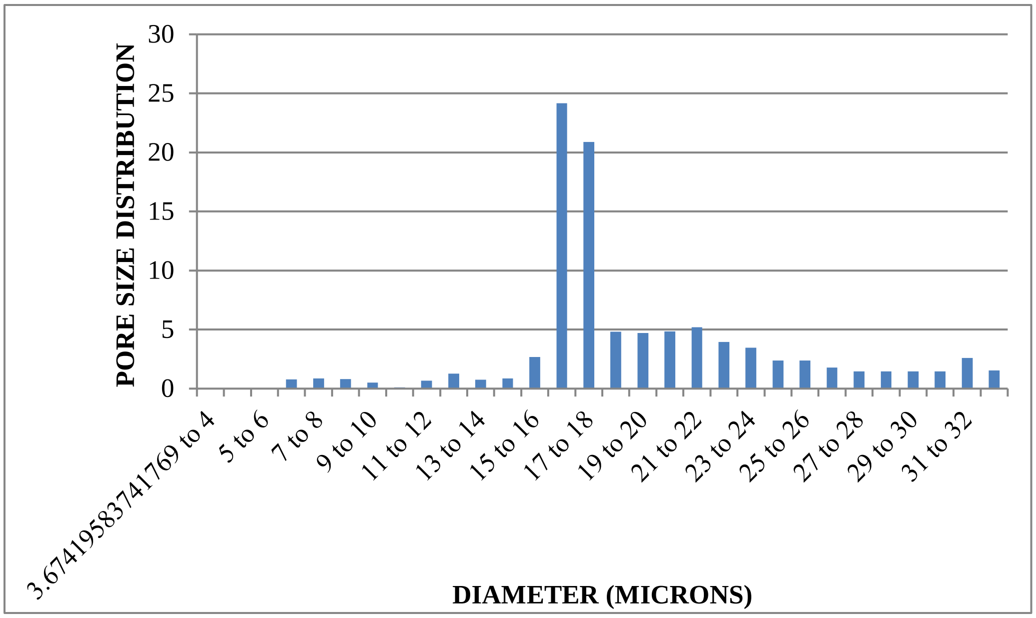


Figure C.3. Pore Distribution vs. Diameter for Sample L2

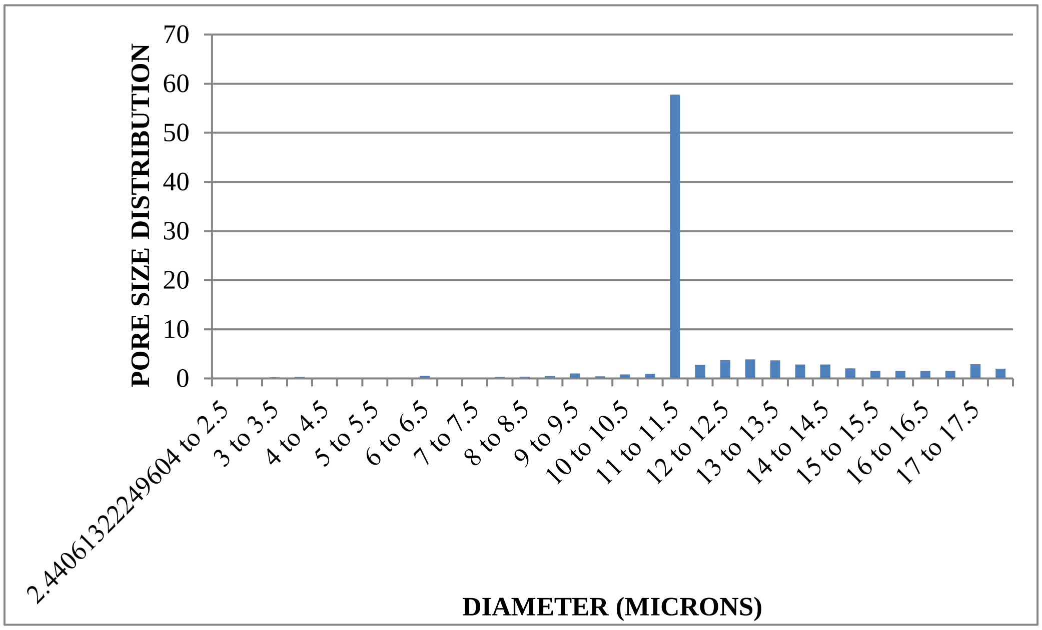


Figure C.4. Pore Distribution vs. Diameter for Sample L3

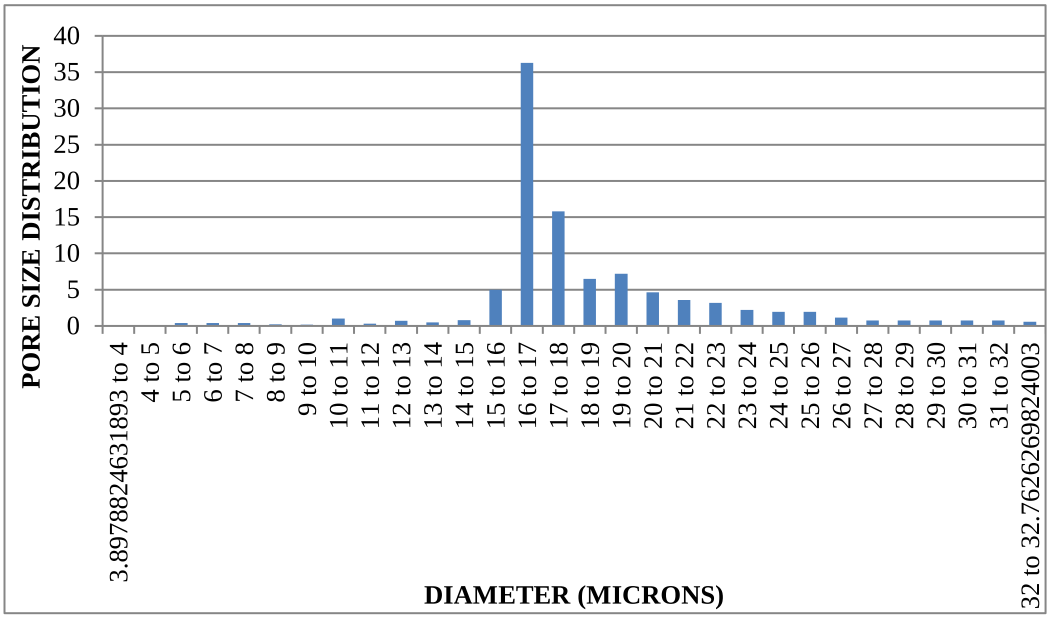


Figure C.5. Pore Distribution vs. Diameter for Sample H0

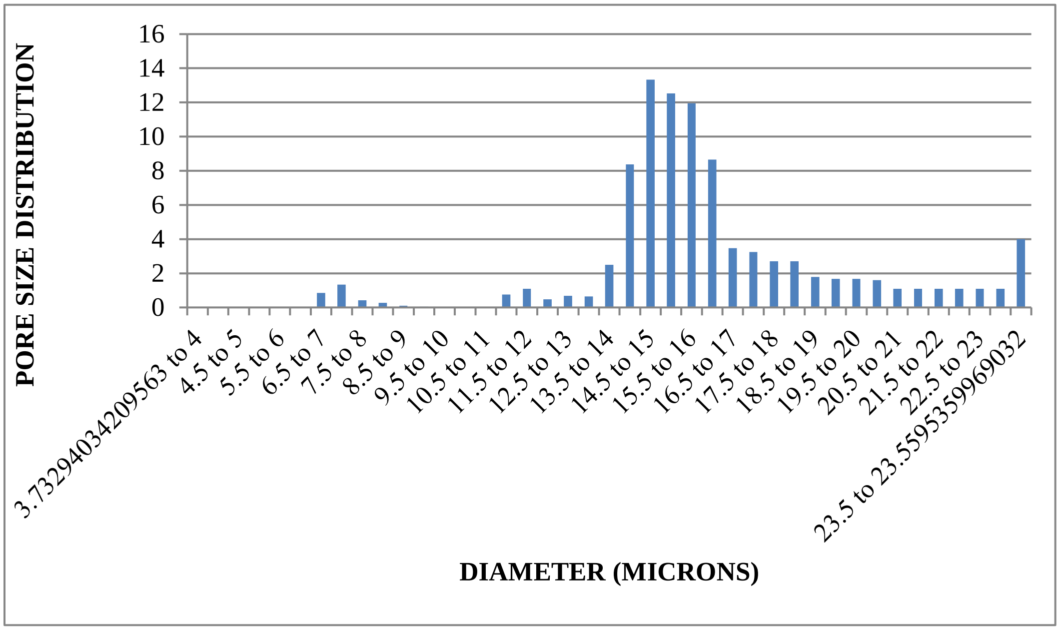


Figure C.6. Pore Distribution vs. Diameter for Sample H1

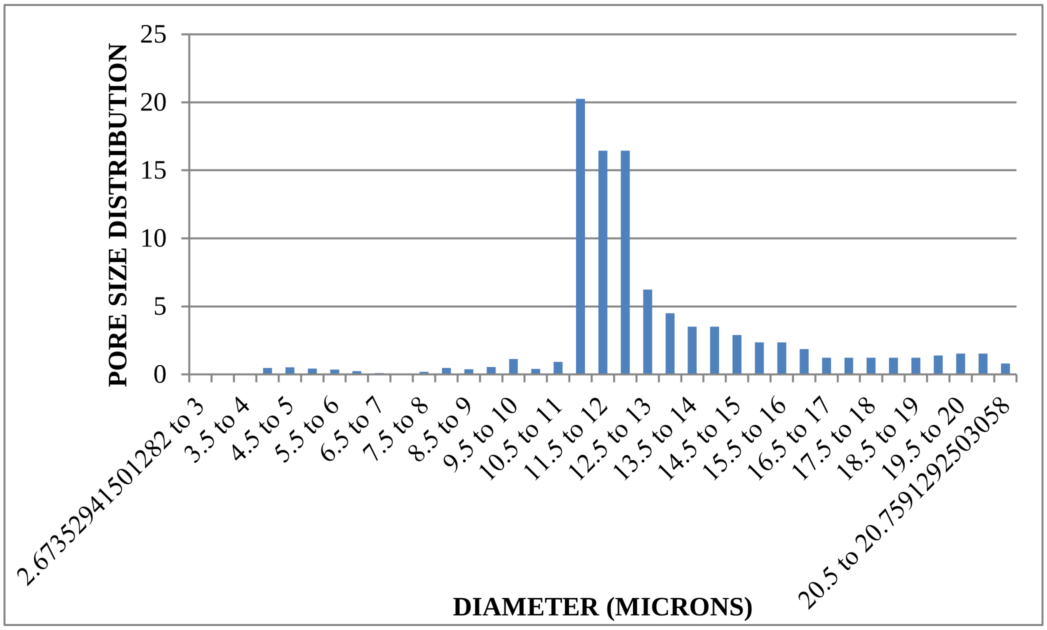


Figure C.7. Pore Distribution vs. Diameter for Sample H2

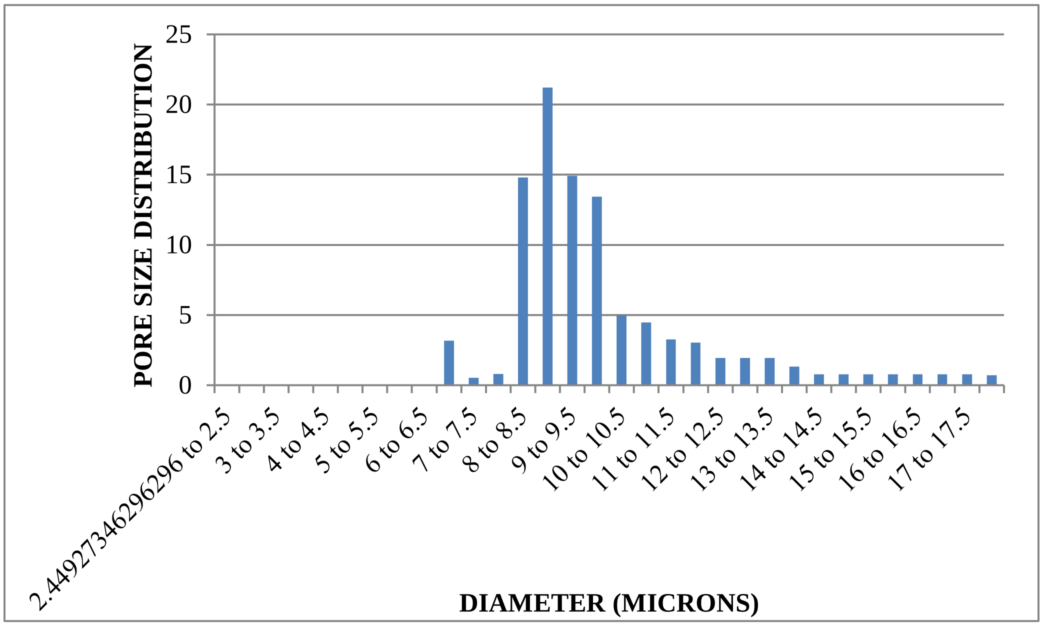


Figure C.8. Pore Distribution vs. Diameter for Sample H3

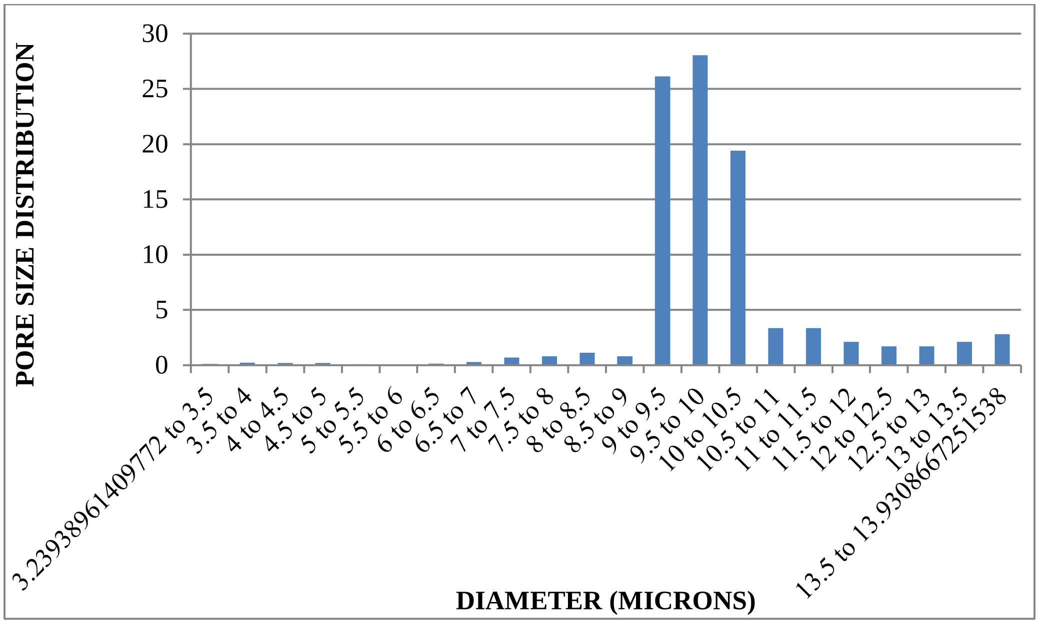


Figure C.9. Pore Distribution vs. Diameter for Sample S1

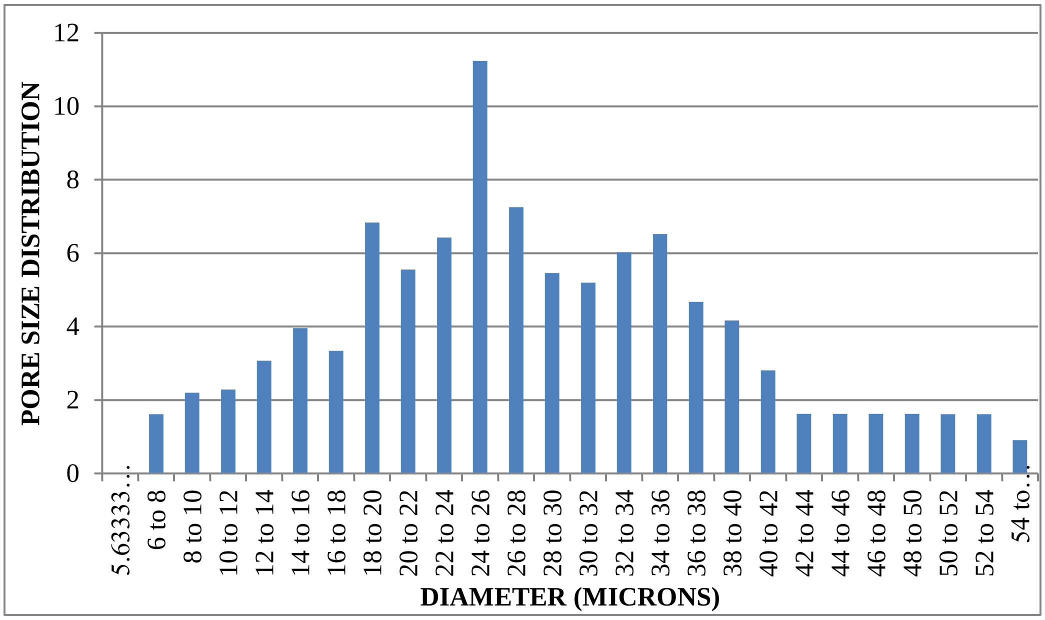


Figure C.10. Pore Distribution vs. Diameter for Sample S2