STRATEGIES TO MANUFACTURE POLY(LACTIC ACID) BLOWN FILMS WITHOUT MELT STRENGTH ENHANCERS

By

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ABSTRACT

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Poly (lactic acid) (PLA), a bio-based polymer derived from renewable resources, is an alternative to petroleum-based polymers because it reduces general dependency on oil availability and environmental concerns of common petroleum-based plastics, among others. Despite these attributes, PLA has relatively few commercial applications, concentrating mainly in the biocompatible biomedical device markets and as a commodity polymer for rigid containers and bottles used for packaging. However, its widespread applicability in flexible sheets/films is limited because of several drawbacks, among which its insufficient melt strength and low thermal stability, leading to narrow processing windows. Melt strength enhancers (MSEs) are often blended with PLA matrix to increase its melt strength, allowing the extrusion blowing and casting of the films. However, these additives are costly and not approved for food applications. Hence, there is a need to manufacture PLA films without any MSEs.

Processing strategies were developed in this study to produce PLA blown films without any MSEs. Using a thermodynamic approach, the effects of various processing conditions and material characteristics on PLA's melt rheology (zero shear, shear and elongational viscosities) and film's blow-up ratio (BUR) were examined. Experimental results indicate that extrusion-blown PLA films could be successfully manufactured without MSEs, irrespective of PLA's degree of crystallinity, by tailoring the melt rheology through processing temperature and controlling other processing conditions such as the film's take-up ratio, as well as internal and external air pressures.

Dedicated to my parents
Sanjay and Mohana Karkhanis

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Chapter 1

INTRODUCTION

1.1 Introduction

Poly(lactic acid) (PLA), a plant-based biodegradable plastic, is a sustainable alternative to petroleum-based polymers because it reduces U.S dependency on foreign oil and provides solutions to the environmental concerns about the use of petroleum-based plastics [1-7]. PLA exhibits many properties equivalent to or better than its petroleum-based counterparts [8]. It has high stiffness, reasonable strength, excellent flavor and aroma barrier, as well as good grease and oil resistance [1-7].

PLA's attractive properties make it a major global market, valued at $304.9 million in 2014, with packaging accounting for 54.6% of its share [9]. Recent statistics forecast a rapid growth in this market and estimate its value at $851.5 million by 2019, registering a compound annual growth rate (CAGR) of 22.8% between 2014 and 2019 [9]. Packaging is expected to remain the dominant application segment over the forecast period [9].

Rigid packaging was reported as the largest contributor to PLA's overall packaging demand in 2013 [10]. However, its applicability in flexible packaging is limited due to several drawbacks such as brittleness, poor water barrier properties, and processing difficulties because of its insufficient melt strength [11, 12] and low thermal stability [13], leading to a narrow processing window [14]. The low melt strength of PLA is attributed to the chain scission reactions that occur when it is subjected to shear and temperature in an extruder. These reactions lower its molecular weight and negatively impact molecular weight dependent properties such as shear and

elongational viscosities, resulting in insufficient melt strength. PLA's inadequate melt strength poses challenges for its processing into flexible film through manufacturing processes that require stretching or orientation, such as blown and cast film extrusion, as well as foaming [15].

In blown film extrusion, a polymer is melted and extruded through an annular die, drawn upward by the take-up rollers, inflated by the introduction of air inside the polymer tube and cooled by an air ring at a certain distance from the die exit to form a film. However, PLA's low melt strength hinders the upward drawing of its extruded melt by the take-up rollers, making the formation of an inflatable polymer tube difficult and leading to accumulation of the polymer near the die exit, known as melt sag.

Furthermore, PLA's insufficient melt strength prevents it from being used in cast film extrusion. In cast film extrusion, the molten polymer is extruded through a slit die, stretched until it touches the surface of a chill roller and quenched and solidified to form a sheet or film. Unfortunately, necking occurs after the extruded PLA exits the die due to its low melt strength [15], resulting in films with non-uniform thickness and smaller width than intended.

Foaming is another process which requires stretching of the polymer, especially during cell growth, wherein, lack of melt strength can lead to cell coalescence, thus affecting the cell morphology of PLA foams [16]. Therefore, PLA's melt strength is extremely vital for its processing into films and foams.

Chain extenders such as multi-functional epoxies [11-13, 17], 1,4-butane di-isocyanate [18] and hexamethylene di-isocyanate [19] among others are often blended with PLA matrix to increase its melt strength. These additives increase PLA's molecular weight by introducing branching, thereby increasing its shear and elongational viscosities. This leads to improved melt

strength which facilitates the blown film extrusion process [11, 12, 20] and other processes such as casting and foaming [13, 17].

Recently, various research efforts have been devoted to increase the melt strength of PLA with the use of multi-functional epoxies for foaming applications. For example, Mihai and co-workers [13] investigated the shear and elongational behaviors of extrusion foamed amorphous and crystalline PLA with the addition of up to 2% multifunctional styrene-acrylic-epoxy copolymer using carbon dioxide (CO_2) as a blowing agent. They reported an increase in the elongational and shear viscosities, as well as strain hardening of PLA with increasing chain extender content, irrespective of PLA's crystallinity. The chain extension facilitated a reduction from 65 to 36 kg/m^3 in foam density of crystalline PLA with 5% CO_2 concentration as a result of better cell wall stabilization due to chain branching at low blowing agent concentration. Nevertheless, amorphous PLA foams were unaffected by chain extenders.

Multi-functional epoxies have also been used to melt strengthen PLA for blown film applications. Recently, investigators [11, 12] used various formulations of PLA with multi-functional epoxy, nucleating agents and plasticizers to melt strengthen and blow PLA film. They have also reported an increase in shear and elongational viscosities of PLA with increasing multi-functionalized epoxy content. These investigators produced extrusion-blown neat PLA films with a blow-up ratio (BUR) of about 3.5 but resorted to melt blending PLA with 0.5% multi-functional epoxy to enlarge its blown film processing window. This PLA/multifunctional epoxy formulation in addition to 10% polyethylene glycol (PEG) as plasticizer, as well as 1% N,N'-ethylenbis (stearamide) (EBSA) and 1% talc as nucleating agents enlarged the processing window even more. However, the obtained film was translucent due to enhanced kinetics of crystallization of PLA enabled by the addition of these additives.

Moreover, two-step reactive modification of PLA with chain extenders such as 1,4-butane di-isocyanate in combination with 1,4-butanediol has been successfully used to increase PLA's viscosity by increasing its molecular weight. Di and coworkers [18] added 1,4-butanediol in the first step to react with PLA's carboxyl group and 1,4-butane di-isocyanate in the second step to react with its hydroxyl group to achieve chain extended PLA. They varied the amounts of these chain extenders to study their effect on the viscosities of PLA and their implications for foaming applications. They reported that excessive 1,4-butanediol degrades PLA while more 1,4-butane di-isocyanate produces highly cross-linked, high molecular weight PLA. The favorably viscous, cross-linked PLA allowed for the production of low-density foams with smaller cell-size and higher cell density compared to neat PLA.

Other techniques such as electron beam irradiation have additionally been carried out on glycidyl methacrylate (GMA)/PLA blends that introduce branching in PLA [21]. Irradiation of PLA induced chain scission reactions, lowering its molecular weight, in the absence of GMA. However, 10kGy irradiation of PLA in the presence of 3 phr GMA, increased the melt strength of PLA significantly.

Although blending PLA with the aforementioned additives increased its shear and elongational viscosities for foaming and other applications, these additives have various drawbacks. For example, multifunctional epoxies have not been approved for food applications. On the other hand, di-isocyanates are under scrutiny due to their toxicity, risk of occupational hazards [22] and their impact on the inherent biodegradability of PLA. Moreover, irradiation, has a low consumer acceptance and is approved for a limited number of food applications only by the United States Food and Drug Administration [23]. Given the additional cost of these additives, unfortunately, the approach of adding additives could also increase the material cost.

Due to the drawbacks of the additives and irradiation used to melt strengthen PLA, an alternative approach should be considered to successfully process PLA into films and foams. One such approach to increase the melt strength of PLA is through processing conditions such as processing temperature and shear rate, among others. To the best of our knowledge, a process to blow PLA films without melt strength enhancers (MSEs) has not been reported. Blowing PLA films without toxic, costly, and petroleum-based MSEs will reduce material cost and broaden the application of PLA films in food packaging without affecting the inherent biodegradability of PLA.

In order to produce PLA films without MSEs, selection in this study designated a control of the melt strength through processing temperatures as a strategy to alter the elongational viscosity during extrusion-blown film. The processing temperature has a great influence on the processability of PLA because of its effect on the shear viscosity, as described by the Arrhenius equation (Equation 1.1). As the equation suggests, the shear viscosity varies inversely with the processing temperature; i.e., the higher the processing temperature, the lower the shear viscosity and, vice versa.

$$\eta = A_0 \exp\left(\frac{E_a}{R \cdot T}\right) \qquad \text{(Equation 1.1)}$$

where η is the shear viscosity, A_0 is a constant, R is the universal gas constant and T is the absolute temperate, and E_a is the activation energy of melt flow [14, 24].

Additionally, the shear viscosity is related to the elongational viscosity as described by the Cogswell's equation (Equation 1.2) [16, 25-27]. Generally, the elongational viscosity varies directly with the shear viscosity, i.e., as the shear viscosity increases, the elongational viscosity increases and vice versa.

$$\eta_e = \frac{9 \cdot (n+1)^2 \cdot (\Delta P_e)^2}{32 \cdot \eta_a \cdot \gamma_a^2} = \frac{9 \cdot (n+1)^2 \cdot (\Delta P_e)^2 \cdot \eta_a}{32 \cdot \tau_a^2} \qquad \text{(Equation 1.2)}$$

where η_e is the elongational viscosity, n is the flow behavior index, ΔP_e is the pressure drop at the capillary entrance, η_a is the apparent shear viscosity, and γ_a is the apparent shear rate which is defined as the ratio of the apparent shear stress, τ_a to η_a.

Since, it is essential to increase the elongational and shear viscosities of PLA through MSEs or irradiation to blow films, it is hypothesized that PLA blown films could be manufactured without MSEs by tailoring the shear and elongational viscosities through a control of the processing temperature. Processing at a lower temperature would lead to an increase in the shear and elongational viscosities and favor the blown film extrusion process of PLA.

Moreover, processing conditions such as take-up ratio (TUR), as well as internal and external air pressures are important processing variables in the blown film extrusion process that have a significant impact on the frost line, in turn affecting the stability of blown films. Hence, it is crucial to optimize these conditions in order to obtain stable PLA films.

The aim of this study was to develop processing strategies to manufacture blown PLA films without any melt strength enhancers. This study examined the effect of temperature on shear and

elongational viscosities in order to identify the optimum temperature for extrusion-blown film. Specifically, the effects of extrusion processing variables and material characteristics on the BUR were evaluated to identify appropriate processing conditions and formulations to blow PLA films without melt strength enhancers.

1.2 Objectives

The goal of this study is to develop processing strategies to manufacture blown PLA films without any MSE. To achieve this objective, the following specific objectives were proposed:

1. Study the effect of temperature on shear and elongational viscosities in order to identify the optimum temperature for extrusion-blown film.

2. Evaluate the influence of extrusion processing conditions such as the TUR and internal air pressure on the BUR and stability of the films to determine appropriate conditions for the manufacture of blown PLA films without MSEs.

3. Gain an in-depth understanding of the effect of material characteristics such as melt flow index and crystallinity of different grades of PLA on the stability and BUR of blown PLA films with the ultimate goal of identifying the optimum formulation for blown film extrusion.

1.3 Hypothesis

This research is intended to test the hypothesis that extrusion-blown PLA films without MSEs could be manufactured by not only controlling the elongational viscosity through the processing temperature but also by controlling the frost line through processing conditions such as TUR, as well as internal and external air pressures.

1.4 Structure of thesis

The first chapter of the thesis introduces the rationale of this research. A background on poly lactic acid and current approaches used to process PLA, specifically blown film extrusion, are reviewed in Chapter 2. The experimental methods, including material specifications, equipment and sample manufacturing are described in Chapter 3. The results of the effect of processing temperature and other processing parameters on the blow-up ratio and feasibility of film production are discussed in Chapter 4. Chapter 5 gives the summary of the findings inferred from the experimental data and proposed future work.

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Chapter 2

BACKGROUND AND LITERATURE REVIEW

2.1 Introduction

Consistent with the scope of this study, a background and literature review on the current approaches used to process and melt strengthen poly (lactic acid) (PLA) are presented in this chapter. The review focuses on the blown film extrusion process used for manufacturing PLA films and the effects of rheological properties on the processing of PLA.

2.2 Poly (lactic acid)

Poly (lactic acid) is a biodegradable and compostable thermoplastic derived from renewable resources such as corn, sugar beets and rice [1]. It exhibits reasonable strength, high stiffness, good heat sealability, excellent flavor and aroma barrier, as well as good grease and oil resistance [2-4].

2.2.1 Synthesis of PLA

Lactic acid, the basic building block of PLA, is a simple chiral molecule which exists as two optically active enantiomers, L and D-lactic acid (Figure 2.1). It can be converted into three types of cyclic dimmers: L-lactide, D-lactide and meso-lactide (Figure 2.2).

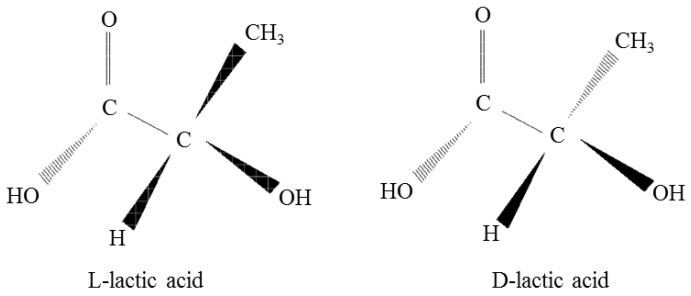


Figure 2.1 Chemical structure of L-Lactic acid and D-Lactic acid

Lactic acid is produced by fermentative or chemical synthesis [5]. The most popular route for producing lactic acid is by bacterial fermentation using genetically modified Lactobacillus to convert sugar and starches into lactic acid [6, 7]. Other routes for chemical synthesis of lactic acid include base-catalyzed degradation of sugars, oxidation of propylene glycol, reaction of acetaldehyde, carbon monoxide, and water at high temperature and pressure, hydrolysis of chloropropionic acid, and nitric acid oxidation of propylene, among others [8].

PLA is usually produced from lactic acid by two methods: (1) direct polycondensation of lactic acid or (2) ring opening polymerization (ROP) of lactide. The direct polycondensation method requires higher reaction times and entails the use of solvent to produce low to intermediate molecular weight PLA. Conversely the ROP method uses catalyst and produces PLA with controlled molecular weight [6, 9]. Cargill Dow LLC is one of the manufacturers of PLA which has exploited the ROP of lactide to produce about 300 million pounds of NatureWorks PLA per year [10].

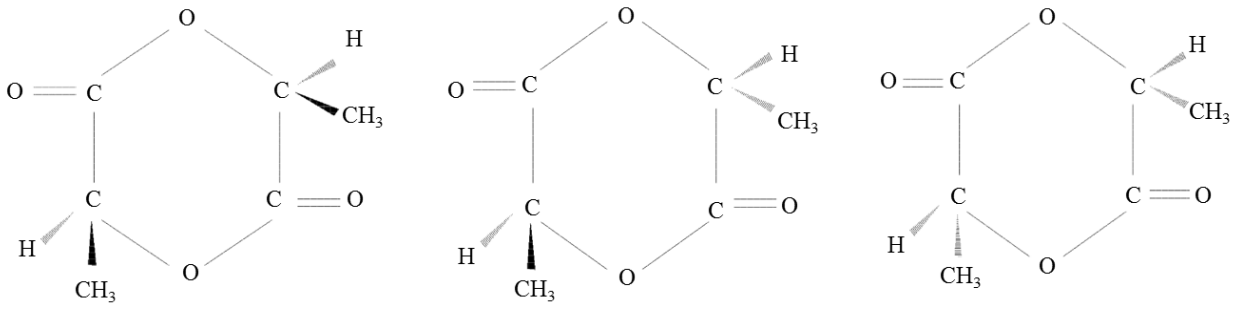


Figure 2.2 Stereochemistry of lactide

The ROP of lactide can be carried out using anionic, cationic or co-ordination mechanisms [11, 12]. Anionic mechanisms often result in back-biting reactions and other side reactions due to the highly active anionic reactants. Moreover, cationic mechanisms result in undesirable side chain reactions due to nucleophilic attacks on the activated monomers or propagating species. These mechanisms result in polymer chains with low molecular weight and low crystallinity. Conversely, coordination polymerization with metal catalysts such as tin (II) octoate, result in high molecular weight polymer chains with a high degree of crystallinity. Consequently, coordination polymerization is the preferred method for the industrial production of PLA [13].

2.2.2 Properties of PLA

The thermal, rheological, mechanical and barrier properties of PLA vary with the degree of crystallinity. The degree of crystallinity of PLA can be controlled by adjusting the relative amounts of L and D-lactide stereoisomers in the polymer. Generally, PLA made from more than 93% L-lactic acid is semi-crystalline while PLA made from 50-93% L-lactic acid is amorphous [14]. Semi-crystalline PLA has higher glass transition and melting temperatures than amorphous PLA. It also tends to have better mechanical, barrier and rheological properties.

2.2.2.1 Thermal properties

PLA has a glass transition temperature between 40 and 70^{o}C and a melt temperature between 130 and 180^{o}C [15]. Thermal properties of PLA vary with the L-lactide content; higher L-lactide content increases T_m and T_g [16].

2.2.2.2 Mechanical properties

PLA has mechanical properties comparable to those of conventional polymers. It has an elastic modulus between 3000-4000 MPa and a tensile strength between 50-70 MPa (Table 2.1) [17]. However, PLA has low impact strength compared to other petroleum-based plastics (Table 2.1). PLA's impact strength increases with increasing molecular weight and crystallinity [18]. It is also highly sensitive to notching and material processing. The notched Izod impact resistance of semi-crystalline PLA ranges from 3-7 kJ/m^2 while the unnotched Izod impact resistance ranges from 18-35 kJ/m^2 [17].

2.2.2.3 Barrier properties

Barrier properties of packaging materials determine the ability of the material to obstruct the flow of permeants such as water vapor, oxygen (O_2) and carbon dioxide (CO_2). These properties are particularly useful in determining the applications of polymers in food packaging. For instance, a dry food product is more likely to be packaged in a plastic that is a good barrier to water vapor to prevent water absorption and consequently sogginess of the product.

Barrier properties of materials are generally characterized by parameters such as permeability, diffusivity and solubility. Higher permeability of a material decreases its barrier properties. Auras and co-workers reported that PLA has O_2 and CO_2 permeability coefficients

comparable to those of polyethylene terephthalate (PET), but lower than polystyrene (PS) [19]. A comparison of PLA's barrier properties with those of other petroleum-based polymers is listed in Table 2.1.

Table 2.1 Comparison of PLA properties with other petroleum-based polymers [19-22]

Properties	PLA	PET	PS	PP
T_g (^{0}C)	55	75	105	-10
Density (g/cc)	1.24	1.33	1.05	0.9
Tensile Strength at Break (MPa)	53.09	54.47	44.82	31.03
Tensile Modulus (MPa)	3447	2758	2896	896
% Elongation	6	130	7	120
Gardner impact (kg-cm)	0.58	3.23	5.18	8.06
Water vapor permeability at 23^{0}C (10^{-13} kg-m/m^2-s-Pa)	80-360	110	670	225
Oxygen permeability at 25^{0}C, 70% RH (10^{-17} kg-m/m^2-s-Pa)	0.121	0.0188	27	498
Carbon dioxide permeability at 25^{0}C, 0% RH (10^{-17} kg-m/m^2-s-Pa)	2.77	0.173	15.5	1080

2.2.2.4 Rheological properties

Rheology is the study of flow and deformation of matter. It is extremely important to understand the flow behavior (or rheology) of a plastic because plastics are usually shaped into articles in their molten state. Generally, flow properties of a plastic are measured by measuring their shear viscosity. Shear viscosity of a fluid is defined as its resistance to flow when subjected to shear. The shear viscosity of plastics is molecular weight and temperature dependent; higher molecular weight increases the shear viscosity while higher temperature decreases it [23].

Figure 2.3 shows a typical curve for logarithmic shear viscosity vs logarithmic shear rate. At very low shear rates, the viscosity is independent of shear rate. This region of the graph is known as the Newtonian region. In contrast, the region where the viscosity varies with shear rate is known as the power-law region or the non-Newtonian region. The viscosity in the Newtonian region, at very low shear rates is known as the zero shear viscosity whereas the viscosity in the non-Newtonian region is known as the shear viscosity. In this study, both the zero shear and shear viscosities of PLA were measured at various temperatures to determine the effect of temperature on PLA's flow behavior.

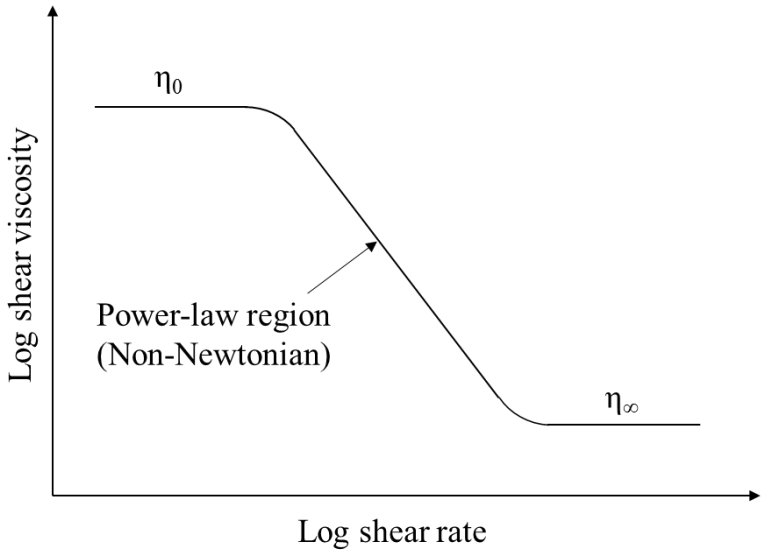


Figure 2.3 Typical viscosity vs shear rate curve

Another important rheological parameter is melt strength. Melt strength is the maximum force required to break an extruded strand and is related to shear and elongational viscosities of plastics. Elongational viscosity can be defined as the resistance of a fluid in extension. Higher shear and elongational viscosities result in higher melt strength.

Melt strength is especially important in blown and cast film extrusion, as well as foaming. Low shear and elongational viscosities of PLA resulting in low melt strength limit its processing into films by blown and cast film extrusion [24]. In blown film extrusion, PLA's lack of melt strength hinders the formation of an inflatable polymer tube and leads to accumulation of the polymer near the die exit, known as melt sag. Researchers have blended PLA with additives [25-30] in order to increase its molecular weight and consequently melt strength. Some of these strategies have been described in the previous chapter. However, these additives have various drawbacks. Hence, alternate strategies to overcome this issue should be considered.

It is important to note that PLA is susceptible to hydrolytic and thermal degradations, which affect viscosity measurements and processing of PLA. It is hence crucial to dry the material before processing. Additional stabilizers may be added to prevent polymer degradation [23].

2.3 Processing technologies of PLA

Melt processing is most widely adopted for converting PLA resins into useful end products. This process involves melting PLA above its melting point to reshape it, followed by cooling it below its glass transition temperature to freeze its dimensions. Melt processed PLA has been converted into thermoformed containers and cups, injection stretch molded bottles and extruded cast films for packaging applications. Moreover, it has been melt-spun into textiles and carpets [24]. In this section of the chapter, blown film extrusion will be described in detail. Additionally, cast film extrusion and other processing methods such as thermoforming and blow molding will be discussed.

2.3.1 Drying

PLA is subject to hydrolytic degradation. Therefore, PLA resins should be dried before melt processing to prevent the loss of physical properties. It is generally dried to less than 250ppm moisture before processing. Typically, a temperature between 60^0C-90^0C is used to dry it. PLA should preferably be dried below its T_g to prevent sticking of pellets. The time required to dry PLA depends on the drying temperature [24].

2.3.2 Extrusion

Extrusion is one of the most common technique for producing a homogenous PLA melt which can then be shaped into bottles using blow molding, or into sheets and films using cast and blown film extrusion processes. A conventional extruder consists of three main sections: (1) the feed section that receives the polymer and conveys the polymer into the screw; (2) the compression section that has a decreasing screw diameter to compress the polymer pellets; (3) the metering section that acts as a pump to meter the required quantity of polymer to the forming die [24]. Dies are used to convert the polymer melt into the desired shape. Flat dies (or slit dies) are used in cast film extrusion to produce films and sheets, annular dies are used in blown film extrusion to produce pipes or tubular films, and capillary dies are used to produce rods and filaments.

2.3.2.1 Blown film extrusion

Blown film extrusion is one of the most widely used method for manufacturing films. In fact, blown film extrusion accounts for 85% of polyethylene film production [31]. In blown film extrusion, a polymer is melted and extruded through an annular die to form a polymer tube which is inflated into a bubble by blowing air into the tube. The formed bubble is cooled by an air ring at a certain distance from the die exit, and flattened and drawn upward by the take-up rollers. The cooled and flattened film is then collected by a winder. The inflation of the tube results in the film's orientation in the transverse direction while the drawing action of the take-up rollers results in orientation in the machine direction. Thus, the formed bi-axially oriented film has better balance of mechanical properties in both directions. Moreover, another advantage of the blown film extrusion process is that films of various widths and thicknesses can be produced using the same

die without significant trimming by varying the internal air pressure, rotational screw speed and take-up roller speed.

The following section summarizes the rheological requirements of a material to be processed in the blown film extrusion process. It also describes the variables of the blown film extrusion process and the defects encountered during the process.

2.3.2.1.1 Rheological requirements of material

Materials used with the blown film extrusion process should have a high melt strength in order to be processed. Lower melt strength of polymers can result in sagging of the polymer upon exiting the die before being solidified. Shear and elongational viscosities are measured to estimate the melt strength of a polymer.

A study was performed on two linear low density polyethylenes (LLDPEs), one with a melt index of 0.5 and another with a melt index of 1.0. The melt index was used to estimate the shear viscosity of a polymer. Generally, a lower melt index results in a higher shear viscosity and consequently higher melt strength. In this study, the researchers found that the LLDPE with a lower melt index and consequently higher melt strength had better bubble stability [32].

Furthermore, studies have been performed on low density polyethylene (LDPE) and LLDPE in order to evaluate their elongational viscosities and hence their melt strength. The effect of the difference in their elongational viscosities on the processability of these plastics in the blown film extrusion process has been studied. Researchers have found that LDPE has a higher elongational viscosity than LLDPE due to its branched structure. In the film blowing process,

LDPE bubbles exhibit more stability than the LLDPE bubbles due to their higher elongational viscosity [33].

To summarize, higher shear and elongational viscosities result in better bubble stability. Thus, high shear and elongational viscosities are often desired in materials to be processed by the blown film extrusion process. However, it is worth mentioning that studies have shown that elongational viscosity has a more profound effect on the bubble stability than shear viscosity. Shear viscosity plays a more important role in determining the extruder power consumption and extrusion pressures during the process [33].

PLA has low shear and elongational viscosities. It is thus difficult to obtain PLA blown films. Researchers often use chain extenders to increase PLA's shear and elongational viscosities to blow PLA films [25-30]. However, chain extenders are often not approved for food applications and add to the material cost. Thus, the goal of this study is to manufacture PLA blown films without the use of any additives.

2.3.2.1.2 Processing parameters affecting film quality

Processing temperature, take-up ratio (TUR), internal and external air pressures have been found to be important processing variables in the blown film extrusion process that have a significant impact on the stability of blown films [34].

The processing temperature, TUR, internal and external air pressures have a significant effect on the frost line height (FLH), which in turn has an impact on the stability of films. The frost line (FL) can be defined as the point at which the polymer solidifies and is no longer able to stretch. The distance from the die exit to the FL is known as the FLH. FLH has a significant impact on the

stability of the films. The FLH should not be too low or too high to process a film without defects. If the FLH is too high, the polymer tube may not be able to support its own weight until the FLH, resulting in melt sag. Conversely, if the FLH is too low, the bubble will stop expanding very close to the die exit, resulting in a thick film with a low bubble diameter. The following section describes the importance of the processing variables and their impact on the FLH and hence bubble stability.

2.3.2.1.2.1 Temperature profile

The temperature profile refers to the temperatures of the different zones in an extruder. The temperature profile in an extruder should be high enough to melt a polymer. Additionally, the temperature profile can also be used to control the viscosity of a polymer. As mentioned earlier, the blown film extrusion process requires high shear and elongational viscosities of a polymer. These properties of a polymer are temperature dependent. A lower processing temperature results in higher shear and elongational viscosities [35, 36]. This known scientific fact will be used in this study to increase the shear and elongational viscosity of PLA in order to manufacture PLA blown films.

2.3.2.1.2.2 Take-up ratio (TUR)

The TUR is the ratio of the velocity of the take-up rollers to the velocity of the rotational screw of the extruder. It basically determines how fast the polymer tube is being pulled away from the die exit. The drawing or pulling action of the polymer tube results in its orientation in the machine direction. Mechanical and barrier properties increase with increasing orientation. Generally, increasing the TUR increases the FLH [37]. As the TUR increases, the take-up roller speed increases and the formed film is pulled away from the die exit and external cooling air faster.

Thus, the film is subjected to cooling for less time and solidifies slowly away from the die exit, resulting in a higher FLH.

2.3.2.1.2.3 Internal air pressure

The internal air pressure is used to inflate a polymer tube and has a significant impact on the blow-up ratio (BUR) of films. The BUR is defined as the ratio of the diameter of the blown film to the diameter of the annular die. Obviously, as the pressure used to inflate the polymer tube increases, the diameter of the bubble increases. Consequently, the BUR increases. The internal air pressure is responsible for the film's orientation in the transverse direction.

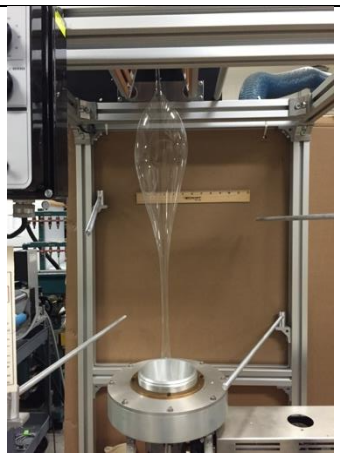
The FLH decreases with increasing BUR [37]. This occurrence can be explained by the more rapid heat transfer arising due to a large bubble diameter and hence a large surface area at a high BUR. Thus, a larger bubble solidifies faster and closer to the die exit, lowering the FLH.

2.3.2.1.2.4 External air pressure

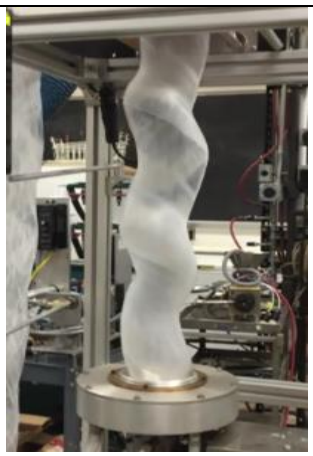
The external air pressure is used to cool the film. As the external air pressure increases, the polymer tube is cooled faster and closer to the die exit. Thus, the FLH is lowered [38].

2.3.2.1.3 Defects

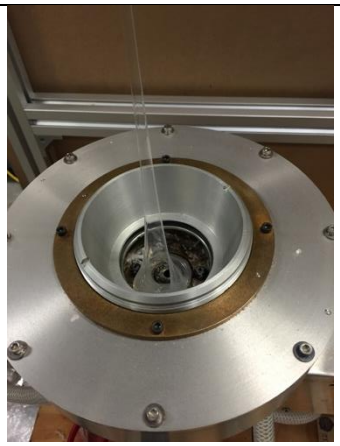
Improper temperature profile, TUR, internal and external air pressure can result in unsuitable FLH and can result in various film defects as shown in Figure 2.4 from our preliminary experiments.



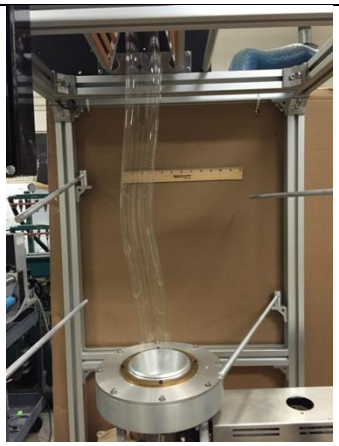
(a) Draw resonance



(b) Helical instability



(c) Melt sag



(d) Bubble dancing

Figure 2.4 Bubble instabilities in blown film extrusion produced in our laboratory

Han and Park studied the blown film extrusion process of high density polyethylene (HDPE), LDPE and polypropylene (PP) [39]. They reported draw resonance of films when the TUR exceeded a certain critical value. Draw resonance was characterized by a varying bubble diameter which resulted in a non-uniform film thickness (Figure 2.4 (a)). They also reported a wave-type bubble instability in LDPE caused by a small change in TUR. In this type of instability, the surface of the bubble resembled a travelling wave. Additionally, they found that increasing the melt temperature worsens the stability of bubbles [39]. Han and Shetty, in a different study,

concluded that the stability of bubbles in blown film extrusion can be enhanced by increasing the elongational viscosity of the polymer [40]. Another type of bubble instability, wherein the bubble diameter fluctuated drastically with time was observed at low BUR for PP. The magnitude of bubble diameter fluctuations worsened over time and eventually led to bubble breakage. A FLH instability was also reported for HDPE, LLDPE and PP. The bubble diameter fluctuated slightly along with pressure oscillations inside the bubble. Additionally, a helical instability was reported at high BURs (Figure 2.4 (b)). Helical instabilities have been reported as a development of helical motion between the die and nip rolls when the FLH moves from the upper limit to the lower one [41]. Melt sag has also been observed due to lack of melt strength [33]. Melt sag is the sagging of melt upon die exit prior to being cooled at the frost line (Figure 2.4 (c)). Another defect observed due a very low FLH is bubble dancing (Figure 2.4 (d)). Bubble dancing causes wrinkles and inconsistencies in film thickness [42].

2.3.2.2 Cast film extrusion

Cast film extrusion has been used to produce 10-12% of all polyethylene films [31]. In cast film extrusion, the extruded melt is forced through a flat die. The film exiting the die tangentially contacts a highly polished, water cooled chill roll wherein it is cooled and then carried to the winder. The film is stretched in the machine direction between the die and the chill rolls to the desired thickness [31]. Tenter frames are sometimes used to orient the film in the cross machine direction.

A common problem associated with cast film extrusion is necking, wherein the final width of the film is smaller than the initial die width. This problem is largely encountered while processing polymers with a low melt strength. The necking phenomenon usually takes place after

exiting the die and before touching the chill rollers. Various melt strength enhancers have been added to polymers such PLA which are subject to necking due to their low melt strength [25-30]. Additionally, PLA can be co-extruded with other polymers to enhance its properties forming multi-layer films.

2.3.2.3 Extrusion blow molding

Extrusion blow molding is a technique used to manufacture hollow products such as bottles and jugs. In the extrusion blow molding process, a parison is formed by extruding a thermoplastic through an annular die. Closing mold halves pinch off the continuously extruded parison. Air is blown into the parison to inflate it into the shape of the cavity after closing the mold. The thermoplastic cools on contact with the mold. The formed part is then ejected and trimmed. This process ensures stretching of the polymer in the radial direction by blowing air [43].

Materials processed using this method need to have a high melt strength. Without the appropriate melt strength, the parison will not have enough strength to support its own weight until the mold closes around it. It may elongate too much before the mold closes, if it is being extruded in the downward direction and can sag backwards on the die if it is being extruded upward.

2.3.3 Injection

Injection molding is a process used for manufacturing parts that require exacting tolerances. It is commonly used for manufacturing closures. It is also used for manufacturing preforms that are later converted into bottles using the injection blow molding or injection stretch blow molding process. In injection molding, polymers are heated and melted in an injection unit. The injection unit consists of a barrel, screw and nozzle. The screw resides in the barrel and

compresses, melts and conveys the plastic to the mold through the nozzle. The molten plastic is shaped in the mold which is opened, closed and clamped together by the clamping unit. Ejector pins are used to eject the formed plastic part after solidification from the mold. Injection molding requires polymers with low viscosity that flow easily to fill the molds [44].

2.3.3 1 Injection blow molding

The injection blow molding process is used to produce hollow shaped containers such as bottles. Bottles formed from this process require less trimming and are of higher quality compared to those produced by the extrusion blow molding process. Additionally, plastics with low melt strength can be processed with this method of manufacture.

In the injection blow molding process, a preform is produced from the injection molding process. The produced preform can be blown into bottles at a later stage. When the preform is ready to be blown into a bottle, it is placed inside a mold cavity and is reheated to soften. The mold cavity closes around the preform and air is blown into the preform. The preform stretches in the radial direction and conforms to the contours of the mold cavity. The formed part is then allowed to cool and ejected [44].

2.3.3 2 Injection stretch blow molding

The injection stretch blow molding process is distinguished from the injection blow molding process by an additional stretching step. In this process, the preform is stretched vertically by a plug in addition to being blown in the radial direction. Thus, the formed article is oriented in both machine and cross directions. This orientation offers better mechanical and barrier properties [44].

PLA is better suited for processing using injection blow molding that extrusion blow molding due to its low melt strength.

2.3.4 Thermoforming

Thermoforming is a widely used process to manufacture polymers with thin walls at a low cost. In this process, a sheet is heated and shaped into a three dimensional article around or into a mold. The molded article is then cooled, ejected and trimmed. PLA has been molded into disposable cups and trays for food packaging applications. Aluminum molds are commonly used when thermoforming PLA containers [45].

2.3.5 Foaming

PLA's competitive material and processing costs, as well as good mechanical properties make it a potential replacement to petroleum-based polystyrene foams. Additionally, PLA foams have been used in tissue engineering and medical implant applications due to its biocompatibility [45-48].

Foaming of PLA starts with the introduction of a blowing agent into the PLA matrix. The temperature of the process is increased or the pressure is decreased to induce nucleation of the bubbles. The foam cells are then vitrified below the T_g to stabilize the bubbles [45]. However, PLA's low melt strength poses challenges to manufacture low-density PLA foams. It's low melt strength leads to cell coalescence affecting the cell morphology of the foams [35].

Various approaches have been examined to melt strengthen PLA and control the cell morphology of its foams. Chain extenders have been added to PLA to prevent cell coalescence, as well as to reduce foam density and increase mechanical properties [28, 29]. However, chain

extenders have several drawbacks such as toxicity among others. Hence, a thermodynamic approach was implemented by Matuana and Diaz to melt strengthen PLA and control the cell morphology of its foams [36]. They reported a significant increase in the cell nucleation rate of PLA at low processing temperatures because of increased melt viscosity and consequently high pressure drop rates in the extrusion system. High pressure drop rates resulted in higher cell population densities. This finding was then successfully used to produce micro-cellular PLA foams with a cell density of 10^9 cells/cm^3 and an average cell size of less than 10 microns through a continuous extrusion process [36]. A similar thermodynamic approach to melt strengthen PLA through processing conditions was employed in this study to produce extrusion-blown PLA films without additives.

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Chapter 3

EXPERIMENTAL

3.1 Materials

Various PLA grades (2003D, 3052D, 4043D and 8302D) obtained from NatureWorks® LLC (Minnetonka, MN) were used as the resins in this study. The difference between these grades of commercial polymers is their D-lactide content, which affects their crystallinity and other related properties [1]. Relevant properties of these polymers measured in this study using the methods described later in this section are summarized in Table 3.1. The Melt Flow Index (MFI) and thermal properties were measured as described below.

Table 3.1 Characteristics of different PLA grades measured in this study

PLA Grade	D-lactide (%)	Melt Properties[a]		Thermal Properties[b]		
		MFI (g/10 mins)	δ_m (g/cc)	T_g (^{0}C)	T_m (^{0}C)	χ_c (%)
2003D	4-4.5[2]	39.93	1.204	61.69	167.03	11.92
3052D	4[1]	27.80	1.138	61.43	165.93	4.12
4043D	4.8 [3]	41.07	1.179	62.11	167.68	12.38
8302D	10[4]	18.47	1.119	60.06	-	-

[a] MFI and δ_m are the melt flow index and melt density of different PLA grades, respectively.

[b] T_g, T_m and χ_c are the glass transition temperature, melting temperature and percent crystallinity of different PLA grades, respectively.

3.1.1 Melt flow index (MFI)

The MFI and melt density (δ_m) of various grades of PLA (Table 3.1), dried at 50^0C, were measured using a Melt Indexer (model LMI 4000) supplied by Dynisco Polymer Testing (Franklin, MA). Methods A and B outlined in ASTM 1238 were employed simultaneously to measure the MFI and melt volume rate (MVR). This information was then used to calculate the δ_m of the samples using the following equation:

$$\delta_m = \frac{MFI}{MVR} \qquad \text{(Equation 3.1)}$$

The test was carried out at 190^0C with a dead load of 2.16 kg. Three replicates were tested.

The MFI and δ_m of PLA 2003D were also measured at 175^0C, 183^0C, 200^0C and 210^0C to obtain the zero shear viscosity (η_0) at these temperatures using the following equation [5, 6]:

$$\eta_0 = \frac{\delta_m \cdot W \cdot R^4}{8 \cdot MFI \cdot L \cdot R_A^2} = 4.8547 \times \frac{\delta_m \cdot W}{MFI} \qquad \text{(Equation 3.2)}$$

where R (1.0475 mm) is the bore radius of the die, R_A (4.775 mm) is the bore radius of the cylinder where the polymer melts, L (8 mm) is the length of the die and W (2160 g) is the applied dead load.

3.1.2 Thermal properties

The thermal properties of various grades of PLA were investigated using a Q100 differential scanning calorimeter (TA Instruments, New Castle, DE) and the results are listed in Table 3.1. Nitrogen, flowing at a constant rate of 70 mL/min was used to purge the DSC cell. A set of heating and cooling cycles were carried out to erase the thermal history of the sample. The samples weighing 2.5-5 mg were heated to 180^0C at a rate of 10^0C/min, cooled to 20^0C, and finally reheated to 180^0C at the same rate. The glass transition temperature (T_g), the melt peak temperature (T_m), the enthalpy of the cold crystallization process (ΔH_c), and the total enthalpy of the melting peaks (ΔH_m) were determined using the software Universal Analysis 2000, V4.5 (TA Instruments, Delaware). The percentage crystallinity (% χ_c) was calculated from the first heat curve using the following equation [6, 7]:

$$\%\chi_c = \frac{\Delta H_c - \Delta H_m}{\Delta H_m \infty} \times 100 \qquad \text{(Equation 3.3)}$$

The melt enthalpy of a spherulite of infinite size ($\Delta H_m \infty$) value used for PLA was 93 J/g [6, 7].

3.2 Sample manufacturing

The following section describes the sample manufacturing. Unless otherwise mentioned, most of the work presented in this study was performed using PLA 2003D matrix.

3.2.1 Rheological measurements

Online capillary rheometry was performed to study the effect of processing temperature on shear viscosity to determine the optimum temperature profile giving the highest shear viscosity. The advantage of using the online capillary rheometer compared to a traditional capillary rheometer is that the online capillary rheometer mimics high shear rates experienced during extrusion and generates test results at actual processing conditions [8].

3.2.1.1 Shear viscosity

Online capillary rheometry measurements were performed on an Intelli-Torque Plasticorder torque rheometer (C.W. Brabender Instruments, South Hackensack, NJ) equipped with a 32 mm conical counter-rotating twin screw extruder (L/D ratio of 13:1) to determine the shear viscosity of the melt at different temperature profiles. WinExt version 3.2.1 (C.W. Brabender Instruments, South Hackensack, NJ) was the software used for data analysis. A capillary die with three different inserts of lengths 40, 20 and 20 mm, all with a diameter of 2 mm, were used. The temperature profile in the extruder and die was kept constant to maintain a constant melt temperature for accurate viscosity measurements. The experiment was performed with all of the heating zones set to 170^0C, 185^0C or 200^0C. The rotational screw speed varied from 10 to 80 rpm to generate different shear rates during the experiments [7-9]. Preliminary results indicated that using rotational screw speeds below 10 rpm resulted in very low shear rates, rarely used in the

extrusion process whereas using rotational screw speeds above 80 rpm resulted in extremely high values of torque and undesirable shear heating of PLA. Experiments were performed in accordance with ASTM standard D5422. The melt density used in the viscosity calculations was measured as described above.

Apparent shear stress (τ_a) and apparent shear rate (γ_a) were calculated using the following equations:

$$\tau_a = \frac{\Delta P}{2 \cdot (L/R)} \quad \text{(Equation 3.4)}$$

$$\gamma_a = \frac{4 \cdot Q}{\pi \cdot R^3} \quad \text{(Equation 3.5)}$$

where ΔP is the pressure drop across the capillary die, L/R is the length-to-radius ratio of the capillary die, Q is the volumetric flow rate of the polymer melt and R is the radius of the capillary.

Bagley correction was performed to account for the excess pressure drop at the capillary entrance. Measurement of viscosity at the same shear rate with at least two different capillary lengths was needed to apply the Bagley correction. Bagley corrected shear stress was calculated using the following equation:

$$\tau_w = \frac{\Delta P}{2 \cdot (e + L/R)} \quad \text{(Equation 3.6)}$$

where e is the Bagley end correction and can be calculated as the intercept of the linear plot of pressure drop across the capillary die versus L/R for each rotational screw speed of the extruder [9].

The apparent shear rate gives only the Newtonian behavior (constant viscosity) and hence Rabinowitsch correction was performed to correct the shear rate for pseudoplastic fluids (viscosity is shear rate dependent) in order to obtain the shear rate at the wall (γ_w). The following equation was used to calculate γ_w:

$$\gamma_w = \frac{3n + 1}{4n} \times \gamma_a \qquad \text{(Equation 3.7)}$$

where n is the flow behavior obtained as the slope of the linear plot of log γ_a vs log τ_a.

The true shear viscosity (η) was then calculated from the corrected shear stress and shear rate as follows:

$$\eta = \frac{\tau_w}{\gamma_w} \qquad \text{(Equation 3.8)}$$

3.2.1.2 Elongational viscosity

The extensional viscosity fixture on the ARES rotational rheometer (TA instruments, New Castle, DE) was used to measure the elongational viscosity of PLA as a function of time at 160^0C, 170^0C and 180^0C to understand the effect of temperature on elongational viscosity. Rectangular samples with dimensions 18 × 10 × 0.78 mm were compression molded at 180^0C. Elongational viscosity was measured at a fixed Hencky strain rate of 0.1 s^{-1} as described by Matuana and Diaz [9] as well as Hadinata and co-workers [10].

From this experiment, the temperature profile which gave the highest shear and elongational viscosities was selected and used to manufacture PLA blown film.

3.2.2 Extrusion-blown PLA films

PLA pellets were dried in an oven at 50^0C for at least 24 hours to remove moisture before processing. A 19 mm single screw extruder (C.W. Brabender Instruments, South Hackensack, NJ), powered by a 3.73 kilowatt (5 hp) Prep Center® D52 (C.W. Brabender Instruments, South Hackensack, NJ) was used to blow PLA films. The single screw extruder had a length:diameter ratio of 30:1 and was fitted with an annular die of diameter 25.4 mm and die opening of 0.889 mm. Starting from the hopper to the die, the temperature profile of the extruder was set at 170-170-170-170^0C. This temperature profile was optimum to ensure the melting of PLA while giving the highest melt strength amongst other temperature profiles investigated.

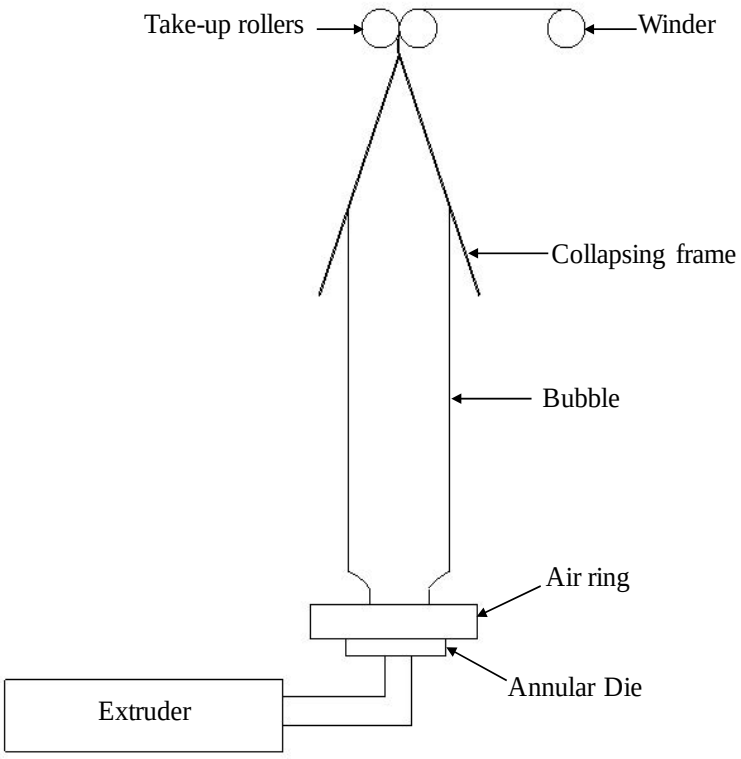

Figure 3.1 Schematic representation of the blown film extrusion process

Take-up ratio (TUR) and internal air pressure used to inflate the films have been found to be key processing variables in controlling the stability and BUR of blown films [11]. Various researchers have reported bubble instabilities or defects such as draw resonance, helical instability, frost line oscillation, among others as a result of improper control of the TUR and internal air pressure [12, 13]. Variation of these crucial parameters can significantly affect the bubble stability and thickness and hence the mechanical and physical properties of the manufactured films. Consequently, this study aimed at evaluating the effects of TUR and the internal air on the blow-up ratio (BUR) and stability of the blown films.

The TUR was defined as the ratio of the speed of take-up rollers to the rotational screw speed of the extruder, and was calculated using the following equation [14]:

$$\text{TUR} = \frac{\text{Speed of take-up rollers}}{\text{Speed of extruder's screw}} \qquad \text{(Equation 3.9)}$$

where the speed of the take-up rollers or extruder's screw is given as:

$$\text{Speed of take-up rollers or extruder's screw} = \frac{\pi \cdot D \cdot N}{60} \qquad \text{(Equation 3.10)}$$

where D is the diameter of the take-up rollers (63.5 mm) or extruder (19 mm), and N is the angular velocity of the take-up rollers or extruder in rpm.

The BUR was defined as the ratio of the diameter of the blown film to the diameter of the annular die. BUR was calculated using the following equation [11, 14]:

$$\text{BUR} = \frac{\text{Final Bubble Diameter}}{\text{Die Diameter}} \qquad \text{(Equation 3.11)}$$

Unless otherwise mentioned, the rotational screw speed of the extruder was set at 35 rpm, while the speed of the take-up roller varied from 32 rpm to 64 rpm by 5 rpm increments to obtain different TUR's. For each TUR, the internal air used to inflate the film varied from 0.03 psi to 0.19 psi, in intervals of 0.02 psi. The external cooling air was fixed at 1 psi. The BUR obtained for each condition of TUR and internal air giving stable film was recorded. A stable film was defined as a

film that showed no defects, such as bubble dancing, melt sag or draw resonance, among others for at least 5 minutes.

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Chapter 4

RESULTS AND DISCUSSION

4.1 Effect of temperature on shear and elongational viscosities

PLA's low shear and elongational viscosities result in low melt strength and pose challenges for its processing into blown films. The proposed strategy to blow PLA films was to control its shear and elongational viscosities through the processing temperature. Consequently, it was of utmost importance to understand the effect of temperature on the shear and elongational viscosities of PLA in order to select the optimum temperature profile for blowing PLA film. A temperature profile giving the highest shear and elongational viscosities would favor the blown film extrusion process of PLA. Online capillary rheometry measurements were performed to study the effect of temperature on the shear viscosity of PLA. The plot of true viscosity of PLA as a function of true shear rate at various temperatures is shown in Figure 4.1.

Two distinct trends were observed in this figure. First, increasing the shear rate reduced the viscosity of PLA, irrespective of the temperature. The results suggest that increasing the shear rate makes the polymer melt less viscous. This trend could be attributed to decreased interaction between polymer chains due to their better orientation and disentanglement [1, 2]. Such behaviour is characteristic of typical pseudoplastic (n<1), shear-thinning fluids in the non-Newtonian region. The results indicate that the melt obeyed power law:

$$\eta = K \cdot (\gamma_w)^{n-1} \qquad \text{(Equation 4.1)}$$

where K and n (Table 4.1), obtained from a linear regression of the curves in Figure 4.1, represent the melt viscosity coefficient and flow index, respectively.

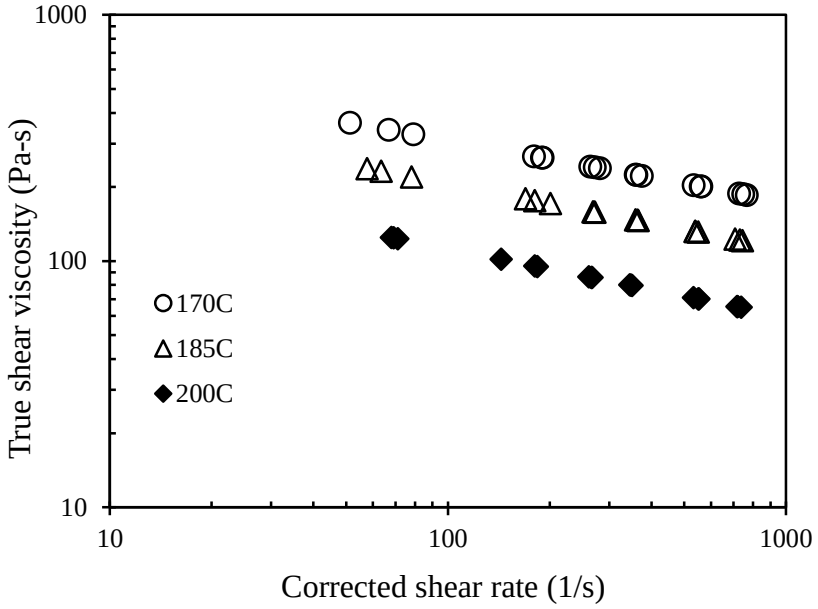


Figure 4.1 True shear viscosity of semicrystalline PLA (2003D) as a function of corrected shear rate at various temperatures (170, 185, 200^0C)

Second, increasing the test temperature resulted in a reduction of melt viscosity coefficient (K) suggesting that the melt became less viscous (Table 4.1). Similar results were reported by Matuana and Diaz [1]. At high temperatures, PLA molecular chains have a higher free volume for motion. Therefore, the polymer chains possess more mobility, leading to low resistance to flow between the melt layers and consequently low viscosity [1]. The values of n were lower than 1 and remained fairly constant with varying temperature suggesting that the melt was pseudoplastic ($n<1$) and the temperature did not have any effect on the pseudoplasticity of PLA (Table 4.1).

Table 4.1 Melt viscosity coefficient (K) and power law index (n) for semicrystalline PLA 2003D measured at various temperatures

	Regression Parameters $\eta=K\gamma_w^{n-1}$		
Temperature (^oC)	K (Pa. s^n)	n	R^2
170	974.78	0.751	1
185	690.19	0.737	1
200	397.63	0.725	1

Moreover, the reduction of viscosity as a function of processing temperature followed the Arrhenius relationship (Equation 1.1) as the logarithmic viscosity of PLA varied linearly with the reciprocal temperature (Figure 4.2). The activation energy (E_a) and Arrhenius constant (A_0) were estimated from the plot of logarithmic true shear viscosity of PLA versus the reciprocal temperature as the slope and intercept, respectively (Table 4.2). The activation energy of the melt increased with increasing shear rate indicating that the effect of processing temperature on the shear viscosity of the polymer melt became more pronounced at higher shear rates, in agreement with the work reported in literature [1].

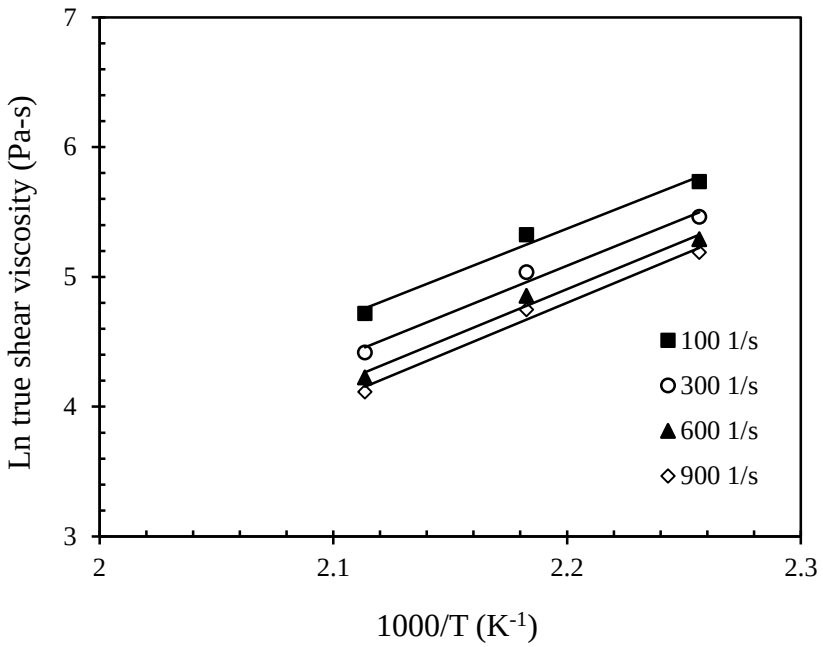


Figure 4.2 Logarithmic true shear viscosity of semicrystalline PLA (2003D) as a function of reciprocal temperatures (1000/T) at various shear rates (100, 300, 600, 900 1/s)

Table 4.2 Activation energy (E_a) and Arrhenius constant (A_0) of semicrystalline PLA 2003D at various shear rates (100, 300, 600, 900 1/s)

	Shear Rate (1/s)			
Temperature (^{0}C)	100	300	600	900
E_a (kJ/mol)	58.92	60.58	61.62	62.24
A_0 ($\times 10^{-5}$)	3.651	1.768	1.119	0.857
R^2	0.9831	0.9842	0.9848	0.9852

Online capillary rheometry measurements performed did not provide the flow properties of PLA at zero shear rate because of a software limitation that could not extrapolate its viscosity at this shear rate. Consequently, melt flow index measurements were performed to estimate the zero shear viscosity at various temperatures because such measurements are performed at very low shear rates. Figure 4.3 shows the zero shear viscosity as a function of temperature. As expected, the zero shear viscosity decreased with increasing temperature, following the Arrhenius relationship (Figure 4.4). The E_a and A_0 were 80.4 kJ/mol and 2.7×10^{-7}, respectively.

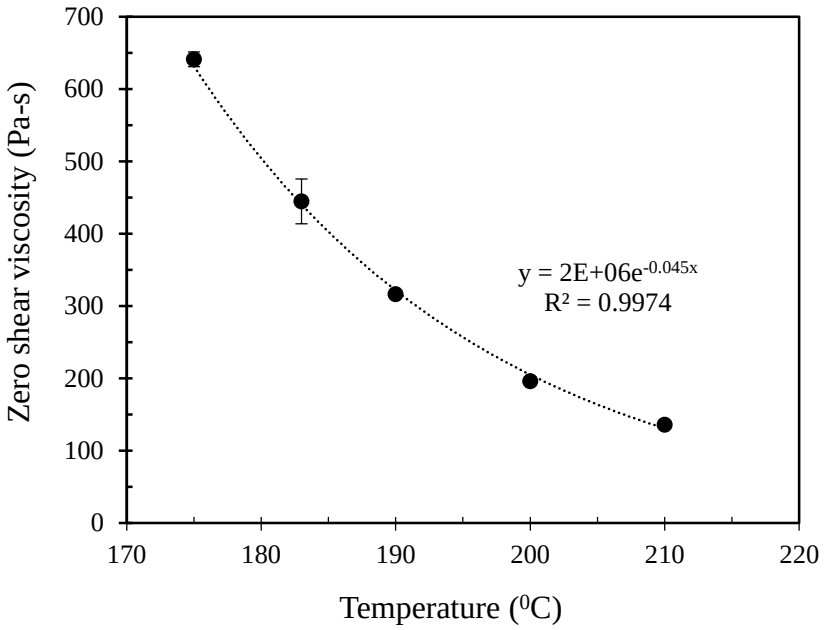


Figure 4.3 Zero shear viscosity of semicrystalline PLA (2003D) as a function of temperature

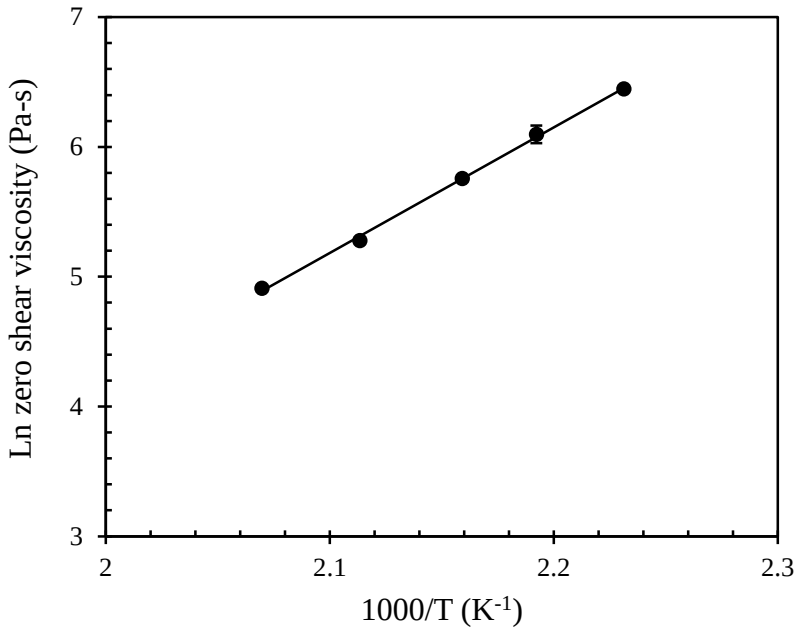


Figure 4.4 Logarithmic zero shear viscosity of semicrystalline PLA (2003D) as a function of reciprocal temperatures (1000/T)

Besides shear viscosity, elongational viscosity plays an important role in blown film processing. Low elongational viscosity can result in bubble instabilities in blown film extrusion. The elongational viscosity of PLA measured at a constant strain rate of 0.1 s^{-1} and various temperatures is shown in Figure 4.5. As hypothesized, the elongational viscosity increased as the temperature decreased. A similar trend was observed by Han and Park for polyethylenes and polypropylenes [3]. The elongational viscosity of PLA at all the temperatures tested showed strain hardening behavior before rupture, irrespective of the temperature. Strain hardening is usually exhibited when the rate of relaxation is considerably higher than the rate of molecular deformation. This effect is most significant in polymers with long chain branching because branching introduces longer relaxation times. Even though most researchers have not observed strain hardening in PLA, Dorgan and co-workers reported significant strain hardening of PLA with a high L-lactide content

[4]. The strain hardening behavior of PLA observed in this study could be attributed to its high L-lactide content.

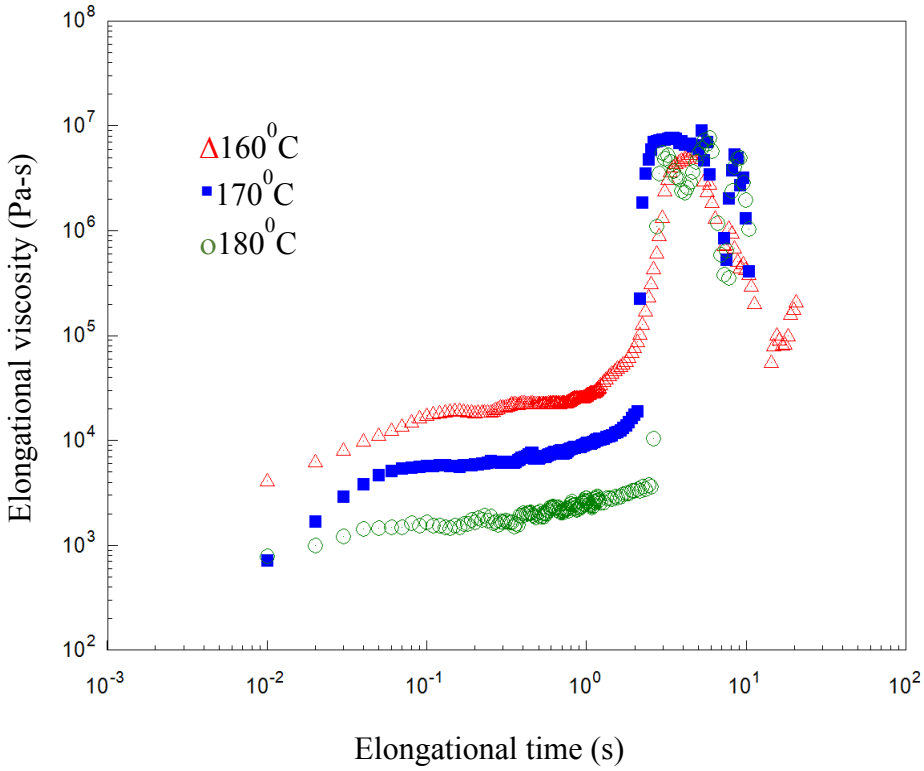


Figure 4.5 Elongational viscosity of semicrystalline PLA (2003D) as a function of elongational time at various temperatures (160, 170, 180^{0}C)

It is worth mentioning that the temperature profiles investigated for measuring the zero shear, shear and elongational viscosity are different. It was difficult to measure the elongational viscosity of PLA at temperatures above 180^{0}C in the capillary rheometer since PLA was extremely soft and could not support its own weight above this temperature. Consequently, lower temperature profiles were selected for the measurement of elongational viscosity. Moreover, a temperature of

at least 175^0C was required to melt PLA for the measurement of zero shear viscosity in the melt indexer and hence a higher temperature range was selected for zero shear viscosity measurements.

The experimental results for shear and elongational viscosity confirmed our hypothesis that the shear (Figure 4.1) and elongational (Figure 4.5) viscosities are highest at the lowest temperature profile. Consequently, a temperature profile above PLA's melting point giving the highest melt strength was selected for processing PLA blown films.

4.2 Effect of TUR and internal air pressure on BUR

After selecting the optimum temperature profile, the next objective of this study was to investigate the effects of processing conditions such as the TUR and internal air pressure on the stability and BUR of the films.

TUR and internal air pressure have been found to be major processing variables in controlling the frost line height (FLH), which in turn influences the stability of blown films [5]. Figure 4.6 shows the plot of BUR as a function of TUR and internal air pressure at a constant external cooling air pressure of 1 psi. The TUR and internal air pressure had a significant effect on the BUR of the film.

A critical value of TUR below 3.5 did not yield a stable film because the rotational screw speed of the extruder was very high compared to the take-up roller speed resulting in a large output of polymer melt being pulled away from the die exit very slowly. Consequently, a substantial amount of polymer melt accumulated at the die exit without solidifying. The unsolidified melt could not self-support itself into a polymer tube and sagged at the die exit resulting in melt sag, as seen in Figure 4.7(a). No frost line was observed at TURs below 3.5.

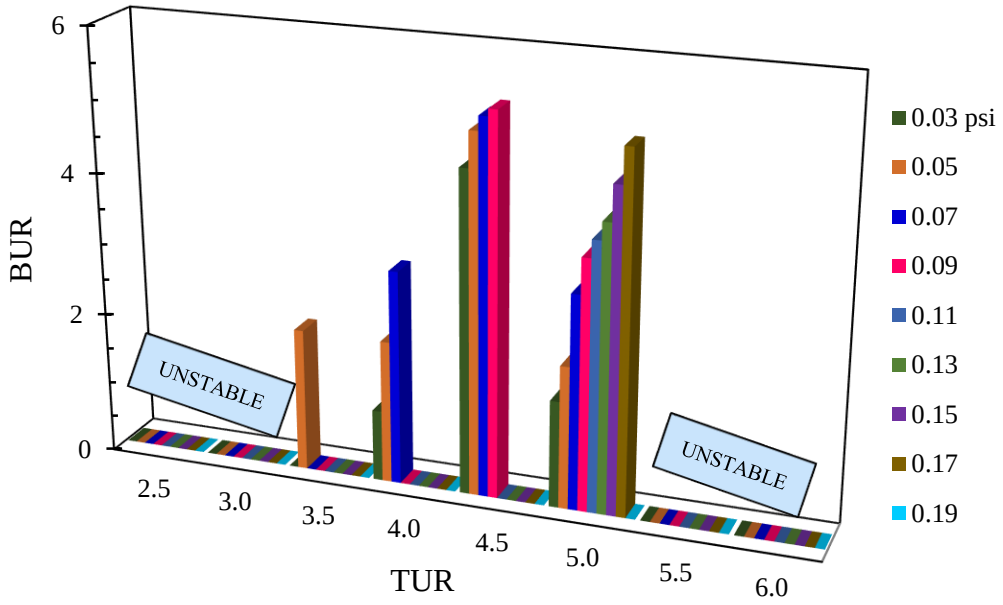
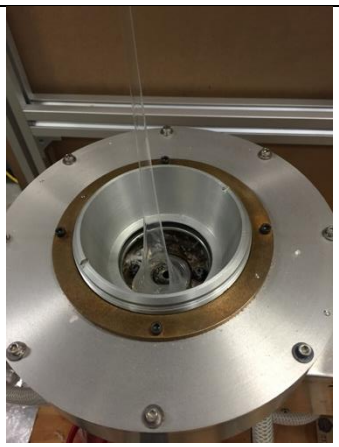


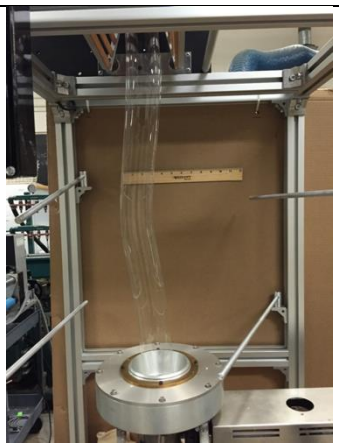
Figure 4.6 Effect of TUR and internal pressure on BUR of PLA films

At a TUR of 3.5, stable film was produced when blown with an internal air pressure of 0.05 psi only. Internal air pressures lower or greater than 0.05 psi did not yield stable films because of the difficulty experienced in controlling the FLH. Bubble dancing (Figure 4.7(b)) was observed at this TUR due to the low FLH obtained. Bubble dancing can cause variations in the diameter and thickness of the formed film. This defect could be corrected by increasing the TUR and producing an adequate FLH.

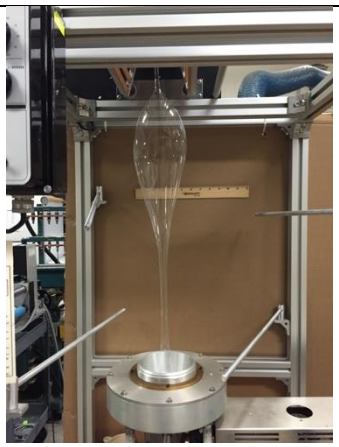
At optimum TURs, between 4.0 and 5, stable PLA films were obtained. As expected, at a particular TUR, the increase in the internal air pressure led to higher BUR as the film stretched more when the internal air pressure was increased. At a TUR of 5, the increasing BUR lowered the FLH. After a critical BUR of 5, the bubble solidified too close to the exit and it was not possible to get a higher BUR.



(a) Melt Sag



(b) Bubble Dancing



(c) Draw resonance

Figure 4.7 Bubble defects observed during blown film extrusion of PLA

At TURs higher than 5, fluctuations in the FLH and internal air pressure inside the bubble were observed. These pressure fluctuations caused the film diameter to vary, as seen in Figure 4.7(c). This defect has been reported in literature as draw resonance [3]. Moreover, the diameter fluctuations aggravated with time and lead to bubble rupture. Hence, no stable film was obtained at a TUR above 5.

The most optimum conditions for blowing PLA to 5" were found at a TUR of 5, with 0.17 psi internal air pressure. Figure 4.8(a) shows a stable PLA film at these conditions. The internal air was ideal to blow PLA to 5" and the TUR was appropriate to eliminate die defects such as melt sag, bubble dancing and draw resonance. Figure 4.8(b) shows a stable film of PLA blown to 3.5" at a TUR of 5, and internal air pressure of 0.09 psi. It is worth mentioning that a TUR of 5 was selected as the optimum TUR because it gave the flexibility to produce film with a wide range of BURs as the internal air pressure varied.

(a) Good film with BUR 5

(b) Good film with BUR 3.5

Figure 4.8 Stable films at TUR of 5

4.3 Effect of processing at a constant TUR obtained through a combination of various take-up roller speeds and extruder's rotational screw speeds on the BUR of films

All films in this study were produced by varying the TUR obtained as a result of changing winder speeds at a constant extruder's rotational screw speed. It was of interest to investigate the effect of different combinations of take-up roller speeds and extruder's rotational screw speeds that result in the same and constant TUR of 5 on the stability and BUR of the films. Figure 4.9 shows the effect of these different speed at a constant air pressure of 0.17 psi.

As seen in Figure 4.9, the different combinations resulting in the same TUR had no significant effect on the film stability and BUR. This is in corroboration with expected results as a constant TUR, internal air pressure, external cooling air and melt temperature would result in a constant FLH. Since all the variables of the blown film process remained constant, a stable film

with a constant BUR of approximately 5 was observed. Thus, it was obvious that maintaining a TUR of 5 is more important than the values of individual speeds needed to achieve it.

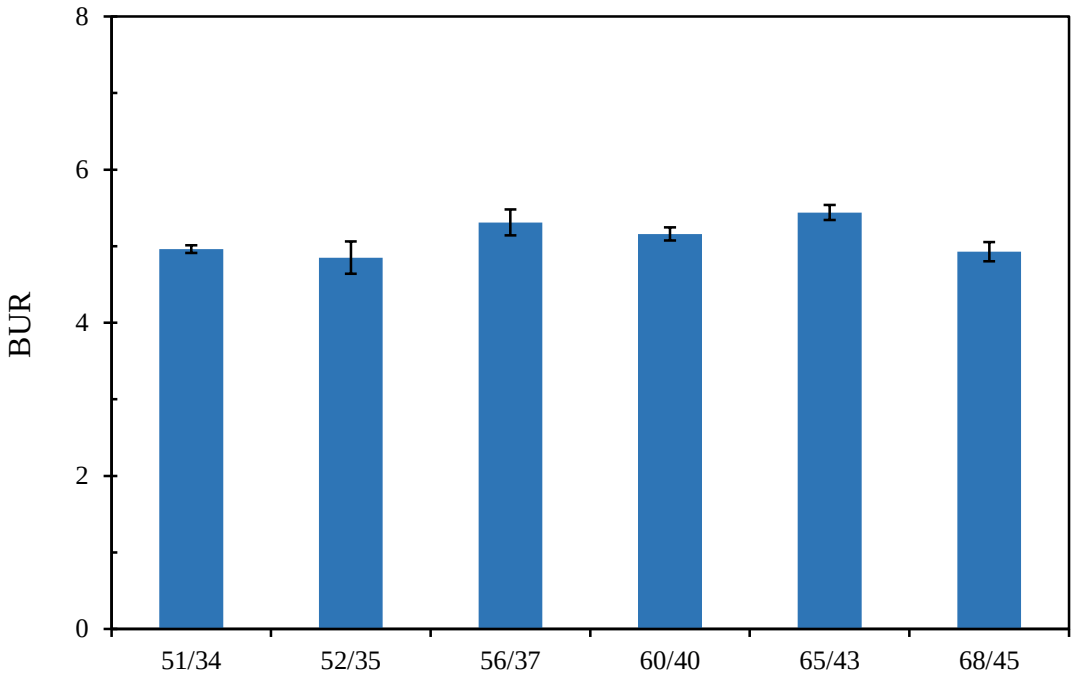


Figure 4.9 Effect of processing at a constant TUR of 5 obtained through a combination of various take-up roller speeds and rotational screw speeds of extruder on the BUR of films

4.4 Effect of material characteristics on the BUR of films

The effect of material characteristics such as MFI and crystallinity of various PLA grades on the stability and BUR of the blown films is illustrated in Figure 4.10. In addition to PLA 2003D, three additional PLA grades (3052D, 4043D and 8302D) with different MFI and crystallinity (Table 3.1) were blown using a TUR of 5 and an internal air pressure of 0.17 psi. No significant difference in the BUR of the films was observed on changing the PLA grades. Thus, it was

apparent that the differences in the crystallinity and MFI of PLA grades within the range investigated had no noteworthy effect on the BUR of the films when processed at the designated optimum processing conditions. This result was in corroboration with the findings of Mallet and co-workers who investigated the processability of different PLA grades (2002D, 3051D, 4032D and 4060D) at various TURs, ranging from 2 to 16. When processed at a TUR of 5, they obtained stable films with a BUR of only 3, irrespective of the PLA grades [6].

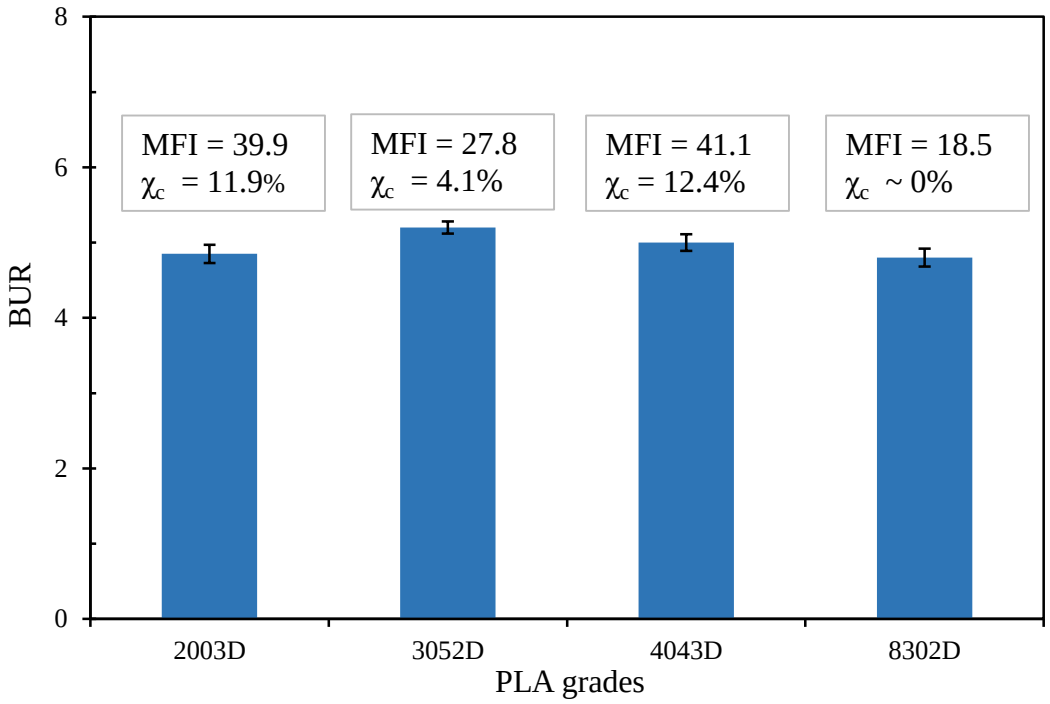


Figure 4.10 Effect of material characteristics on the BUR of films at constant TUR and internal air pressure of 5 and 0.17 psi, respectively

APPENDICES

APPENDIX A

Effect of temperature on shear viscosity of semicrystalline PLA (2003D)

Table A.1 Uncorrected viscosity of semicrystalline PLA (2003D) as a function of shear rate at 170^0C

No.	L / D (mm/mm)	Speed (rpm)	Temp (^{0}C)	ΔP (PSI)	ρ (g/min)	Q (cm^3/min)	γ_a (sec^{-1})	τ_a (Pa)	η_a (Pa-s)
1	20/2	10	170.8	185	3.85	3.44	72.9	31902	437.3
2	20/2	20	170.9	289	9.23	8.24	174.9	49796	284.7
3	20/2	30	170.9	411	13.25	11.83	251.0	70875	282.3
4	20/2	40	171.6	548	17.58	15.70	333.1	94383	283.4
5	20/2	60	171.5	790	27.23	24.31	515.9	136152	263.9
6	20/2	80	171.6	935	37.32	33.32	707.1	161242	228
7	30/2	10	171.7	221	2.50	2.23	47.4	25353	535.2
8	30/2	20	171.5	464	8.75	7.81	165.8	53279	321.4
9	30/2	30	171.5	634	12.84	11.46	243.3	72801	299.2
10	30/2	40	171.4	821	17.49	15.62	331.4	94290	284.5
11	30/2	60	171.4	1078	25.99	23.21	492.4	123848	251.5
12	30/2	80	171.5	1255	36.37	32.47	689.1	144240	209.3
13	40/2	10	171.3	281	3.25	2.90	61.6	24241	393.7
14	40/2	20	171.3	586	9.27	8.28	175.6	50473	287.4
15	40/2	30	171.6	860	13.72	12.25	260.0	74076	285
16	40/2	40	171.5	1097	18.25	16.29	345.8	94525	273.4
17	40/2	60	171.5	1415	27.33	24.40	517.8	121953	235.5
18	40/2	80	171.8	1613	35.39	31.60	670.5	139043	207.4

Table A.2 Corrected viscosity of semicrystalline PLA (2003D) as a function of shear rate at 170^0C

No.	Entrance Correction	τ_w (Pa)	γ_w (sec^{-1})	η (Pa-s)
1	0.531	25886	79	327.7
2	0.445	49902	189.4	263.5
3	0.412	65459	271.9	240.7
4	0.386	80936	360.8	224.3
5	0.349	112400	558.8	201.1
6	0.323	142399	765.8	185.9
7	0.577	18720	51.3	364.9
8	0.450	47941	179.6	267.0
9	0.415	63933	263.5	242.6
10	0.387	80625	358.9	224.6
11	0.353	108536	533.3	203.5
12	0.325	139670	746.3	187.1
13	0.549	22795	66.7	341.8
14	0.445	50064	190.2	263.2
15	0.409	67194	281.5	238.7
16	0.383	83240	374.5	222.3
17	0.348	112709	560.8	201.0
18	0.327	136836	726.2	188.4

Table A.3 Uncorrected viscosity of semicrystalline PLA (2003D) as a function of shear rate at 185^0C

No.	L / D (mm/mm)	Speed (rpm)	Temp (^{0}C)	ΔP (PSI)	ρ (g/min)	Q (cm^3/min)	γ_a (sec^{-1})	τ_a (Pa)	η_a (Pa-s)
1	20/2	10	186.9	126	3.78	3.38	71.6	21664	302.5
2	20/2	20	187	185	9.74	8.70	184.5	31833	172.5
3	20/2	30	186.9	262	13.14	11.73	249.0	45242	181.7
4	20/2	40	187.2	369	17.71	15.81	335.6	63683	189.8
5	20/2	60	187	516	26.10	23.3	494.5	88980	179.9
6	20/2	80	187	610	36.05	32.19	683.0	105125	153.9
7	30/2	10	186.8	156	2.79	2.49	52.9	17942	339.4
8	30/2	20	186.9	290	8.22	7.34	155.7	33358	214.2
9	30/2	30	187.1	426	13.18	11.77	249.7	49008	196.2
10	30/2	40	186.9	510	17.62	15.73	333.8	58645	175.7
11	30/2	60	186.9	694	26.17	23.37	495.8	79746	160.8
12	30/2	80	186.4	848	35.42	31.63	671.1	97470	145.2
13	40/2	10	187	180	3.07	2.74	58.2	15535	267.1
14	40/2	20	186.2	368	8.75	7.81	165.8	31708	191.3
15	40/2	30	186.3	522	13.01	11.62	246.5	44962	182.4
16	40/2	40	185.8	700	17.38	15.52	329.3	60351	183.3
17	40/2	60	187.2	906	26.67	23.81	505.3	78083	154.5
18	40/2	80	187.8	1077	34.29	30.62	649.7	92819	142.9

Table A.4 Corrected viscosity of semicrystalline PLA (2003D) as a function of shear rate at 185^0C

No.	Entrance Correction	τ_w (Pa)	γ_w (sec^{-1})	η (Pa-s)
1	0.418	17115	78.0	219.4
2	0.4	34400	201.0	171.1
3	0.397	42895	271.2	158.2
4	0.394	53446	365.5	146.2
5	0.392	71113	538.6	132.0
6	0.392	90201	743.9	121.2
7	0.425	13678	57.6	237.6
8	0.402	30356	169.6	179.0
9	0.397	42991	272.0	158.1
10	0.394	53245	363.6	146.4
11	0.392	71254	540.1	131.9
12	0.392	89038	730.9	121.8
13	0.423	14679	63.4	231.7
14	0.402	31787	180.6	176.0
15	0.397	42582	268.5	158.6
16	0.394	52710	358.7	147.0
17	0.392	72254	550.4	131.3
18	0.392	86938	707.6	122.9

Table A.5 Uncorrected viscosity of semicrystalline PLA (2003D) as a function of shear rate at 200^0C

No.	L / D (mm/mm)	Speed (rpm)	Temp (^{0}C)	ΔP (PSI)	ρ (g/min)	Q (cm^3/min)	γ_a (sec^{-1})	τ_a (Pa)	η_a (Pa-s)
1	20/2	10	201.2	72	3.33	2.97	63.1	12470	197.6
2	20/2	20	201.4	130	6.93	6.19	131.3	22375	170.4
3	20/2	30	201.4	202	12.6	11.25	238.7	34806	145.8
4	20/2	40	201.8	255	16.79	14.99	318.1	43984	138.3
5	20/2	60	201.4	359	26.63	23.78	504.6	61878	122.6
6	20/2	80	201.6	434	35.53	31.72	673.2	74787	111.1
7	30/2	10	202	118	3.43	3.06	65.0	13527	208.1
8	30/2	20	202.7	183	8.86	7.91	167.9	21064	125.5
9	30/2	30	202.3	252	12.86	11.48	243.7	28989	119.0
10	30/2	40	202.6	328	16.89	15.08	320.0	37679	117.7
11	30/2	60	202.1	476	26.54	23.7	502.9	54655	108.7
12	30/2	80	202.2	569	34.68	30.96	657.1	65341	99.4
13	40/2	10	202.2	126	3.28	2.93	62.1	10888	175.2
14	40/2	20	201.8	244	8.71	7.78	165.0	20992	127.2
15	40/2	30	202.1	323	12.82	11.45	242.9	27824	114.5
16	40/2	40	202.5	415	16.64	14.86	315.3	35793	113.5
17	40/2	60	202	572	25.66	22.91	486.2	49340	101.5
18	40/2	80	201.9	718	34.52	30.82	654.1	61852	94.6

Table A.6 Corrected viscosity of semicrystalline PLA (2003D) as a function of shear rate at 200^0C

No.	Entrance Correction	τ_w (Pa)	γ_w (sec^{-1})	η (Pa-s)
1	1.251	8587	69.1	124.3
2	1.305	14619	143.7	101.7
3	1.35	22556	261.3	86.3
4	1.373	27776	348.2	79.8
5	1.411	38804	552.3	70.3
6	1.435	47820	736.9	64.9
7	1.253	8774	71.1	123.3
8	1.323	17471	183.8	95.1
9	1.352	22892	266.7	85.8
10	1.374	27896	350.3	79.6
11	1.411	38709	550.5	70.3
12	1.433	46988	719.3	65.3
13	1.25	8493	68.0	124.8
14	1.322	17256	180.7	95.5
15	1.352	22841	265.9	85.9
16	1.372	27596	345.1	80.0
17	1.408	37774	532.2	71.0
18	1.433	46831	716.0	65.4

Table A.7 Activation energy (E_a) and Arrhenius constant (A_0) of semicrystalline PLA (2003D) at various shear rates (100, 300, 600, 900 1/s)

Shear rate (1/s)	**Temperature T (^{0}C)**	**T (K)**	**1/T (1000K^{-1})**	**ln Viscosity**	**ln A_0**	**A_0 (×10^5)**	**E_a/R^a (K)**	**Ea (kJ/ mol)**
100	170	443.15	2.257	5.736	-10.218	3.651	7086.4	58.916
	185	458.15	2.183	5.326				
	200	473.15	2.113	4.719				
300	170	443.15	2.257	5.462	-10.943	1.768	7286.2	60.577
	185	458.15	2.183	5.037				
	200	473.15	2.113	4.417				
600	170	443.15	2.257	5.289	-11.400	1.120	7412.2	61.625
	185	458.15	2.183	4.855				
	200	473.15	2.113	4.226				
900	170	443.15	2.257	5.188	-11.667	0.857	7485.9	62.237
	185	458.15	2.183	4.748				
	200	473.15	2.113	4.115				

[a]R is the universal gas constant (8.314 J mol^{-1} K^{-1})

Table A.8 Zero shear viscosity of semicrystalline PLA (2003D) as a function of temperature

Temperature (^{0}C)	Replicate	Melt flow index (g/10 mins)	Melt density (g/cc)	Zero shear viscosity η_0 (Pa-s)	Average η_0 (Pa-s)	Standard deviation
175	1	18.60	1.137	641.31	641.31	10.27
	2	18.95	1.122	621.16		
	3	18.90	1.131	627.80		
183	1	24.30	1.113	480.52	444.82	30.92
	2	27.10	1.102	426.61		
	3	27.30	1.112	427.33		
190	1	40.40	1.228	318.74	316.18	4.77
	2	39.20	1.193	319.13		
	3	40.20	1.191	310.67		
200	1	60.60	1.111	192.25	195.88	5.06
	2	58.50	1.125	201.66		
	3	60.40	1.116	193.75		
210	1	86.55	1.119	135.57	135.66	0.59
	2	85.95	1.117	136.28		
	3	87.00	1.121	135.11		

Table A.9 Activation energy (E_a) and Arrhenius constant (A_0) of semicrystalline PLA (2003D) at zero shear rate

	Temperature, T (^{0}C)	**T (K)**	**1/T (1000K^{-1})**	**ln viscosity**	**Average ln viscosity**	**Standard Deviation**
	175	448.15	2.231	6.464 6.432 6.442	6.446	0.016
	183	456.15	2.192	6.175 6.056 6.058	6.096	0.068
	190	463.15	2.159	5.764 5.766 5.739	5.756	0.015
	200	473.15	2.113	5.259 5.307 5.267	5.277	0.026
	210	483.15	2.070	4.910 4.915 4.906	4.910	0.004
E_a/R^a (K)				9670.9		
ln A_0				15.13		
A_0				2.70E-07		

[a]R is the universal gas constant (8.314 J mol^{-1} K^{-1})

APPENDIX B

Effect of temperature on elongational viscosity of semicrystalline PLA (2003D)

Table B.1 Elongational viscosity of semicrystalline PLA (2003D) as a function of elongational time at various temperatures (160, 170, 180^{0}C)

Time (s)	**Elongational viscosity (Pa-s)**		
	160^{0}C	170^{0}C	180^{0}C
0.01	2219.16	724.638	650.019
0.02	7484.96	1701.89	1013.8
0.03	5324.51	2911.41	1336.35
0.04	2583.53	3804.38	1580.2
0.05	7086.35	4655.63	1617.44
0.06	16598.1	5100.34	1613.86
0.07	23955.8	5371.75	1601.69
0.08	21510.5	5535.39	1600.62
0.09	14624.4	5602.02	1754.18
0.1	12234.5	5663.7	1804.55
0.11	19258	5753.57	1901.59
0.12	26147.7	5848.74	1798.37
0.13	26787.8	5861.34	1782.16
0.14	18658.5	5727.74	1686.24
0.15	13904.1	5688.01	1746.74
0.16	16066.2	5648.5	1719.83
0.17	23388.8	5764.92	1844.7
0.18	27378.4	5792.24	1728.81
0.19	22963.7	5785.19	1775.14
0.2	17817.7	5888.59	1631.53
0.21	13627.3	5885.49	1745.89
0.22	14766.9	5988.9	1771.08
0.23	13669.4	6052.14	1810.87
0.24	12731.1	6182.8	1827.12
0.25	15822.8	6351	1774.75
0.26	24955.1	6282.21	1768.94
0.27	24892.1	6287.27	1725.79
0.28	20328.3	6279.66	1823.59
0.29	15479.8	6162.7	1861.74
0.3	18447.3	6168.92	1826.68
0.31	25377.5	6122	1716.87

Table B1 (cont'd)

0.32	29314.2	6259.4	1761.55
0.33	22377.4	6122.59	1716.46
0.34	16249.3	6138.25	1866.58
0.35	16957.6	6156.23	1886.34
0.36	24273.6	6204.73	1847.79
0.37	29383.5	6431.25	1882.02
0.38	26151.8	6572.17	1782.9
0.39	20338.2	6823.28	1753.63
0.2	17817.7	5888.59	1631.53
0.4	14597.3	6790.05	1626.81
0.41	20731.7	6962.81	1761.5
0.42	27741.8	7053.75	1721.87
0.43	28812.7	7306.15	1872.17
0.44	22539.5	7397.33	1814.04
0.45	15778.1	7579.12	1945.89
0.46	17255.5	7599.83	1828.36
0.47	26159.1	6736.43	1982.76
0.48	29638	6682.81	1865.67
0.49	22560.2	6777.39	1998.16
0.5	17273.9	6704.37	1891.81
0.51	18826.5	6795.17	1945.26
0.52	26967.2	6920.87	1855.97
0.53	27776.3	7005.41	1900.48
0.54	21244	7086.79	1829.67
0.55	13807.8	6965.44	1828.36
0.56	19475.9	7094.54	1928.29
0.57	26893.5	7173.58	1787.45
0.58	28909.6	7373.73	1841.86
0.59	20652.2	7411.53	1826.42
0.6	18216.1	7433.25	1884.02
0.61	20856	7488.04	1807.23
0.62	28757.8	7617.85	1876.41
0.63	28858.7	7719.57	1812.27
0.64	20740.4	7723.43	1901.22
0.65	14952.3	7639.26	1861
0.66	17760.5	7672.84	1865.79

Table B1 (cont'd)

0.67	26872.7	7852.4	1931.67
0.68	31460	7884.92	1990.57
0.69	24292.2	8007.96	2089.73
0.7	14764.7	7766.29	1989.21
0.71	16933.8	7663.82	2040.18
0.72	25605.8	7463.53	1827.77
0.73	31538.4	7584.56	2006.45
0.74	23645.2	7628.56	1882.46
0.75	15719.3	7908.19	2185.9
0.76	17410.7	7979.37	2056.01
0.77	25048.6	8144.7	2136.54
0.78	28385.1	8141.4	1916.28
0.79	21986.1	8407.67	1959.34
0.8	17246	8294.47	1827.91
0.81	22410	8426.38	1851.66
0.82	32087.4	8470.26	1791.95
0.83	33585	8569.48	1940.43
0.84	27685.7	8625.35	1951.58
0.85	18711.5	8553.24	1975.57
0.86	21615.8	8635.53	2043.63
0.87	29165.9	8619.45	1918.88
0.88	34515.3	8733.24	2041.57
0.89	27148.6	8687.31	1917.93
0.9	19839.2	8678.17	2068.05
0.91	16345.6	8609.75	2040.37
0.92	24497	8735.15	2031.12
0.93	31051.4	8892.25	2003.33
0.94	30039.7	8985.35	2024.1
0.95	21482.9	9031.04	2059.26
0.96	18225.3	9060	2114.48
0.97	25361.7	9216.01	2038.92
0.98	31642.9	9229.76	1997.98
0.99	28914.5	9365.89	1957.99
1	20457.8	9303.79	1858.77
1.01	23133.3	9457.9	2033.2
1.02	30667.6	9269.44	1955.71

Table B1 (cont'd)

1.03	36777.7	9521.3	2182.91
1.04	30132	9343.78	1944.85
1.05	22858.3	9507.07	2141.02
1.06	21812.1	9326.99	1991.35
1.07	29791.1	9474.28	2161.04
1.08	35948.2	9450.71	2118.68
1.09	32774.2	9717.18	2239.46
1.1	26109.1	9701.63	2203.14
1.11	21037	9706.71	2225.54
1.12	26515.3	9741.74	2178.06
1.13	31684.3	9889.68	2187.26
1.14	30411	10068	2225.81
1.15	23810.6	10172.2	2177.09
1.16	23974.6	10154.1	2213.91
1.17	30330.1	10048.5	2054.91
1.18	37711.1	10129.3	2095.99
1.19	37010.9	10182.2	1995.83
1.2	29566.1	10377.8	2166.16
1.23	34496.2	10235.1	2049.18
1.28	37780.8	10403.8	2145.24
1.33	39578.9	10847.7	2377.19
1.385	41063.6	11034.4	2170.38
1.445	46678.8	11171.7	2190.28
1.505	49941.6	11898.6	2319.36
1.565	52711.3	12078.7	2222.09
1.63	54139.7	12493.9	2420.68
1.695	54040.4	13207.6	2350.1
1.76	56231.5	13895.2	2221.36
1.835	58497.2	15040.9	2451.46
1.915	56717.4	16338	2490.45
1.995	63440.8	17700.8	2446.9
2.075	67344.8	19113.2	2507.13
2.155	62837.4	2.24E+05	2450.93
2.24	66479.6	1.84E+06	2607.98
2.335	68797	3.53E+06	2645.21
2.435	69106.5	4.80E+06	4.81E+05

Table B1 (cont'd)

2.535	68644.8	5.97E+06	3.43E+06
2.635	70402.3	6.97E+06	6.37E+06
2.74	5.86E+05	7.15E+06	6.95E+06
2.855	1.88E+06	7.24E+06	6.58E+06
2.975	3.21E+06	7.34E+06	4.77E+06
3.095	3.52E+06	7.43E+06	3.30E+06
3.22	4.00E+06	7.54E+06	2.37E+06
3.355	4.01E+06	7.65E+06	2.28E+06
3.495	4.11E+06	7.62E+06	2.20E+06
3.635	4.28E+06	7.50E+06	1.97E+06
3.78	4.82E+06	6.91E+06	2.41E+06
3.935	4.51E+06	7.12E+06	2.55E+06
4.1	4.84E+06	6.64E+06	3.29E+06
4.27	5.36E+06	6.59E+06	3.84E+06
4.445	5.19E+06	6.78E+06	4.90E+06
4.625	5.38E+06	6.41E+06	5.46E+06
4.815	4.95E+06	6.53E+06	6.33E+06
5.015	5.58E+06	6.09E+06	7.14E+06
5.22	7.81E+06	8.96E+06	9.37E+06
5.435	5.43E+06	4.70E+06	9.60E+06
5.655	9.82E+06	7.01E+06	9.11E+06
5.885	5.02E+06	3.46E+06	2.49E+06
6.13	-2.10E+06	-1.63E+06	1.13E+06
6.38	-3.61E+06	-1.51E+06	2.33E+05
6.64	-1.53E+06	-1.83E+06	-7.55E+05
6.915	-4.25E+05	-8.17E+05	-80508
7.2	-5.58E+05	8.56E+05	6.68E+05
7.495	-3.37E+05	5.31E+05	4.80E+05
7.8	-1.88E+05	2.05E+06	2.10E+06
8.12	2.85E+06	3.76E+06	5.78E+06
8.455	3.63E+06	5.31E+06	6.88E+06
8.8	4.87E+06	4.98E+06	4.31E+06
9.16	2.21E+06	2.70E+06	3.35E+06
9.535	1.44E+06	3.23E+06	2.62E+06
9.925	1.02E+06	1.32E+06	1.12E+06
10.335	-1.59E+05	4.14E+05	4.26E+05

Table B1 (cont'd)

10.76	-2.11E+05	-3.97E+05	-3.55E+05
11.2	-80579	-6.86E+05	-3.51E+05
11.66	-2889.2	-1.02E+06	-2.47E+05

APPENDIX C

Effect of take-up ratio and internal air pressure on the blow-up ratio of semicrystalline PLA (2003D) films

Table C.1 Effect of TUR and internal pressure on BUR of semicrytsalline PLA (2003D) films

TUR	**BUR***								
	Internal air pressure (psi)								
	0.03	0.05	0.07	0.09	0.11	0.13	0.15	0.17	0.19
2.5	0	0	0	0	0	0	0	0	0
3.0	0	2	0	0	0	0	0	0	0
3.5	1	2	3	0	0	0	0	0	0
4.0	4.5	5	5.2	5.3	0	0	0	0	0
4.5	1.5	2	3	3.5	3.75	4	4.5	5	0
5.0	0	0	0	0	0	0	0	0	0
5.5	0	0	0	0	0	0	0	0	0

* A BUR of 0 means that the film was unstable**.**

APPENDIX D

Effect of processing at a constant TUR obtained through a combination of various take-up roller speeds and extruder's rotational screw speeds on the BUR of semicrytsalline PLA (2003D) films

Table D.1 Effect of processing at a constant TUR obtained through a combination of various take-up roller speeds and rotational screw speeds of the extruder on the BUR of semicrytsalline PLA (2003D) films

Take-up roller speed (rpm)/ Extruder's rotational screw speed (rpm) (TUR = 5)	**BUR**										**Average**	**Standard Deviation**
	Number of replicates											
	1	2	3	4	5	6	7	8	9	10		
51/34	4.9	5.0	5	4.9	5	5	4.9	5	5	4.9	4.96	0.05
52/35	5.0	5.0	5.0	5.0	4.75	4.75	4.5	4.5	5.0	5.0	4.85	0.21
56/37	5.5	5.25	5.1	5.4	5.3	5.4	5.1	5.1	5.5	5.5	5.31	0.17
60/40	5.1	5.1	5.2	5.2	5.1	5.2	5.0	5.2	5.3	5.2	5.16	0.08
65/43	5.5	5.5	5.5	5.3	5.5	5.5	5.3	5.5	5.3	5.5	5.44	0.10
68/45	4.8	4.7	4.9	4.9	5.0	5.0	4.9	5.1	5.1	4.9	4.93	0.13

APPENDIX E

Effect of material characteristics on the blow-up ratio of semicrystalline and amorphous PLA films

Table E.1 Effect of material characteristics on the BUR of semicrystalline and amorphous PLA films at constant TUR and internal air pressure of 5 and 0.17 psi, respectively

PLA Grades	BUR										Average	Standard Deviation
	Number of replicates											
	1	2	3	4	5	6	7	8	9	10		
2003D (MFI 39.9, χ_c = 11.92)	5.00	5.00	5.00	4.75	4.75	4.50	4.50	5.00	5.00	5.00	4.85	0.21
3052D (MFI 27.8, χ_c = 4.12)	5.30	5.00	5.25	5.00	5.00	5.25	5.30	5.30	5.30	5.30	5.20	0.14
4043D (MFI 41.07, χ_c = 12.38)	4.9	4.9	4.9	4.9	5.1	5.1	5.1	5.1	5.1	4.9	5.00	0.11
8302D (MFI 18.47, χ_c = 0)	4.75	4.75	4.75	4.50	5.00	4.75	5.00	4.75	5.00	4.75	4.80	0.16

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Chapter 5

CONCLUSIONS

5.1 Conclusions

The aim of this study was to blow PLA films using the conventional blown film extrusion process without the addition of any melt strengthening additives. To achieve this goal, the effect of temperature on the shear and elongational viscosities of PLA was investigated in order to determine the temperature profile which results in the highest shear and elongational viscosity, and hence the highest melt strength. After selecting the optimum temperature profile, the effect of processing variables such as TUR and internal air pressure on the BUR and stability of the films was studied. Additionally, the effect of different take-up roller speeds and rotational screw speeds of the extruder, leading to the same and constant TUR of 5, on the BUR and stability of PLA films was examined. The effect of differences in MFI and crystallinity of different PLA grades on its processing into films was also investigated. The following conclusions were drawn from the study:

1. PLA processed at the lowest temperature profile had the highest shear and elongational viscosities leading to a high melt strength.

    a. The shear viscosity increased as the temperature decreased in accordance with the Arrhenius relationship. The activation energy (E_a) increased with increasing shear rates indicating that the effect of processing temperature on the shear viscosity of the polymer melt became more pronounced at high shear rates. Additionally, PLA exhibited shear thinning behavior irrespective of the processing temperature.

b. The zero shear viscosity of PLA increased as the temperature decreased following the Arrhenius relationship. The activation energy (E_a) and Arrhenius constant (A_0) were 80.4 kJ/mol and 2.7×10^{-7}, respectively.

c. The elongational viscosity increased as the temperature decreased. PLA exhibited strain hardening at all temperatures tested.

2. Processing variables such as TUR and internal air pressure had a significant impact on the stability and BUR of the blown films. Various defects such as melt sag at low TURs, bubble dancing at higher internal air pressures, and draw resonance at high TURs were observed. These defects could be eliminated by appropriate control of processing variables.

3. By optimizing the processing temperature and conditions, PLA films with a BUR of 5 could be manufactured successfully using a conventional blown film extrusion process without the use of additives.

4. Different values of take-up roller speeds and rotational screw speeds, leading to the same and constant TUR of 5 had no effect on the stability and BUR of the PLA films. These results indicate that the ratio of take-up roller speeds to the rotational screw speed had more impact on the BUR and stability of PLA films than the actual values of speeds used.

5. The difference in MFI and crystallinity of the PLA grades investigated had no effect on the stability and BUR of the PLA films suggesting that both semicrystalline and amorphous PLA can be blown into flexible films without MSEs.

5.2 Future work

While this study focused on developing strategies to process extrusion-blown PLA films without MSEs, the performance of these films as packaging materials must also be evaluated. It would be appropriate to measure the optical (clarity, gloss, opacity, color, haze), thermal (glass transition and melting temperatures), mechanical (tensile and impact strength, toughness, hardness, creep, resilience, puncture resistance), sealing (seal strength, hot tack) as well as barrier properties of these films. These properties are important parameters to consider while evaluating package performance. Moreover, the measured properties can be compared to those of films processed with MSEs in order to identify films with better performance