Blown film extrusion of poly(lactic acid) without melt strength enhancers

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ABSTRACT: Processing strategies were developed to manufacture poly(lactic acid) (PLA) blown films without melt strength enhancers (MSEs). The effects of processing temperature on PLA's melt properties (shear and elongational viscosities), PLA grades, and other processing conditions [ratio of take-up roller to extruder's rotational screw speeds or processing speed ratio (PSR) and internal air pressures] on film's blow-up ratio were examined. Experimental results indicate that extrusion-blown amorphous and semicrystalline PLA films can be successfully manufactured without MSEs by controlling melt rheology through processing temperature and other extrusion processing conditions. PLA processed at lower extrusion temperature had higher melt viscosities, which favored the formation of stable films depending on the PSR and internal air pressure used. Inappropriate control of PSR and internal air pressure led to unstable films with various processing defects such as melt sag, bubble dancing, or draw resonance, irrespective of the lower extrusion processing temperature. © 2017 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2017**, *134*, 45212.

INTRODUCTION

Poly(lactic acid) (PLA), a plant-based biodegradable plastic, is a sustainable alternative to petroleum-based polymers because it reduces United States 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 excellent stiffness, reasonable strength, excellent flavor and aroma barrier, as well as good grease and oil resistance.[1–7]

The global PLA market was valued at $304.9 million in 2014, dominated by the packaging segment, which accounted 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 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 due to its insufficient melt strength and low thermal stability, leading to a narrow processing window.[11–14] The low melt strength of PLA is attributed to the chain scission reactions that occur when it is subjected to shear and high temperature in an extruder.[15] These reactions lower its molecular weight and negatively impact molecular weight dependent properties such as shear and elongational viscosities, resulting in insufficient melt strength.[15] PLA's inadequate melt strength poses challenges for its manufacture into flexible film through processes that require stretching or orientation, such as blown and cast film extrusion, as well as foaming.[16]

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, insufficient melt strength of PLA prevents its use in cast film extrusion. In cast film extrusion process, 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, resulting in films with nonuniform thickness and smaller width than intended.[16]

Foaming is another process which requires stretching of the polymer, especially during cell growth, wherein the lack of melt strength can lead to cell coalescence, thus affecting the cell morphology of PLA foams.[17] Therefore, PLA's melt strength is extremely vital for its processing into films and foams.

Chain extenders such as multifunctional epoxies, 1,4-butane di-isocyanate, and hexamethylene di-isocyanate among others are often blended with PLA matrix to increase its melt strength.[11–13,18–20] 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 and other processes such as casting and foaming.[11–13,18,21]

Attempts have recently been made to increase the melt strength of PLA using multifunctional epoxies for foaming applications. For example, Mihai et al. investigated the shear and elongational viscosities of extrusion foamed amorphous and semicrystalline PLA with the addition of up to 2% multifunctional styrene-acrylic-epoxy copolymer using carbon dioxide (CO_2) as a blowing agent.[13] They reported an increase in these viscosities and strain hardening of PLA with increasing chain extender content, irrespective of PLA's crystallinity. The chain extension reduced foam density of crystalline PLA from 65 to 36 kg/m^3 owing to better cell wall stabilization induced by chain branching at low blowing agent concentration (5% CO_2). Nevertheless, amorphous PLA foams were unaffected by chain extenders.

Multifunctional epoxies have also been used to melt strengthen PLA for blown film applications. Recently, Mallet et al. investigated various formulations of PLA with multifunctional epoxy, nucleating agents and plasticizers to melt strengthen and blow PLA film.[11,12] They reported an increase in shear and elongational viscosities of PLA with increasing multifunctionalized epoxy content. Additionally, they 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% multifunctional epoxy to enlarge its processing window. This PLA/multifunctional epoxy formulation blended with 10% poly(ethylene glycol) (PEG), 1% N,N′-ethylenebis (stearamide), and 1% talc 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, a 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 et al. added 1,4-butanediol in the first step to react with PLA's carboxyl group and then added 1,4-butane di-isocyanate in the second step to react with PLA's hydroxyl group to chain-extend PLA.[19] 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 crosslinked, high molecular weight PLA. The favorably

viscous, crosslinked 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.[22] Irradiation of PLA induced chain scission reactions, lowering its molecular weight, in the absence of GMA. However, 10 kGy 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, and their impact on the inherent biodegradability of PLA.[23] 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.[24] 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, an extrusion 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 [eq. (1)].

$$\eta = A_0 \exp\left(\frac{E_a}{R \cdot T}\right) \qquad (1)$$

where η is the shear viscosity, A_0 is a constant, R is the universal gas constant, and T is the absolute temperature, and E_a is the activation energy of melt flow.[14,25]

As eq. (1) 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. Additionally, processing conditions that change the shear viscosity will also affect the elongational viscosity since the shear viscosity is related to the elongational viscosity.[17,26–28] Generally, the elongational viscosity varies directly with the shear viscosity, i.e., as the shear viscosity increases, the elongational viscosity increases, and vice versa.

Table I. Characteristics of Different PLA Grades Measured in This Study

PLA grade	D-lactide (%)	Melt properties[a]		Thermal properties[b]		
		MFI (g 10 min^{-1})	δ_m (g cm^{-3})	T_g (°C)	T_m (°C)	χ_c (%)
2003 D	4–4.5[31]	39.93	1.204	61.69	167.03	11.92
3052 D	4[30]	27.80	1.138	61.43	165.93	4.12
4043 D	4.8[32]	41.07	1.179	62.11	167.68	12.38
8302 D	10[14]	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.

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 controlling 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.

Furthermore, processing conditions such as extruder's rotational screw speed, take-up ratio (TUR) (ratio of the take-up velocity to the velocity of extruded melt as it exits the die), as well as internal and external air pressures are important variables in the extrusion-blown film process that have a significant impact on the frost line (FL), in turn affecting the stability of films.[29] It is crucial to optimize these processing variables to obtain stable PLA films.

The aim of this study was to develop processing strategies to manufacture blown PLA films without any MSEs. 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 MSEs.

EXPERIMENTAL

Materials
Various PLA grades (2003 D, 3052 D, 4043 D, and 8302 D) 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.[30] Relevant properties of these polymers measured in this study using the methods described later in this section are summarized in Table I. [14,30–32] The melt flow index (MFI) and thermal properties were measured as described below.

MFI. The MFI and melt density (δ_m) of various grades of PLA (Table I), dried at 50 °C, 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:

$$\delta_m = \frac{\text{MFI}}{\text{MVR}} \qquad (2)$$

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

The MFI and δ_m of PLA 2003 D were also measured at 175, 183, 200, and 210 °C to obtain the zero shear viscosity (η_0) at these temperatures using the following equation[7,33]:

$$\eta_0 = \frac{\delta_m \cdot W \cdot R^4}{8 \cdot \text{MFI} \cdot L \cdot R_A^4} = 4.8547 \times \frac{\delta_m \cdot W}{\text{MFI}} \qquad (3)$$

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.

Thermal Properties. The thermal properties of various grades of PLA were measured using a Q100 differential scanning calorimeter (TA Instruments, New Castle, DE) and the results are listed in Table I. Nitrogen, flowing at a constant rate of 70 mL min^{-1} 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 to 5 mg were heated to 180 °C at a rate of 10 °C min^{-1}, cooled to 20 °C, and finally reheated to 180 °C 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, DE). The percentage crystallinity (% χ_c) was calculated from the first heat curve using the following equation[5,7]:

$$\%\chi_c = \frac{\Delta H_c - \Delta H_m}{\Delta H_m^\infty} \qquad (4)$$

The melt enthalpy of a spherulite of infinite size $\left(\Delta H_m^\infty\right)$ used for PLA was 93 J g^{-1}.[5,7]

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

Rheological Measurements. 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 capillary rheometer attached to an extruder as employed in this study is that it

mimics high shear rates experienced during extrusion and generates test results at actual processing conditions.[34]

Shear viscosity. 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 20, 30, and 40 mm, all with a diameter of 2 mm, were utilized. Starting from the hopper to the die, the temperature profile of the extruder was kept constant to maintain a constant melt temperature for accurate viscosity measurements with all the heating zones set to 170, 185, or 200 °C. The rotational screw speed varied from 10 to 80 rpm to generate different shear rates during the experiments.[5,17,34] 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 and the melt density used in the viscosity calculations was measured as described above.

Apparent shear stress (τ_a) and apparent shear rate ($\dot{\gamma}_a$) were calculated using the following equations:

$$\tau_a = \frac{\Delta P}{2 \cdot (L/R)} \qquad (5)$$

$$\dot{\gamma}_a = \frac{4 \cdot Q}{\pi \cdot R^3} \qquad (6)$$

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:

$$\tau_w = \frac{\Delta P}{2 \cdot (e + L/R)} \qquad (7)$$

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.

The apparent shear rate gives only the Newtonian behavior (constant viscosity) and hence Rabinowitsch correction was performed to correct the shear rate for pseudo-plastic fluids (viscosity is shear rate dependent) in order to obtain the shear rate at the wall ($\dot{\gamma}_w$). The following equation was used to calculate $\dot{\gamma}_w$:

$$\dot{\gamma}_w = \frac{3n+1}{4n} \times \dot{\gamma}_a \qquad (8)$$

where n is the flow behavior obtained as the slope of the linear plot of log $\dot{\gamma}_a$ versus log τ_a.

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

$$\eta = \frac{\tau_w}{\dot{\gamma}_w} \qquad (9)$$

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, 170, and 180 °C to understand the effect of temperature on elongational viscosity. The reason for selecting different temperatures for elongational viscosity measurements than those used for shear viscosity will be discussed later. Rectangular samples with dimensions 18 × 10 × 0.78 mm were compression molded at 180 °C. Elongational viscosity was measured at a fixed Hencky strain rate of 0.1 s^{-1} as described by Matuana and Diaz as well as Hadinata *et al.*[17,35] From this experiment, the temperature profile resulting in the highest shear and elongational viscosities was selected and used to manufacture PLA blown film.

Extrusion-Blown PLA Films. PLA pellets were dried in an oven at 50 °C for at least 24 h to remove moisture before processing. A 19-mm single screw extruder (C.W. Brabender Instruments, South Hackensack, NJ), powered by a 3.73 KW (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 °C. This temperature profile was optimum to ensure the melting of PLA while giving the highest shear and elongational viscosities amongst other temperature profiles investigated.

Processing speeds (extruder's rotational screw and take-up rollers) as well as 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.[2] Investigators have reported bubble instabilities or defects such as draw resonance, helical instability, FL oscillation, among others as a result of improper control of the extruder's rotational screw and take-up roller speeds as well as internal air pressure.[36,37] 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 processing speeds and the internal air pressure on the BUR and stability of the blown films.

The processing speed ratio (PSR) defined as the ratio of the speed of take-up rollers to the rotational screw speed of the extruder was used as an appropriate and independent variable to control the film's BUR. It was calculated using the following equation:

$$PSR = \frac{\text{Speed of take−up rollers}}{\text{Speed of extruder's rotational screw}} \qquad (10)$$

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

Speed of take−up rollers or extruder's rotational screw

$$= \frac{\pi \cdot D \cdot N}{60} \qquad (11)$$

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's rotational screw 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[12,36]:

$$BUR = \frac{Final\ Bubble\ Diameter}{Die\ Diameter} \qquad (12)$$

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 to 64 rpm by 5 rpm increments to obtain different PSRs. For each PSR, the internal air used to inflate the film varied from 0.03 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 PSR 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 min of processing.

RESULTS AND DISCUSSION

Effect of Temperature on Shear and Elongational Viscosities

Low shear and elongational viscosities of PLA 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 these 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 extrusion-blown film processing of PLA. Capillary rheometry measurements were performed to study the effect of temperature on the shear viscosity of PLA. The plot of PLA's true shear viscosity as a function of its corrected shear rate at various temperatures is shown in Figure 1.

Two distinct trends were observed in this figure (Figure 1). 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.[14,17] Such behavior is characteristic of typical pseudoplastic ($n < 1$), shear-thinning fluids in the non-Newtonian region. The results indicate that the melt obeyed power law:

$$\eta = K \cdot (\dot{\gamma}_w)^{n-1} \qquad (13)$$

where K and n (Table II), obtained from a linear regression of the curves in Figure 1, represent the melt viscosity coefficient and flow index, respectively.

Second, increasing the test temperature resulted in a reduction of melt viscosity coefficient (K) suggesting that the melt became less viscous (Table II). Similar results were reported by Matuana and Diaz.[14] At high temperatures, PLA molecular chains have a
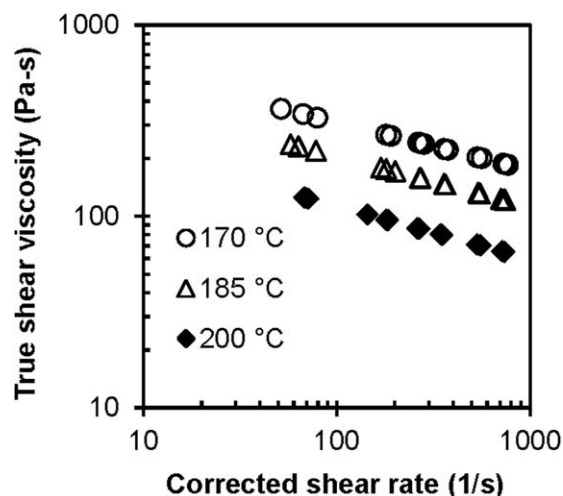

Figure 1. True shear viscosity of semicrystalline PLA (2003 D) as a function of corrected shear rate at various temperatures (170, 185, and 200 °C).

more 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.[14] 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 II).

Moreover, the reduction of viscosity as a function of processing temperature followed the Arrhenius relationship [eq. (1)] as the logarithmic viscosity of PLA varied linearly with the reciprocal temperature (Figure 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 III). 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.[14]

Capillary rheometry measurements performed did not provide the flow properties of PLA at zero shear rate because the shear rates processed in the capillary rheometer were very high. Consequently, MFI measurements were performed to estimate the zero shear viscosity at various temperatures. Figure 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. The E_a and A_0 were 80.4 kJ mol^{-1} and 2.7×10^{-7} Pa s, respectively.

Table II. Melt Viscosity Coefficient (K) and Power Law Index (n) for Semicrystalline PLA 2003 D Measured at Various Temperatures

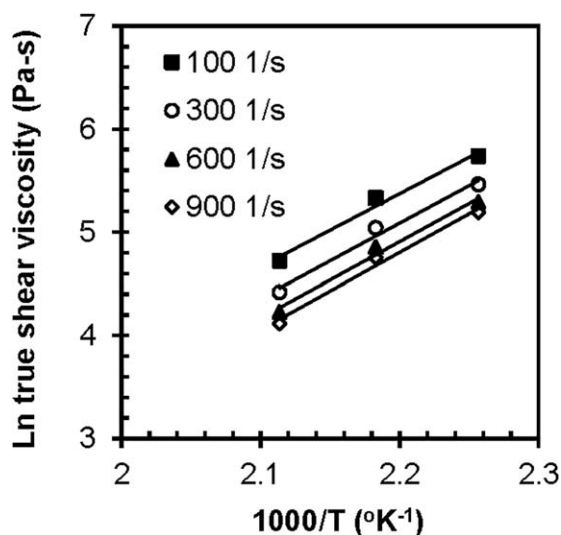| Temperature (°C)	Regression parameters		
	K (Pa s^n)	n	R^2
170	974.8	0.751	1
185	690.2	0.737	1
200	397.6	0.725	1

Figure 2. Logarithmic true shear viscosity of semicrystalline PLA (2003 D) as a function of reciprocal temperatures ($1000/T$) at various shear rates (100, 300, 600, and 900 1/s).
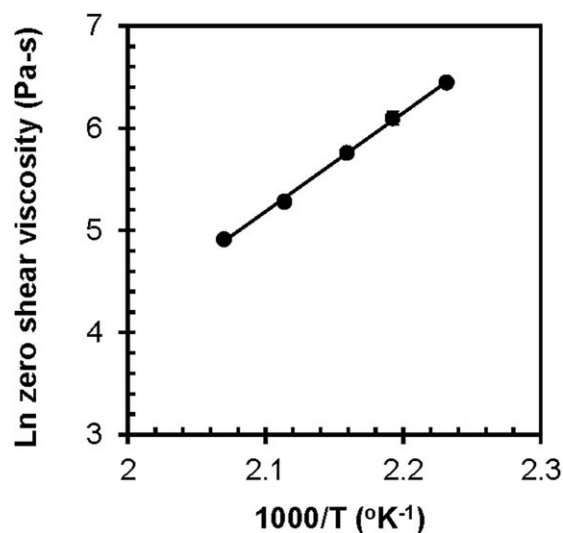

Figure 3. Logarithmic zero shear viscosity of semicrystalline PLA (2003 D) as a function of reciprocal temperatures ($1000/T$).

Besides shear viscosity, elongational viscosity plays an important role in blown film processing. Low elongational viscosity can result in bubble instabilities, whereas polymers with strain hardening, indicative of high elongational viscosity, are good for bubble stability in the blown film extrusion process. Strain hardening is usually exhibited in plastics when the rate of deformation exceeds the rate of molecular relaxation.[38,39] It is most significant in polymers with long chain branching because branching introduces longer relaxation times.[39] Even though strain hardening for linear polymers is uncommon, it has been reported by several investigators.[39–42] For instance, Dorgan *et al.* reported significant strain hardening of linear PLA with L-lactide contents of 96% and 98%, owing to high molecular weight fractions present in the samples.[39,42]

The elongational viscosity of PLA measured at a constant strain rate of 0.1 s^{-1} and various temperatures is shown in Figure 4. As expected, the elongational viscosity increased as the temperature decreased. A similar trend was observed by Han and Park for polyethylenes and polypropylenes.[43] The elongational viscosity of PLA with ~96% L-lactide tested in this study showed strain hardening behavior before rupture, irrespective of the temperature, in agreement with the work of Dorgan *et al.*[39,42]

It is worth mentioning that the temperature profiles investigated for measuring the zero shear, shear and elongational viscosities were different. It was difficult to measure the elongational

viscosity of PLA at temperatures above 180 °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 °C was required to melt PLA for the measurement of zero shear viscosity in the melt indexer. Therefore, a higher temperature range (175–210 °C) was selected for zero shear viscosity measurements.

The experimental results for shear and elongational viscosity confirmed the hypothesis that the shear (Figure 1) and elongational (Figure 4) 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.

Effect of PSR 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 PSR and internal air pressure on the
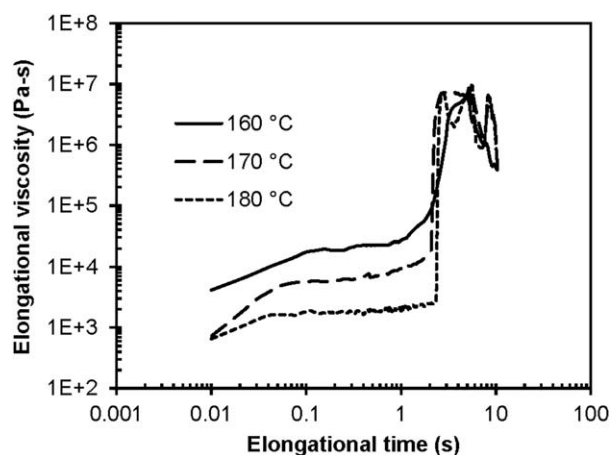
Table III. Activation Energy (E_a) and Arrhenius Constant (A_0) of Semicrystalline PLA 2003 D at Various Shear Rates (100, 300, 600, and 900 1/s)

Temperature (°C)	Shear rate (s$_{-1}$)			
	100	300	600	900
E_a (kJ mol^{-1})	58.92	60.58	61.62	62.24
A_0 (×10^{-5} Pa s)	3.651	1.768	1.119	0.857
R^2	0.9831	0.9842	0.9848	0.9852

Figure 4. Elongational viscosity of semicrystalline PLA (2003 D) as a function of elongational time at various temperatures (160, 170, and 180 °C).
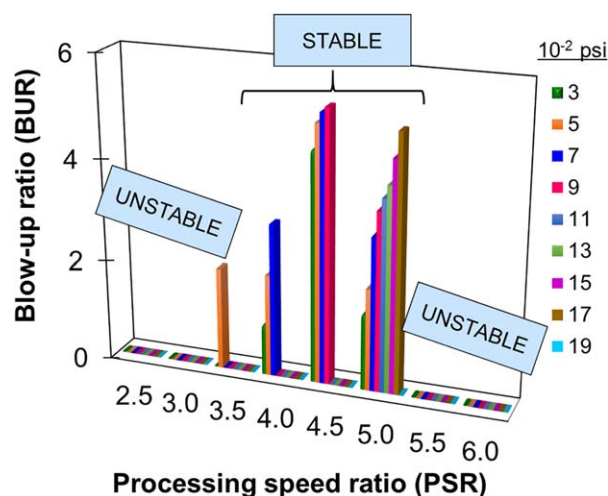
Figure 5. Effect of film's PSR and bubble's internal air pressure (in psi) on the BUR of PLA films.

stability and BUR of the films. Processing speeds of the extruder's rotational screw and take-up rollers as well as the internal air pressure have been found to be major processing variables in controlling the FL height (FLH), which in turn influences the stability of blown films.[2] The FL is the point at which the polymer solidifies and is no longer able to stretch, i.e., the point where no more crystallization occurs and the polymer attains its final solid state.[44] The distance from the die exit to the FL is known as the FLH.

Figure 5 shows the plot of BUR as a function of PSR and internal air pressure at a constant external cooling air pressure of 1 psi. The PSR and internal air pressure had a significant effect on the BUR of the film.

A critical value of PSR 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 6(a). No FL was observed at PSRs below 3.5.

At a PSR 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 6(b)] was observed at this PSR 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 PSR and producing an adequate FLH.

At optimum PSRs, between 4.0 and 5, stable PLA films were obtained. As expected, at a particular PSR, 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 PSR 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.

At PSRs 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 6(c). This defect has been reported in literature as draw resonance.[37] Moreover, the diameter fluctuations aggravated with time and led to bubble rupture. Hence, no stable film was obtained at a PSR above 5.

The optimum conditions for blowing PLA to 5-in. diameter were found at a PSR of 5, with 0.17 psi internal air pressure. At this PSR of 5, the film thickness decreased from 0.032 to 0.014 mm when the BUR changed from 1.5 to 5. Figure 7(a) shows a stable PLA film at these conditions. The internal air was ideal to blow PLA to 5-in. diameter and the PSR was appropriate to eliminate defects such as melt sag, bubble dancing, and draw resonance. Figure 7(b) shows a stable film of PLA blown to 3.5-in. diameter at a PSR of 5, and internal air pressure of 0.09 psi. It is worth mentioning that a PSR of 5 was
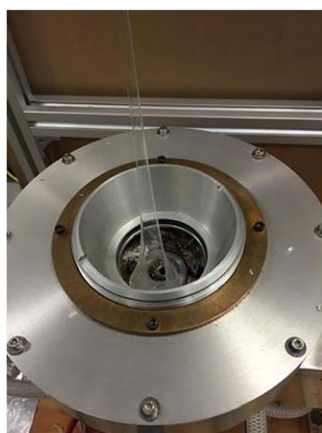
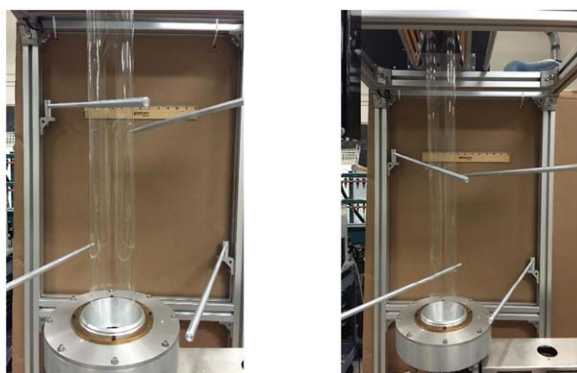**Figure 6.** Bubble defects observed during blown PLA films extrusion.

Figure 7. Stable films with different BUR values processed at a constant PSR of 5 without any defects for at least 5 min of continuous processing.

selected as the optimum PSR because it gave the flexibility to produce film with a wide range of BURs as the internal air pressure varied.

Effect of Processing at a Constant PSR 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 PSR obtained by 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 PSR of 5 on the stability and BUR of the films. Figure 8 shows the effect of these different speeds at a constant air pressure of 0.17 psi.

As seen in Figure 8, the different combinations resulting in the same PSR had no significant effect on the film's BUR. These films showed no defects, such as bubble dancing, melt sag or draw resonance, among others for at least 5 min of processing.
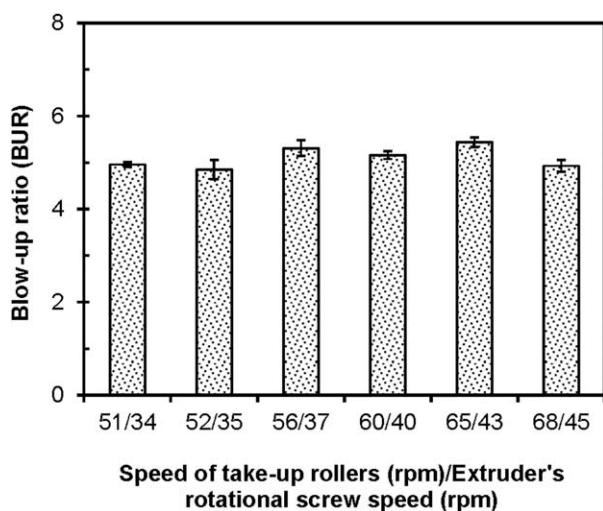

Figure 8. Effect of processing at a constant PSR of 5 obtained through a combination of various take-up roller and extruder's rotational screw speeds on film's BUR.
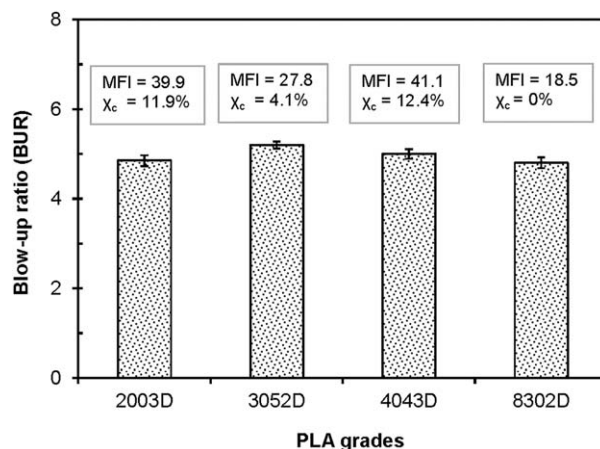

Figure 9. Effect of PLA grades on the BUR of films produced at similar processing conditions.

This was expected as processing at a constant PSR, internal air pressure, external cooling air, and melt temperature would yield a similar FLH. Since all processing variables remained constant, stable films with a constant BUR of approximately 5 were produced. These results imply that maintaining PSR to a constant value of 5 is more important than the setting of individual speed values of the winder and extruder's rotational screw needed to achieve it.

Effect of PLA Grades on the BUR of Films

Four PLA grades (2003 D, 3052 D, 4043 D, and 8302 D) with different MFI and crystallinity values (Table I) were blown at a constant PSR of 5 and an internal air pressure of 0.17 psi to understand whether these optimum processing conditions obtained for PLA 2003 D were applicable to one single grade of PLA or could be used for other grades as well. The effect of various PLA grades on the BUR of the blown films is illustrated in Figure 9. No significant difference in the BUR of the films was observed on changing the PLA grades studied. Also, these films showed no defects, such as bubble dancing, melt sag, or draw resonance, among others for at least 5 min of processing. Thus, it was apparent that the differences in PLA grades investigated had no noteworthy effect on the BUR and stability of the films when processed at the designated optimum processing conditions. This result is in agreement with the findings of Mallet *et al.* who investigated the processability of different PLA grades (2002 D, 3051 D, 4032 D, and 4060 D) at various TURs, ranging from 2 to 16.[12] When processed at a TUR of 5, they obtained stable films with a BUR of only 3, irrespective of the PLA grades.[12]

CONCLUSIONS

PLA has limited applicability in flexible sheets/films because of several drawbacks, among which its insufficient melt strength. MSEs are often blended with PLA matrix to increase its melt strength, allowing the extrusion blowing and casting of the films. However, as these additives are costly and not approved for food applications, there is a need to manufacture PLA films without MSEs.

Extrusion-blown semicrystalline and amorphous PLA films were successfully manufactured without MSEs using a conventional blown film extrusion process by controlling the melt rheology through processing temperature and other processing conditions such as the film's PSR, as well as internal and external air pressures.

PLA processed at the lowest temperature profile had the highest shear and elongational viscosities leading to a high melt strength, which was required for successful manufacture of blown films. Processing variables such as PSR 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 PSRs (2.5–3.0), bubble dancing at PSR of 3.5 and inappropriate internal air pressures (less or more than 0.05 psi), and draw resonance at high PSRs (5.5–6.0) were observed. These defects could be eliminated by appropriate control of processing variables. Stable films with a BUR of 5 were obtained at a PSR of 5, internal air pressure of 0.17 psi, and external air pressure of 1 psi. Moreover, different values of take-up roller speeds and extruder's rotational screw speeds, leading to the same and constant PSR of 5 had no effect on the BUR of the PLA films. These results indicate that the ratio of take-up roller speeds to the extruder's rotational screw speed had more impact on the BUR and stability of PLA films than the actual values of speed used. Furthermore, the difference in 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.

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