# MICROCELLULAR FOAMING OF POLY(LACTIC ACID) BRANCHED WITH FOOD-GRADE CHAIN-EXTENDERS

By

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# ABSTRACT

# MICROCELLULAR FOAMING OF POLY(LACTIC ACID) BRANCHED WITH FOOD-GRADE CHAIN-EXTENDERS

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Poly(lactic acid) (PLA) has become a material of interest in the packaging industry due to its sustainability. It has very low extensional viscosity, which causes problems for the manufacture of high-quality foams. This can be mitigated by increasing its extensional viscosity through chain extenders (CE). Therefore, this study evaluated the effectiveness and efficiency of two food-grade multifunctional epoxies chain extenders (CE) with low and high epoxy equivalent weights (EEW) in branching PLA and improving its foamability.

The chain-extension reaction of PLA with CE was followed by torque rheometry as well as shear and elongational viscosities. The cell morphology, void fraction, volume expansion ratio, and cell-population density of PLA batch-microcellular foamed with $CO_2$ were evaluated. Both CE grades were effective in increasing PLA's viscosity. However, CE with low EEW was more efficient than CE with high EEW due to its high reactivity.

Neat PLA foams showed poor cell morphology and had low expansion, owing to their low elongational viscosity. The chain-extended PLA foams showed uniform cell morphology with higher expansion, irrespective of CE content and grade. High void fraction (up to ~85%) and expansion ratio (up to ~ 8 times) were achieved by chain-branching PLA, suggesting that their melt properties were appropriate for optimum cell growth and stabilization during foaming.

Overall, this study identified the chain extender with low EEW as the most effective grade and 0.25% the threshold of CE content to produce PLA foams with homogeneous structure, small cells, as well as high void fraction, volume expansion ratio, and cell-population density.

Dedicated to my dad Mr. T. Venkatesan, mom Mrs. K. Meenakshi,
the teachers and mentors who inspired me to pursue science.

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# CHAPTER 1

## INTRODUCTION

### 1.1 Introduction

Poly (lactic acid) or PLA is a bio-based polymer which can be synthesized by the condensation polymerization of lactic acid [1]. It is bio-degradable and compostable and so has received a lot of attention in the past years as it provides a more sustainable alternative to petroleum-based polymers [2]. Poly (lactic acid) is considered a non-toxic, safe polymer for food contact [3]. It also has some attractive properties like high aroma barrier, stiffness, modulus of elasticity [2].

These desirable properties have made PLA a polymer of interest in the packaging industry, especially in food packaging and rigid packaging applications. But even though it a promising polymer it does come with its own challenges.

Being a very stiff polymer, its applications are very limited and will not be able to replace very prevalent polymers like polyethylene which is known for its flexibility and toughness.

Microcellular foaming is an established procedure that can be used to increase the toughness of PLA without heavily affecting the elasticity modulus [4], it is useful since it does not necessarily require any toxic additives [5,6]. Microcellular foams are different from regular foams because of their high cell-population densities (in the order of $10^9$ cells/cc) and small cell size ( in the order of 10 μm) [5].

But microcellular foaming of PLA comes with its own challenges because of its low melt strength [7]. Thus, PLA foams often tends to form poor foams with non-homogeneous structure and low void fractions. Increasing melt strength can improve foamability of PLA [8]. For instance, Heidari and Fasihi have reported an increase in the cell-population density and impact strength of polypropylene foams after blending with poly-olefin elastomers to increase the melt strength and extrusion foamed with sodium bicarbonate and azodicarbonamide as blowing agents [9].

The first paper on treating a commercial PLA with chain extenders with expectation of improving its viscoelastic properties for foam processing was reported by Di and co-investigators [8]. PLA with L-lactide >92 wt% was reactively modified in the melt by sequentially adding different amount ratios of two low molecular weight chain extenders, i.e., 1,4-butanediol (BD) and 1,4-butane diisocyanate (BDI) and batch-foamed using $N_2/CO_2$ compressed mixture (80/20) at 16 MPa. Crosslinking occurred in PLA modified with an equimolar amount of BD and BDI as well with an excess amount of BDI and these samples showed significant increase in molecular weight and complex melt viscosity than the unmodified PLA. These chain extended/cross-linked PLA samples allowed the production of PLA foams with smaller cell size, higher cell-population density, and lower foam density compared to the unmodified PLA foam. In contrast, modification with excess amount of BD lowered PLA's complex melt viscosity because it induced more PLA degradation, thus did not enhance its foamability [8].

Recently, long-chain branched polylactide (LCB-PLA) was prepared by UV-induced reaction extrusion with trimethylolpropane triacrylate (TMPTA) and the effect of the long-chain branching structure on the cell morphologies of PLA foamed with supercritical carbon dioxide was studied [10]. Nano-cells were formed in PLA and LCB-PLA branched with 0.5 wt% TMPTA when foamed with supercritical CO2 at 142°C. Additionally, LCB-PLA foams showed better cell morphology (less coalescence, no collapse, and uniform cell distribution) than linear PLA under higher pressure due to their increased matrix strength and higher nucleation potential [10].

A study on the extrusion foaming of chain-extended PLA with $CO_2$ as the blowing agent and talc as the nucleating agent has also been performed [11]. A styrene-acrylic oligomer, a multifunctional epoxy-based chain extender (CE) was used in this study. The authors recorded an increase in the exit die pressure as the CE content increased in the PLA matrix. This resulted in an increase in cell-population density with the addition of 0.7 to 1.0% CE, especially at the die temperatures above 140°C. The addition of CE increased the cell-population density of PLA-talc by approximately one order of magnitude up until 1.0% CE, beyond which it decreased. An increase in expansion ratio was also reported with increased CE content without affecting the cell size due to the nucleation effect caused by talc.

A similar study examined the effect of chain branching of amorphous PLA (aPLA) and semi-crystalline (cPLA) matrices with multifunctional styrene-acrylic epoxy copolymer on their foamability in a one-step extrusion process with up to 9% $CO_2$ [12]. The shear and elongational viscosities of both aPLA and cPLA increased with the CE content. Unfortunately, increased melt elasticity of PLA did not correlate with the foamability of amorphous grade since the foam morphology and density of aPLA were not improved by the presence of the chain-extender, irrespective of the content. This was attributed to the low foaming temperatures achieved during aPLA foaming, which may have limited the reactivity of the chain-extender. In contrast, the cPLA foam morphology and density were affected by the increase of the chain-extender content only at 5% $CO_2$, where chain extended cPLA foams exhibited lower densities and larger cell sizes than neat cPLA counterpart [12].

Improvements in PLA foam characteristics have also been reported with other chain extenders such as multifunctional aziridine [13], polystyrene/poly(glycidyl methacrylate) random copolymer [14], etc. or by the free radical branching/linking of PLA with dicumyl peroxide [15].

Despite promising results, most of the chain extenders used to ease the foamability of PLA are not approved for food contact because of toxicity issues. For instance, trimethylolpropane tri-acrylate has been reported to cause rare types of cancer in mice [16] and isocyanates are also known for their toxicity [17]. The other chain extenders are styrene-based additives, and styrene is a known carcinogen [18].

Recently, novel food-grade multifunctional epoxies with varying reactivities that are approved for food contact by the food and drug administration (FDA) have been developed. Unfortunately, limited studies have been reported on their use to melt strengthen PLA and ease its foamability. The effectiveness and efficiency of two food-grade multifunctional epoxies with low and high epoxy equivalent weights (EEW) in chain extending/branching poly(lactic acid) (PLA) were recently studied in a torque rheometer [2]. Chain extension occurred through the ring-opening reaction of epoxy groups in the CE with PLA's hydroxyl and/or carboxyl groups. CE with lower epoxy equivalent weight was more efficient due to its higher reactivity. Despite this promising result, the effect of these chain-extenders on the foamability of PLA has not been investigated, thus was the main goal of this study.

## 1.2 Objectives

The main goal of this research was to study the effectiveness and efficiency of two food-grade multifunctional epoxies chain extenders (CE) with low and high epoxy equivalent weights (EEW) in improving the melt strength and foamability of PLA. The following specific objectives were proposed to achieve the research goal:

1. To understand the effects of CE content and type (epoxy equivalent weights) on rheological properties to determine their effectiveness and efficiency in chain extending/branching PLA.

2. To study effects of chain extender content and type on the void fraction (density reduction), volume expansion ratio, average cell size, and cell-population density of PLA foams to determine the most suitable formulation for successful manufacture of branched PLA foams.

## 1.3 Hypothesis

This study tested the hypothesis that improvement in the elongational viscosity and the foamability of linear PLA will depend on the epoxy equivalent weight and concentration of the chain extender.

## 1.4 Structure of the thesis

Chapter 1 discusses the rationale for this research, followed by a background on PLA, its properties and various manufacturing techniques used for processing PLA along with a detailed literature review on microcellular foaming with PLA in chapter 2. The materials, methods used for sample preparation and microcellular foaming experiments, as well as rheological and foam property characterization are described in detail in the following chapter. The fourth chapter discusses the rheological and foam property results of chain extended PLA including shear viscosity, extensional viscosity, volume expansion, average cell diameter, and cell-population density. The findings have been summarized in chapter 5 and future work based on these findings have also been proposed.

# REFERENCES

# REFERENCES

1. Cheng, Y., Deng, S., Chen, P., and Ruan, R. (2009). Polylactic acid (PLA) synthesis and modifications: a review. *Frontiers of Chemistry in China,* 4(3), 259-264.

2. Karkhanis, S.S., and Matuana, L.M. (2019). Extrusion blown films of poly(lactic acid) chain-extended with food grade multifunctional epoxies. *Polymer Engineering and Science,* 59 (11): 2211-2219.

3. Conn, R.E., Kolstad, J.J., Borzelleca, J.F., Dixler, D.S., Filer Jr, L.J., LaDu Jr, B.N., and Pariza, M.W. (1995). Safety assessment of polylactide (PLA) for use as a food-contact polymer. *Food and Chemical Toxicology,* 33(4), 273-283.

4. Wang, J., Zhai, W., Ling, J., Shen, B., Zheng, W., and Park, C.B. (2011). Ultrasonic irradiation enhanced cell nucleation in microcellular poly(lactic acid): a novel approach to reduce cell size distribution and increase foam expansion. *Industrial and Engineering Chemistry Research,* 50(24), 13840-13847.

5. Colton, J.S., and Suh, N.P. (1987). Nucleation of microcellular foam: Theory and practice. *Polymer Engineering and Science,* 27(7), 500-503.

6. Ding, W., Jahani, D., Chang, E., Alemdar, A., Park, C.B., and Sain, M. (2016). Development of PLA/cellulosic fiber composite foams using injection molding: Crystallization and foaming behaviors. *Composites Part A: Applied Science and Manufacturing,* 83, 130-139.

7. Matuana, L.M., and Diaz, C.A. (2013). Strategy to produce microcellular foamed poly(lactic acid)/wood-flour composites in a continuous extrusion process. *Industrial and Engineering Chemistry Research,* 52(34), 12032-12040.

8. Di, Y., Iannace, S., Maio, E.D., and Nicolais, L. (2005). Reactively modified poly(lactic acid): properties and foam processing. *Macromolecular Materials and Engineering,* 290, 1083-1090.

9. Heidari, A., and Fasihi, M. (2019). Cell structure-impact property relationship of polypropylene/thermoplastic elastomer blend foams. *eXPRESS Polymer Letters,* 13(5), 429-442.

10. Li, S., He, G., Liao, X., Park, C.B., Yang, Q., and Li, G. (2017). Introduction of a long-chain branching structure by ultraviolet-induced reactive extrusion to improve cell morphology and processing properties of polylactide foam. *Royal Society of Chemistry Advances,* 7(11), 6266-6277.

11. Pilla, S., Kim, S.G., Auer, G.K., Gong, S., and Park, C.B. (2009). Microcellular extrusion-foaming of polylactide with chain-extender. *Polymer Engineering and Science,* 49(8), 1653-1660.

12. Mihai, M., Huneault, M.A., and Favis, B.D. (2009). Rheology and extrusion foaming of chain-branched poly(lactic acid). *Polymer Engineering and Science,* 50, 629-642.

13. Gu, L., Xu, Y., Fahnhorst, G.W., and Macosko, C.W. (2017). Star vs. long chain branching of poly(lactic acid) with multifunctional aziridine. *Journal of Rheology,* 61(4), 785-796. doi:10.1122/1.4985344

14. Zhou, M., Zhou, P., Xiong, P., Qian, X., and Zheng, H. (2015). Crystallization, rheology and foam morphology of branched PLA prepared by novel type of chain extender. *Macromolecular Research*, 23(3), 231-236.

15. Standau, T., Castellón, S.M., Delavoie, A., Bonten, C., and Altstädt, V. (2019). Effects of chemical modifications on the rheological and the expansion behavior of polylactide (PLA) in foam extrusion. *e-Polymers,* 19(1), 297-304.

16. National Toxicology Program. (2012). Toxicology and carcinogenesis studies of trimethylolpropane triacrylate (technical grade)(CASRN 15625-89-5) in F344/N rats and B6C3F1/N mice (dermal studies). *National Toxicology Program Technical Report Series,* (576), 1.

17. Pauluhn, J. (2000). Inhalation toxicity of 1, 6-hexamethylene diisocyanate homopolymer (HDI-IC) aerosol results of single inhalation exposure studies. *Toxicological Sciences*, *58*(1), 173-181.

18. Leibman, K.C. (1975). Metabolism and toxicity of styrene. *Environmental health perspectives,* 11, 115-119.

# CHAPTER 2

## BACKGROUND AND LITERATURE REVIEW

### 2.1 Introduction

Foams are materials that contain a solid matrix within which gas bubbles are trapped closely. Polymer foams can be made from thermoplastic or thermoset polymers based on their final applications. Some common polymers used to manufacture foams include polystyrene, polyurethane, polyethylene, poly(vinyl chloride) (PVC) [1]. These materials are sourced from crude oil and the production of these polymers is contributing significantly to the carbon footprint of the human species. This in turn contributes to global warming and habitat destruction and has created a need for alternatives that are more sustainable in the long term.

Recent innovations in polymer synthesis have led to biopolymers that are synthesized from renewable resources like plant sugars. Rilsan® is a bio-polyamide created by the Arkema group from castor plant [2], BIOVYN® from INOVYN is a bio-based PVC synthesized from bio-attributed ethylene [3], and I'm green® polyethylene from Braskem which is produced from sugarcane [4] are some examples. Even though these polymers are bio-based rather than petroleum-based polymers, they still pose a problem as these plastics are hard to dispose of and stay in landfills. Given that a significant portion of the produced plastics are for single-use and recycling still being very difficult, polymers that are bio-degradable are a better solution.

Poly(lactic acid) (PLA) is a promising material that has been gaining popularity in recent years as it is a biopolymer that can be composted. A rise in its popularity could be mainly because consumers are realizing the need for more sustainable alternatives for single-use plastics. A recent survey found that three-fourths of the participants were in favor of banning single use plastics [5].

Because of this, there has been an increase in the usage of bioplastics in past years and reports estimated that 2.11 million tons of bioplastics were produced in the year 2019 [5]. Even though the quantity of produced bioplastics seems large, it represented only a fraction of the ~360 million tons of plastic produced in 2018 [6]. This fraction also includes the non-biodegradable biopolymers discussed previously. Even though poly(lactic acid) shows potential as a sustainable replacement, it is held back by its limitations in processability and lack of certain properties. Currently, PLA is mainly used in the manufacturing of rigid packaging because of its stiffness. Matuana has reported an increase in PLA's impact strength after foaming [7]. Foaming PLA can reduce material consumption and increase flexibility, thus paving the way for flexible packaging applications. Innovations with foaming PLA can help expand the current market for bioplastics.

This chapter will deliberate the properties of poly(lactic acid), foaming techniques and foaming with PLA. The chapter provides a background and literature review of the processing and foaming techniques of PLA currently in use. The review will focus on the rheological properties of PLA and the use of additives to modify PLA's rheology.

## 2.2 Poly(lactic acid)

PLA is a linear biopolymer; it is synthesized from natural resources and is biodegradable under industrial composting conditions. It has many properties comparable to petroleum-based polymers. It has good tensile properties, stiffness, heat-sealability, and aroma barrier [8].

### 2.2.1 Producing PLA

Poly(lactic acid) is commonly manufactured from monomers or dimers that are synthesized from bacterial fermentation of plant sugars like those obtained corn starch and sugar cane commonly using a bacterium from the species '*lactobacillus*' [9].

There are two main polymerization processes used to manufacture PLA. They are condensation polymerization of lactic acid and ring-opening polymerization of lactide.

#### *2.2.1.1 Condensation polymerization of lactic acid*

Lactic acid ($C_3H_6O_3$) is a molecule that plays a role in many biological processes. It is present naturally in food substances like Greek yogurt and is also produced as a waste byproduct during normal metabolic activities in the body. It is a chiral molecule and hence has two stereoisomers, D-lactic acid and L-lactic acid (Figure 2-1).

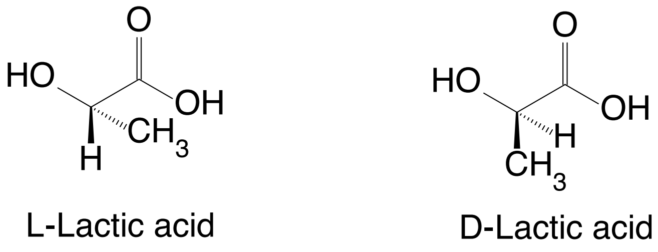

*Figure 2-1: Stereoisomers of lactic acid.*

Lactic acid can be polymerized into poly(lactic acid) by the removal of water molecules. The reaction takes place as follows [9]:

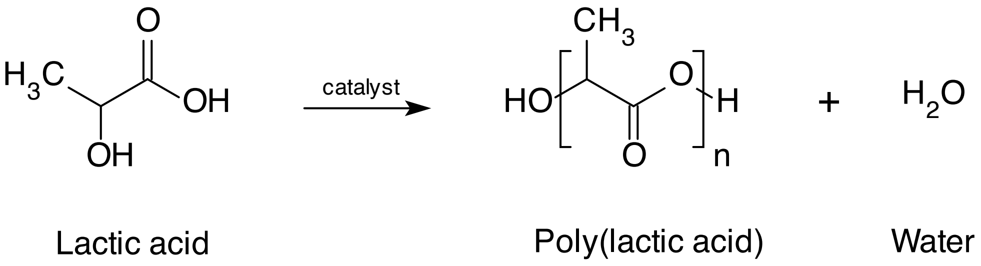

*Figure 2-2: Condensation polymerization of PLA.*

This is the less expensive route to synthesize PLA however, high molecular weight cannot be achieved using this method [9].

### *2.2.1.2 Ring-opening polymerization of lactide*

Lactides are cyclic dimers of lactic acid. They have three stereoisomers, namely D, L, and meso lactide, as shown in figure 2-3. They are produced mainly by de-polymerization of low-molecular weight poly(lactic acid) under low pressure conditions [9].

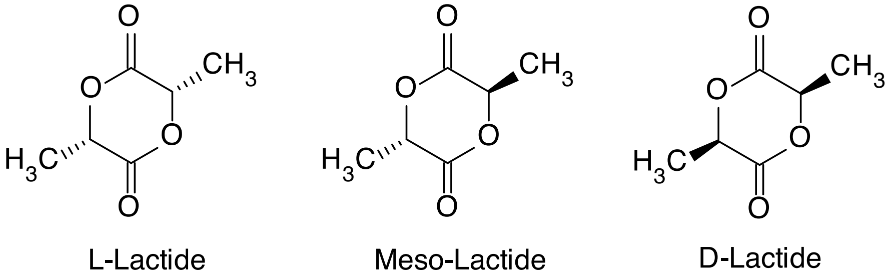

*Figure 2-3: Stereoisomers of lactide [9].*

Ring-opening polymerization of lactide can produce high molecular weight PLA. The ring-opening can be initiated by either cationic or anionic mechanisms based on the catalytic environment. Figure 2-4 shows the ring-opening polymerization reaction of lactide into PLA.

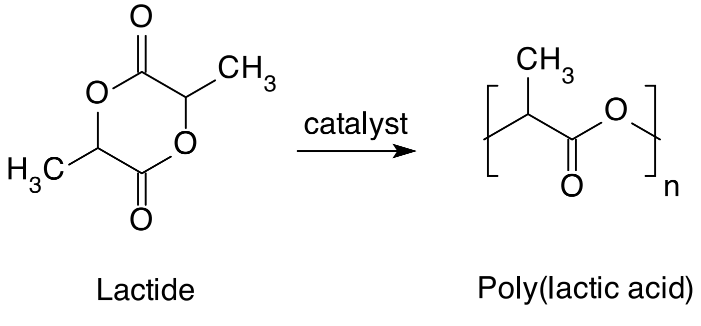

*Figure 2-4: Ring-opening polymerization of lactide [9].*

It has been found that high molecular weights can be achieved when transition metal compounds are used as catalysts [9]. Tin(II) bis-2-ethyl hexanoic acid is one such catalyst used in the polymerization of PLA mainly because of its low toxicity and high catalytic efficiency.

### 2.2.2 Manufacturing processes

Polymer resins should be processed into desired shapes and structures so that they can be used for specific applications. A myriad of processing techniques is used for forming plastics depending on the final requirement, some common techniques include the followings.

#### *2.2.2.1 Compression molding*

Compression molding is a batch process that can be used to produce sheets or containers of plastic. This process can be used in research and development to produce small quantities of sheets of various compositions. The compression molding process is also used industrially to manufacture certain products like electrical housings, dinner plates, bowls, etc. [10]. The sheets are often machined into desired shapes that can be used as test samples for various tests such as tensile, impact, etc.

In this process, a calculated amount of polymer resin is placed in a flat, heated platen, which melts and compresses the resin into a flat uniform sheet of desired thickness, the polymer is then cooled under pressure so that it maintains it shape, this process is shown in Figure 2-5 [10]. Melt flow is a key parameter in this process as higher melt flow prevents trapped air bubbles and other such defects. The same approach is used to produce 3D shaped containers using a mold.

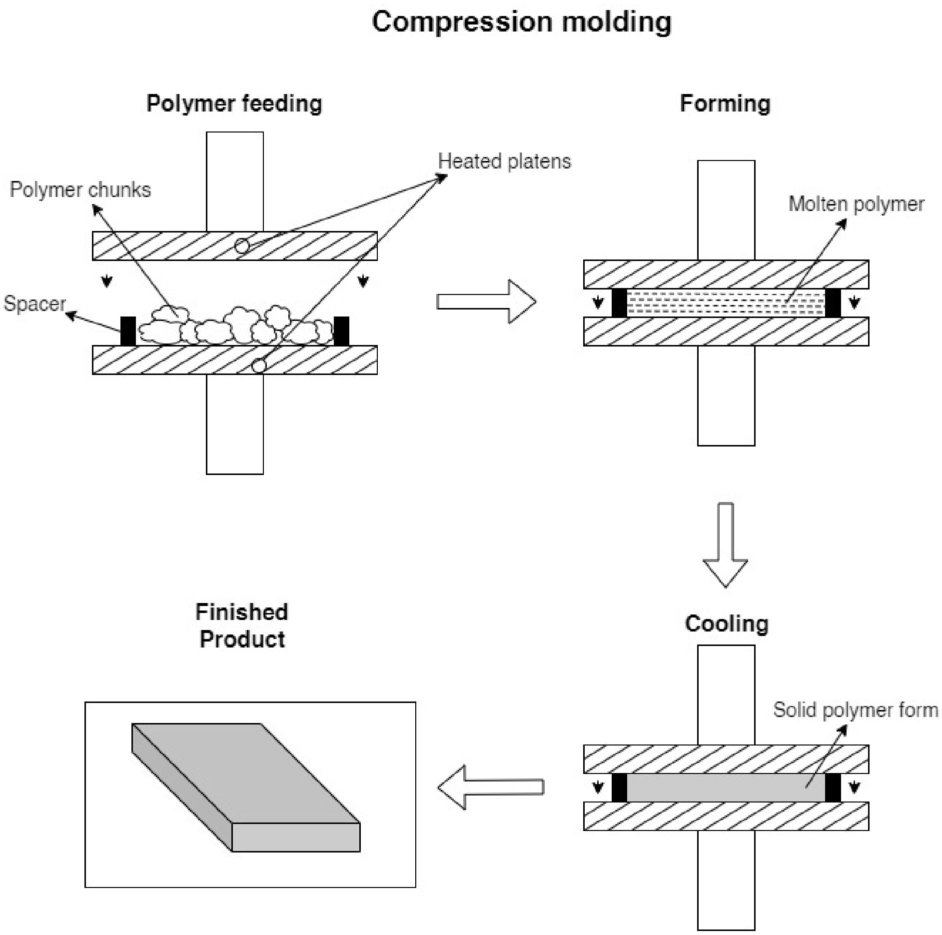

*Figure 2-5: Process of compression molding [10].*

### *2.2.2.2 Injection molding*

Injection molding is the process for producing more complex shapes using plastics. The apparatus for injection molding consists of the barrel, a nozzle, and a mold (Figure 2-6). The polymer is fed through a hopper into the barrel where it is heated and molten. The polymer melt is then squeezed into the negative mold cavity from the barrel through a nozzle [10].

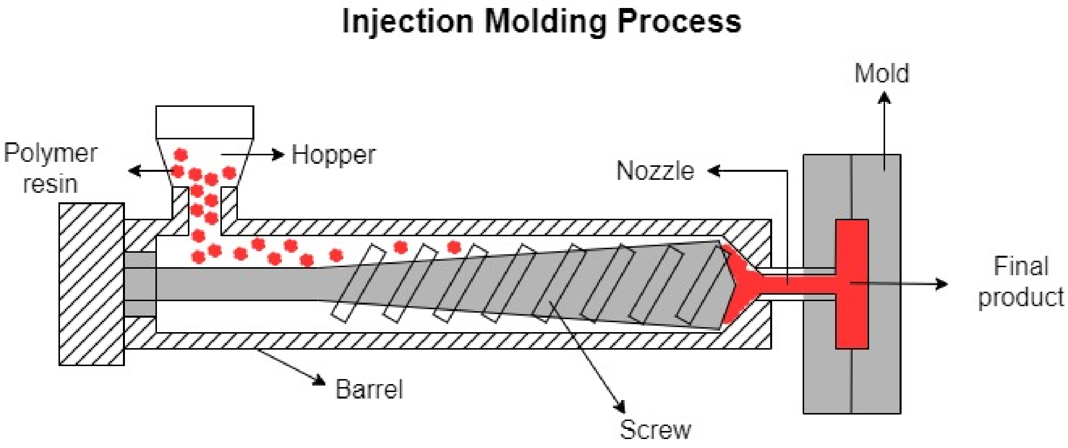

*Figure 2-6: Injection molding process [10].*

The molten polymer conforms to the shape of the mold and the mold is cooled. The shaped plastic is then removed when the mold opens, and ejector pins push the piece out. This method produces shapes with high dimensional accuracy and is very easily scaled-up. This process is used for making many products such as closures, mechanical parts, etc. [10]

The complexity of the shape that can be made in this process is limited by mold design; two-piece reusable molds cannot be designed for some complex shapes. Compared to compression molding, injection molding can also be used with polymers that have much lower melt flow index (MFI) as the injection pressure helps the melt flow and fill the molds.

The process produces a lot of flashing; thus, a lot of waste is generated by injection molding. Mold pressure is very important and insufficient mold pressure can cause flashing, which in turn leads to more material wastage.

### *2.2.2.3 Thermoforming*

Thermo-forming, as the name implies, is the process of using heat to form sheets of polymers into desired mold shapes [10]. This can be a batch or continuous process and is relatively easy to scale up. An illustration of the thermoforming process is shown in figure 2-7. The plastic sheets are feed into a chamber where the heat makes them pliable and are formed around a die often with the help of a vacuum or air pressure.

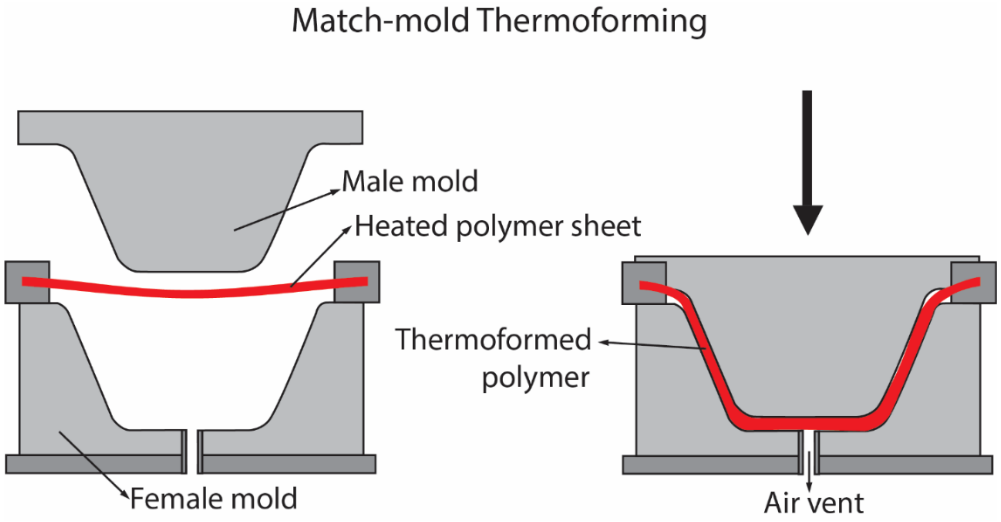

*Figure 2-7: Process of thermoforming.*

Since a flat sheet of plastic is formed into a 3D shape, it is hard to achieve uniform wall thicknesses on all sides [10]. The distribution of material depends mainly on the type of mold being used - male or female. Melt strength is a crucial parameter in this processing as other problems like sagging can occur with the processing of low melt strength materials.

All thermoforming techniques are stretching processes. The stretching of a flat sheet of plastic material into a larger shape results in a reduction in the sheet's original thickness. The thinning down of the sheet's original thickness is not necessarily uniform. Therefore, wall thickness non-uniformity of thermoformed containers is one of the drawbacks of these techniques [10].

However, certain techniques like plug-assist, bubble, and match-mold thermoforming can be used to improve wall thickness uniformity [10]. Again, this process is limited by its mold design, very complex designs cannot be manufactured with this process as it might be difficult to produce corresponding molds that easily release the plastic after forming.

#### *2.2.2.4 Additive manufacturing*

Most manufacturing processes such as lathe and computer numerical control machining, are subtractive processes and work by starting with a block of larger material and selectively remove material to form the finished product. Additive manufacturing, however, is the process in which the material is selectively added to create a finished product [11].

One of the more recent additive manufacturing technologies is 3D printing. There are many different 3D printing techniques, one of which is fused deposition modeling (FDM). FDM works by melting a filament of polymer and depositing the melt to selective positions through a nozzle to form the desired shape (Figure 2-8).

The advantage of additive manufacturing is that it allows for creating much more complex designs that cannot be produced using other traditional methods. It can also be used to create prototypes for testing or even for the manufacture of a master which can be used to create a mold. Depending on the shape of the product, the wastage produced in this method can be almost negligible, however the support material may be required for certain structures.

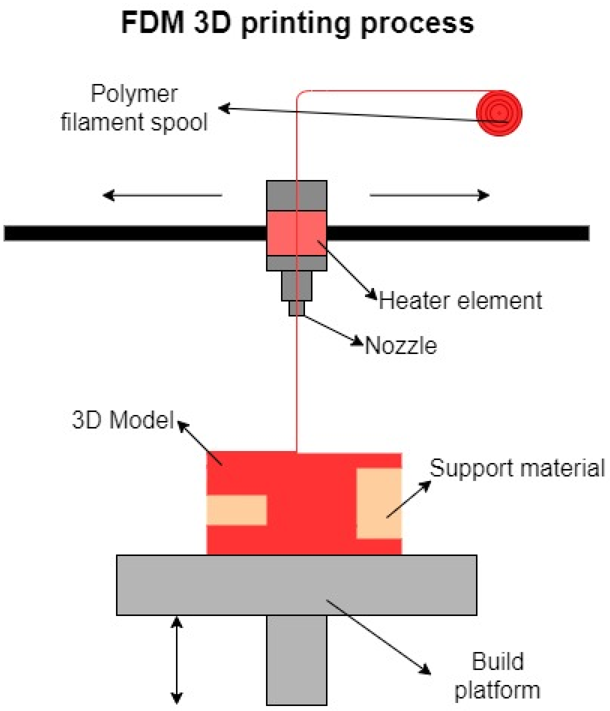

*Figure 2-8: Schematic diagram of the fused deposition modeling process.*

This technology is still in its developing phase and manufacturing with FDM is much slower than other traditional techniques and FDM may not produce details as fine as some other techniques [11].

The MFI of the polymer is important for this technique too as the melting and fusing of polymer is much faster and more accurate if the MFI is high. PLA’s high MFI makes it a suitable material for FDM, and PLA is widely used in FDM 3D printing [11].

#### *2.2.2.5 Extrusion*

The extrusion process is broader than just plastics and is also for large scale production in the food industry. In plastics manufacturing, extrusion is the process of using an extruder to melt the polymer and continuously produce polymer melt with the help of an extrusion screw. The process of cast film extrusion is shown in figure 2-9. The extruder contains the barrel which houses the extrusion screw and is constantly heated using numerous band heaters. The screw is connected to a high-torque drive unit, usually an electrical motor. The polymer resin is fed through the hopper and it passes through the three zones (*feeding, compression, and metering*) in an extruder's barrel, after which it comes out as a uniform stream of polymer melt [12].

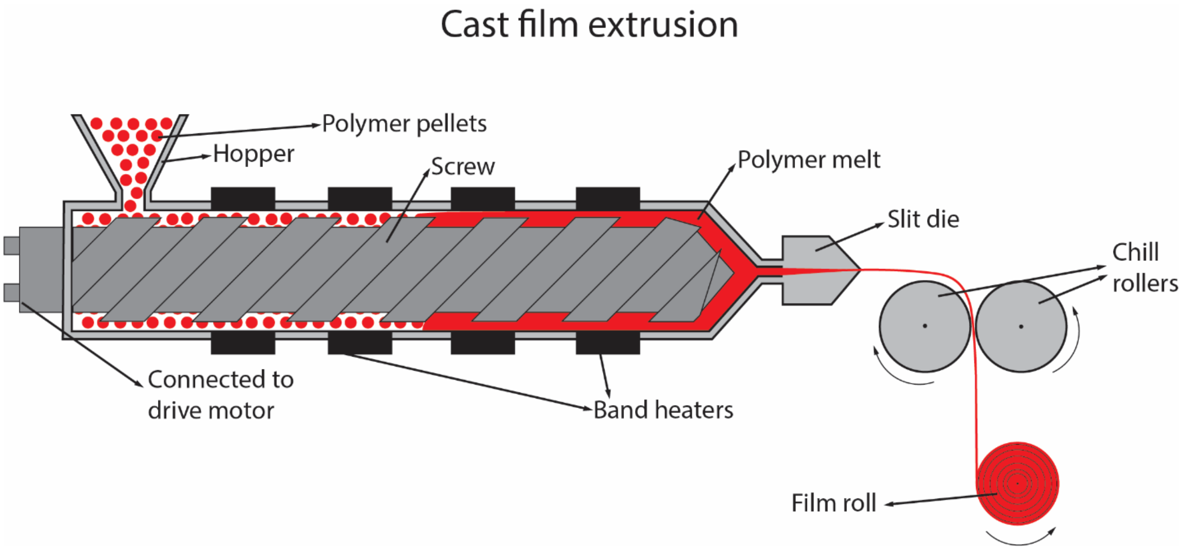

*Figure 2-9: Process of cast film extrusion.*

The *feeding* section is the section of the extruder connected to the hopper and this is where the polymer pellets enter the barrel. From there, as the screw is turned, the pellets reach the *compression* zone where they melt because of the heat and are compressed to remove any air bubbles or voids. From the compression zone, the pellets travel to the *metering* zone, which lets the melt flow through at a uniform rate. After the melt exits the barrel, it flows through a die, and depending on the die, the extruded product can be a wire, tube, sheet, or film. In packaging, extrusion is mainly used to produce films and sheets. Film extrusion is broadly classified into cast film and blown film based on the techniques and processes involved in their manufacture. Properties of the manufactured film depend on the manufacturing technique used.

#### *2.2.2.5.1 Cast film extrusion*

In this process, the polymer melt is passed through a slit die, which has a slit-shaped opening. Figure 2-9 illustrates the process of cast film extrusion. The melt forms into a film as it is extruded through the die and is immediately cooled when it encounters the chill roller [12]. This quenches the polymer film and prevents crystallization, which produces a film with high clarity. The cooled film is then wound onto a reel. Melt strength is crucial for this process, if the polymer does not have enough melt strength then it can cause problems like sagging, which is when the hot film starts drooping between the die and the chill roller. Low melt strength can also cause necking, and this is when the film width reduces after leaving the die producing a ‘neck’ [13].

#### *2.2.2.5.2 Blown film extrusion*

Figure 2-10 shows the blown film extrusion process. In this process, the extrudate is sent through an annular die which has a ring-shaped opening. The melt comes out through the die as a tube, air is then blown into this tube inflating it into a bubble. This process stretches the blown film and eventually cools it. The cooled film then passes through the nip rollers which pinch and flatten the bubble. Then the tube-shaped film is either slit and separated into two layers or kept as such depending on end-use. Since the cooling rate of the film during blown film process is lower than during cast film, the resulting blown films tend to have higher degree of crystallinity than cast films [8]. The air blown into the film stretched the tube and hence orients it, this imbues the film with superior mechanical properties compared to cast film extrusion [10].

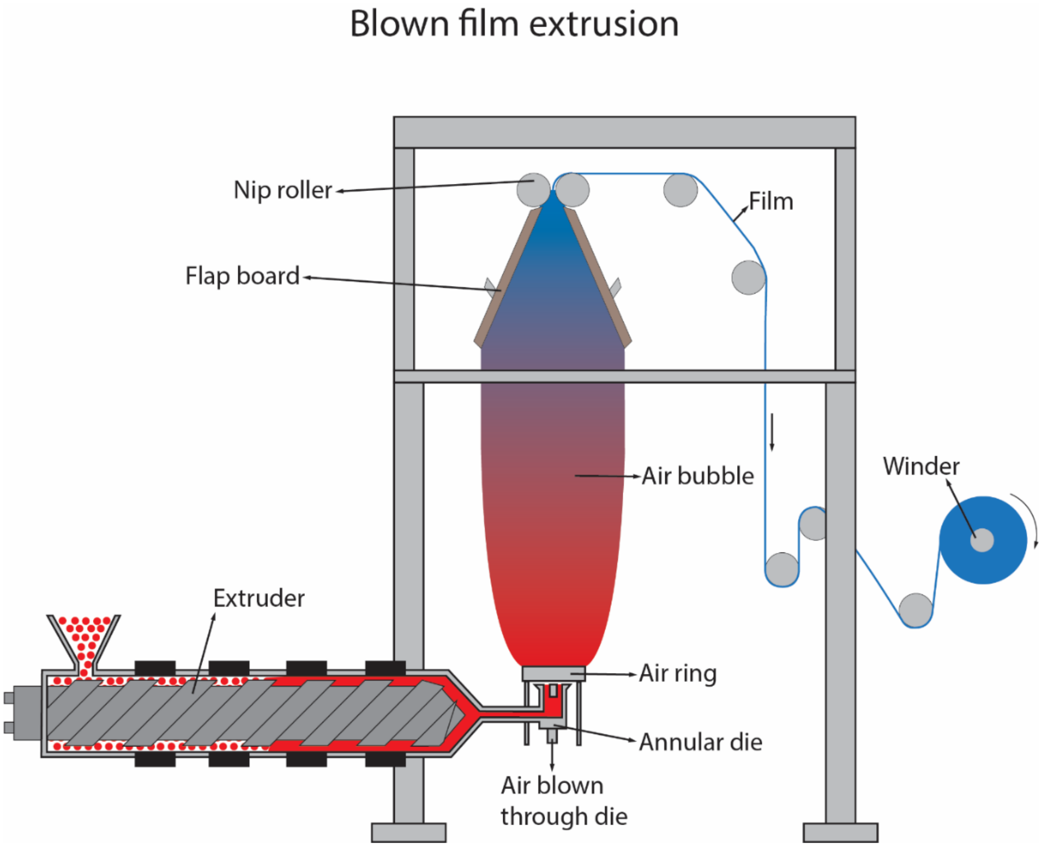

*Figure 2-10: Blown film extrusion process.*

Since the polymer is extruded against the forces of gravity, high melt strength is required for the polymer melt. Lower melt strength polymer will sag or will cause problems with bubble stability [13].

#### *2.2.2.6 Blow molding*

Blow molding is the process used to create hollow structures like bottles, jugs, hollow figurines, etc. [10] The idea of blow molding is like glass blowing where a blob of molten glass is blown into a bubble through a hollow pipe and formed into various shapes manually. Blow molding is mainly comprised of two types: Injection blow molding and extrusion blow molding.

### *2.2.2.6.1 Injection blow molding*

The process of injection blow molding is illustrated in figure 2-11. In this process, a preform or a parison is made using the injection molding process. Once the parison has been produced, it is then placed into another mold where it is heated and inflated by blowing air [10]. This causes the polymer to take the shape of the mold while still being hollow. This method is mainly used for soda bottles made with PET.

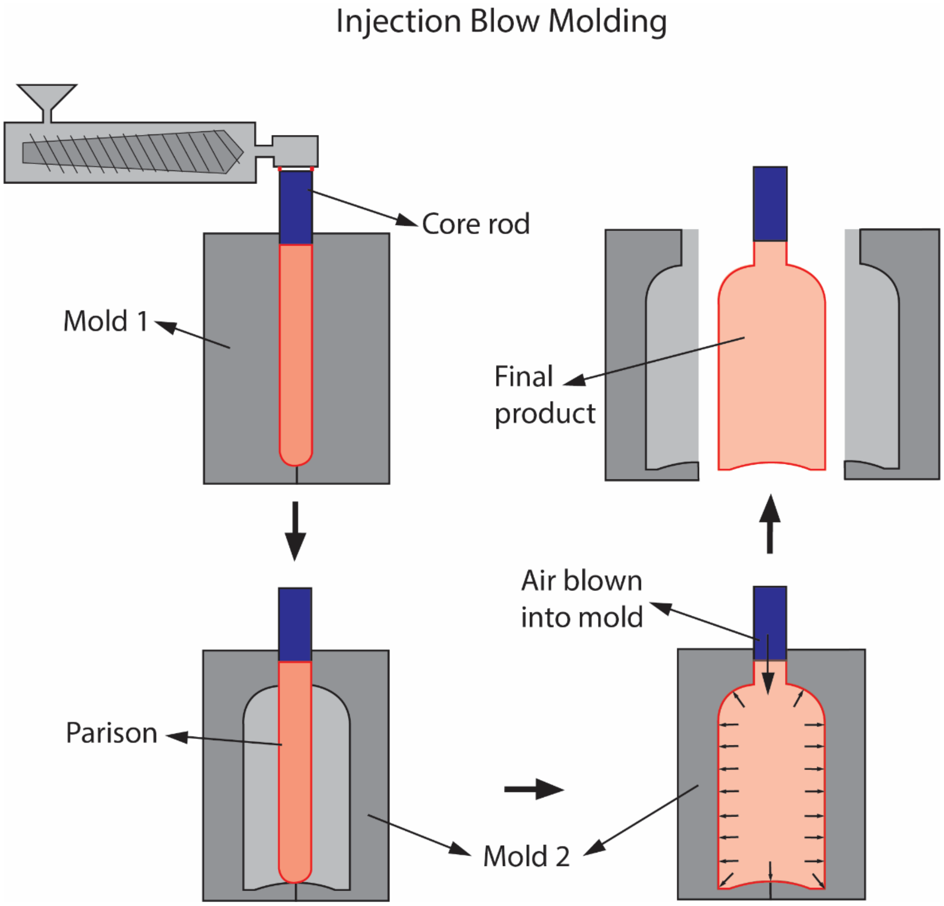

*Figure 2-11: Injection blow molding process.*

A variation of this process is the injection-stretch blow molding. In this process, the parison is stretched with a mechanical rod as it is inflated [10]. This process works better for shapes that are narrow and long like bottles. The process produces high quality bottles, which also have high clarity. Injection molding is excellent for bottles as the necks have high dimensional accuracy and thus fit perfectly with threaded closures.

#### *2.2.2.6.2 Extrusion blow molding*

The difference between this process and the former is that this one does not involve any preform as shown in figure 2-12. A tube is extruded in between the halves of the mold, this tube acts as a preform. The mold halves close and pinch off the top and bottom, and air is pushed into the tube to blow it. The tube is inflated and takes the shape of the mold. A weld line is visible in the bottom where the tube was pinched off.

Unlike injection blow molding, this method is more suitable for materials with high melt strength. The tube that is being extruded needs to hold its shape without sagging; thus, a material with higher melt strength is better for this process [10].

Extrusion blow molding can produce complex shapes like bottle/jugs with handles that are not possible with injection blow molding. Thus, it is used for producing a variety of household products like reservoirs, tanks, watering cans, detergent bottles, etc. This process also produces more waste than injection molding. The tube, which is pinched off produces flash, which must be trimmed off.

Other than these two methods, there is also the lesser-known compression blow molding where the preform is compression molded instead.

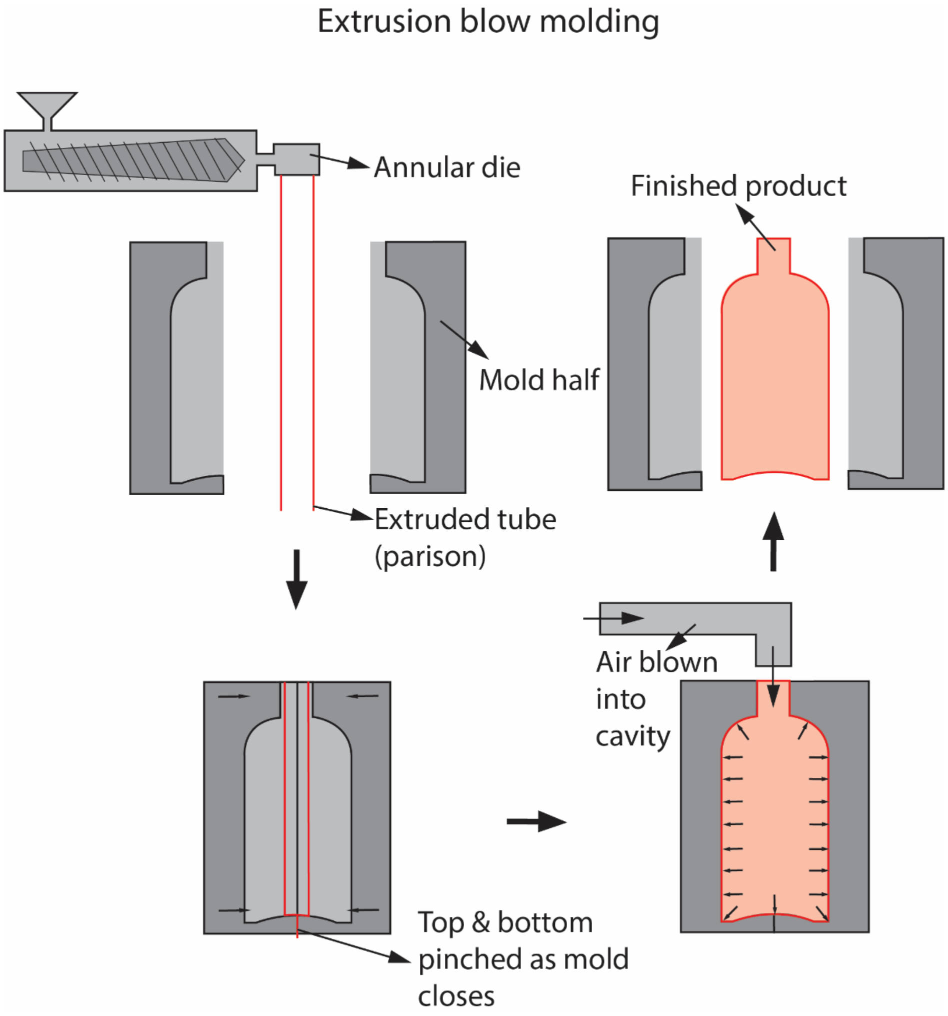

*Figure 2-12: Extrusion blow molding process.*

## 2.3 Properties of PLA

### 2.3.1 Factors affecting PLA's properties

Like many other polymers, several PLA's properties vary based on its crystallinity. PLA can be amorphous or up to 40% crystalline depending on certain conditions and parameters. They are as follows:

#### *2.3.1.1 Stereochemistry of monomers*

As previously mentioned, PLA can be manufactured from lactic acid and lactide, both of which exhibit stereo-merism. The stereochemistry of these monomers influences the shape of the polymer chain that forms. Some stereoisomers produce a very linear chain that can stack parallelly and thus easily crystallize, others however, form a bent polymer backbone which makes crystallization difficult. For instance, PLA synthesized from mostly L-lactide (> 93%) is semi-crystalline, whereas those from a lower concentration of L-lactide (50-93%) are amorphous [14]. Most of the synthesized PLA has at least some percentage of D and D, L-lactide as there are some meso-lactide impurities in the starting material. The presence of these impurities affects the polymer chain morphology and thus reduce the crystallization.

#### *2.3.1.2 Processing conditions*

Studies have concluded that the rate of crystallization of PLA is rather slow, just as observed in poly(ethylene terephthalate) (PET) [15]. This rate is slow enough that normal processing conditions can affect the crystallinity of the finished product. For instance, quenching is the process of rapidly cooling the polymer melt, this produces a polymer with a low crystallinity as the polymer chains do not have enough time to form the crystalline structure. Similarly, annealing which is the opposite of quenching produces PLA with higher crystallinity [10].

Processing methods can also influence the crystallinity of PLA [12, 15]. For instance, cast film extrusion with a chill roller that rapidly cools the extruded polymer film will have lower crystallinity compared to a process where the cooling rate is not this high.

Like PET, orienting polymer chains also influences PLA's crystallinity [12]. Uni or bi-directional stretching can orient the polymer chains, which may decrease their activation energy and make it easier to crystallize. Thus, certain processes like blown film extrusion produce films with unique properties because of the bi-directional stretching [8].

#### *2.3.1.3 Presence of additives*

Additives added to the polymer can directly influence the crystallinity. Depending on their property, they can either increase crystallinity or inhibit crystallization [16]. Certain molecules act as nucleation spots to which polymer chains can attach and start forming crystals. This usually occurs with molecules that have an affinity to the polymer. These molecules are called nucleating agents. For instance, in research conducted by Karkhanis and Matuana, they have concluded that cellulose nanocrystals (CNC) can act as a nucleating agent, increasing the percent crystallinity of PLA [16].

Other additives such as plasticizers can impact the crystallinity differently. Plasticizers are molecules of lower molecular weight, often oils, which occupy the space between two polymer chains. Since they are in the middle of two polymer chains, they prevent the chains from packing closely, i.e., to form crystals. Thus, in general addition of plasticizers increase the free volume in the polymer matrix and decrease the percent crystallinity of the polymer [18].

There are other additives that are added to polymers during processing to improve various desirable properties. Some of these additives like branching agents, chain-extenders can also react with the polymer chain and change their length, the degree of branching, etc. These additives such as chain-extenders, plasticizers, antioxidants, fillers, impact modifiers, etc. can influence the properties of the polymer [10].

In addition to polymer's crystallinity, other parameters such as the polymer's processing thermal history, molecular weight, aging, etc. also affect its properties [19].

### 2.3.2 Physical properties of PLA

Physical properties are any of the properties that can be measured without changing the chemistry of the material. Physical properties are important when processing the polymers and can also help us choose the most appropriate material required for a specific application.

For instance, the density of a material is used to determine the amount required to fill a mold or calculate how much a structure will weigh. It is also used to calculate specific properties which are density normalized mechanical properties of the material. Weight average molecular weight is the molecular weight average calculated by taking the size of each polymer chain into account, and this is an important factor for predicting rheological properties. Heat deflection temperature is the temperature at which the polymer starts to deform under load. Glass transition temperature is the temperature below which the polymer behaves hard and brittle. Melting temperature is the temperature at which the crystalline structures in a polymer melt and change into a liquid phase.

Light transmission property determines how much of a certain wavelength of light can pass through the polymer. Visible light transmission is important in packaging as there is a lot of demand for see-through or transparent packages. UV transmission can be important in deciding the processing of certain products within a package, for instance, certain foods cannot be UV sterilized if they are inside a package that absorbs most of the UV light, there are also scenarios where UV absorption is desired. Certain products should be shielded from UV rays, here polymers that absorb UV radiation can come in handy. Some of PLA's physical properties are listed in table 2-1.

*Table 2-1: Physical properties of PLA.*

| Properties | Units | Values | References |
|---|---|---|---|
| *Weight average molecular weight* ($M_w$) | Kg/mol | 65 - 210 | [17] |
| *Density* | | | [17] |
| Specific gravity | | 1.27 | |
| Solid density | g/cm$^3$ | 1.21 - 1.25 | |
| Melt density | g/cm$^3$ | 1.07 - 1.12 | |
| *Thermal properties* | | | |
| Heat deflection temperature | °C | 55 | [20] |
| Glass transition temperature ($T_g$) | °C | 40 - 70 | [21] |
| Melting temperature ($T_m$) | °C | 130 - 180 | [21] |
| *Optical Properties* (UV transmission) | | | [22] |
| Middle UV (190 - 220 nm) | % | < 5 | |
| (225 - 250 nm) | % | 85% | |
| Near UV (> 300 nm) | % | 95% | |
| Visible light transmission (400 - 700 nm) | % | 95% | |

### 2.3.3 Mechanical properties of PLA

Mechanical properties determine how the material will behave with the application of mechanical forces. These properties are important as materials come across a variety of forces and stresses in their lifespan.

For instance, in packaging, packages are stacked on top of another to optimally use space; this causes compressive forces in the packages. The right material must be chosen such that the packages can hold their shape when even when under compression. Other properties such as tensile, impact, flexural, hardness, and heat deflection are also important. In products like polymer handbags, the weight of the bag pulls the handle down and thus exerts tensile forces, a polymer with high enough tensile strength can be chosen such that the handles can safely deal with the weight of the bag without yielding.

Flexural strength is a measure of how much load it can hold in bending mode before yielding. Stiffness is the extent to which an object resists deformation in response to an applied force. Impact strength is a measure of how much energy it takes to fracture a sample, and it is related to the toughness of a material.

Shear modulus is how much shear stress it takes for a material per unit shear strain. Poisson's ratio is the ratio of change in the lateral direction to a proportional change in the length of a sample and this property is important for closures used in bottles. Hardness gives information about how easy it is to scratch or indent a smooth surface of a material. Some of these mechanical properties of PLA are listed in table 2-2.

*Table 2-2: Mechanical properties of PLA.*

| Properties | Units | Values | References |
|---|---|---|---|
| *Tensile* | | | [17] |
| Ultimate strength | MPa | 47 - 166 | |
| Yield strength | MPa | 70 | |
| Elongation at break | % | 3 - 160 | |
| Elastic modulus | GPa | 3.4 - 4.1 | |
| *Flexural and impact* | | | |
| Flexural strength | MPa | 106 | [23] |
| Notched Izod impact | J/m | 26 | [25] |
| *Others* | | | |
| Shear modulus | GPa | 1.29 | [17] |
| Poisson's ratio | - | 0.36 | |
| Rockwell hardness | | 82 - 88 | [23,25] |

### 2.3.4 Rheological properties of PLA

Rheology is the study of flow and deformation of materials, mainly liquids and viscoelastic materials. Viscosity is an important flow property, which determines how the liquid will flow. Shear viscosity is the viscosity of a fluid measured when there are shear forces in the liquid. The rheology of a polymer is crucial for processing as polymers are molded into required shapes by melting them. This means that the rheological properties of a polymer can determine how easy or suitable it is for certain manufacturing processes. There are various factors that determine the rheological properties of a material. Some of them are briefly discussed below.

#### *2.3.4.1 Polymer chemistry*

The structure of a polymer chain determines how well the polymer can slide past one another in a melt state, i.e., the flow behavior of a polymer depends on the chain structure [24]. Some of the features of the polymer chain that affect rheology are discussed below.

##### *2.3.4.1.1 Chain length*

Chain length is a measure of how long the polymer chain is. Measuring the molecular weight of the polymer gives a general idea of the length of the chain as it tells us how many monomer units make up the polymer chain. The chain contour-length can be estimated by multiplying $M_w$ (weight average molecular weight) and the molecular length of the monomer. Intuitively, it can be expected that polymers with longer (heavier) chains have more resistance to flow and thus exhibit a higher viscosity than shorter polymer chains. This is generally true and has been commonly observed by many researchers like Mark and Houwink who have come up with the following empirical relationship between molecular weight and viscosity of the polymer [26]:

$$\eta = KM^{\alpha} \tag{2.1}$$

where η is the viscosity of the material, M stands for the molecular weight of the polymer, and K, α are constants related to temperature and polymer-solvent system, α is a parameter that is related to the polymer chain stiffness.

#### *2.3.4.1.2 Chain branching and pendant groups*

Chain branching plays a key role in determining the polymers' rheology. Heavily branched chains tend to entangle and exhibit very different rheological properties to their linear counterparts [24]. There are some techniques that are used to measure branching. The branching index (BI), which is the ratio of the radius of gyration of the branched polymer to the radius of gyration of a linear polymer of the same molecular weight, gives a good idea about the degree of branching in a polymer chain. Branched chains find it harder to slide along other chains because the side branches create an entanglement effect, which inhibits flow. Thus, branched polymers generally exhibit higher viscosity than linear counterparts at lower shear rates [24]. The viscosity relation between the branched and linear polymers change based on the geometry of the polymer chains. Pendant groups have a similar effect to branching in that they cause entanglement albeit lesser [27].

Other properties such as polarity of the chain, presence of secondary force interactions, etc. can also affect the rheological properties of the polymer. The presence of polar functional groups can induce dipoles, and cause dipole interactions or stronger interactions like hydrogen bonding [28]. These interactions cause strong chain entanglement, which can affect the rheology of the polymer.

### *2.3.4.2 Flow conditions*

Just as the intrinsic properties of the polymer affect its rheology, so do the environmental conditions. Take this example, water will flow faster from a hole in a pouch if it is squeezed. It is important to understand the relation between the flow conditions and the polymer rheology of polymers so that we can use that knowledge to our advantage when it comes to processing these materials. Two main conditions that affect the rheology of material in shear flow are the temperature and shear rate, both of which are briefly discussed below.

#### *2.3.4.2.1 Temperature*

Temperature directly influences the rheological properties of polymers. This can be understood better with the help of the kinetic theory of fluids, which forms a relationship between kinetic energy of the molecules and the temperature of the system [29]. This can also be understood with the help of activation energy, we can imagine more molecules have the required activation for the process of flow when the temperature is higher [16]. Thus naturally, polymers flow more easily at higher temperatures. This is explained by the following Arrhenius equation [16]:

$$K = Ae^{[-E_a/RT]} \tag{2.2}$$

where, K is the rate of the process, A is the temperature-independent constant, $E_a$ is the activation energy for the process, R is the gas constant, and T is the absolute temperature.

This can be observed in a home kitchen where one might have observed that substances like corn starch solution congeal when cooled and flow easily when heated. This holds true for most polymers including PLA.

### *2.3.4.2.2 Shear*

Shear occurs when there is relative movement between adjacent layers of a material. This condition occurs in many materials flowing in a pipe due to the drag from the pipe wall. A true Newtonian fluid does not get affected by the shear rate. Some examples of Newtonian include water, oil, and alcohol. Figure 2-13 shows Newtonian fluid's viscosity is unaffected by shear rate.

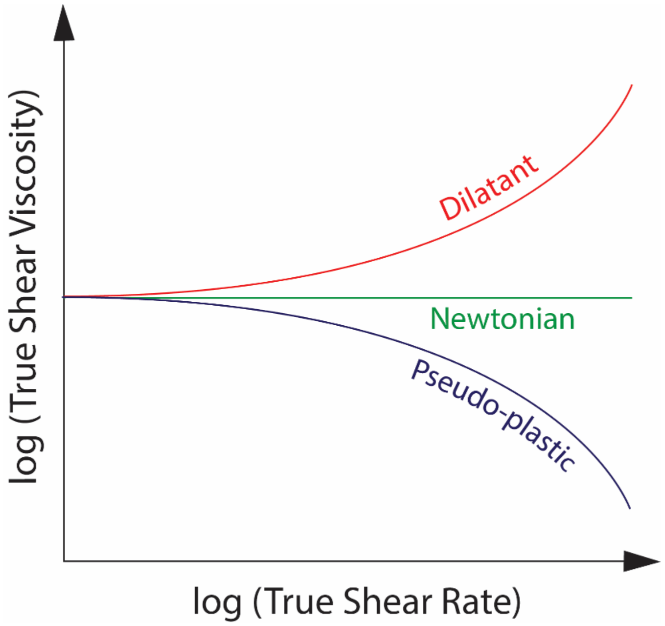

*Figure 2-13: Newtonian and non-Newtonian fluid behaviors[10].*

There are other categories of fluids that are affected by shear rate, these are called non-Newtonian fluids. Non-Newtonian fluids are further sub-divided into two types based on how they are affected by shear. They are dilatant or shear-thickening fluids and pseudo-plastics or shear-thinning fluids.

Dilatant fluids' viscosity has a positive relationship with shear rate i.e. the viscosity of these materials increases with an increase in shear rate (Figure 2-13). An example of dilatant is a mixture of cornstarch and water.

Pseudo-plastics behave opposite to dilatant fluids with the application of shear. This means they flow better or have lower viscosity when the shear rate is higher. Figure 2-14 below shows the typical behavior of a pseudo-plastic's shear viscosity over shear rate (also shown in Fig. 2-13).

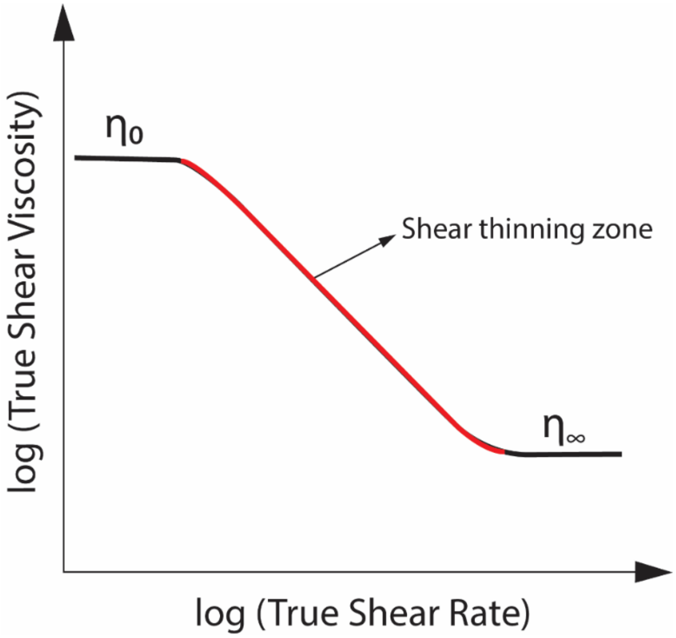

*Figure 2-14: Shear-thinning behavior of pseudo-plastics.*

From figure 2-14, we can see three clear zones. There are two regions where the viscosity is unaffected by shear rate and there is a middle region where shear thinning occurs. At lower shear rates, the material behaves as though there is no shear present and exhibits no shear-thinning, this region is called the Newtonian plateau and the constant viscosity in this zone is called zero-shear viscosity ($\eta_0$). Beyond the Newtonian plateau we have the shear thinning zone where the material's viscosity drops with increase in shear rate.

The shear-thinning zone can be approximated into a model using the power-law, which gives the relationship between the shear rate and shear viscosity of a shear-thinning fluid. It is as follows [23]:

$$\eta = m(\dot{\gamma}_w)^{n-1} \tag{2.3}$$

where $\eta$ is the true shear viscosity of the polymer melt, $\dot{\gamma}_w$ is the true shear rate; m and n are consistency index and flow index, respectively. ‘m’ and ‘n’ are constants that pertain to the nature and chemistry of the polymer.

Beyond the shear-thinning zone, the viscosity does not drop anymore and reaches another plateau. This is the third zone and is called the infinite shear viscosity plateau where the fluid has a constant viscosity called infinite shear viscosity ($\eta_\infty$). The viscosity does not drop with shear rate anymore in this region.

#### ***2.3.4.3 Additives***

As mentioned earlier additives can modify the properties of PLA. Some additives used to alter the rheology are deliberated below:

##### *2.3.4.3.1 Plasticizers*

Plasticizers are additives that when added to the polymer, tend to soften it, make it stretchable and flexible. Plasticizers are compounds of smaller molecular weight and are completely miscible with the polymer. These plasticizers disperse throughout the polymer matrix and lodge themselves in between the polymer chain. This works to increase the free volume of the polymer and hence increase flexibility but can negatively affect mechanical properties like tensile strength.

Plasticizers can also affect the rheology of polymers. This is because they are molecules of smaller weight and thus bring down the total molecular weight average [30]. Since we know that heavier molecules have higher viscosity and vice versa from the Mark-Houwink relation, we can expect a polymer melt with plasticizers to flow better than those without any plasticizers.

The most common plasticizer used for PLA is poly(ethylene glycol) (PEG) which has high compatibility with PLA [31]. Researchers have also established epoxidized soybean oil as a compatible plasticizer for PLA [31]. Because of its polarity PLA is also miscible with citrate-based plasticizers like triethyl citrate (TEC) and acetyl tributyl citrate (ATBC) [31]. Other researchers have also reported that $CO_2$ mixed with PLA for continuous foam extrusion process also acts as a plasticizer for PLA [23].

#### *2.3.4.3.2 Lubricants*

Lubricants are also known as flow promoters. Lubricants are additives that, when added to the polymer will reduce the friction. Lubricants are of two types based on their function, they are: external and internal lubricants [33]. External lubricants mainly reduce the friction between the polymer and the surface it is in contact with, they reduce the wear in processing equipment, reduce processing noise, etc.

Internal lubricants are also called slip agents. They promote the slippage between polymer chains and thus work to reduce the viscosity. These materials work by weakening chain entanglement and secondary force interaction between polymer chains. Adding slip agents helps the melt to flow and fill narrow and intricate structures in the mold.

PLA has high melt flow and usually does not require slip agents. Common slip agents are generally made of fatty acid esters, fatty acid amides, ethyl-vinyl acetate (EVA) waxes, etc. [33].

#### *2.3.4.3.3 Heat stabilizers*

PLA being a bio-degradable polymer, is more susceptible to thermal degradation than other polymers like low density polyethylene (LDPE). Heat stabilizers are additives that stabilize the polymer chain from thermal degradation during processing [33].

Heat stabilizers work by either preventing or neutralizing the free radicals that form under heat. Since free radicals go and attack active chain-sites to cause chain scission, addition of such heat stabilizers increases the thermal stability of polymers.

PLA might require heat stabilization especially if there is a pre-processing step like melt compounding involved. Since thermal degradation cause changes in chain length which in turn cause change in rheological properties, it can be said that thermal stabilizers prevent change in rheology of the polymer.

Common thermal stabilizers used in the food industry are derivatives of epoxidized soybean oil, linseed oil and sunflower oil [31].

#### *2.3.4.3.4 Impact modifiers*

Impact modifiers are used to increase the impact strength of brittle polymers. Polymers that are brittle fracture easily on impact, this is often undesirable. Thus, rubbery materials are added to the compounds to increase the flexibility and impact strength of the polymer [34].

These do not react chemically with the polymer and are like plasticizers. The difference is that impact modifiers are always rubber-like materials, whereas plasticizers can be fluids like oils.

For PLA, the rubber resins like polybutadiene and acrylics have been grafted with a rigid polymer phase to make it miscible with PLA [34]. An example is Paraloid BPM-515, introduced by Dow chemicals as an impact modifier for PLA. It is an acrylic-based impact modifier that can increase impact strength without reducing clarity.

#### *2.3.4.3.5 Chain extenders/branching agents*

Chain extenders and branching agents contain reactive functional groups which chemically react with the polymer chains and can form longer/ branched chains. Since chain length and degree of branching directly influence rheology, these additives affect the rheology of the melt [24,36,37].

Chain extenders increase the chain length and therefore increase the shear viscosity of the melt. Branching agents increase chain entanglement and cause an increase in shear as well as extensional viscosity. Since extensional viscosity is related to melt strength, branching agents also act as melt strength enhancers.

Mihai et. al. improved the melt strength of PLA by branching it with multifunctional styrene-acrylic-epoxy copolymer, and reported increase in shear and elongational viscosity while reducing the density of foamed from 65 kg/m$^3$ for linear PLA to 30 kg/m$^3$ [35].

Zhou et. al. also branched PLA with polystyrene/poly(glycidyl methacrylate) random copolymer and reported an increase in complex viscosity and elongational viscosity after branching [36].

Similarly, other branching agents such as multi-functional epoxies or diisocyanate based agents have been used by various researchers to modify the rheology of PLA [37,38].

#### *2.3.4.3.6 Fillers*

Fillers are inexpensive minerals/materials added to the polymer to reduce the amount of resin being used. They help reduce the cost of production as they reduce the weight of resin used [39]. Fillers modify the rheology of the polymer and are mainly made up of inexpensive materials like clay, talc, etc.

These materials do not melt and stay as solid particulates in the melt. The presence of these solid particulates in the melt hinder the flow and thus causes an apparent increase in the viscosity.

Some common filler materials include calcium carbonate, talc, silica, carbon black, kaolin etc. Some researchers have also used plant/bio-fibers as filler material for PLA. For instance, Fehlberg et. al. has used the orange peel from the juicing industry as a filler material for PE [39].

## 2.4 Foaming

Foaming is the process of creating a structure by trapping gas bubbles into another phase, i.e., liquid or gas. This chapter will discuss the process of foaming and literature review on PLA foams relevant to the research objective.

### 2.4.1 Components of a foam

All foams contain two main components, including the (i) gas phase and (ii) matrix phase as discussed below:

#### *2.4.1.1 Gas phase/ blowing agent*

The gas phase is a gaseous or a volatile material that is used to create the bubbles or voids in the foam. The gaseous phase is supplied to the foam during its formation by a blowing agent (foaming agent). Based on its composition, blowing agents are primarily divided into two broad categories that are chemical blowing agents (CBA) and physical blowing agents (PBA).

##### *2.4.1.1.1 Chemical blowing agents*

Chemical blowing agents (CBA) are chemical compounds that when added to the matrix create gases during the foam formation either from a chemical reaction or by decomposition.

Baking soda added to a cake batter reacting with acids and forming $CO_2$ is an example of a chemical foaming agent in day-to-day life. In fact, baking soda is also used in the industry to produce polymer foams [40]. Other examples of chemical foaming agents include azodicarbonamide, isocyanates, titanium hydride, etc. [41]

Chemical foaming agents are subdivided into two types based on the nature of the chemical reaction through which they produce blowing agent. They are endothermic and exothermic CBA. Endothermic foaming agents absorb heat in the process of decomposition, hence produce a cooling effect. Exothermic foaming agents produce more heat during decomposition.

The disadvantage of exothermic chemical blowing agents is that they leave behind by-products when they react or decompose to produce gases. This poses a problem with polymer foams as these by-products can change the chemistry and rheology of the polymer melt which can have unpredictable debilitating effects on the foam. Thus, low density foams are hard to produce by just using chemical blowing agents.

#### *2.4.1.1.2 Physical blowing agents*

Physical blowing agents (PBA) are different from chemical blowing agents in that they do not undergo a chemical reaction to produce gases. Instead, they go through a physical change in their phase to form into a gas [32]. This process can be compared to incorporating air into whipping cream with a whisk. Usually, physical blowing agents are mixed with the polymer during foam manufacturing, where they evaporate into a gas and aid in foam growth.

Examples of physical blowing agents include compressed gases like $CO_2$, $N_2$ or volatile compounds like hydrocarbons or Chlorofluorocarbons (CFCs). The disadvantage of physical blowing agents is that some of them can be harmful to the environment (CFCs) or are hazardous (hydrocarbons are inflammable). However, low density foams are easier to manufacture with physical blowing agents compared to the chemical blowing agents.

#### *2.4.1.2 Matrix phase*

The matrix phase is the part that gives foam its structure. The matrix phase is either a liquid (in case of soap) or solid (in polymer foams) that serves as a backbone and holds the voids in place. Polymer foams are primarily made up of thermoset and thermoplastic foams.

Thermoset foams are primarily made from materials like polyurethane, phenol-formaldehyde, silicone, etc. which are thermoset polymer. This means that these foams cannot be molded into new shapes after they are made. Thermoplastic foams are made from thermoplastics which can be heated and reshaped numerous times, thus making recyclable foams. Materials like polyethylene (PE), polystyrene (PS), poly(vinyl chloride) (PVC) are some common resins used to manufacture thermoplastic foams.

Both chemical and physical blowing agents can be used to produce foams with either closed or open-cell structure. The closed-cell foam structure is formed when each bubble inside foam is covered entirely by a closed wall, thus isolating the bubble from surrounding bubbles. Closed-cell foams are used mainly as insulators due to their excellent thermal insulation properties. Open-celled foams, on the other hand, have bubbles that are not completely encapsulated by the wall and are connected to their adjacent cells. This allows for fluids to move freely through the foam and are softer than closed-cell foams. Open-cell foams are mainly used as cushioning materials [42].

### 2.4.2 Mechanism of foaming

There are many types of foams that we encounter in our daily lives, from the froth in a bubble bath to egg whites in a meringue are all examples of foams. But the basic mechanism of foaming is the same. This mechanism is explained below:

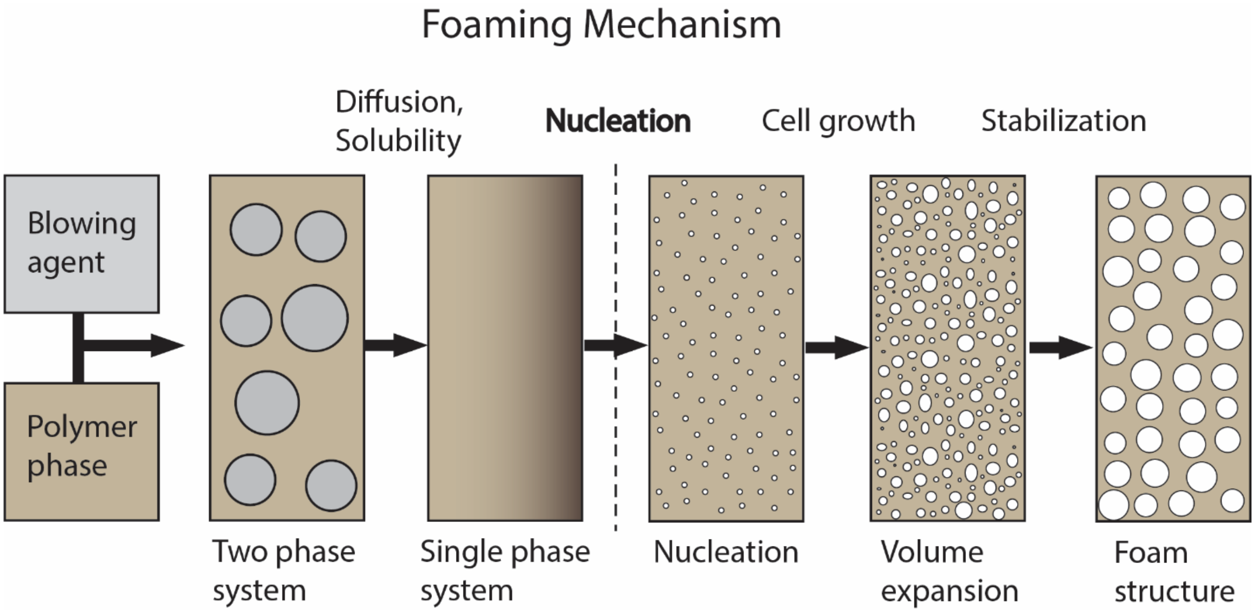

*Figure 2-15: Steps involved in the mechanism of foaming [43].*

#### *2.4.2.1 Step 1: Gas dissolution [42]*

As mentioned earlier, foams contain two main phases - (i) the gas phase, which forms the voids or cells in foam, and (ii) the solid phase that forms the foam matrix that provides structural integrity to foam. The first step towards foaming is combing these two phases to make a single-phase solution. The conditions are maintained such that the thermodynamics favor high solubility of the gas in the polymer. This is a similar process to adding $CO_2$ to water to make soda/carbonated water. Soda is a single-phase solution, which contains dissolved $CO_2$ gas.

#### *2.4.2.2 Step 2: Nucleation*

The single-phase solution is an equilibrium condition for the thermodynamic system and will remain as such if left in the same environment. To create gas separation, a change in the thermodynamic system should be induced, this is called a thermodynamic instability. In general, increasing temperature or decreasing pressure reduces gas solubility and creates nucleation, which is the process by which gas molecules combine at a small point to form a gas phase. This mechanism explains why a can of soda starts fizzing when opened, the reduction in pressure creates a thermodynamic instability.

The classical nucleation theory models the process of nucleation which creates a relation between the rate of nucleation and various relevant factors in the system [32]:

$$N_{nucl} = C_0 f_0 e^{\left(\frac{-\Delta G}{kT}\right)} \tag{2.4}$$

where, $N_{nucl}$ is the rate of nucleation, $C_0$ the concentration of gas molecules, $f_0$ the frequency factor, ΔG is Gibb's free energy, k the Boltzmann constant, and T the absolute temperature.

Thus, in general, nucleation is directly proportional to the concentration of gas molecules and the temperature of the system.

Nucleation is mainly divided into two types, homogeneous and heterogenous nucleation. Homogeneous nucleation happens in a single-phase system and is driven by random chance and Gibb's free energy. Gibb's free energy for homogenous nucleation is given by classical nucleation theory as follows [32]:

$$\Delta G_{homogeneous} = \frac{\pi \gamma_{bp}^3}{3\Delta p^2} \tag{2.5}$$

where, $\gamma$ is the surface energy at the bubble-polymer interface and $\Delta p$ is the pressure drop in the polymer/gas system.

Heterogenous nucleation is the nucleation that happens at the phase boundary of a system. It is more common than homogenous nucleation and sometimes takes lesser energy. The Gibb's free energy for a homogeneous system is also given by classical nucleation as follows [32]:

$$\Delta G_{heterogenous} = \Delta G_{homogeneous} \times f(\theta) \tag{2.6}$$

where, $f(\theta)$ is a function of contact angle at the phase boundary of the nucleus site.

#### *2.4.2.3 Step 3: Cell growth*

Once the nucleation has taken place, the cells keep expanding as more and more gas molecules join the nucleus to form the gas phase. This is facilitated in polymer foams by increasing the temperature and soften the polymer to make it conducive to growth. This process, if left unchecked, can reach a critical point beyond which the matrix cannot support the bubble and hence, can cause cell collapse (opposing cell walls touch) or coalescence (rupture of cell walls).

#### *2.4.2.4 Step 4: Cell stabilization*

The matrix phase of the foam should be stabilizing to arrest cell growth and prevent cell collapse [42]. In polymer foams, cell stabilization is done by cooling down the thermoplastic such that it no longer allows for the expansion of gases.

### 2.4.3 Properties of foams

The properties of solid foams depend on their density, average cell size, and cell-population density. Since these properties are affected by the type of blowing agent used in foam production, it is evident that the property of foamed samples is also dependent on the type of foaming agent used in their production. The table below lists the various properties of foams manufactured with chemical and physical blowing agents.

*Table 2-3: Properties of samples foamed with CBA and PBA.*

| Properties | CBA foams [40] | PBA foams [32] |
|---|---|---|
| Cell size (µm) | > 100 | ~ 0.001-10 |
| Cell-population density (cells/cm$^3$) | $\leq 10^6$ | $\geq 10^9$ |
| Wall thickness (mm) | ≥ 4 [44] | ≤ 2 [44] |

Samples foamed with PBA having properties listed in Table 2-3 are also called microcellular foams. These microcellular foams also have unique properties compared to samples foamed conventionally using CFA.

Microcellular foams are generally defined as having an average cell diameter of the order of 10 microns and cell-population density in the order of $10^9$ cells per cm$^3$. The small gas bubbles in the foam act as spots which release the stress in the material, hence arrest crack propagation. Generally, microcellular foamed plastics have better improvement in impact strength compared counterparts foamed with CFA. Improvement in impact strength of plastic foamed with CBAs usually comes at the expense of other mechanical properties like specific tensile modulus and tensile strength. This deleterious effect of foaming with CBAs is not observed for microcellular plastic foams. Research has found out that microcellular foams maintain their specific tensile properties [45].

Other than the foaming agent, the property of foams also depends on processing parameters like saturation pressure, foaming temperature, etc. and material properties like melt strength, gas solubility coefficient [46].

### 2.4.4 Microcellular foam process

The basic theory behind manufacturing microcellular foams is the same as mentioned. But based on the technique used, they are mainly divided into two types.

#### *2.4.4.1 Batch process*

In this process, the polymer pre-form is first made using a common manufacturing technique like injection molding or compression molding. Then this sample is placed in a pressurized chamber and saturated with the blowing gas (Figure 2-16). Due to higher pressure, the gas diffuses slowly into the sample and forms a single-phase solution in accordance with Henry's law that states that the concentration of dissolved gas in a medium is directly proportional to the pressure, given by the following equation [7]:

$$c = H \times p \tag{2.7}$$

where, c is the concentration of dissolved gas, H the Henry's constant and p the partial pressure of gas.

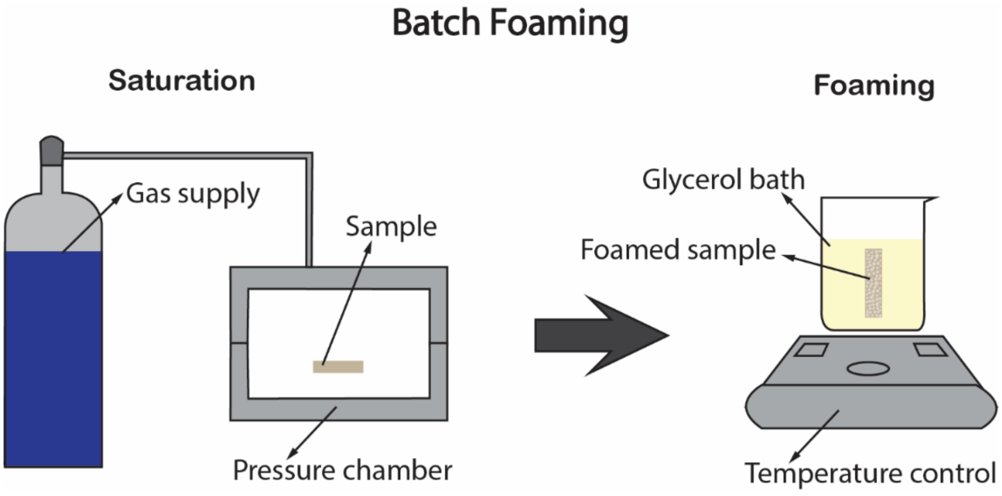

*Figure 2-16: Batch foaming process.*

This process of dissolution can either be done at room temperature or at higher temperatures. Increasing the saturation temperature increases the rate of gas diffusion. Once the sample has reached an equilibrium state with a given amount of gas dissolved, a thermodynamic instability is created by rapidly decreasing the pressure and increasing the temperature by immersing it into a hot bath to foam the sample (Figure 2-16). This causes a thermodynamic instability, which causes nucleation and cell growth. After sufficient cell growth has been achieved, the sample is then cooled to harden the polymer and cease further cell growth/collapse.

#### *2.4.4.2 Continuous process*

In the continuous process, the blowing agent is injected into the extrusion barrel in a supercritical state (Figure 2-17). It is important that the gas is supercritical or else it will be difficult to achieve a homogeneous polymer/gas single-phase solution before the melt exits from the barrel. Other auxiliary components like a static mixer may be incorporated to improve the mixing of polymer melt and blowing agent to achieve a homogeneous polymer/gas single-phase solution [32]. When the melt exits the extrusion barrel through a die, there is a pressure drop that creates the thermodynamic instability required for foaming. The sample can be air-cooled to stabilize the foam. Unlike the batch process, the main advantage of this process is that it allows for continuous production with minimal supervision and hence can be easily scaled-up at the industrial level.

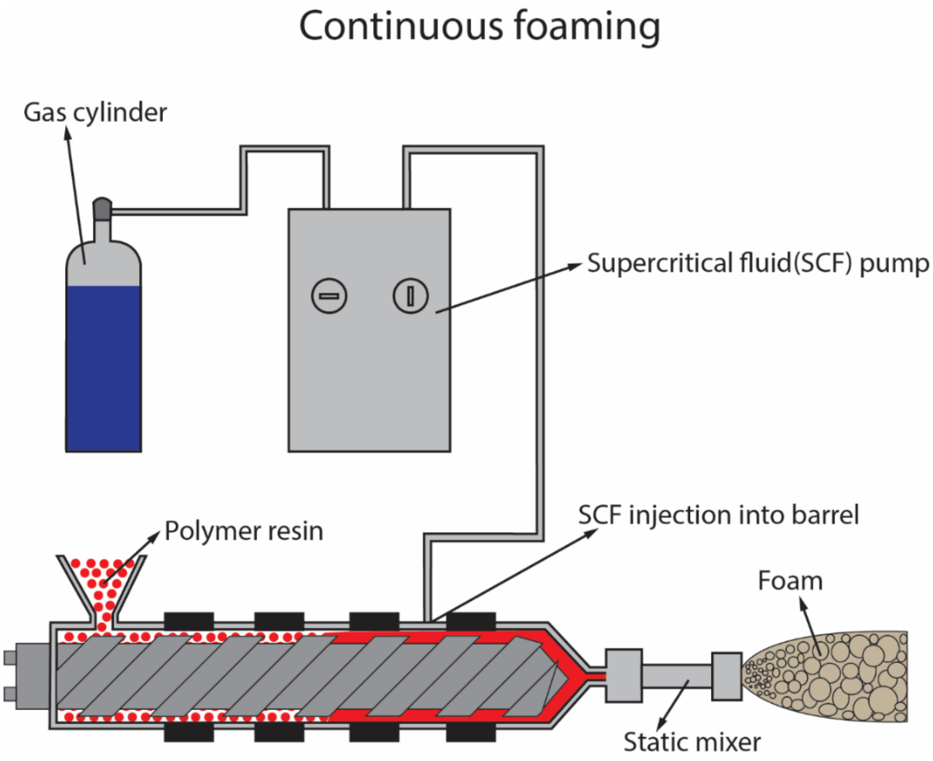

*Figure 2-17: Continuous foaming process [32].*

### 2.4.5 Important factors for foaming

Not all materials can produce good and stable foam structures. Several factors have significant effects during the foaming process, including the gas solubility and diffusivity, the rheological properties of the melt, especially extensional viscosity, among others. Some of these factors are discussed below.

#### *2.4.5.1 Gas solubility and diffusivity*

According to the classical nucleation theory, the rate of nucleation is given by [32]:

$$N_{nucl} = C_0 f_0 e^{\left(\frac{-\Delta G}{kT}\right)} \tag{2.8}$$

The rate of nucleation $N_{nucl}$ is directly proportional to the concentration of gas molecules ($C_0$) in the system (gas solubility). Thus, for creating foams with high cell-population density and expansion ratio, a high concentration of gas is ideal.

Gas diffusivity is a measure of how fast a gas can diffuse through the material. This is very important during the process of foaming. If material has very high gas diffusivity, then a lot of the blowing gas can escape through diffusion during the foaming process instead of contributing to foam expansion.

#### *2.4.5.2 Polymer Rheology*

Just as it is important for the polymer to have higher gas solubility to have more nucleation, it is also important for the polymer to be able to structurally hold the cells during cell growth. Since cell growth in thermoplastic foams happen in their molten state, the rheological properties of the polymer melt are crucial for achieving good quality, high expansion foams.

When the bubbles are expanding during the growth phase of the foam, the walls should hold them stably even as they get thinner. This ability to hold its shape is quantified by a parameter called melt strength. This is also directly related to the extensional viscosity of the melt. If the polymer does not have enough melt strength, then the walls will rupture, and this will either collapse the cell leading to the gas escape or it will cause cell coalescence, i.e., rupture of the walls between two or more cells forming a single bigger cell. This can cause problems with producing high expansion foams and may also produce other defects in the foam, such as blister formation.

PLA resin has very low melt strength and extensional viscosity; this creates issues with producing high-quality PLA foams. Improving the melt strength of PLA can improve the quality of its foams. Various novel techniques have been employed to improve the foamability of PLA, and some of them are reviewed in the following sections.

### 2.4.6 Approaches to improve PLA foamability

Several novel approaches have been used to improve the foamability of PLA, and some of them are reviewed below.

#### *2.4.6.1 Modifying processing parameters*

It has been established that viscosity and other rheological properties depend on external conditions like shear rate and temperature. Since most polymers, including PLA, exhibit shear-thinning behavior, they have higher apparent viscosity at lower shear rate. Also, polymers tend to have a lower flow rate at lower temperatures, as discussed earlier.

Given the right processing conditions, it is possible to produce microcellular foams with PLA. Diaz and Matuana have produced microcellular PLA foam without the use of any additives by controlling the processing parameters such as temperature [32].

Others have also optimized processing parameters in chain-extended PLA to produce nanocellular foams. For example, Tiwary et. al. reported that PLA modified with a coagent crosslinking agents and foamed close to crystallization temperature yielded sub-micron size cells and the foam had a high cell-population density in the order of $10^{11}$ cells/cm$^3$ [47].

But various studies have reported that neat PLA cannot reach a very high expansion rate and are also very difficult to produce because of PLA’s narrow processing window. Many studies have also reported cell rupture in neat PLA foams due to its low melt strength [48].

#### *2.4.6.2 Copolymerization*

Copolymerization is the process of making a polymer from two or more monomers. Copolymerization imparts the material with desirable properties of the mono-polymers of all the monomers used for the process. Block, random, graft co-polymerization are some different types of co-polymerization divided based on the positioning of the different monomers in the polymer chain. However, this process has a high economic cost unless made in a large-scale.

Foams have been manufactured from PLA-glycolic acid copolymer (PLGA) for applications in the bio-medical field due to the materials increased biocompatibility. PLGA is synthesized by ring-opening polymerization of cyclic lactide and glycolic acid. Mohammadi et. al. reported that PLGA produced highly porous foams when supercritical $CO_2$ was used and discussed their application as scaffolds for tissue engineering [49].

#### *2.4.6.3 Blends*

Blending is the process of mixing two or more polymers together. The difference from copolymerization is that, in blending two polymers are mixed, but the polymer chains are not chemically bonded together as in copolymers. Depending on the chemistry of the polymers, they can form miscible or immiscible blends. Miscible blends are considered a homogeneous mixture and exhibit a synergistic increase in mechanical properties. A compatibilizer may be used to increase miscibility when two immiscible polymers are used.

Poly(butylene succinate) (PBS) is another biodegradable polymer that is blended with PLA to increase its toughness. However, blend still does not have high melt viscosity because none of the polymers flaunt that property [50,51].

Microcellular foaming of uncompatibilized PLA/poly(butylene adipate-co-terephthalate) (PBAT) blends and compatibilized PLA/PBAT blends produced in an extrusion process using CO2 as blowing agent, with or without talc, the nucleating agent [52]. In general, the addition of talc compatibilization have decreased the average cell size and volume expansion but increased the cell density [52].

Foaming of PLA/acrylonitrile-butadiene-styrene (ABS) binary blends with supercritical $CO_2$ has also been reported [53]. Microcellular foams with a blend containing 30% ABS was successfully produced at various foaming conditions and ABS played an important role in the stabilization of the foam [53]. However, the authors did not compare the results of foamed blends with neat PLA foam.

#### *2.4.6.4 Composites/Nanocomposites*

Polymer composites are materials that are formed by mixing filler or reinforcer materials with the polymer. Most fillers/reinforcers do not melt and remain solid inside the barrel during processing. Therefore, the addition of materials like clay, wood flour, wood fibers, etc., tend to decrease the flow rate of the melt and provide an apparent increase in viscosity.

Diaz and Matuana have reported that pine wood flour in PLA acts as a heterogeneous nucleating agent and they also reported one order of magnitude increase in the extensional viscosity of the melt after addition of 20% wood flour [54]. However, there was no significant increase seen in the void fraction of PLA foam after the addition of wood flour.

PLA/cellulosic fiber composites based on fibers from northern bleached softwood kraft (NBSK) and black spruce medium density fiberboard (MDF) with poly(ethylene glycol) (PEG) as a lubricant were microcellular injection molded [55]. The incorporation of 25 phr NBSK and MDF fibers led to higher cell density, smaller cell size, and narrower cell size distribution (more uniform cell structure) compared to that of foamed PLA/PEG samples. This improved foam morphology was attributed to the cell nucleating effects of fibers and the increase in the melt strength of PLA/PEG by the addition of NBSK and MDF fibers [55].

Microcellular foamed PLA was successfully produced in a batch processing using up to 10% wt. talc [56]. An approximately 45% decrease in cell size from 15.4 μm to 8.5 μm, as well as a 298% increase in cell-population density, were reported with 3 wt.% talc loading. This improvement in foamed samples was also attributed to the heterogeneous nucleation caused by talc, which significantly increased the crystallinity of the PLA matrix [56].

The addition of nanomaterials like nanoclay, cellulose nanocrystals, etc., produce polymer nanocomposites. Many nanomaterials also have been reported to increase the nucleation rate even at low concentration. The dispersion of nanomaterials in these polymer materials depends on their compatibility with the polymer. If the nanomaterial is incompatible, it will form agglomerates and will show poor dispersion. If the nanomaterial is compatible, it will either be exfoliated or intercalated depending on the level of compatibility.

Ameli and coworkers have foamed PLA and PLA/nanoclay composites using low-pressure foam injection molding (FIM) and high-pressure FIM (HPFIM) equipped with mold opening and gas counter pressure [57]. Not only the addition of nanoclay Cloisite® 30B into PLA matrix enhanced its ductility, but it also significantly improved the cell morphology of foamed sample. Nanocomposite foams with average cell size less than 50 μm and void fraction as high as 55% were achieved in PLA by adding nanoclay [57].

Similarly, another type of clay, organophilic montmorillonite (OMMT) was employed to improve the foaming performance PLA/PBS blends. The impact toughness of PLA/PBS blends by 50% with 3 wt % OMMT in the blend. The results also indicated that OMMT could improve the effect of foaming markedly. The blends also showed a six-fold increase in the cell-population density and 45% decrease in average cell size from 475.6 μm to 261.4 μm [51].

The effect of biobased nanofillers on foam cellular morphology, thermal and wettability behavior of biodegradable PLA/cellulose nanocrystals (CNCs) composite microcellular foam has been recently investigated [58]. PLA and PLA/CNC foams were fabricated by using sucrose particles as a porogen medium by casting and leaching methodology. The authors reported approximately 6.1 folds reduction in the density of PLA and the nanocomposite foams compared to neat PLA. Additionally, PLA/CNC foams had an almost ∼1.7 and ∼2.2-fold increase in storage modulus for the compressive and tensile mode, respectively, compared to the neat PLA counterpart [58].

#### *2.4.6.5 Chain extension and branching/cross-linking*

PLA is a linear polymer and thus has low melt strength due to a lack of chain entanglement. This can be mitigated by inducing branching in the polymer chain. Usually, branching is induced in PLA with the help of additives known as chain extenders, which catalyze chain extension and branching in the polymer. Examples of these additives include diisocyanates, epoxides, anhydrides, carbodiimide, etc.

Branched and chain-extended PLA generally shows improved melt strength and extensional viscosity and is better suited for foaming.

Yang and coworkers have synthesized star-shaped long-chained (LCB) PLA via transesterification with trimethylolpropane triacrylate (TMPTA) and ZnO nanoparticles as an accelerant for transesterification. They have reported an increase in the torque recorded in the torque curve which they relate to apparent viscosity [59]. They reported an average cell diameter of 52 μm for LCB-PLA compared to 140 μm for neat PLA, they also reported an increased cell density and lower occurrence of collapsed cells in LCB-PLA.

Similarly, Li and coworkers prepared long-chain branched polylactide (LCB-PLA) by UV-induced reaction extrusion with trimethylolpropane triacrylate (TMPTA) and investigated the effect of the long-chain branching structure on the cell morphologies of PLA foamed with supercritical carbon dioxide as the blowing agent [60]. They reported a higher cell density and reduction in cell diameter when foamed at 142°C. When foamed under 8 MPa and 12 MPa, the expansion ratio of linear PLA was bigger than that of LCB-PLA branched with 1.0 wt% TMPTA, and the opposite trend was reported when pressure was higher than 12 MPa.

Branching of PLA with multifunctional styrene-acrylic-epoxy copolymer chain extender (CE) was performed by Mihai and collaborators [35]. They showed that amorphous neat PLA control had a zero-shear viscosity of around 1600 Pa·s whereas this value went up to 2600 after the addition of 0.5% chain extender. Due to chain extension, the density of PLA foamed with 9% $CO_2$ decrease from 27 to 19 $kg/m^3$ after the addition of 2% CE.

The use of dicumyl peroxide (DCP) modified PLA in foam extrusion was described the first time by Standau et al. who also compared their results with those obtained with PLA branched with multifunctional epoxide (MFE) [61]. DCP is a free radical initiator and encourages random branching in PLA. Both modifications lead to an increase in melt strength, but the highest increase was shown for the PLA modified with dicumyl peroxide that also showed strain hardening. Neat

PLA showed foam density similar to that of MFE modified PLA, while there was a 28.9% decrease in the density of PLA treated with DCP. They also reported that the latter had twice the compression strength of untreated PLA despite its lower density. DCP was found to be more efficient than MFE as it showed more improvement, even at a fifth of the concentration of the latter.

PLA with L-lactide >92 wt% was reactively modified in the melt by sequentially adding different amount ratios of two low molecular weight chain extenders, i.e., 1,4-butanediol (BD) and 1,4-butane diisocyanate (BDI) and batch-foamed using $N_2/CO_2$ compressed mixture (80/20) at 16 MPa [62]. Crosslinking occurred in PLA modified with an equimolar amount of BD and BDI as well with an excess amount of BDI, and these samples showed a significant increase in molecular weight and complex melt viscosity than the unmodified PLA. These chain extended/cross-linked PLA samples allowed the production of PLA foams with smaller cell size, higher cell-population density, and lower foam density compared to the unmodified PLA foam [62]. In contrast, modification with an excess amount of BD lowered PLA's complex melt viscosity because of induced PLA degradation, thus did not enhance foamability [62].

Karkhanis and Matuana have successfully used food-grade multifunctional epoxy chain extenders of different epoxy-equivalent weight to chain-extend PLA. They have reported an increase in zero-shear viscosity, shear viscosity, molecular weight after reactive extrusion [37]. However, foaming with this chain extended PLA has not been attempted.

# REFERENCES

# REFERENCES

1. Kitamori, Y. (1994). Foamed polyolefin process development. Plastics age. In *Thermoplastic Foam Conference sponsored by Industrial Technology Research Institute, Taipei, Taiwan*, pp. 40.

2. Lao, S.C., Kan, M.F., Lam, C.K., Chen, D.Z., Koo, J.H., Moon, T., and Pilato, L. (2010). Polyamide 11-carbon nanotubes nanocomposites: processing, morphological, and property characterization. In *Twenty-First International SFF Symposium–An Additive Manufacturing Conference, Austin, TX, USA*, pp. 451-467.

3. *Inovyn | INOVYN launches world's first commercially available grade of bio-attributed PVC*. (2019). inovyn.com. https://www.inovyn.com/news/inovyn-launches-worlds-first-commercially-available-grade-of-bio-attributed-pvc/. Site accessed on July 15, 2020

4. de Andrade Coutinho, P.L., Morita, A.T., Cassinelli, L.F., Morschbacker, A., and Do Carmo, R. W. (2013). Chapter 6: Braskem's ethanol to polyethylene process development. Imhof, P, van der Waal, J.C, *Catalytic Process Development for Renewable Materials*. Wiley-VCH Verlag, Berlin. pp. 151-167.

5. Goldsberry, C. (2020). *Widespread use of bioplastics held back by lagging innovation, claims report*. Plasticstoday.com. https://www.plasticstoday.com/packaging/widespread-use-bioplastics-held-back-lagging-innovation-claims-report. Site accessed on July 7, 2020.

6. Zeng, C., and Hu, Q. (2019). 2018 petroleum and chemical industry development report. *Chinese Journal of Chemical Engineering*, 27(10), 2606-2614.

7. Matuana, L.M. (2008). Solid state microcellular foamed poly (lactic acid): morphology and property characterization. *Bioresource Technology*, 99(9), 3643-3650.

8. Karkhanis, S.S., Stark, N.M., Sabo, R.C., and Matuana, L.M. (2018). Performance of poly(lactic acid)/cellulose nanocrystal composite blown films processed by two different compounding approaches. *Polymer Engineering and Science*, 58 (11): 1965-1974.

9. Avérous, L. (2008). Chapter 21 - Polylactic acid: synthesis, properties and applications. Belgacem, M. N., and Gandini, A., *Monomers, Polymers and Composites from Renewable Resources*. Elsevier, New York. pp. 433-450.

10. Harper, C. A. (2006). *Handbook of Plastic Processes*. Wiley, Hoboken.

11. Chacón, J.M., Caminero, M.A., García-Plaza, and E., Núñez, P.J. (2017). Additive manufacturing of PLA structures using fused deposition modelling: Effect of process parameters on mechanical properties and their optimal selection. *Materials and Design*, 124, 143-157.

12. Liu, Y., and Matuana, L.M. (2019). Surface texture and barrier performance of poly(lactic acid)/cellulose nanocrystals extruded cast films. *Journal of Applied Polymer Science*, 136 (22), 47594.

13. Karkhanis, S.S., Stark, N.M., Sabo, R.C., and Matuana, L.M. (2017). Blown film extrusion of poly(lactic acid) without melt strength enhancers. *Journal of Applied Polymer Science*, 134 (34): article 45212 (10 pages).

14. Avérous, L., and Pollet, E. (2012). Biodegradable polymers. In L. Avérous, and E. Pollet, *Environmental Silicate Nano-Biocomposites*. Springer-Verlag, London. pp. 13-39.

15. Saeidlou, S., Huneault, M.A., Li, H., and Park, C.B. (2012). Poly (lactic acid) crystallization. *Progress in Polymer Science*, 37(12), 1657-1677.

16. Karkhanis, S.S., Stark, N.M., Sabo, R.C., and Matuana, L.M. (2018). Water vapor and oxygen barrier properties of extrusion-blown poly (lactic acid)/cellulose nanocrystals nanocomposite films. *Composites Part A: Applied Science and Manufacturing*, 114, 204-211.

17. Garlotta, D. (2001). A literature review of poly (lactic acid). *Journal of Polymers and the Environment*, 9(2), 63-84.

18. Sarasua, J., Arraiza, A.L., Balerdi, P., and Maiza, I. (2005), Crystallinity and mechanical properties of optically pure polylactides and their blends. *Polymer Engineering and Science,* 45, 745-753.

19. Muller, J., Jiménez, A., González-Martínez, C., and Chiralt, A. (2016). Influence of plasticizers on thermal properties and crystallization behavior of poly(lactic acid) films obtained by compression molding. *Polymer International*, 65: 970-978.

20. Farah, S., Anderson, D.G., and Langer, R. (2016). Physical and mechanical properties of PLA, and their functions in widespread applications-A comprehensive review. *Advanced drug delivery reviews*, 107, 367-392.

21. Mehta, R., Kumar, V., Bhunia, H., and Upadhyay, S.N. (2005). Synthesis of poly (lactic acid): a review. *Journal of Macromolecular Science, Part C: Polymer Reviews*, 45(4), 325-349.

22. Auras, R., Harte, B., and Selke, S. (2005). Polylactides. A new era of biodegradable polymers for packaging application. *SPE-ANTEC Papers*, 320-324.

23. Perego, G., Cella, G.D., and Bastioli, C. (1996). Effect of molecular weight and crystallinity on poly (lactic acid) mechanical properties. *Journal of Applied Polymer Science*, 59(1), 37-43.

24. Kasehagen, L. J., and Macosko, C. W. (1998). Nonlinear shear and extensional rheology of long-chain randomly branched polybutadiene. *Journal of Rheology*, 42(6), 1303-1327.

25. Hartmann, M.H. (2013). Chapter 15: High molecular weight polylactic acid polymers. In D.L. Kaplan (Ed.), *Biopolymers from Renewable Resources,* Springer-Verlag, Berlin. pp. 367–412.

26. Wagner, H.L. (1985). The Mark-Houwink-Sakurada equation for the viscosity of linear polyethylene. *Journal of Physical and Chemical Reference Data*, 14(2), 611-617.

27. Chinai, S.N., and Guzzi, R.A. (1959). Poly-N-lauryl methacrylate. V. Dilute solution properties by viscosity and light scattering. *Journal of Polymer Science,* 41(138), 475-485.

28. Cui, Z., Wang, X., Chen, W., Hu, E., and Liu, K. (2012). Synthesis, spectral and dyeing properties of phenylazopyrazolone-containing acylamide disperse dyes designed for poly (lactic acid). *Coloration Technology*, 128(4), 283-289.

29. Kauzmann, W. (1966). *Kinetic Theory of Gases.* W.A. Benjamin, New York.

30. Hallwachs, M.R., Hanson, H.E., Link, W.E., Salomons, N.S., and Widder, C.R. (1971). Gel permeation chromatography analysis of plasticizer blends. *Journal of Chromatography A*, 55(1), 7-13.

31. Vijayarajan, S., Selke, S.E.M., and Matuana, L.M. (2014), Continuous blending approach in the manufacture of epoxidized soybean-plasticized poly(lactic acid) sheets and films. *Macromolecular Materials and Engineering*, 299 (5), 622-630.

32. Matuana, L.M., and Diaz, C.A. (2010). Study of cell nucleation in microcellular poly (lactic acid) foamed with supercritical $CO_2$ through a continuous-extrusion process. *Industrial and engineering chemistry research*, *49*(5), 2186-2193.

33. Hahladakis, J.N, Velis, C.A, Weber, R., Iacovidou, E., and Purnell, P. (2018). An overview of chemical additives present in plastics: Migration, release, fate and environmental impact during their use, disposal and recycling. *Journal of Hazardous Materials,* 344, Pages 179-199.

34. Afrifah, K.A., and Matuana, L.M., (2010). Impact modification of polylactide with a biodegradable ethylene acrylate copolymer. *Macromolecular Materials and Engineering,* 295 (9), 802-811.

35. Mihai, M., Huneault, M.A., and Favis, B.D. (2010). Rheology and extrusion foaming of chain-branched poly (lactic acid). *Polymer Engineering and Science*, 50(3), 629-642.

36. Zhou, M., Zhou, P., Xiong, P., Qian, X., and Zheng, H. (2015). Crystallization, rheology and foam morphology of branched PLA prepared by novel type of chain extender. *Macromolecular Research*, 23(3), 231-236.

37. Karkhanis, S.S., and Matuana, L.M. (2019). Extrusion blown films of poly (lactic acid) chain-extended with food grade multifunctional epoxies. *Polymer Engineering and Science*, 59(11), 2211-2219.

38. Liu, C., Jia, Y., and He, A. (2013). Preparation of higher molecular weight poly (L-lactic acid) by chain extension. *International Journal of Polymer Science,* 2013, article 315917 (6 pages).

39. Fehlberg, J., Lee, C.L., Matuana, L.M., and Almenar, E. (2020). Orange peel waste from juicing as raw material for plastic composites intended for use in food packaging. *Journal of Applied Polymer Science,* 137(26), article 48841 (12 pages).

40. Li, Q., and Matuana, L.M. (2003). Foam extrusion of high-density polyethylene/wood-flour composites using chemical foaming agents. *Journal of Applied Polymer Science,* 88(14), 3139-3150.

41. Matuana, L.M., Faruk, O. and Diaz, C.A. (2009). Cell morphology of extrusion foamed poly(lactic acid) using endothermic chemical foaming agent. *Bioresource Technology*, 100 (23), 5947-5954.

42. Matuana, L.M. (2010). Chapter 17: Foaming. R. Auras, L.T. Lim, S.E. Selke, and H. Tsuji, *Poly(lactic acid): Synthesis, Structure, Properties, Processing and Applications.* John Wiley and Sons, Inc., Hoboken. pp. 273-291.

43. Standau T., and Altstädt V. (2019) Chapter 10: Foams. Karger-Kocsis J., Bárány T. (eds) *Polypropylene Handbook*. Springer, Cham. 580-634.

44. Kishbaugh, L. (2019). Chemical vs physical foaming. From https://trexel.com/chemical-vs-physical-foaming. Site accessed on July 7, 2020.

45. Kumar, V., VanderWel, M., Weller, J., and Seeler, K.A. (1994). Experimental characterization of the tensile behavior of microcellular polycarbonate foams. *Journal of Engineering Materials and Technology*, 116, 439-445.

46. Matuana, L.M., Faruk, O. (2010). Effect of gas saturation conditions on the expansion ratio of microcellular PLA/wood-flour composites. *eXPRESS Polymer Letters,* 4 (10), 621-631.

47. Tiwary, P., Park, C.B., and Kontopoulou, M. (2017). Transition from microcellular to nanocellular PLA foams by controlling viscosity, branching and crystallization. *European Polymer Journal*, 91, 283-296.

48. Li, B., Zhao, G., Wang, G., Zhang, L., and Gong, J. (2018). Fabrication of high-expansion microcellular PLA foams based on pre-isothermal cold crystallization and supercritical $CO_2$ foaming. *Polymer Degradation and Stability*, 156, 75-88.

49. Mohammadi, M.S., Bureau, M.N., and Nazhat, S.N. (2014). Chapter 11: Polylactic acid (PLA) biomedical foams for tissue engineering. Netti, P.A., *Biomedical Foams for Tissue Engineering Applications*. Woodhead Publishing, Cambridge. pp. 313-334.

50. Gigante, V., Coltelli, M.B., Vannozzi, A., Panariello, L., Fusco, A., Trombi, L., Donnarumma, G., Danti, S., and Lazzeri, A. (2019). Flat die extruded biocompatible poly

(lactic acid)(PLA)/poly (butylene succinate)(PBS) based films. *Polymers*, 11(11), article 1857 (27 pages).

51. Zhou, J., Yao, Z., Zhou, C., Wei, D., and Li, S. (2014). Mechanical properties of PLA/PBS foamed composites reinforced by organophilic montmorillonite. *Journal of Applied Polymer Science*, 131(18), article 40773 (8 pages).

52. Pilla, S., Kim, S.G., Auer, G.K., Gong, S., and Park, C.B. (2010). Microcellular extrusion foaming of poly (lactide)/poly (butylene adipate-co-terephthalate) blends. *Materials Science and Engineering: C*, 30(2), 255-262.

53. Kamrani, M.R., Sanchez-Soto, M., Aghili, A., and Ramezannejad, A. (2018). An investigation on the effect of pressure and temperature on microcellular foams of polylactic acid (PLA)/acrylonitrile-butadiene-styrene (ABS) binary blends. In *International Seminar on Polymer Science and Technology* (pp. 52-55). Springer, Cham.

54. Matuana, L.M., and Diaz, C.A. (2013). Strategy to produce microcellular foamed poly (lactic acid)/wood-flour composites in a continuous extrusion process. *Industrial and Engineering Chemistry Research*, 52(34), 12032-12040.

55. Ding, W., Jahani, D., Chang, E., Alemdar, A., Park, C.B., and Sain, M. (2016). Development of PLA/cellulosic fiber composite foams using injection molding: crystallization and foaming behaviors. *Composites Part A: Applied Science and Manufacturing*, 83, 130-139.

56. Huang, A., Yu, P., Jing, X., Mi, H.Y., Geng, L.H., Chen, B.Y., and Peng, X.F. (2016). The effect of talc on the mechanical, crystallization and foaming properties of poly (lactic acid). *Journal of Macromolecular Science, Part B*, 55(9), 908-924.

57. Ameli, A., Jahani, D., Nofar, M., Jung, P.U., and Park, C.B. (2014). Development of high void fraction polylactide composite foams using injection molding: Mechanical and thermal insulation properties. *Composites Science and Technology*, 90, 88-95.

58. Borkotoky, S.S., Dhar, P., and Katiyar, V. (2018). Biodegradable poly (lactic acid)/cellulose nanocrystals (CNCs) composite microcellular foam: effect of nanofillers on foam cellular morphology, thermal and wettability behavior. *International journal of biological macromolecules*, 106, 433-446.

59. Yang, L., Yang, Z., Zhang, F., Xie, L., Luo, Z., and Zheng, Q. (2018). Star shaped long chain branched poly (lactic acid) prepared by melt transesterification with trimethylolpropane triacrylate and nano-ZnO. *Polymers*, 10(7), article 796 (19 pages).

60. Li, S., He, G., Liao, X., Park, C.B., Yang, Q., and Li, G. (2017). Introduction of a long-chain branching structure by ultraviolet-induced reactive extrusion to improve cell morphology and processing properties of polylactide foam. *RSC advances*, 7(11), 6266-6277.

61. Standau, T., Castellón, S.M., Delavoie, A., Bonten, C., and Altstädt, V. (2019). Effects of chemical modifications on the rheological and the expansion behavior of polylactide (PLA) in foam extrusion. *e-Polymers*, 19(1), 297-304.

62. Di, Y., Iannace, S., Di Maio, E., and Nicolais, L. (2005). Reactively modified poly (lactic acid): properties and foam processing. *Macromolecular materials and engineering*, 290(11), 1083-1090.

# CHAPTER 3

## EXPERIMENTAL

### 3.1 Materials

Poly(lactic) acid (PLA 4044D) with less than 4% D-lactide content [1], a melt flow rate of 3.95 g/10 min (190ºC, 2.16 kg) and density of 1.24 g/cm$^3$ [2-4], obtained from NatureWorks® LLC (Minnetonka, MN) was used as the resin in this study. Two grades of epoxy-functionalized and food grade approved chain extenders (CE), i.e., Joncryl® ADR4400 (or CE 4400) and Joncryl® ADR4468 (or CE 4468), were provided by BASF Corporation. These CEs have different epoxy equivalent weights (EEW) of 485g/mol and 310g/mol for CE 4400 and CE 4468, respectively. For the foaming, commercially available carbon dioxide gas was used as a foaming agent.

### 3.2 Compounding of PLA with chain extenders

The PLA resin was dried in an oven at 60℃ for at least 12 hours before processing to remove any moisture. Compounding of PLA pellets with both grades of multifunctional epoxies took place in an electrically heated 60 ml three-piece internal mixer/measuring head (3:2 gear ratio) with counter-rotating roller style mixing blades (C.W. Brabender Instruments, South Hackensack, NJ) at 200ºC for 5 minutes with the rotor speed set at 35 rpm as described in previous work [2,5-7]. This processing time was selected for successful completion of the reaction between PLA and each CE since a residence time of at least two minutes is recommended by the manufacturer for the reaction of these CEs to be over 99% complete at 200ºC [2]. A 5.6 kW (7.5 hp) Intelli-Torque Plasti-Corder torque rheometer (C.W. Brabender Instruments) powered the mixer. Four different compositions of PLA/CE blends of each CE grade were made by mixing

PLA with 0.25%, 0.50%, 0.75%, and 1.00% weight fractions of each CE grade. Neat PLA was also compounded at the same condition as control.

## 3.3 Melt rheology evaluation

### 3.3.1 Torque rheometry

The torque and stock temperature data were recorded as a function of mixing time from the compounding experiments of PLA with CEs in shear flow conditions in the three-piece internal mixer/measuring head described above. These data were analyzed to assess the effectiveness of these chain extenders on branching PLA matrix and identify the most efficient one. Example of typical curves obtained from the Brabender torque rheometer for the torque and stock temperature of PLA as a function of mixing time is shown in Figure 3.1. Similar curves were obtained for PLA blended with various CE contents for both grades of CE but are not shown. As mentioned, a minimum residence time of 120 s is recommended by the manufacturer for the reaction of these CEs to be over 99% complete at 200°C. Therefore, the times required to reach 200°C were recorded the torque rheometer curves, as described by Karkhanis and Matuana [2]. Since the total processing time was held constant at 300 s, the residence times provided to PLA/CE samples at a minimum of 200°C were calculated by the difference between the total mixing times and the times taken to reach 200°C (Figure 3.1).

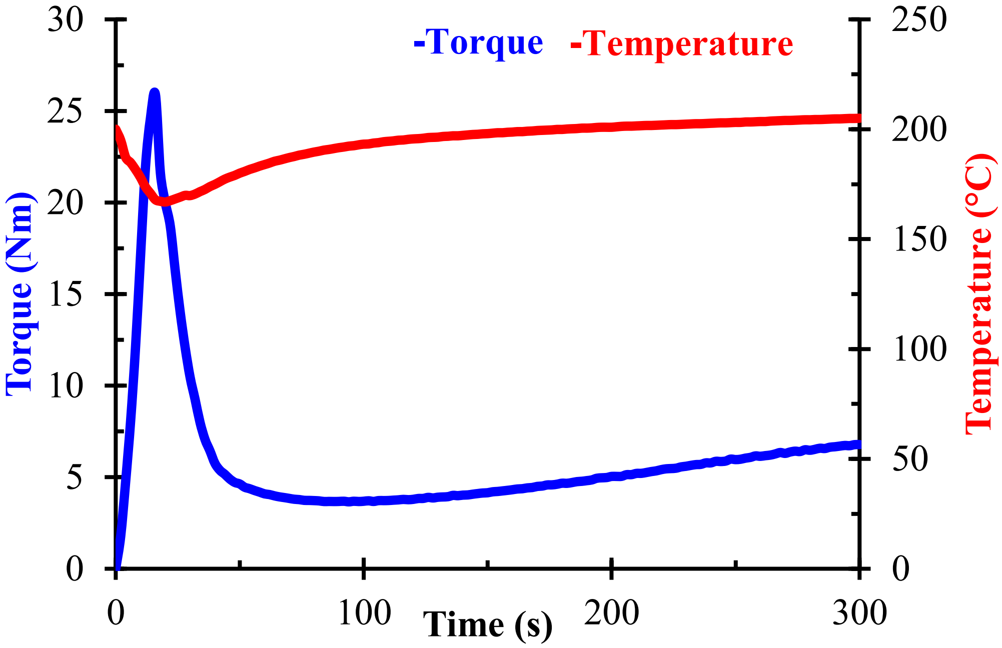

*Figure 3-1: Typical torque rheometry graph.*

### 3.3.2 Capillary extrusion

The shear viscosities of neat PLA and PLA blended with 1% CE of both grades of CE were measured as a function of shear rates at a constant temperature. PLA and CE were dry blended in a high-intensity mixer (Waring Commercial Xtreme) for 30 seconds at 30,000 rpm at ambient temperature. The viscosities of PLA/CE blends and neat PLA (control) were measured on an Intelli-Torque Plasticorder® Torque Rheometer (C.W. Brabender Instruments Inc.) equipped with a 32-mm conical counter-rotating twin-screw extruder (L/D ratio 13:1) as previously described [8-10]. Different L/D ratios (10:1, 15:1, and 20:1) of capillary inserts were used. The temperature profile of the extruder was maintained at 200-205-210-210°C in the heating zones from the feed to the die. However, the speed of the screws was varied from 10 rpm to 80 rpm to generate different shear rates during experiments. Die pressure and flow rate of extruded melts were recorded to calculate apparent shear viscosity of neat PLA and PLA blended with 1% CE of both CE grades according to ASTM standard D5422.

The apparent shear stress ($\tau_a$) and apparent shear rate ($\dot{\gamma}_a$) in a capillary die are given by using the following equations [8-10]:

$$\tau_a = \frac{\Delta P}{4(L/D)} \tag{3.1}$$

$$\dot{\gamma}_a = \frac{32Q}{\pi D^3} \tag{3.2}$$

where, ΔP is the pressure drop in the capillary die, L/D the length over diameter ratio of the capillary die, and Q is the volumetric flow rate of the polymer melt.

The apparent viscosity ($\eta_a$) is the ratio of apparent shear stress to the shear rate.

$$\eta_a = \frac{\tau_a}{\dot{\gamma}_a} \tag{3.3}$$

### 3.3.3 Extensional viscosity

The information collected during the capillary rheometry was used to calculate the extensional viscosity of the polymer melt. The entrance pressure of the die calculated in the capillary rheometry was used along with Cogswell relation to calculate the apparent extensional strain rate ($\dot{\varepsilon}_A$) and apparent extensional shear stress ($\sigma_E$) were calculated as follows [8,11-13]:

$$\dot{\varepsilon}_A = \frac{4\dot{\gamma}_a^2\eta_a}{3(n+1)\Delta P_{end}} \tag{3.4}$$

and

$$\sigma_E = \frac{3}{8}(n+1)\Delta P_{end} \tag{3.5}$$

where $\Delta P_{end}$ is the end pressure correction calculated from the plot of the total pressure in the capillary die (recorded during experiments) versus L/D for each processing screw speed using a linear extrapolation (Bagley correction). Whereas the flow behavior index (n) was obtained from the slope of the plot between the Bagley corrected or true shear stress log ($\tau_w$) and the apparent shear rate log ($\dot{\gamma}_a$).

From these, the apparent extensional viscosity ($\eta_e$) can be calculated as,

$$\eta_e = \frac{\sigma_E}{\dot{\varepsilon}_A} = \frac{9(n+1)^2(\Delta P_{end})^2}{32 \cdot \eta_a \cdot \dot{\gamma}_a^2} \tag{3.6}$$

### 3.4 Compression molding of PLA and PLA/CE samples

The PLA/CE blends and neat PLA were melt compounded into the internal mixer as described above (section 3.1) and then compression molded into panels in a Carver hot press (Carver Inc., Wabash, IN) at platen temperature of 160°C and 0.96 MPa constant pressure for 1 minute. Pressed samples were cooled under pressure by supplying water into the platens before their release. The thickness of the panels measured around 1.0 mm. Manufacturing neat PLA panel followed a similar process, as illustrated in Figure 3.2.

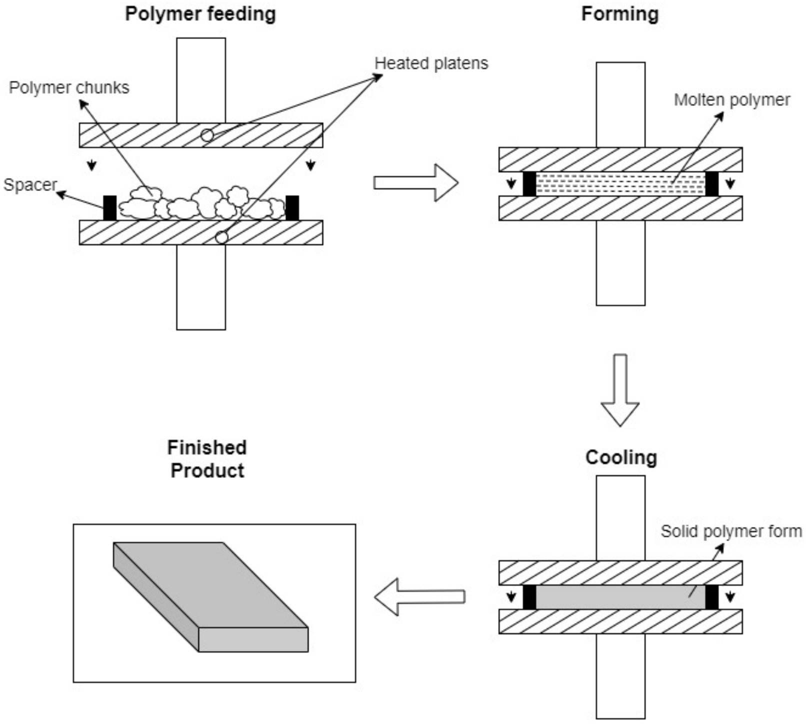

*Figure 3-2: Compression molding process.*

Compression-molded samples were cut into 1.27 cm×2.54 cm rectangular specimens using the RYOBI BS 903 band saw. The edges were then smoothened using 100 grit emery paper and labeled appropriately for foaming experiments.

### 3.5 Saturation and foaming

The labeled rectangular samples were then placed in a pressure chamber (Fig. 3.3) and saturated with $CO_2$ at 400 psi pressures (2.76 MPa) at room temperature for at least 4 days.

This lower saturation pressure was selected since it produced foamed PLA specimens with homogeneous morphology and high volume expansion from the work performed by Matuana and Faruk [14], who studied the influence of $CO_2$ saturation pressure and time on the $CO_2$ solubility and expansion ratio of batch-microcellular foamed PLA. Their results suggest the need for a critical gas concentration of approximately 9.4% for significant foam expansion to occur in PLA (ten-fold expansion over unfoamed PLA). Increasing the concentration of $CO_2$ beyond this critical value has a deleterious effect on the volume expansion, i.e., foam expansion decreases significantly. The foaming conditions associated with such an elevated expansion ratio involved a lower gas saturation pressure up to 2.76 MPa, which corresponds to a critical gas concentration of approximately 9.4%. At this condition, the saturation time of 4 days was required for $CO_2$ diffusion in 1.5-2.0 mm thick PLA samples used in their study [14].

Although not quantified, a large amount of $CO_2$ was dissolved in the 1.0 mm thick samples used in this study after 4 saturation days at 2.76 MPa (400 psi).

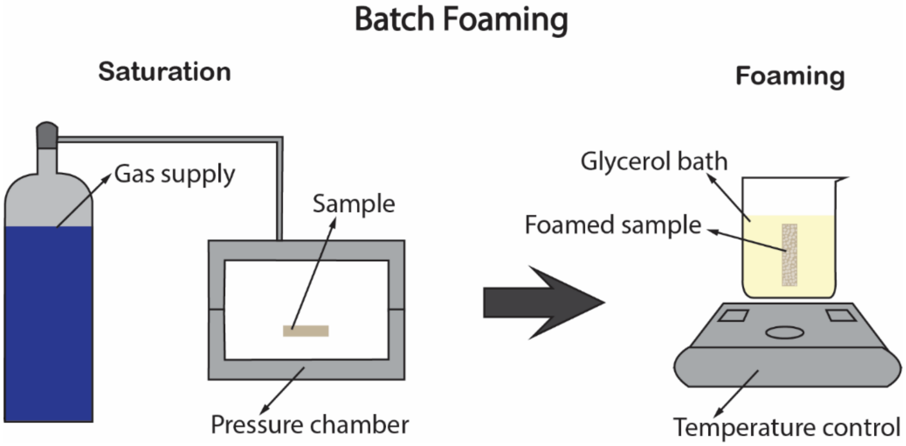

*Figure 3-3: Schematic of two steps involved in batch-microcellular foaming.*

After saturation, the $CO_2$-saturated samples were then removed from the chamber and immediately immersed into a glycerol hot bath set up at 150℃ to create a thermodynamic instability and thus induce gas nucleation (Fig. 3.3). The samples were kept inside the hot bath for 15 seconds to allow the cells to expand and then removed and immediately dipped into a water bath to freeze the foam structure and minimize the deterioration of cells through cell coalescence during bubble growth [8,9,14,15]. The foaming temperature and time were optimized from our preliminary tests.

### 3.6 Characterization of foams

The foam density was measured using the ASTM D792 test standard. The density(ρ) of the foamed sample is given by,

$$\rho_{foam} = \frac{Wt_{sample\ in\ air}}{Wt_{sample\ in\ water}} \times 0.9976 g/cm^3 \qquad (3.7)$$

The Void fraction ($V_f$) which is the percentage decrease in density and the volume expansion ratio (φ) were determined using the following equations [8,14,15]:

$$V_f = \frac{[\rho_{solid} - \rho_{foam}]}{\rho_{solid}} \times 100\% \quad (3.8)$$

$$\varphi = \frac{V_{(foam)}}{V_{(solid)}} = \frac{\rho_{solid}}{\rho_{foam}} = \frac{1}{1 - V_f} \quad (3.9)$$

The foamed samples were then frozen in liquid nitrogen and cracked to image the cross-section in a scanning electron microscope (SEM). The samples were sputter-coated with gold for 180 seconds at 20 mA. The scanning voltage was set to 10KV and micrographs of the cross-sections of all the compositions were taken at various magnification levels. The micrographs that were obtained were then processed in ImageJ image-processing software, which was used to identify the cell diameters of 200 random cells for each composition. The cell-size distribution was plotted, and the average cell diameter was calculated for each composition. The number of cells within a specific area of SEM micrograph was manually counted, and the number of cells nucleated per unit volume of the original unfoamed polymer or cell-population density ($N_0$) was then calculated by [9]:

$$N_0 = \left[\frac{NM^2}{A}\right]^{3/2} \times \varphi \quad (3.10)$$

where N is the number of cells counted in the given area (A), M is the magnification factor and φ is the volume expansion ratio.

### 3.7 Statistical analysis

Ten replicates were done for all the samples in foaming and triplicates for torque rheology and cell-population density. The average values and standard deviations are reported. A one-way T-Test ANOVA with an α of 0.05 was conducted on the data to verify for statistical significance.

# REFERENCES

# REFERENCES

1. Gendron, R., and Mihai, M. (2016). Chapter: 5 Extrusion foaming of polylactide. In S.T. Lee (Ed), *Polymeric foams: innovations in processes, technologies, and products.* Taylor and Francis Group LLC, Boca Raton. pp.107-157.

2. Karkhanis, S.S., and Matuana, L.M. (2019). Extrusion blown films of poly(lactic acid) chain-extended with food grade multifunctional epoxies. *Polymer Engineering and Science,* 59 (11): 2211-2219.

3. Karkhanis, S.S., Stark, N.M., Sabo, R.C., and Matuana, L.M. (2018). Performance of poly(lactic acid)/cellulose nanocrystal composite blown films processed by two different compounding approaches. *Polymer Engineering and Science*, 58 (11), 1965-1974.

4. Karkhanis, S.S., Stark, N.M., Sabo, R.C., and Matuana, L.M. (2018). Water vapor and oxygen barrier properties of extrusion-blown poly(lactic acid)/cellulose nanocrystals nanocomposite films. *Composites Part A: Applied Science and Manufacturing,* 114, 204-211. https://doi.org/10.1016/j.compositesa.2018.08.025

5. Faruk, O., and Matuana, L.M. (2008). Reinforcement of rigid PVC/wood-flour composites with multi-walled carbon nanotubes. *Journal of Vinyl and Additive Technology,* 14 (2), 60-64.

6. Faruk, O., and Matuana, L.M. (2008). Nanoclay reinforced HDPE as a matrix for wood-plastic composites. *Composites Science and Technology,* 68 (9), 2073-2077.

7. Matuana, L.M., and Kim, J.W. (2007). Fusion characteristics of wood-flour filled rigid PVC by torque rheometry. *Journal of Vinyl and Additive Technology,* 13 (1), 1-13.

8. Matuana, L.M., and Diaz, C.A. (2013). Strategy to produce microcellular foamed poly(lactic acid)/wood-flour composites in a continuous extrusion process. *Industrial and Engineering Chemistry Research,* 52(34), 12032-12040.

9. Matuana, L.M., and Diaz, C.A. (2010). Study of cell nucleation in microcellular PLA foamed with supercritical $CO_2$ through a continuous extrusion process. *Industrial and Engineering Chemistry Research,* 49 (5), 2186-2193.

10. Shah, B.L., and Matuana, L.M. (2004). Online measurement of rheological properties of PVC/wood-flour composites. *Journal of Vinyl and Additive Technology,* 10 (3), 121-128.

11. Dealy, J.M., and Wissbrun, K.F. (1990). *Melt rheology and its role in plastics processing.* Springer, Boston.

12. Huang, J.C., and Leong, K.S. (2002). Shear viscosity, extensional viscosity, and die swell of polypropylene in capillary flow with pressure dependency. *Journal of Applied Polymer Science*, 84, 1269-1276.

13. Tzoganakis, C., Vlachopoulos, J., Hamielec, A.E., and Shinozaki, D.M. (1989). Effect of molecular-weight distribution on the rheological and mechanical properties of polypropylene. *Polymer Engineering and Science,* 29, 390-396.

14. Matuana, L.M., and Faruk, O. (2010). Effect of gas saturation conditions on the expansion ratio of microcellular poly (lactic acid)/wood-flour composites. *eXPRESS Polymer Letters*, 4(10), 621-631.

15. Matuana, L.M. (2008). Solid state microcellular foamed PLA: Morphology and property characterization. *Bioresource Technology,* 99 (9), 3643-3650.

# CHAPTER 4

## RESULTS AND DISCUSSION

### 4.1 Chain extension of PLA

Generally, linear polymers are branched by adding chain extenders [1-5]. For PLA for example, this chain-extension increases its zero-shear viscosity and molecular weight, resulting in a modified PLA with enhanced melt viscosity and elasticity, properties needed for successful production of PLA foam [1-11].

This study examined the effectiveness and efficiency of two food-grade multifunctional epoxies chain extenders (CE) with low and high epoxy equivalent weights (EEW) in chain extending/branching PLA and its foamability. The chain extension reaction of PLA with CE was followed by torque rheometry since an increase in torque is associated with chain extension [5] as well as by other rheological properties such as shear and elongational viscosities [2,4,7,9-11].

#### *4.1.1 Torque rheometry of PLA/CE blends*

A residence time of at least 2 minutes is recommended by the manufacturer for the chain extension reaction of PLA with both grades of multifunctional epoxies used in this study to be over 99% complete at a minimum of 200ºC [5]. The total residence times provided to PLA/CE blends at or above 200ºC are summarized in Table 4-1 along with the equilibrium torque (end torque value) taken at 300 s from the torque versus mixing time curves (Fig. 3-1).

The results listed in Table 4-1 clearly indicate that the chain extension reaction between PLA and both multifunctional epoxy grades was over 99% complete, regardless of the CE content, since the experimental residence times for complete reaction exceeded the 2 minutes recommended by the manufacturer.

It should be mentioned that PLA/CE blends experienced temperatures greater than 200ºC because the stock temperature continued to increase above the set temperature of 200ºC to reach 211ºC due to shear generated during processing. Karkhanis and Matuana reported that this additional heat could have accelerated the chain extension reaction between the PLA and multifunctional epoxy-based CE that occurred through the ring-opening reaction of epoxy groups in the CE with PLA's hydroxyl and/or carboxyl groups [5].

*Table 4-1: Mixing times and end torque values of PLA and PLA blended with both grades of multifunctional epoxies in torque rheometer.*

| **C.E Concentration (wt/wt%)** | **Total time at ≥ 200°C (min)** | | **End torque (N·m)** | |
|---|---|---|---|---|
| | **CE 4400** | **CE 4468** | **CE 4400** | **CE 4468** |
| 0 | 2.0 ± 0.0 | 2.0 ± 0.0 | 2.8 ± 0.4 | 2.8 ± 0.4 |
| 0.25 | 2.1 ± 0.1 | 2.1 ± 0.1 | 3.2 ± 0.4 | 3.4 ± 0.4 |
| 0.50 | 2.1 ± 0.0 | 2.2 ± 0.1 | 4.8 ± 0.2 | 5.6 ± 0.3 |
| 0.75 | 2.1 ± 0.0 | 2.4 ± 0.0 | 5.5 ± 0.4 | 6.9 ± 1.5 |
| 1.00 | 2.4 ± 0.1 | 2.5 ± 0.1 | 6.6 ± 0.3 | 8.1 ± 0.7 |

Additionally, the end torque was used to monitor the chain extension reaction of PLA with CE (Table 4-1) since an increase in torque is associated with chain extension. The end torque of PLA during mixing increased linearly with the CE content for both multifunctional CEs. This result implies that both multifunctional epoxies chain extended and branched PLA effectively. Similar results have been reported in previous work [5]. Generally, an increase in the end torque values indicates an increase in the viscosity and molecular weight due to the formation of longer and/or branched chains [5,8,12,13].

### *4.1.2 Shear viscosity of PLA/CE blends*

Successful chain extension of PLA with multifunctional epoxies was further studied by evaluating the effect of CE addition on the shear viscosity of PLA melt. It can be seen in figure 4-1 that neat PLA exhibited typical Newtonian behavior in the low shear rate region. The zero-shear viscosity was well defined at around 400 Pa·s for neat PLA and the onset of its shear-thinning behavior occurred at higher shear rates (at around 300 1/s), which is a characteristic for linear polymers [4]. In contrast, PLA/CE blends had higher viscosities than neat PLA for all shear rates due to the increased number of molecular chain entanglements in modified PLA [5]. The zero-shear viscosity of PLA/CE blends were not observed in the measured shear rate range because they shifted upward to higher values, and the onset of their shear-thinning behaviors occurred at lower shear rates (by extrapolation), suggesting a significant increase in the molecular weight of PLA. The zero-shear viscosity of polymer melt depends on the polymer's average molecular weight and the number of entanglements between branching points [10]. As a result, a polymer with higher molecular weight will also have an increased zero-shear viscosity due to molecular chain entanglement, as expected from the Mark-Houwink relation [5,14]. Therefore, the increased viscosity of PLA/CE blends obtained in this study supports the successful chain extension of PLA.

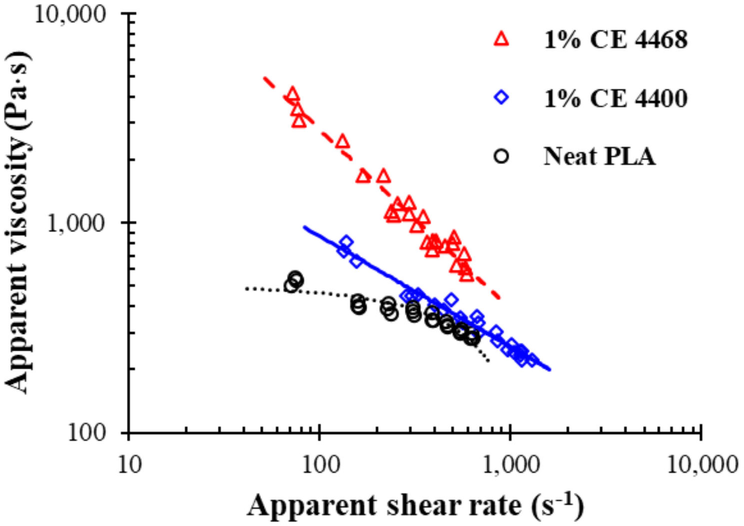

*Figure 4-1: Apparent shear viscosity vs. apparent shear rate of PLA and PLA/1%CE blends.*

The chain-extended PLA also shows a more prominent shear thinning behavior from the steeper slope occurring at lower shear rates than neat PLA. The shear viscosities of chain-extended PLA were ~8 times greater than that of neat PLA at lower shear rates, but only twice as viscous at high shear rates. This could be evidence of long-chain branching as a high degree of shear-thinning is associated with long-chain branched polymer chains [2,4,7,15]. Moreover, the reduced degree of crystallinity of PLA caused by the addition of CE into the matrix reported in the previous study corroborates this chain branching [5].

### *4.1.3 Extensional viscosity of PLA/CE blends*

Successfully chain extension and branching of PLA with multifunctional epoxies have been demonstrated by torque rheometry and shear viscosity results. Extensional viscosity is another important parameter for foaming as higher extensional viscosity would allow the polymer melt to maintain stable bubbles, thus forming a uniform foam cell structure [4,5,11,16,17].

The apparent extensional viscosities of linear and branched PLA plotted as a function of apparent extensional strain rate are illustrated in figure 4-2. Irrespective of the strain rate, the branched PLA had higher extensional viscosities than linear PLA, suggesting that the addition of CE significantly improves the melt strength of PLA due to chain extension. This result was expected because long-chain branching leads to greater chain entanglement, which causes an increase in extensional viscosity. Similar results were reported by other investigators [4,11].

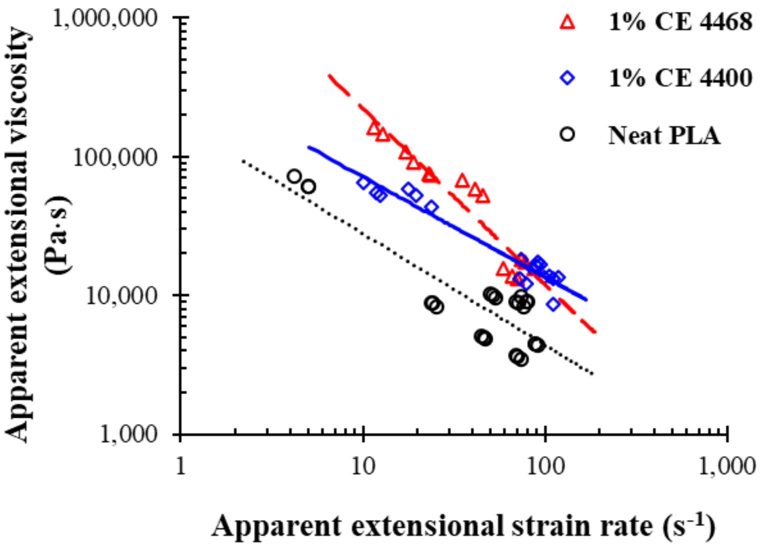

*Figure 4-2: Apparent extensional viscosity measured by online capillary rheometry of PLA and chain-extended PLA with 1% multifunctional epoxies.*

### 4.2 Foam characteristics and cell morphology

In general, branched/chain-extended PLA with higher elongational viscosity or melt strength, than unmodified PLA is be better suited for foaming [1-4,6-11]. Thus, it is important to examine the foamability of the PLA chain extended with various concentrations of food-grade multifunctional epoxies of low and high epoxy equivalent weights.

The SEM micrographs of microcellular foamed PLA branched with various amounts of chain extender showing thickness expansion, and cell size growth are illustrated in figures 4-3 (low magnification) and 4-4 (high magnification), respectively, whereas the effect of CE content on the void fraction and volume expansion ratio of PLA foams is shown in Figure 4-5.

Neat PLA samples showed poor morphology with irregular cell sizes (Figs. 4-3 and 4-4) and low expansion (Fig. 4-5). Neat PLA did not provide polymer matrix suitable enough for withholding the gas for bubble growth, because of their lower elongational viscosity, as seen in Fig. 4-2. High magnification SEM micrograph in Fig. 4-4a clearly illustrates the inhomogeneous cell structure of neat PLA foams with areas without nucleated cells (dead zones) (Fig. 4-6). It is believed that its elongational viscosity was not high enough so that either the evolving gas was not sufficiently trapped for cell growth or the bubbles collapsed to a certain degree during the foaming process [19-21]. Moreover, a large variation in average cell size is seen through its cellular structure (Fig. 4-6).

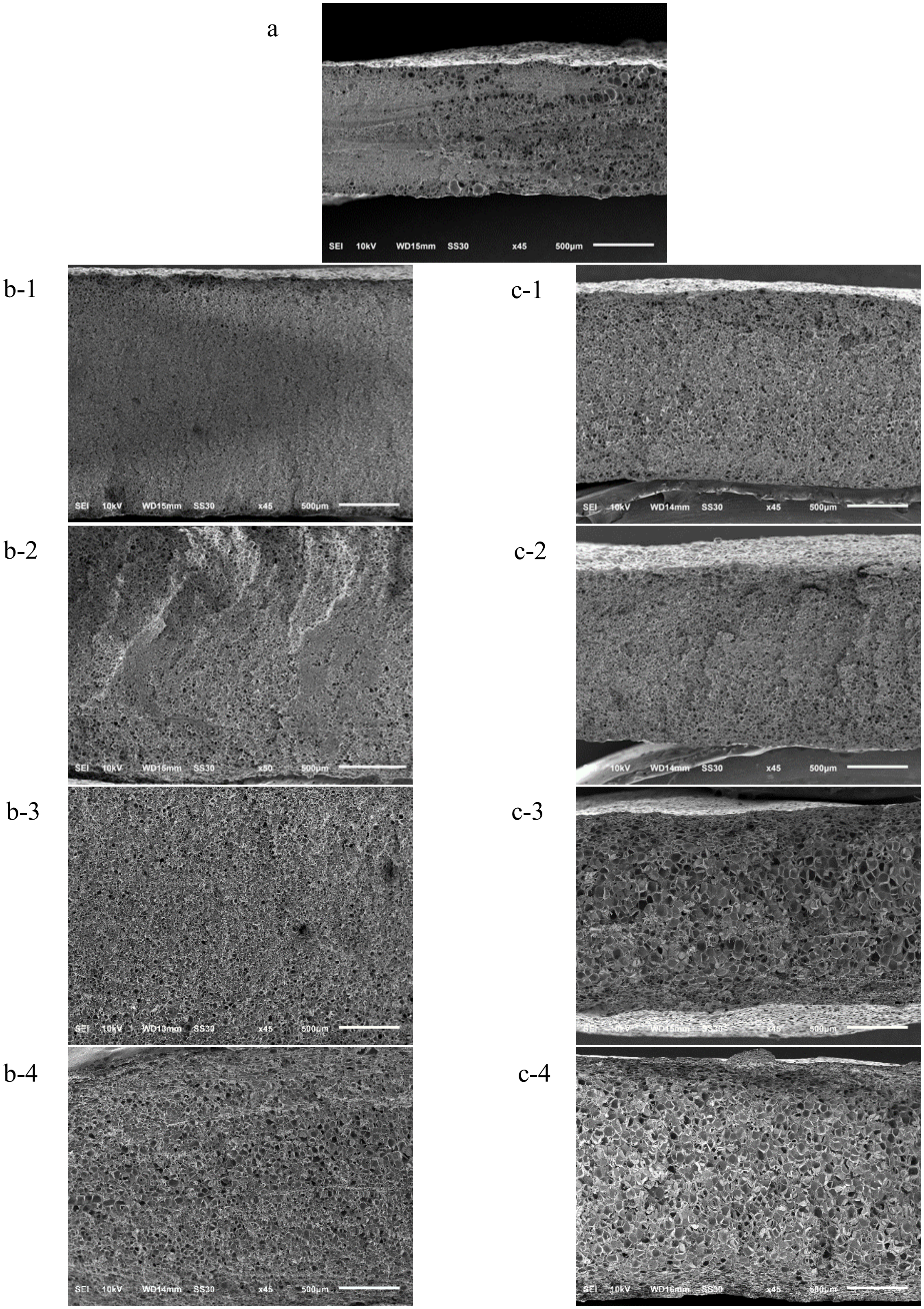

*Figure 4-3: SEM micrographs (45x) of (a) neat PLA as well as PLA branched with (b) CE 4468, and (c) CE 4400. Samples 1, 2, 3, 4 contained 0.25; 0.5; 0.75; and 1% CE, respectively.*

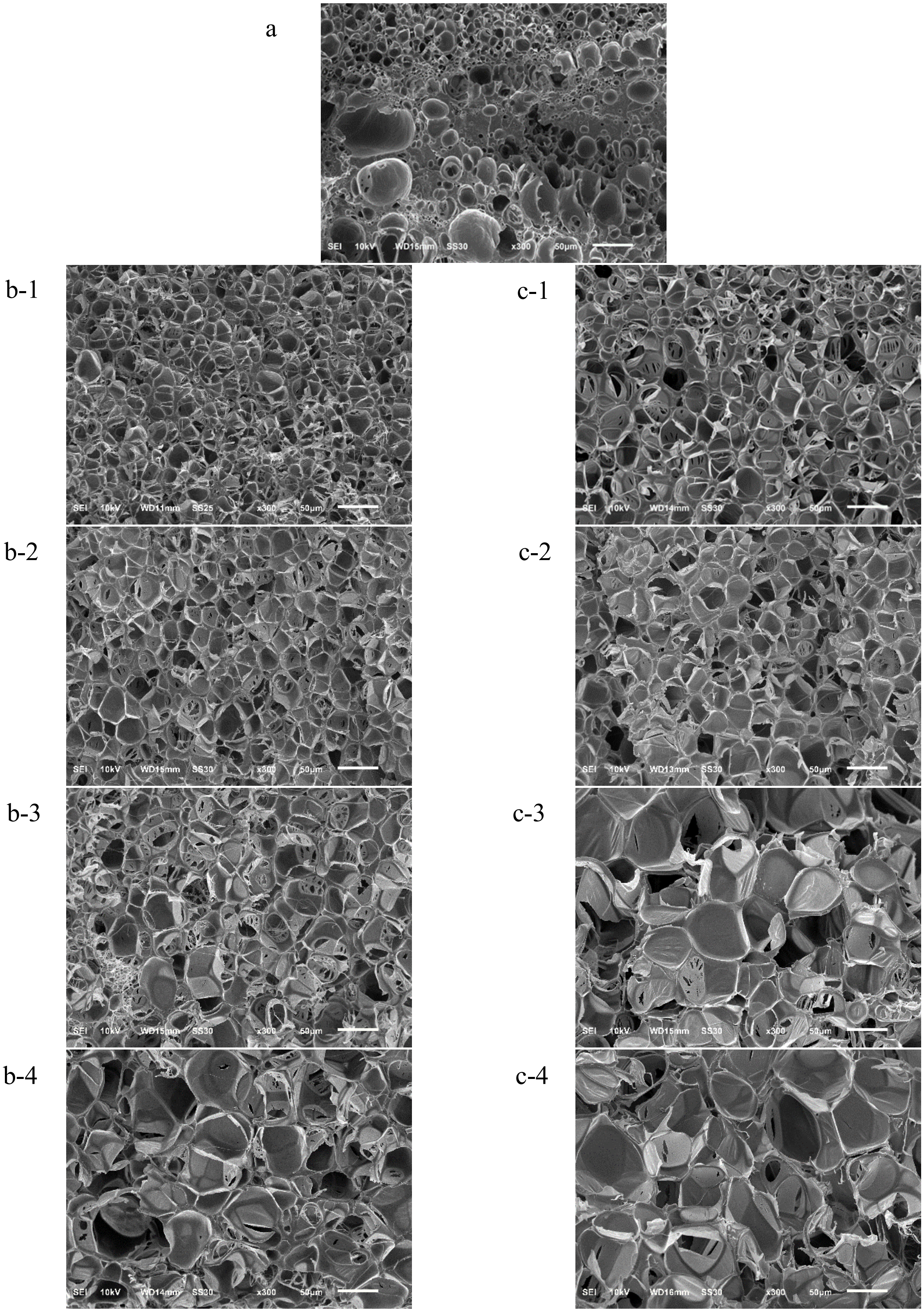

*Figure 4-4: SEM micrographs (300x) of (a) neat PLA as well as PLA branched with (b) CE 4468, and (c) CE 4400. Samples 1, 2, 3, 4 contained 0.25; 0.5; 0.75; and 1% CE, respectively.*

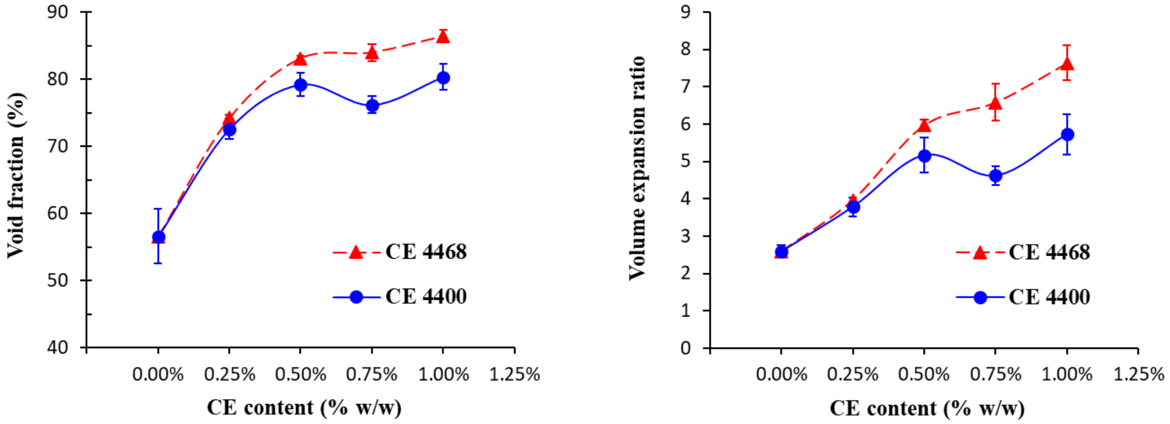

*Figure 4-5: Effect of CE content on the void fraction and volume expansion ratio of PLA foams.*

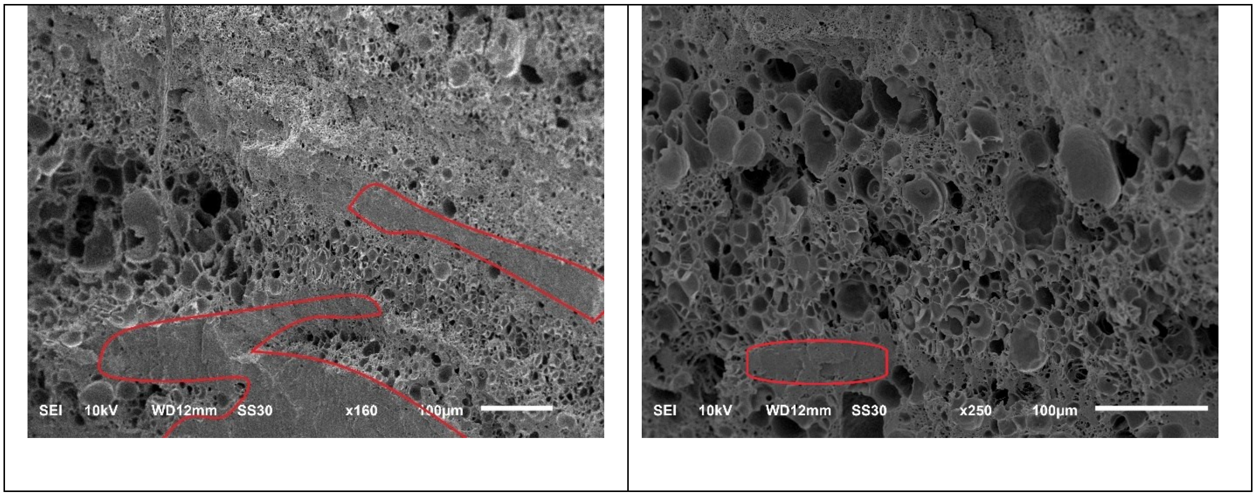

*Figure 4-6: SEM micrographs taken at magnifications of 160x (left) and 250x (right) showing dead zones (outlined in red line) in neat PLA foam.*

By contrast, there was a stark change in the uniformity of the PLA foam structure caused by its branching. Chain-extended PLA foams showed uniform cell morphology (Figs. 4-3 and 4-4.) with the highest expansion (Fig. 4-5), mainly due to their high elongational viscosities. As the CE content increased, both the void fraction and expansion ratio increased, reaching a maximum value at 0.5% CE, after which they remained constant as the CE content further increased above 0.5%, irrespective of CE grade. This tendency can be attributed to the growth and stabilization of nucleated cells, which were favored by the increased elongational viscosities of branched PLA. Once the cells are nucleated, they continue to grow if there is enough gas to diffuse into the nucleated cells so that the polymer could be expanded [16-21]. Since increased melt viscosity prevents the diffusion loss of gas from the nucleated cells to the environment, it is believed that the dissolved gas was effectively used for cell growth of branched samples because of their high elongational viscosity. The Stokes-Einstein equation that relates viscosity (η) and diffusion (D) supports the fact the gas diffusion decreases by increasing the melt viscosity [22].

$$D = \frac{K_B T}{6\pi\eta r} \tag{4.1}$$

where $K_B$ is the Boltzmann constant, T is the absolute temperature, and r is the radius of the fluid drop. Overall, chain-extended PLA foams exhibited larger cells than the neat PLA because of their high extensional viscosity. These results agree with those published by Mihai and coworkers showing a decrease in foam density (or increase in void faction) by the increase of the chain extender content for semi-crystalline PLA microcellular foamed with 5% $CO_2$ [2]. A ten times increase in volume expansion ratio of PLA has also been reported by the addition of 5 phr CE [11].

The void fraction and expansion ratio appeared to increase with CE content above 0.5% CE, particularly for the CE with low epoxy equivalent weight (CE 4468). Nevertheless, this increase was not statistically significant compared to the one observed below 0.5%. Additionally, statistical analysis suggested a strong dependence of both void fraction and expansion ratio on the chain extender grade (epoxy equivalent weight or EEW) and content. Chain extenders with both low EEW (CE 4468) and high EEW (CE 4400) performed similarly in increasing both the void fraction and expansion ration of PLA up to 0.25% CE. Different trend was observed above this concentration, where the chain extender with low EEW outperformed the counterpart with high EEW, probably due to their different effect during cell growth as will be discussed later.

Significant improvements in both void fraction (up to ~85% density reduction) and expansion ratio (an eightfold expansion over unfoamed PLA) were achieved by chain branching PLA, suggesting that melt properties of branched PLA were appropriate for optimum cell growth and stabilization during foaming. Changes in the average cell diameter of foamed PLA as a function of chain extender content are listed in Table 4-2.

*Table 4-2: Average cell diameter of branched PLA foams calculated manually and with an image processing software (ImageJ).*

| **CE types** | | **Average cell size (μm)* as a function of CE content** | | | | |
|---|---|---|---|---|---|---|
| | | **0%** | **0.25%** | **0.50%** | **0.75%** | **1.00%** |
| *CE 4400* | *Manual* | 10.4 ± 13.6$^a$ | 15.3 ± 4.9$^a$ | 17.1 ± 6.6$^a$ | 22.1 ± 14.7$^a$ | 32.2 ± 21.0$^a$ |
| | *ImageJ* | 10.6 ± 7.4$^a$ | 15.0 ± 4.1$^a$ | 17.1 ± 7.6$^a$ | 23.5 ± 13.3$^a$ | 29.9 ± 12.0$^a$ |
| *CE 4468* | *Manual* | 10.4 ± 13.6$^a$ | 7.96 ± 2.3$^a$ | 15.8 ± 5.5$^a$ | 15.5 ± 3. 8$^a$ | 23.2 ± 14.8$^a$ |
| | *ImageJ* | 10.6 ± 7.4$^a$ | 8.13 ± 1.9$^a$ | 16.4 ± 4.3$^a$ | 15.7 ± 4.2$^a$ | 19.2 ± 9.7$^a$ |

*The superscript letter denotes a one-way ANOVA within the same column comparing manual vs. ImageJ method for each CE type. Similar superscript letters within the same column are not significantly different based on the T-Test results at a 5% significance level.

Statistically, the cell sizes calculated manually yielded similar results to those calculated with an image processing software (ImageJ), validating the accuracy of the manual method. The average cell size was strongly dependent on the chain extender content, increasing almost linearly with the chain extender content, regardless of the CE grade because branched PLA had elongational viscosity suitable for cell growth (Table 4-2). However, a slight downward trend was only observed for PLA branched with 0.25% of low EEW chain extender, which exhibited finer cells (<10 μm) compared to neat and other branched PLA formulations (Table 4-2 and Fig. 4-4). Thus, 0.25% appears to be the threshold of CE content that provides melt viscosity appropriate to produce PLA foams with a homogeneous structure and fine cells. Similar results were reported by Chen et al. [11] and Mihai et. al. [2] for semi-crystalline PLA foamed with 5% $CO_2$, which showed an increase in cell size from 130 up to 300 μm as the CE content increased to 2% [2]. An opposite trend showing a decrease in cell size with the increase in CE content has also been reported and attributed to the intrinsically high viscosity and elasticity of branched samples, which restricted the expansion of cells [4,7]. This discrepancy could be due to different methods and foaming conditions during foam manufacture.

Comparison between the two chain extender grades with different epoxy equivalent weights (EEW) indicated that chain extender with high EEW (CE 4400) produced foams with larger cells than their counterparts with low EEW (CE 4468), irrespective of CE content, attributed to its lower elongation viscosity (Fig. 4-2) that offered less resistance to cell growth [19-21].

Overall, the cell-population density appeared to slightly decrease with the increased CE content due to increased cell size, but this change was not statistically significant (Figure 4.7). Except, the effect of CE content on cell-population density was noticeable only in PLA branched with 0.25% of low EEW chain extender, due to its finer cells as previously discussed (Table 4-2 and Fig. 4-4).

PLA branched with 0.25% of the low EEW foam (CE 4468) had the highest cell density, which was around five times higher than the other formulations. Thus, 0.25% was found to be the optimum CE content and chain extender with low epoxy equivalent weight (CE 4468), the most effective grade for producing foams with higher cell density. This optimum 0.25% CE concentration agrees with the initial trial dosage of 0.2% recommended by the manufacturer of the multifunctional epoxies used in this study.

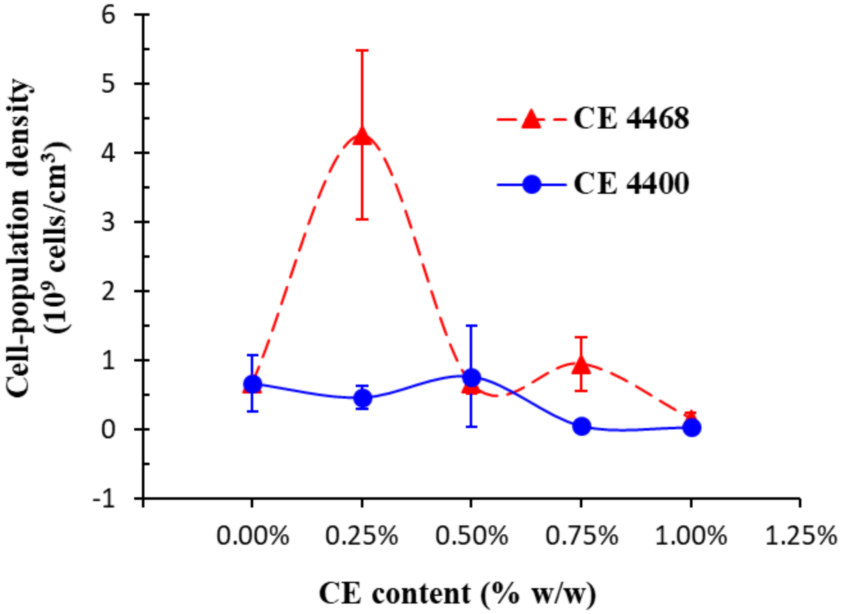

*Figure 4-7: Effect of CE content on the cell-population density of PLA foams.*

# APPENDIX

# APPENDIX

*Table A-1: Capillary rheometry raw data: PLA 4044D.*

| L/D [mm/mm] | Speed [rpm] | Temp. [°C] | ΔP [PSI] | ρ [g/min] | Q [$cm^3$/min] | γ [1/s] | τ [Pa] | η [Pas] |
|---|---|---|---|---|---|---|---|---|
| 20/2 | 10 | 205.7 | 237 | 3.99 | 3.53 | 74.9 | 40,843 | 545.1 |
| 20/2 | 20 | 205.6 | 392 | 8.47 | 7.5 | 159.1 | 67,617 | 425.1 |
| 20/2 | 30 | 205.4 | 545 | 12.18 | 10.78 | 228.7 | 93,926 | 410.6 |
| 20/2 | 40 | 205.1 | 706 | 16.44 | 14.55 | 308.7 | 121,649 | 394.0 |
| 20/2 | 50 | 205.3 | 833 | 20.57 | 18.2 | 386.3 | 143,624 | 371.8 |
| 20/2 | 60 | 205.4 | 912 | 24.67 | 21.83 | 463.3 | 157,196 | 339.3 |
| 20/2 | 70 | 204.9 | 1009 | 29.57 | 26.17 | 555.3 | 173,893 | 313.1 |
| 20/2 | 80 | 205.2 | 1072 | 33.1 | 29.29 | 621.6 | 184,716 | 297.2 |
| 30/2 | 10 | 205.1 | 350 | 4.03 | 3.57 | 75.7 | 40,204 | 531.2 |
| 30/2 | 20 | 205.3 | 550 | 8.53 | 7.55 | 160.2 | 63,178 | 394.4 |
| 30/2 | 30 | 205.8 | 766 | 12.7 | 11.24 | 238.5 | 88,062 | 369.2 |
| 30/2 | 40 | 205.9 | 994 | 16.75 | 14.82 | 314.6 | 114,170 | 363.0 |
| 30/2 | 50 | 205.6 | 1180 | 20.95 | 18.54 | 393.4 | 135,548 | 344.5 |
| 30/2 | 60 | 205.1 | 1315 | 24.94 | 22.07 | 468.4 | 151,131 | 322.7 |
| 30/2 | 70 | 205.2 | 1447 | 29.12 | 25.77 | 546.9 | 166,234 | 304.0 |
| 30/2 | 80 | 204.9 | 1559 | 33.69 | 29.81 | 632.7 | 179,198 | 283.2 |
| 40/2 | 10 | 205.7 | 416 | 3.8 | 3.36 | 71.4 | 35,870 | 502.7 |
| 40/2 | 20 | 206.1 | 734 | 8.39 | 7.42 | 157.6 | 63,283 | 401.6 |
| 40/2 | 30 | 205.4 | 1033 | 12.1 | 10.71 | 227.2 | 89,051 | 391.9 |
| 40/2 | 40 | 204.9 | 1346 | 16.29 | 14.42 | 305.9 | 116,033 | 379.3 |
| 40/2 | 50 | 205.2 | 1550 | 20.68 | 18.3 | 388.4 | 133,565 | 343.9 |
| 40/2 | 60 | 205.2 | 1735 | 25.05 | 22.17 | 470.4 | 149,563 | 317.9 |
| 40/2 | 70 | 205 | 1881 | 29.12 | 25.77 | 546.9 | 162,117 | 296.5 |
| 40/2 | 80 | 204.9 | 1997 | 32.6 | 28.85 | 612.2 | 172,079 | 281.1 |

*Table A-2: Capillary rheometry raw data: PLA 4044D + 1% CE4468.*

| L/D [mm/mm] | Speed [rpm] | Temp. [°C] | ΔP [PSI] | ρ [g/min] | Q [cm$^3$/min] | γ [1/s] | τ [Pa] | η [Pas] |
|---|---|---|---|---|---|---|---|---|
| 20/2 | 10 | 204.9 | 1731 | 3.82 | 3.38 | 71.7 | 298,347 | 4158.9 |
| 20/2 | 20 | 205.1 | 1890 | 6.99 | 6.19 | 131.3 | 325,724 | 2481.4 |
| 20/2 | 30 | 204.6 | 1839 | 13.57 | 12.01 | 254.8 | 316,978 | 1243.8 |
| 20/2 | 40 | 205 | 1813 | 17.12 | 15.15 | 321.5 | 312,423 | 971.8 |
| 20/2 | 50 | 204.8 | 1829 | 20.64 | 18.27 | 387.6 | 315,314 | 813.5 |
| 20/2 | 60 | 204.6 | 2035 | 24.02 | 21.26 | 451.1 | 350,788 | 777.7 |
| 20/2 | 70 | 204.5 | 2300 | 26.49 | 23.44 | 497.5 | 396,375 | 796.8 |
| 20/2 | 80 | 204.1 | 2085 | 31.1 | 27.52 | 584 | 359,384 | 615.3 |
| 30/2 | 10 | 204.8 | 2107 | 4.15 | 3.67 | 77.9 | 242,068 | 3106.1 |
| 30/2 | 20 | 205.3 | 2471 | 8.98 | 7.95 | 168.6 | 283,958 | 1683.8 |
| 30/2 | 30 | 204.9 | 3203 | 11.58 | 10.25 | 217.5 | 368,025 | 1692.3 |
| 30/2 | 40 | 204.5 | 2838 | 15.75 | 13.94 | 295.8 | 326,178 | 1102.8 |
| 30/2 | 50 | 204.6 | 2588 | 19.52 | 17.27 | 366.6 | 297,410 | 811.3 |
| 30/2 | 60 | 204.1 | 2494 | 20.56 | 18.19 | 386.1 | 286,572 | 742.2 |
| 30/2 | 70 | 204.2 | 3748 | 26.71 | 23.64 | 501.6 | 430,680 | 858.6 |
| 30/2 | 80 | 203.5 | 3550 | 30.3 | 26.81 | 569 | 407,973 | 717 |
| 40/2 | 10 | 205.1 | 3135 | 4.09 | 3.62 | 76.8 | 270,185 | 3517.7 |
| 40/2 | 20 | 204.5 | 3139 | 12.63 | 11.18 | 237.2 | 270,557 | 1140.7 |
| 40/2 | 30 | 203.4 | 3095 | 13.08 | 11.58 | 245.6 | 266,772 | 1086.1 |
| 40/2 | 40 | 203.9 | 4286 | 15.72 | 13.91 | 295.2 | 369,378 | 1251.2 |
| 40/2 | 50 | 203.6 | 4351 | 18.43 | 16.31 | 346.1 | 375,008 | 1083.5 |
| 40/2 | 60 | 203.5 | 3921 | 21.8 | 19.29 | 409.4 | 337,953 | 825.5 |
| 40/2 | 70 | 203.1 | 3793 | 27.55 | 24.38 | 517.4 | 326,890 | 631.8 |
| 40/2 | 80 | 202.9 | 3902 | 31.4 | 27.79 | 589.7 | 336,320 | 570.4 |

*Table A-3: Capillary rheometry raw data: PLA 4044D + 1% CE4400.*

| L/D [mm/mm] | Speed [rpm] | Temp. [°C] | ΔP [PSI] | ρ [g/min] | Q [cm³/min] | γ [1/s] | τ [Pa] | η [Pas] |
|---|---|---|---|---|---|---|---|---|
| 20/2 | 10 | 206.5 | 332 | 10.26 | 9.08 | 193.0 | 28,573 | 148.3 |
| 20/2 | 20 | 206.6 | 596 | 24.2 | 21.42 | 454.0 | 51,401 | 113.1 |
| 20/2 | 30 | 206.4 | 746 | 38.07 | 33.69 | 715.0 | 64,302 | 89.9 |
| 20/2 | 40 | 205.6 | 807 | 52.95 | 46.86 | 994.0 | 69,511 | 69.9 |
| 20/2 | 50 | 206.3 | 907 | 68.51 | 60.63 | 1287.0 | 78,193 | 60.8 |
| 20/2 | 60 | 206.1 | 920 | 79.6 | 70.44 | 1495.0 | 79,313 | 53.1 |
| 20/2 | 70 | 205.6 | 948 | 104.68 | 92.64 | 1966.0 | 81,731 | 41.6 |
| 20/2 | 80 | 206.8 | 1000 | 96.04 | 84.99 | 1804.0 | 86,220 | 47.8 |
| 30/2 | 10 | 206.4 | 392 | 11.16 | 9.88 | 210.0 | 45,044 | 214.9 |
| 30/2 | 20 | 206.3 | 561 | 21.58 | 19.1 | 405.0 | 64,447 | 159 |
| 30/2 | 30 | 206.1 | 902 | 32.32 | 28.6 | 607.0 | 103,620 | 170.7 |
| 30/2 | 40 | 205.8 | 1163 | 50.92 | 45.06 | 956.0 | 133,632 | 139.7 |
| 30/2 | 50 | 206.2 | 1253 | 63.92 | 56.57 | 1200.0 | 144,021 | 120 |
| 30/2 | 60 | 206.1 | 1340 | 83.36 | 73.77 | 1565.0 | 153,995 | 98.4 |
| 30/2 | 70 | 205.8 | 1392 | 95.28 | 84.32 | 1789.3 | 159,961 | 89.4 |
| 30/2 | 80 | 206 | 1460 | 107.44 | 95.08 | 2018.0 | 167,737 | 83.1 |
| 40/2 | 10 | 205.8 | 848 | 7.96 | 7.04 | 149.5 | 73,104 | 489 |
| 40/2 | 20 | 205.6 | 1267 | 16.55 | 14.65 | 310.8 | 109,175 | 351.3 |
| 40/2 | 30 | 205.2 | 1906 | 27.76 | 24.57 | 521.3 | 164,293 | 315.2 |
| 40/2 | 40 | 204.9 | 2424 | 31.57 | 27.94 | 592.9 | 208,953 | 352.4 |
| 40/2 | 50 | 205.2 | 2522 | 38.69 | 34.24 | 726.6 | 217,355 | 299.2 |
| 40/2 | 60 | 204.6 | 2901 | 50.8 | 44.96 | 954.0 | 249,992 | 262 |
| 40/2 | 70 | 204.5 | 2970 | 58.05 | 51.37 | 1090.0 | 255,966 | 234.8 |
| 40/2 | 80 | 204.2 | 3071 | 66.85 | 59.16 | 1255.0 | 264,687 | 210.8 |

*Table A-4: Extensional viscosity raw data for PLA 4044D, PLA 4044D + 1% CE4468, PLA 4044D + 1% CE4400.*

| *PLA 4044D* | | | *PLA 4044D + 1% CE4468* | | | *PLA 4044D + 1% CE4400* | | |
|---|---|---|---|---|---|---|---|---|
| Time [s] | Extensional Strain rate [$\varepsilon_A$] | Extensional viscosity [$\eta_{EC}$] | Time [s] | Extensional Strain rate [$\varepsilon_A$] | Extensional viscosity [$\eta_{EC}$] | Time [s] | Extensional Strain rate [$\varepsilon_A$] | Extensional viscosity [$\eta_{EC}$] |
| 0.20 | 5.03 | 60,395.0 | 0.06 | 16.51 | 39,236.9 | 0.08 | 11.85 | 55,241.6 |
| 0.04 | 25.52 | 8,259.0 | 0.09 | 11.51 | 161,473.3 | 0.04 | 23.96 | 43,430.6 |
| 0.02 | 47.15 | 4,829.2 | 0.04 | 23.35 | 74,075.1 | 0.04 | 25.42 | 80,771.1 |
| 0.01 | 73.50 | 3,475.0 | - | - | - | 0.02 | 45.38 | 38,668.2 |
| 0.02 | 53.58 | 9,663.8 | 0.02 | 66.24 | 13,927.7 | 0.01 | 110.56 | 8,603.8 |
| 0.01 | 91.55 | 4,344.4 | - | - | - | 0.01 | 99.24 | 13,500.8 |
| 0.01 | 75.96 | 8,365.5 | 0.02 | 41.19 | 58,116.1 | 0.01 | 110.95 | 13,102.9 |
| 0.01 | 80.16 | 8,935.1 | 0.01 | 78.00 | 17,247.5 | 0.01 | 118.12 | 13,485.5 |
| 0.20 | 5.01 | 60,672.3 | 0.07 | 14.55 | 44,506.3 | 0.08 | 12.38 | 52,866.7 |
| 0.04 | 24.01 | 8,780.0 | 0.08 | 12.88 | 144,318.3 | 0.05 | 19.71 | 52,802.8 |
| 0.02 | 46.11 | 4,938.4 | 0.04 | 23.15 | 74,718.1 | 0.05 | 18.57 | 110,578.8 |
| 0.01 | 70.33 | 3,631.6 | - | - | - | 0.03 | 29.78 | 58,924.8 |
| 0.02 | 51.49 | 10,056.5 | 0.02 | 59.09 | 15,611.3 | 0.01 | 72.22 | 13,171.9 |
| 0.01 | 89.00 | 4,468.9 | - | - | - | 0.01 | 85.32 | 15,702.9 |
| 0.01 | 71.54 | 8,882.6 | 0.02 | 45.12 | 53,055.0 | 0.01 | 105.41 | 13,791.4 |
| 0.01 | 79.14 | 9,050.7 | 0.01 | 86.28 | 15,591.8 | 0.01 | 95.04 | 16,760.5 |
| 0.24 | 4.22 | 72,066.8 | 0.06 | 16.02 | 40,432.5 | 0.10 | 10.03 | 65,296.3 |
| 0.04 | 23.66 | 8,909.5 | 0.06 | 17.27 | 107,628.2 | 0.06 | 17.68 | 58,872.3 |
| 0.02 | 44.42 | 5,126.7 | 0.05 | 18.94 | 91,305.2 | 0.06 | 16.15 | 127,136.3 |
| 0.01 | 69.48 | 3,676.0 | - | - | - | 0.03 | 30.41 | 57,709.5 |
| 0.02 | 50.10 | 10,335.1 | 0.01 | 70.34 | 13,115.2 | 0.01 | 79.02 | 12,038.4 |
| 0.01 | 88.43 | 4,497.9 | - | - | - | 0.01 | 73.93 | 18,120.9 |
| 0.01 | 69.78 | 9,107.3 | 0.03 | 35.33 | 67,764.1 | 0.01 | 89.94 | 16,164.0 |
| 0.01 | 73.54 | 9,739.2 | 0.01 | 73.72 | 18,247.3 | 0.01 | 91.63 | 17,385.4 |

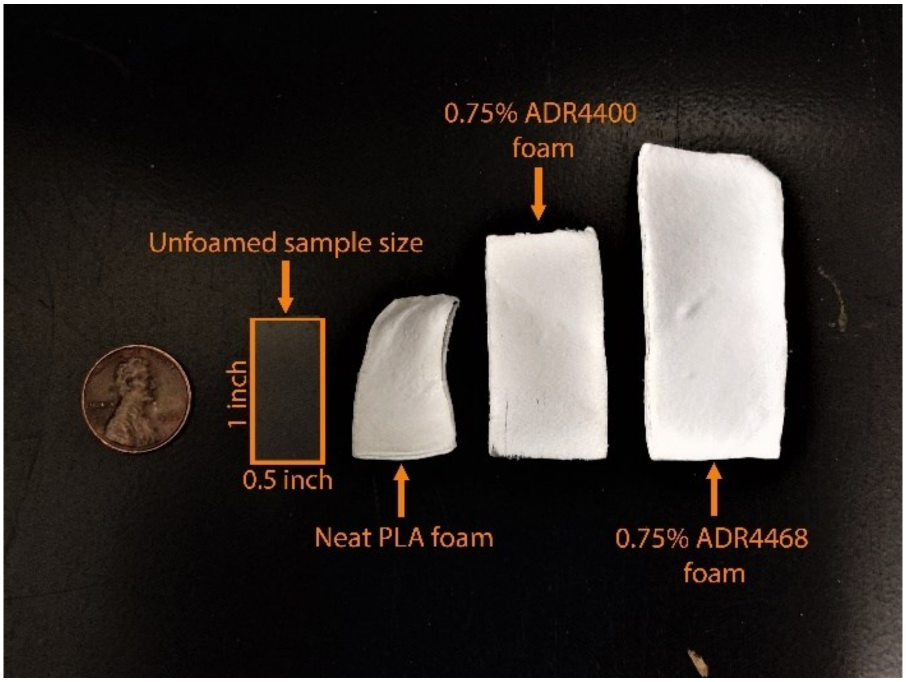

*Figure A-1: From left to right: A U.S penny, un-foamed sample size, Foamed neat PLA sample, Foamed sample of PLA with 0.75% high EEW CE (ADR4400) and foamed sample of PLA with 0.75% low EEW CE(ADR4468).*

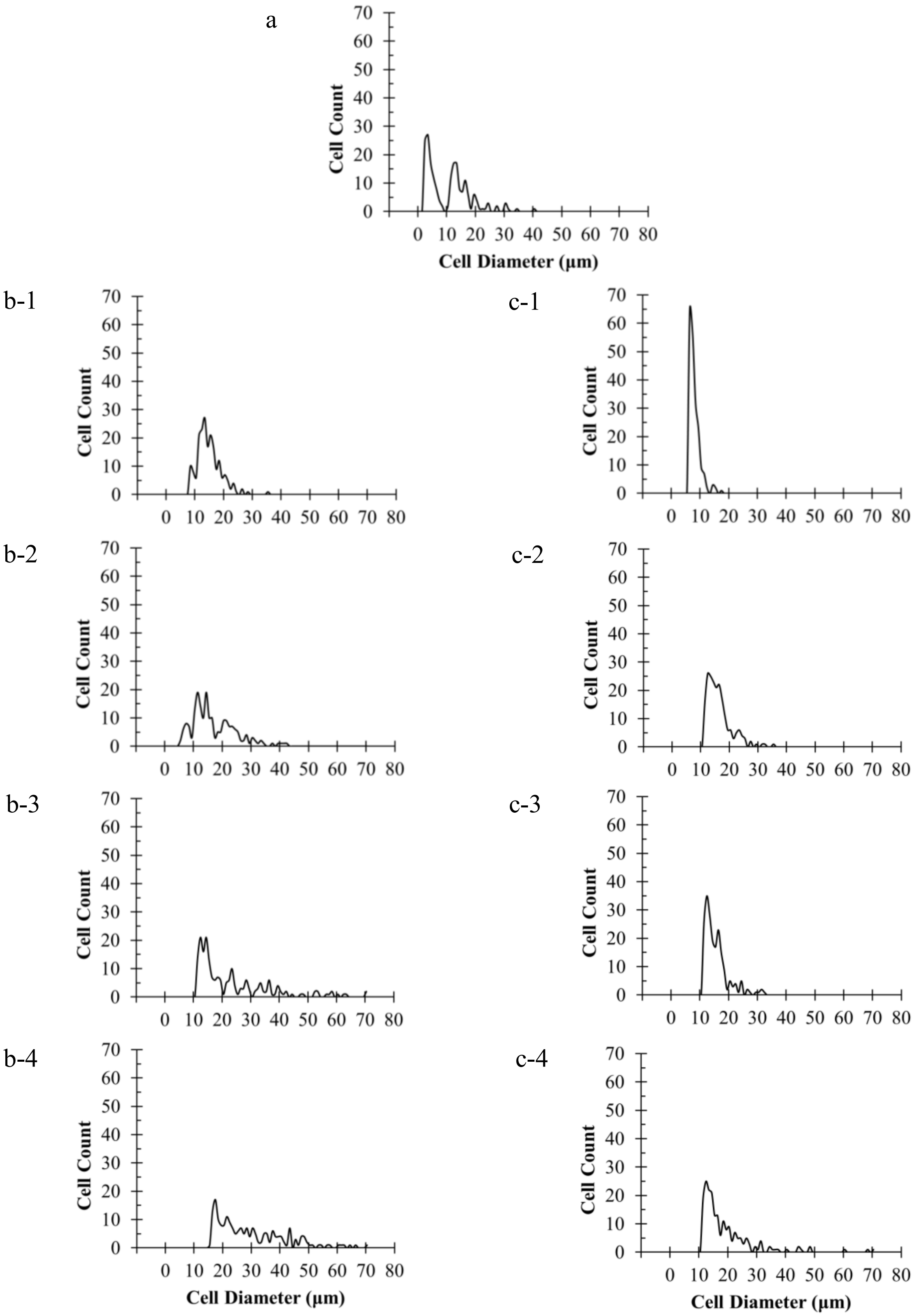

*Figure A-2: Cell diameter distribution (45x) of (a) neat PLA and PLA branched with (b) CE 4468, and (c) CE 4400. Samples 1, 2, 3, 4 contained 0.25; 0.5; 0.75; and 1% CE, respectively.*

# REFERENCES

# REFERENCES

1. Li, S., He, G., Liao, X., Park, C.B., Yang, Q., and Li, G. (2017). Introduction of a long-chain branching structure by ultraviolet-induced reactive extrusion to improve cell morphology and processing properties of polylactide foam. *Royal Society of Chemistry Advances,* 7(11), 6266-6277.

2. Mihai, M., Huneault, M.A., and Favis, B.D. (2009). Rheology and extrusion foaming of chain-branched poly(lactic acid). *Polymer Engineering and Science,* 50, 629-642.

3. Gu, L., Xu, Y., Fahnhorst, G.W., and Macosko, C.W. (2017). Star vs. long chain branching of poly(lactic acid) with multifunctional aziridine. *Journal of Rheology,* 61(4), 785-796. doi:10.1122/1.4985344

4. Zhou, M., Zhou, P., Xiong, P., Qian, X., and Zheng, H. (2015). Crystallization, rheology and foam morphology of branched PLA prepared by novel type of chain extender. *Macromolecular Research*, 23(3), 231-236.

5. Karkhanis, S.S., and Matuana, L.M. (2019). Extrusion blown films of poly(lactic acid) chain-extended with food grade multifunctional epoxies. *Polymer Engineering and Science,* 59 (11), 2211-2219.

6. Wang, J., Zhai, W., Ling, J., Shen, B., Zheng, W., and Park, C.B. (2011). Ultrasonic irradiation enhanced cell nucleation in microcellular poly(lactic acid): a novel approach to reduce cell size distribution and increase foam expansion. *Industrial and Engineering Chemistry Research,* 50(24), 13840-13847.

7. Di, Y., Iannace, S., Maio, E.D., and Nicolais, L. (2005). Reactively modified poly(lactic acid): properties and foam processing. *Macromolecular Materials and Engineering,* 290, 1083-1090.

8. Pilla, S., Kim, S.G., Auer, G.K., Gong, S., and Park, C.B. (2009). Microcellular extrusion-foaming of polylactide with chain-extender. *Polymer Engineering and Science,* 49(8), 1653-1660.

9. Standau, T., Castellón, S.M., Delavoie, A., Bonten, C., and Altstädt, V. (2019). Effects of chemical modifications on the rheological and the expansion behavior of polylactide (PLA) in foam extrusion. *e-Polymers,* 19(1), 297-304.

10. Standau,T. Zhao, C., Castellón, S.M., Bonten, C., and Altstädt, V. (2019). Chemical modification and foam processing of polylactide (PLA). *Polymers*, 11, 306-344.

11. Chen, P., Wang, W., Wang, Y., Yu, K., Zhou, H., Wang, X., and Mi, J. (2017). Crystallization-induced microcellular foaming of poly (lactic acid). *Polymer Degradation and Stability*, 144, 231-240.

12. Liu, J., Lou, L., Yu, W., Liao, R., Li, R., and Zhou, C. (2010). Long chain branching polylactide: structures and properties. *Polymer*, 51(22), 5186-5197.

13. Arruda, L.C., Magaton, M., Bretas, R.E.S., and Ueki, M.M. (2015). Influence of chain extender on mechanical, thermal and morphological properties of blown films of PLA/PBAT blends. *Polymer Testing*, 43, 27-37.

14. Wagner, H.L. (1985). The Mark-Houwink-Sakurada equation for the viscosity of linear polyethylene. *Journal of Physical and Chemical Reference Data*. 14(2), 611-617.

15. Kasehagen, L.J., and Macosko, C.W. (1998). Nonlinear shear and extensional rheology of long-chain randomly branched polybutadiene. *Journal of Rheology*, 42(6), 1303-1327.

16. Matuana, L.M., and Diaz, C.A. (2013). Strategy to produce microcellular foamed poly(lactic acid)/wood-flour composites in a continuous extrusion process. *Industrial and Engineering Chemistry Research,* 52(34), 12032-12040.

17. Diaz. C.A., and Matuana, L.M. (2009). Continuous extrusion production of microcellular rigid PVC. *Journal of Vinyl & Additive Technology*, 15 (4), 211-218.

18. Matuana, L.M., Park, C.B., and Balatinecz, J.J. (1997). Processing and cell morphology relationships for microcellular foamed PVC/wood-fiber composites. *Polymer Engineering and Science*, 37, 1137-1147.

19. Matuana, L.M. (2008). Solid state microcellular foamed poly (lactic acid): morphology and property characterization. *Bioresource technology*, 99(9), 3643-3650.

20. Matuana, L.M., and Faruk, O. (2010). Effect of gas saturation conditions on the expansion ratio of microcellular PLA/wood-flour composites. *eXPRESS Polymer Letters*, 4 (10), 621-631.

21. Matuana, L.M., Faruk, O., and Diaz, C.A. (2009). Cell morphology of extrusion foamed poly(lactic acid) using endothermic chemical foaming agent. *Bioresource Technology*, 100 (23), 5947-5954.

22. Radoev, B., Nedjalkov, M., and Djakovich, V. (1992). Brownian motion at liquid-gas interfaces. 1. Diffusion. *Langmuir,* 8(12), 2962-2965.

# CHAPTER 5

## CONCLUSIONS

### 5.1 Conclusions

PLA resin is a linear polymer that has very low extensional viscosity due to a lack of chain entanglement. This poses issues with producing PLA foams that are of good quality. Increasing the extensional viscosity of PLA through molecular chain branching improves the quality of its foams. Therefore, the main goal of this research was to study the effectiveness and efficiency of two food-grade multifunctional epoxies chain extenders (CE) with low (CE 4468) and high (CE 4400) epoxy equivalent weights (EEW) in branching and improving the foamability of PLA. The study was performed in two phases.

During the first phase, efforts were centered on examining the effects of CE content and type (epoxy equivalent weights) on rheological properties to determine their effectiveness and efficiency in chain extending/branching PLA. The chain extension reaction of PLA with CE was followed by torque rheometry as well as shear and elongational viscosities. In the second phase of this study, the emphasis was placed on assessing the role of molecular chain extension/branching on the foamability of PLA. The effects of chain extender content and type on the void fraction (density reduction), volume expansion ratio, average cell size, and cell-population density of PLA foams were evaluated to determine the most suitable formulation for the successful manufacture of branched PLA foams. The following conclusions were drawn from the experimental results:

1. Both CE grades were effective at chain extending PLA because they significantly increased PLA's end torque during mixing. The end torque of PLA increased linearly with the CE content for both multifunctional CEs during mixing. Generally, an increase

in the end torque values indicates an increase in the viscosity and molecular weight due to the formation of longer and/or branched chains. Nevertheless, the CE with low epoxy equivalent weight (CE 4468) was more efficient in increasing the torque of PLA compared to its counterpart with high epoxy equivalent weight (CE 4400) due to its higher reactivity.

2. Evidence of PLA chain extension was further confirmed by its shear and elongational viscosities, which increased significantly by the addition of CE. Chain-extended PLA showed a more pronounced and high degree of shear-thinning behavior associated with long-chain branched polymer chains than neat, linear PLA. Similarly, chain-extended PLA had higher extensional viscosities than linear PLA, suggesting that the addition of CE significantly improved the melt strength of PLA because long-chain branching leads to greater chain entanglement.
3. Neat PLA foams showed poor cell morphology with inhomogeneous cell structure of irregular cell sizes with areas without nucleated cells and had a low expansion, owing to the lack of melt strength (low elongational viscosity). By contrast, there was a considerable change in the morphology of the PLA foam structure caused by its branching. Chain-extended PLA foams showed uniform cell morphology with the highest expansion, mainly due to their high elongational viscosities, irrespective of CE content and grade.
4. The void fraction and expansion ratio increased with CE content, and significant improvements in both void fraction (up to ~85% density reduction) and expansion ratio (an eightfold expansion over unfoamed PLA) were achieved by chain branching PLA, irrespective of CE type, suggesting that melt properties of branched PLA were

appropriate for optimum cell growth and stabilization during foaming. Generally, the average cell size increased with CE content, causing a slight decrease in cell-population density.

5. Overall, this study identified the chain extender with low epoxy equivalent weight (CE 4468) as the most effective grade and 0.25% the threshold of CE content that provided melt viscosity appropriate to produce PLA foams with a homogeneous structure, fine cells, as well as a high void fraction, volume expansion ratio, and cell-population density. This optimum 0.25% CE concentration corresponds to the initial trial dosage of 0.2% recommended by the manufacturer of the multifunctional epoxies used in this study.

Using food-safe additives like those investigated in this study to improve PLA foam characteristics can help expand its applications; thus, providing tremendous opportunity to replace petroleum-based polymers in the food packaging industry.

## 5.2 Future works

This study investigated the microcellular foaming of chain-extended PLA at a fixed saturation pressure as well as fixed foaming temperature and time. The effects of these parameters should also be studied to gain an in-depth understanding of the role of branching on the foamability of PLA. Additionally, the batch foaming method of this study cannot be scaled because it is a time-consuming process involving multiple steps to produce foam. The foamability of PLA branched with these CEs must also be attempted in a large scale through a continuous extrusion or injection process. Finally, since 0.25% appeared the threshold of CE content, it would be appropriate to investigate further the foamability of PLA branched with low CE content in the 0-0.25% range, with the expectation of producing PLA with better quality foam.