ASSESSMENT OF THE PROPERTIES OF POLY (LACTIC ACID) SHEETS WITH DIFFERENT AMOUNTS OF POST-CONSUMER RECYCLED POLY (LACTIC ACID)

By

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ABSTRACT

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The main objective of this research was to evaluate the properties of sheet containing mechanically recycled post-consumer polylactic acid (PLA) bottle flakes blended with virgin PLA resin. PLA bottles were flaked, cleaned, blended with virgin resin and then extruded and thermoformed into trays. The molecular weight, physical, optical, thermal and mechanical properties of sheet containing 0, 20, 40, 60, 80 and 100 wt.-% recycled content were evaluated. Cleaning conditions were evaluated using response surface methodology, and conditions of 15 min, 85°C, 1 wt.-% NaOH, and 0.3 wt.-% surfactant were adopted for cleaning the PLA flake. Virgin PLA sheet possessed superior properties to recycled sheet with statistically significant differences at $\alpha=0.05$. PLA sheets were darker and absorbed more UV light in the 260 to 285 nm range when 20% or more recycled content was added. At 40% recycled content, the sheet had increased blue and red tones and the mechanical properties in the cross-machine direction decreased. At 60% recycled content or above, reduction of weight average molecular weight (M_W), tensile strength and tensile strength at yield in the machine direction (MD) were found. At 80% recycled content, the melting temperature and modulus of elasticity in the MD decreased. All of the sheet samples were successfully thermoformed into trays.

Dedicated to my father and mother

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KEY TO SYMBOLS OR ABBREVIATIONS

ABBREVIATIONS

ANOVA	Analysis of variance
ASTM	American Society for Testing and Materials
ATR	Attenuated total reflectance
CD	Cross machine direction
CFR	Code of federal regulations
DSC	Differential scanning calorimeter
EPA	US Environmental Protection Agency
FTIR	Fourier transform infrared spectroscopy
HSD	Honestly significant difference
HDPE	High density polyethylene
IR	Infrared
LSD	Least significant difference
MD	Machine direction
MFR	Melt flow rate
MSW	Municipal solid waste
NIR	Near-infrared sorting system
PET	Polyethylene terephthalate
PLA	Poly (lactic acid)

PHBV	Poly-3-hydroxy butyrate-co-3hydroxyvalerate
PBAT	Polybutylene adipate-co-terephthlate
PS	Polystyrene
PDI	Polydispersity index
RSM	Response surface methodology
ROP	Ring open polymerization
THF	Tetrahydrofuran
WRAP	Waste Resources Action Program

SYMBOLS

100V	100% virgin PLA
80V	80% virgin PLA, 20% recycled PLA
60V	60% virgin PLA, 40% recycled PLA
40V	40% virgin PLA, 60% recycled PLA
20V	20% virgin PLA, 80% recycled PLA
100R	100% recycled PLA
α	alpha (Mark–Houwink constant)
a^*	Radii of chromaticity
b^*	Radii of chromaticity
E_{act}	Average energy of activation
ΔE	Color difference
ΔH_c	Enthalpy of crystallization
ΔH^0_m	Enthalpy of 100% crystalline
ΔH_m	Enthalpy of melting
K	K (Mark–Houwink constant)
L^*	Lightness variable in the CIELAB system
M_w	Weight average molecular weight
M_n	Number average molecular weight ()

T_g	Glass transition temperature
T_m	Melting point
$T_{d,0}$	Initial decomposition temperature
χ_c	Crystallinity

CHAPTER 1

INTRODUCTION

Background

Plastics are used in many applications across the world such as building and construction materials, electronic goods, furniture, fabrics and packaging applications. Their versatile properties such as light weight, high durability and ease of shaping are reasons for the high demand for plastics. There are many types of plastics, and they can be modified to meet the requirements of the end-products. Packaging applications are the largest business for plastics. In 2009, 32% of thermoplastic resins market sales were in packaging applications (23,391 million pounds) [7]. One of the reasons for using plastics in packaging is their light weight (low density). It reduces the energy necessary for the distribution of packaged products. In general, plastics are safe enough to use as a food contact packaging and in medical applications [8]. The wide use of plastics requires a proper method for their end of life management.

According to the EPA, plastics in municipal solid waste (MSW) within the USA increased from less than 1% in 1960 to approximately 12% in the year 2009. Thirty million tons of plastic wastes were generated in 2009, with the largest portion of plastic wastes categorized as packaging containers (13 million tons) [9]. The low density of plastics (high volume but very low weight) fills the valuable space in the landfill very quickly. In general, petroleum-based plastics have high durability and they are non-biodegradable, making them stay intact for a very long period of time in a landfill.

An alternate waste management method such as recovery is used for reducing the wastes in the landfill. In 2008, one third of the MSW management in the US was done by recovery, which consisted of composting or recycling the waste. According to EPA, “the recycling rate with composting in the USA has increased from below 10 percent in 1980 to more than 33 percent of MSW generated in 2008”. This resulted in a decrease of MSW discarded in landfills from 89 percent of total MSW generated in 1980 to 54 percent in 2008 [10].

Composting is a method to convert organic materials into a soil-like substance or compost by microorganisms. The compost products - humus - can be used as a nutrient replenishment for soils and for covering the surface of landfills. Also, composting can take some biodegradable wastes out of the landfill and increase the space for handling other MSW [11]. On the other hand, recycling is a process to transform non-valuable or non-usable waste into new products. The function of the new valuable goods may be the same or different. Recycling is another proper way to manage MSW. It also reduces utilization of raw materials, some of which are obtained from non-renewable resources [10].

If MSW is sorted by product category, packaging applications are the biggest proportion of generated MSW by weight (almost 30 percent). In 2009, approximately 48 percent of waste in packaging and containers was recovered. Due to the wide variety of plastic types, around 14% of plastic packaging was recycled. Most of them were HDPE and PET bottles with recycling rates of 29 and 28%, respectively. There is a large market demand for both post-consumer resins. For example, recycled PET is a raw material for fiber, cloth, carpet and textiles and HDPE can be recycled into new bottles. The demands for recycled post-consumer products now exceed the available plastic waste recovered from the waste stream [9, 12].

Most petroleum based plastic packaging is engineered to have high durability, and good microbial and water resistance. So, normal plastic packaging is not appreciably decomposed by microorganisms in reasonable time frames and ends up in the landfill. Biodegradable polymers must be able to completely degrade by microorganisms in proper environmental conditions in a reasonably short period of time. The byproduct of this process must also be compatible with soil, plants and animals. Biodegradable plastics also have some comparable properties with synthetic petroleum-based plastics.

There are several biodegradable polymers such as polylactic acid (PLA), starch based thermoplastic, poly-3-hydroxy butyrate-co-3hydroxyvalerate (PHBV) and polybutylene adipate-co-terephthlate (PBAT) [13]. One of the promising biodegradable plastics for packaging applications is PLA, which can be produced from renewable resources and is considered a bio-based polymer. The base structure of PLA consists of lactic acid monomers. It can be derived from agricultural crops such as corn, sugar cane and starch. Initially, PLA production cost was high and it was mainly used in medical applications. However, now with the lactide ring opening polymerization technology, PLA can be synthesized with lower cost and the resin price has become more affordable for packaging applications. PLA is a stiff and brittle polymer that is compostable. It has mechanical properties similar to PS. PLA is safe and can be used as food contact packaging such as fresh produce containers or disposable cups and utensils. It can also be fabricated into sheet and film. PLA consumption is increasing in packaging applications.

Waste management for PLA is not limited to biodegradation. PLA is also recyclable by chemical recycling methods [14]. In chemical recycling, the post-consumer or post-industrial

PLA wastes are hydrolyzed at high temperature and yield lactic acid [15]. The drawbacks of chemical recycling for PLA are that it requires expensive and complicated processes.

Mechanical recycling involving regrinding plastic wastes and reprocessing them by conventional melt process is generally easier and cheaper than chemical recycling. However, little is known about mechanical recycling of PLA.

Objectives

The main goal of this thesis was to compare the properties of extruded virgin PLA sheet with PLA sheet contained varying recycled content obtained by mechanical recycling. The following are the specific objectives:

- Evaluation of the optimal cleaning conditions to obtain clean PLA flakes from post-consumer PLA packages.
- Evaluation of the properties of PLA sheet incorporating different proportions of mechanically recycled PLA.
- Evaluation of the thermoformability of recycled content PLA sheet.

CHAPTER 2
LITERATURE REVIEW

Poly (lactic acid), PLA

The history of PLA can be traced back to 1932 when a scientist from Du Pont, Wallace Carothers, heated lactic acid under vacuum and successfully fabricated a low molecular weight PLA [16]. With an additional improvement, this process was patented by Du Pont in 1954 [17]. Then in 1988, Cargill Inc. planned to develop PLA to be a new commercialized product. Eventually with a joint venture of Cargill Inc. and Dow Chemical Company, Cargill Dow LLC was formed in 1997 and PLA was commercialized under the trade name of NatureWorks^{TM} , nowadays Ingeo^{TM}[18].

PLA polymer did not have many applications until a couple of decades ago due to limited molecular weight, low accessibility and high cost compared with other commercial plastics. However, PLA has good compatibility with the human body. As a result, PLA was mainly used in medical applications such as implant parts and controlled drug release applications. With modern polymer synthesis technology, ring open polymerization (ROP), PLA can be produced at much lower cost [5, 16, 17, 19]. At present, PLA is used in a wide range of applications from fabrics to dinnerware [20].

PLA is an aliphatic polyester. It is a compostable and biodegradable plastic, which is derived from renewable resources. Normally, PLA is produced from carbohydrate based agricultural products such as corn, potato, and cassava. In the USA, corn is used as the raw material to produce PLA because it is cheap and abundant [18].

In addition to NatureWorks LLC's PLA manufacturing plant with 140,000 metric ton capacity in Blair, Nebraska, USA, Futerro opened a bioplastic production plant with a capacity of producing 1,500 tons per year of PLA in April, 2010 [21]. Also Purac and Indorama Ventures PLC plan to set up a PLA production plant in Thailand with initial capacity of 10,000 metric tons and a maximum potential of 100,000 metric tons [22].

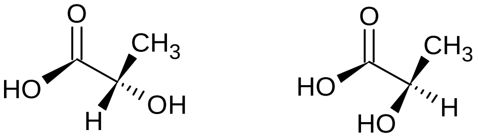
PLA synthesis

PLA is produced from lactic acid (2-hydroxy propionic acid). It possess two optical isomers which are L(+) and D(-) lactic acid. It can be derived from either fermentation of carbohydrates or chemical synthesis. In PLA synthesis, lactic acid is mainly derived from bacterial fermentation. Corn is the main raw material for this process in the USA. The fermentation process begins with separation of the starch from the cooked corn by grinding and screening. Starch is then changed to sugar and bacteria such as lactobacillus are used to converted sugar into lactic acid [5, 19, 23].

There are three major routes to produce PLA, which are direct condensation polymerization, azeotropic dehydrative condensation and polymerization through lactide formation or ROP [5, 19]. In direct condensation polymerization, PLA is derived by using solvent under high vacuum and temperature. It is the least expensive method and has fewer processing steps. However, it is not easy to produce high molecular weight polymer with this method due to the presence of water and other byproducts [5, 18, 24, 25].

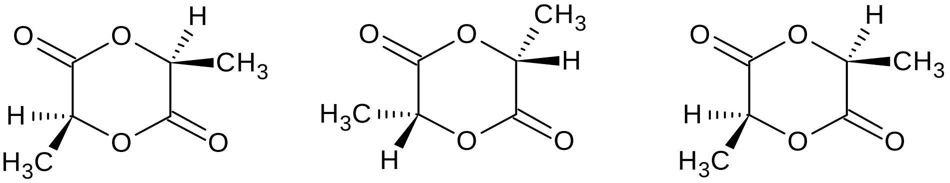
Azeotropic dehydrative condensation can provide high molecular weight PLA. This method was commercialized by Mitsui Toatsu Chemicals in Japan. The general concept of this process involves removing water from lactic acid by reducing the distillation pressure in the vessel for 2-3 hours at 130°C. Then catalyst and diphenyl ester are added and a molecular sieve tube is connected to the vessel. The solvent is then refluxed through the sieve for 30 – 40 hrs at 130°C. After the process, the catalyst is removed and the polymer is then passed through a purification process [5, 26-28].

Polymerization through lactide formation or ring opening polymerization is the method that NatureWorks LLC uses to produce commercial PLA. This method was developed by DuPont in 1954 [28]. In this process, lactic acid is polymerized into PLA pre-polymer with low molecular weight. Then the pre-polymer is depolymerized using a catalyst under low pressure and is transformed to lactide. Since there are two optically active isomers for lactic acid, lactide, which is a cyclic dimer, has three stereoisomer forms: L-L-lactide (consisting of two L-lactic acids), D-D-lactide (consisting of two D-lactic acids) and meso-lactide (consisting of L-lactic acid and D-lactic acid). After lactide is sorted into a low D-lactide stream, and a high D-lactide and meso-lactide stream, high molecular weight PLA is produced by using ring opening of L-lactide. According to Auras *et al*, the ring opening polymerization can be cationic using methyl trifluoromethanesulfonic acid or trifluoromethanesulfonic acid, or anionic using the nucleophilic reaction of an anion with the carbonyl and subsequent acyl-oxygen cleavage [5, 28].



L-Lactic acid D-Lactic acid

Figure 2-1: Chemical structure of L and D- lactic acid



LL-Lactide DD-Lactide LD-Lactide (meso lactide)

Figure 2-2: Chemical structure of LL, DD and LD-Lactid

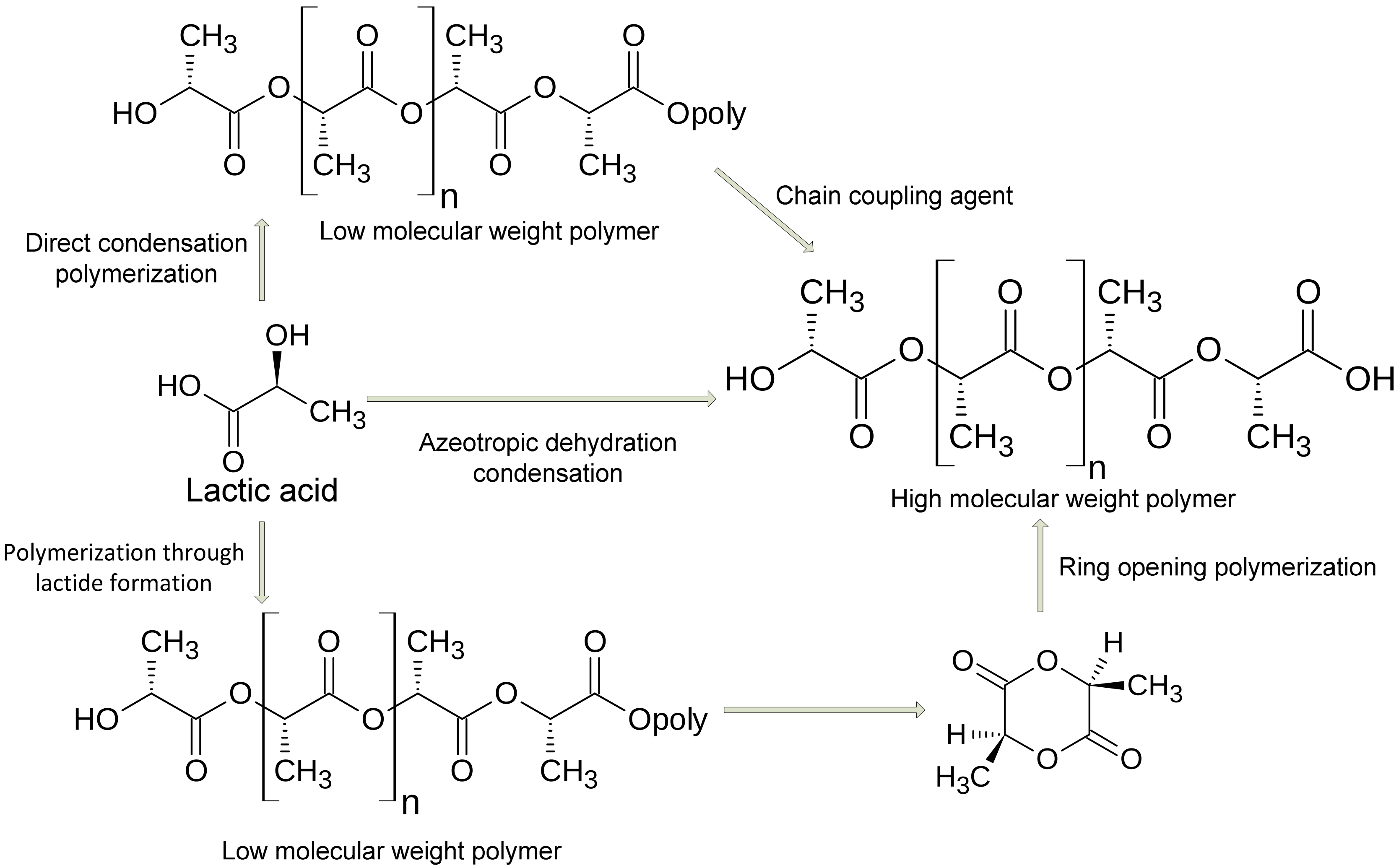


Figure 2-3: PLA synthesis methods from lactic acid, adapted from [5]

Morphology and Properties

PLA is a linear polymer and the monomer itself contains a functional group that does not have internal plane symmetry. As a result, properties of PLA are significantly affected by the stereochemical composition of the polymer. Since most of the commercial PLA is derived from lactide ROP, there are three possible forms of lactide as mentioned above. By controlling lactide formation, the properties of PLA can be manipulated. In commercial PLA synthesis, most of the lactic acid is acquired from bacterial fermentation, which yields mostly L-lactic acid. The homo-polymer (L-lactide) has a melting peak of approximately 180°C. Usually, the temperature for melt processing is above the melting point by 40 to 50°C. This result in thermal degradation in the polymer during the processing since the degradation temperature of PLA is about 200°C Copolymerization of LL-polylactide and D,D-polylactide by introducing meso-lactide in the ring opening polymerization process can reduce the melting temperature of the copolymer, and it can also increase the crystallization rate. However, a drawback is the decrease in crystallinity [29]. The D- and meso-lactide tend to interrupt the regularity of the crystal structure of poly(L-lactide). As a result, PLA becomes amorphous when it is derived from lactic acid with L-content less than 93% [5]. The crystallinity of the polymer can be also manipulated by applying stress at temperatures approximately 10°C above the glass transition temperature (T_g), during processing. This process will increase the orientation of the polymer [30].

Properties of PLA are versatile and depend on various aspects such as the structure, amount of stereoisomer, degree of crystallinity and molecular weight. As a result, PLA can be modified to have properties that meet the requirements of a particular application. PLA is a transparent thermoplastic polymer. It is stiff and brittle. Similar to other thermoplastic polymers, at temperatures above T_g it can be deformed. As mentioned above, the stereochemistry affects the developed crystalline structure in the polymer [31]. PLA can be either an amorphous or a semicrystalline polymer. The T_g of semi-crystalline PLA is approximately 50 to 60°C and the T_m ranges from 130 to 180°C, depending on the degree of crystallinity of the polymer and the molecular weight. Commercial PLA is normally a poly(L-lactic acid) and poly(D,L-lactic acid) copolymer and has a semicrystalline structure with high molecular weight (above 100 kDa) [19]. It possesses mechanical and barrier properties comparable with polystyrene (PS) but slightly inferior to polyethylene terephthalate (PET) [1, 5]. The main problem with the mechanical properties of PLA is its brittleness, resulting in poor impact resistance, but this can be improved by using some additives. PLA can be processed by most conventional processing methods. However, the thermal stability is inferior to conventional polymers used for thermoplastic applications [31]. PLA suffers from low melt strength and tends to experience sagging and necking during extrusion. Therefore, it is difficult to obtain PLA films through extrusion blow molding. This problem can be solved by using additives or blending with high molecular weight polymer to increase the chain entanglement. The properties of PLA have been extensively studied [1, 5, 19, 25, 28, 30, 31]. The general properties of PLA are shown in Table 2-1, and the properties of commercial PLA resins are shown in Table 2-2 and Table 2-3.

Table 2-1: General properties of PLA, adapted from [1]

Properties	
Clarity	Clear–yellow
Density amorphous, $kg \cdot m^{-3}$	1250
Density 100% crystalline, $kg \cdot m^{-3}$	1490
Glass-transition temperature (T_g), °C	55–65
Melting temperature (T_m), °C	130–180
Initial decomposition temperature ($T_{d,0}$), °C	335
Half decomposition temperature, ($T_{d,1/2}$), °C	395
Average energy of activation (E_{act}), $kJ \cdot mol^{-1}$	205–297
Enthalpy (ΔH_m),100%, $J \cdot g^{-1}$	93
Crystallinity, %	0–40
Heat deflection temperature, °C	55–65
$K \times 10^{-4}$, $DL \cdot g^{-1}$ (Mark–Houwink constants)	8.5
α (Mark–Houwink constants)	0.66
Tensile strength at yield, MPa	0.88
Elastic modulus, GPa	8.6
Elongation at break, %	3–30

Table 2-1 (Continued)

Flexural strength, MPa	70
Flexural modulus, GPa	3.8
Unnotched Izod impact, $J \cdot m^{-1}$	106
Notched Izod impact, $J \cdot m^{-1}$	26
Rockwell hardness	88
Impact strength	Poor
Oxygen × 10^{-18}, $kg \cdot m \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$ at 25°C	1.21 ± 0.07
Oxygen activation energy, $kJ \cdot mol^{-1}$ (25–45°C)	41.43 ± 3.5
Carbon dioxide × 10^{-17}, $kg \cdot m \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$ at 25°C	2.77 ± 0.05
Carbon dioxide activation energy, $kJ \cdot mol^{-1}$ (25–45°C)	15.65 ± 0.63
Water × 10^{-14}, $kg \cdot m \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$ at 25°C	1.75 ± 0.05
Water activation energy, $kJ \cdot mol^{-1}$	–9.73 ± 0.27

Table 2-2: Properties of Ingeo^{TM} biopolymer 2003D PLA resin for fresh food packaging and food service ware from NatureWorks LLC , adapted from [2]

Properties	**Ingeo 2003D**
Specific Gravity	1.24
MFR, g/10 min (210°C, 2.16kg)	6
Clarity	Transparent
Tensile Strength at Break, psi (MPa)	7,700 (53)
Tensile Yield Strength, psi (MPa)	8,700 (60)
Tensile Modulus, kpsi (GPa)	500 (3.5)
Tensile Elongation, %	6.0
Notched Izod Impact, ft-lb/in (J/m)	0.3 (16)
Heat Distortion Temperature (°C)	55

Table 2-3: Properties for Ingeo^{TM} biopolymer 7001D PLA resin for injection blow molded bottles from NatureWorks LLC , adapted from [3]

Properties	**Ingeo 7001D**
Specific Gravity	1.24
MFR, g/10 min (210°C, 2.16 kg)	6
Glass Transition Temperature	55-60°C
Crystalline Melt Temperature	145-160°C
O_2 Transmission Rate	675 cc-mil/m^2-24hr-atm
CO_2 Transmission Rate	2,850 cc-mil/ m^2-24hr-atm
Water Vapor Transmission Rate	375 g-mil/ m^2-24hr
Clarity	Transparent
Preform Temperature	80-100°C (176-212°F)
Stretch Rod Speed	1.2-2 m/sec
Mold Temperature	21-38°C (70-100°F)

Industrial applications

PLA has been studied for medical applications for more than 30 years. It is used as a wound dressing film, and for implants and drug release control systems because it has good compatibility with the human body [5, 32-34]. Even though the development of new PLA synthesis methods enables production of high molecular weight PLA at a reasonably economical cost, PLA resin is still more expensive than high density polyethylene (HDPE) or PET [35]. However, current commodity plastics are derived from crude oil, which is a limited resource. With the high demand for energy resources, oil prices have had high fluctuations since 2007 [36]. Some countries need to import petroleum resources from foreign countries to produce energy and products. On the other hand, PLA, which is produced from renewable resources and generally produced from domestic renewable resources, can be an alternative plastic for a number of applications. PLA is also used by many companies to claim a carbon footprint reduction [35].

More recently, other European countries, Japan and the USA have started to use PLA for fresh produce packaging, disposable containers, cups, packaging film, and blister packaging. PLA is also used in agriculture film and yard bags since it is biodegradable and compostable [5, 18]. PLA is used in many types of processes such as sheet or film extrusion, injection blow molding and thermoforming. The methods involve heating PLA either between T_g and T_m or above its melting point. In any of these methods, a shape of softened or molten polymer is formed and then it is cooled down to retain the polymer dimensions. In addition, each fabrication process requires PLA with different properties so selecting the proper PLA resin for each processing technique is also important. As mentioned, commercial PLA resin is a copolymer of LL-polylactide and D,L-polylactide. The concentration of LL-lactide affects the properties of the resin. Examples of NatureWorks LLC PLA resin types for each type of application are listed in table Table2-4.

Table2-4: Types of PLA resin from NatureWorks LLC for different applications and products

Resin series	Applications	Products
2000	Extrusion/thermoform	Serviceware, blister packaging fresh produce packaging, disposable packaging,
3000	Injection molding	Durable goods
4000	Film and sheet	Cards, folding cartons, films for food contact, shrink wrap, bags laminated coatings and multi-layered structure
6000	Fiber and nonwovens	Apparel, fabric, fiber, yarn, home textiles, furniture, baby care products
7000	Injection stretch blow molded	Bottles, multi-layer or co-injection bottles
8000	Foam	Protective foam, foam sheet for meat and vegetable packaging,

Polymer sheet extrusion

The beginning of plastic packaging processes usually involves transforming the solid plastic into desired shapes by using melt processing. Normally, an extruder is used to convert plastic resins into a homogeneous melt by heating them above the melting point. The melt then passes through a die to form a film or a sheet, or it can be delivered to other equipment such as blow molding or injection molding machines. The basic single screw extruder usually consists of a feeding port, an extruder barrel with a screw inside and a shaping part, which in sheet extrusion is a die.

Plastic pellets are fed through a hopper and get into the extruder barrel via the feeding port. The hopper can be equipped with an auger or a stirrer to help force the materials into the extruder barrel. Some extruders contain more than one feeding port, for example for adding fillers into a molten plastic. The extruder barrel is where the melting of the pellets takes place [8, 37].

The barrel is hollow with a helical screw inside. The function of the screw is to melt the plastics and to pump molten solution to the die. The screw can be divided into three sections: the solids feeding section, the melting or compression section and the metering section. In the solid feeding section, plastic pellets are received from the feeding port and transferred further inside the barrel to the second part of the screw for melting. In the compression section, the screw channels are gradually decreased to compress the pellets and also force them against the barrel wall. The friction between the plastic and the barrel and the shearing between pellets provide the heat for melting. An external heater and a cooling system are commonly provided to control the processing temperature. The last part of the screw is the metering section where the flight depth of the screw is shallow and constant. This section is designed to deliver a uniform stream of molten polymer to the shaping device at the desired rate [8, 37].

The extrusion processes for plastic film and sheet are identical. In general, the molten polymer is pumped through a slit-shaped die. The extruded product is rectangular in shape and the width of the products is greater than the thickness. Usually the plastic sheets are more than 0.25 mm in thickness and the films are less than 0.076 mm. The die gap for sheet or film extruding is normally set at 10% greater than the desired product thickness [8, 37].

Polymer thermoforming

Thermoforming is a method to form products from plastic sheets by using heat and pressure. The heating process is not intended to fully melt the plastic, but instead, the sheets are heated until they are soft enough to form into a shape with molds. Usually thermoforming is used to form simple shaped products such as trays, cups and blister packaging. In general, the thermoforming process is inexpensive. The machine and the processing method are quite simple when compared with injection molding. It can use a single-surface mold to form products. The drawbacks of this process are the difficulty of producing products with uniform thicknesses or with complicated shapes [8].

There are several thermoforming methods, for example drape forming, vacuum forming, pressure forming, plug-assist thermoforming, matched mold forming and skin packaging. During the molding, heated plastic is stretched to form a shape. As the stretching continues, the thickness of the sheet is also decreasing until it touches the mold surface. The thickest part of the product is where the first contact between the plastic sheet and the mold takes place. This can vary depending on the type of mold. For example, drape forming uses a convex shape (positive) single-face mold so the bottom of the product is the thickest part and the thinnest part is the rim. On the other hand, vacuum forming uses a concave shape (negative) mold and as a result, the thickest part of the product is on the rim and the thinnest part is the bottom of product [8].

Degradation

Hydrolytic degradation

PLA is vulnerable to degradation from hydrolysis. The reaction rate and mechanism depend on both material properties such as structure, crystalline character and molecular weight, and also environmental factors such as temperature, humidity, time and catalysts. The mechanism of hydrolysis in neutral conditions is initiated by the presence of water. Generally, the polymer is degraded by random chain scissions of ester groups in the structure. The location of the chain cleavage is usually on the surface where the water is in contact, resulting in surface erosion. On the other hand, bulk erosion, erosion in which the degradation occurs throughout in the material, dominates if the diffusion rate of water in the PLA is rapid. Amorphous regions are more highly susceptible to hydrolysis than crystalline structures since water cannot diffuse through crystal structures in order to hydrolyze the polymer chains inside. Chain cleavage in amorphous structures produces water-soluble oligomers and monomers. Hydrolysis of PLA is also affected by the surrounding medium. The hydroxide ions in an alkaline environment increase the degradation rate as do elevated temperatures. At temperatures above T_g, the diffusion rate of water molecules increases due to the flexibility of the amorphous regions. Also, hydrolysis can occur homogenously and rapidly in the polymer structure when the surrounding temperature is above T_m [1, 5, 38].

Thermal degradation

Thermal degradation of PLA is mainly caused by random chain scission and unzipping depolymerization reactions and usually occurs during melt processing of PLA. [37, 39]. Thermal degradation mechanisms are complicated as has been reported in many studies. For example, Kopinke et al. reported “five degradation mechanisms occurring at temperature above 200°C: intra- and intermolecular ester exchange, cis-elimination, radical and concerted nonradical reactions, radical reaction and Sn-catalyzed depolymerization” [40]. Also, McNeill and Leiper reported the byproducts of degradation of PLA: at 230°C, lactide, acetaldehyde and carbon monoxide are formed; at 270°C, carbon dioxide is generated; and at 320°C or above, methylketene with a small amount of methane is formed. They proposed the mechanism of thermal degradation in PLA as “a non-radical, backbiting ester interchange reaction involving the OH chain ends” [41]. Residual polymerization catalysts increase the degradation of PLA by reverse depolymerization and cause molecular weight loss, which impact the mechanical properties of PLA. Jamshidi et al. reported a significantdifference in M_w between purified PLLA and unpurified PLLA with catalyst. [42]

End of life of PLA

Landfilling, incineration and recycling are common waste management processes for petroleum–based plastics. PLA has an additional option for its end of life. Being a bio-based and biodegradable polymer, PLA can be composted in composting facilities in a reasonably short period of time. The disposal of PLA is not limited only to composting. PLA can also be managed by conventional waste disposal methods [14, 43, 44].

Biodegradation of PLA begins with hydrolysis. The molecular weight is reduced by random chain scission of the ester groups. The byproducts of the hydrolysis reaction such as low molecular weight PLA, oligomers and lactic acid are then decomposed by microorganisms. The products of the biodegradation are H_2O, CO_2 and humus [5, 14, 45]. Biodegradability of PLA is affected by many factors, such as material properties of the polymer and the environmental conditions. High humidity and temperature (50-60°C) are suitable to initiate rapid hydrolysis in PLA structures [30, 46, 47]. PLA is quite stable under normal environmental condition. Ho *et al*, reported the biodegradation of PLA in soil and compost rows. In soil conditions, the degradation rate resulted in no visible degradation of PLA until after six months of soil burial. On the other hand, PLA degradation in compost rows takes only around 2 – 3 weeks [48]. Ohkita and Lee also reported similar results [49].

Almost 12% of MSW is managed by using combustion with energy recovery. The facilities can be managed by private organizations or local government, and they are regulated by 40 CRF part 60 subchapter C. In the US, more than 20 percent of Incineration facilities can separate recyclable wastes out of MSW before burning. Incineration can be considered as another end of life for PLA [4]. At a combustion temperature of 1000°C, 1 lb of PLA provides 8,338 BTU compared to 7,300 BTU/lb and 5400 BTU/lb for wood and average MSW, respectively. Energy values for combustion of other materials are shown in Table 2-5. The volatile and residual substances released during combustion are also listed in Table 2-5.

Table 2-5: Energy values for combusting MSW materials at 1000^{o}C, adapted from [4].

Materials	**Energy provided (BTU.lb^{-1})**
Fuel Oil	20,900
HDPE	18,700
Rubber and leather	12,800
PET	10,900
Wyoming coal	9,600
Textiles	9,400
PLA	8,368
Newspaper	8,000
Wood	7,300
Corrugated boxes (paper)	7,000
Average MSW	5,900
Yard waste	2,900
Food waste	2,900

Table 2-6: Residues and volatiles released during PLA combustion, adapted from [4].

Compounds	Amount released, $mg.g^{-1}$
carbon monoxide	<0.1
carbon dioxide	2020
water	>260
volatiles	< 0.001
semi-volatiles	< 0.01
residue	0.01

Recycling

Recycling involves producing a new product from an old, unwanted or waste material. The end-product can be either the same or different functionality, for example recycling an old glass bottle into a new one or recycling a plastic bottle into fabric, respectively. EPA claims that recycling provides many benefits to the nation such as increasing job opportunities, reducing greenhouse gases and pollution from producing new materials, decreasing burdens in landfill and incineration, and preserving energy and natural resources [10]. In contrast to reuse, recycled waste materials are reprocessed by converting the material to a basic structure. The processes differ for each recyclable material, for example breaking down paper to fiber, de-polymerizing plastic to monomer or re-melting glass or metal. The end-products of the process are used to manufacture new items. The recycling process is not limited to reprocessing the waste material, but also includes gathering, sorting and separating types of waste, and manufacturing and marketing of the recycled products. An inability to accomplish any element will result in ineffective recycling.

Raw material sources and management

The raw materials for recycling processes usually come from unwanted items or wastes. According to EPA [6], in 2009, 243 million tons of MSW was generated in the USA (Figure 2-4 and Figure 2-5); this large amount of wastes should be sufficient as a feedstock for recycling processes. However, without efficient sorting, it will be impossible to have economical recycling because of the high degree of contamination of the waste.

Recyclable materials collection systems differ. There are four general methods, curbside collection, drop-off centers, deposit systems and buy-back centers. After the recyclable goods are collected, they usually end up at a material recovery facility (MRF) to be sorted. There are several methods available for materials separation processes, such as using an electromagnetic to separate ferrous materials out of other wastes, or hand-sorting for separating major types of wastes, such as glass, papers, plastics and metal. Recyclable plastics are normally collected at the curbside or at drop-off centers. Usually, after plastics are sorted from other recyclables, they are sent to a reclaiming facility for cleaning and grinding. Then, the plastic flakes are passed through another sorting process to separate the contaminants and types of plastic. In general, density differences are used to sort plastic types.

There are special issues for new materials such as PLA, which were not long ago introduced to the packaging business. They are not used as extensively as HDPE or PET products. Thus, it may be hard to start a recycling business for PLA since there is an inadequate supply of recyclable raw materials compared to other conventional recyclable plastics.

However, products such as PLA bottles can be considered as potential recyclable materials because some drinking water brands have started to use PLA bottles due to their perceived environmental benefits. PLA bottles are also being used for noncarbonated soft drinks [50, 51]. Another hindrance in recycling PLA is the sorting. The recovery facilities may not want to start a new processing line for PLA due to the cost. Hence, post consumer PLA is mostly not accepted by the collectors or MRF. In order to solve this problem, in 2005, Natureworks established a "Buy Back" program to accept the curbside bales of PLA bottles. This strategy was set up to increase the demand and encourage the marketing of post consumer PLA bottles until the market matured. More information about this program can be found elsewhere [52].

The most recyclable plastic bottles in MSW are PET and HDPE [9]. In general, the sorting is done by flotation in a water tank. Because the density of water is 1 g-cm^{-3}, PET, which has a density higher than water (1.4 g-cm^{-3}) sinks under water. On the other hand, HDPE floats in water since its density is approximately 0.9 g-cm^{-3}. As for PLA, there are some concerns that PLA will contaminate the PET recycle stream because the density of PLA is also higher than water, around 1.24 g-cm^{-3}, closer to PET. Although PLA can be separated from HDPE, PET or other plastics by hand either at the source by customers or at the collection facility, a near-infrared sorting system (NIR) is another alternative for sorting PLA. This system operates by identifying specific absorption regions of different plastics in the near-IR region of the electromagnetic spectrum between 750 and 2500 nm [53]. According to the Waste Resources Action Program (WRAP), NIR efficiently sorts PLA from other packaging waste with a resulting purity of 97% [54].

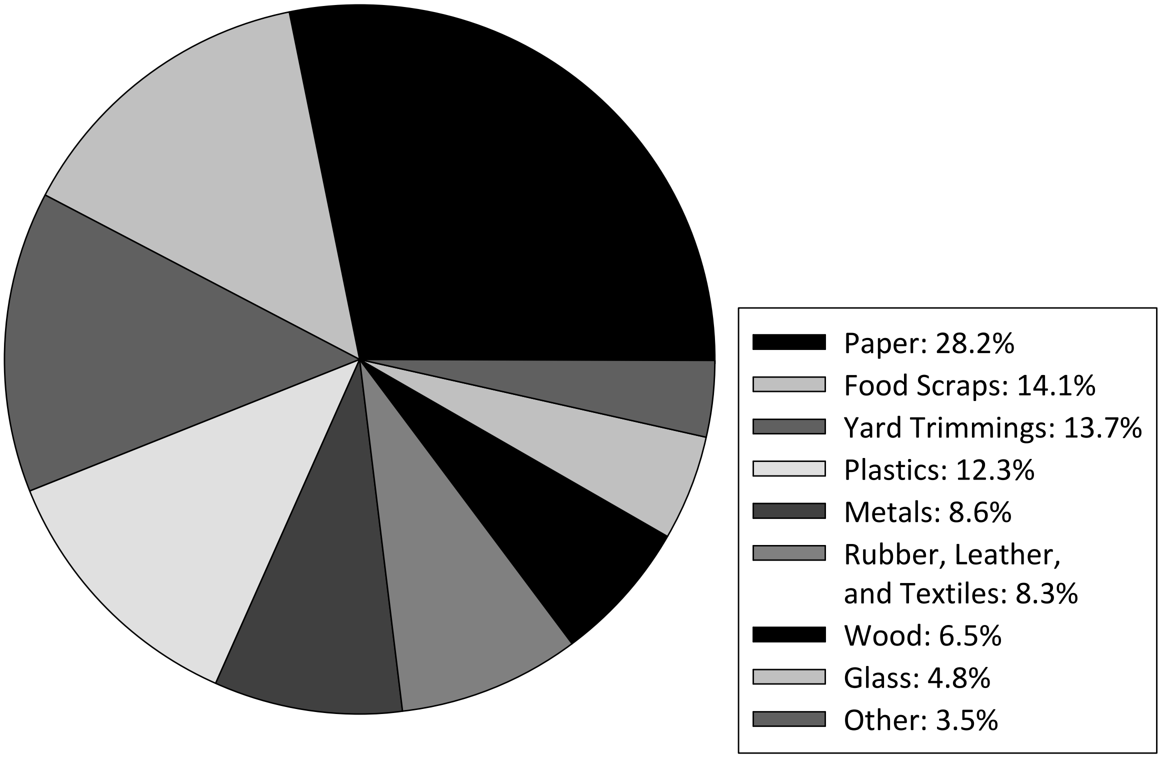


Figure2-4: Total MSW generated in 2009 sorted by materials (243 million tons) [6]

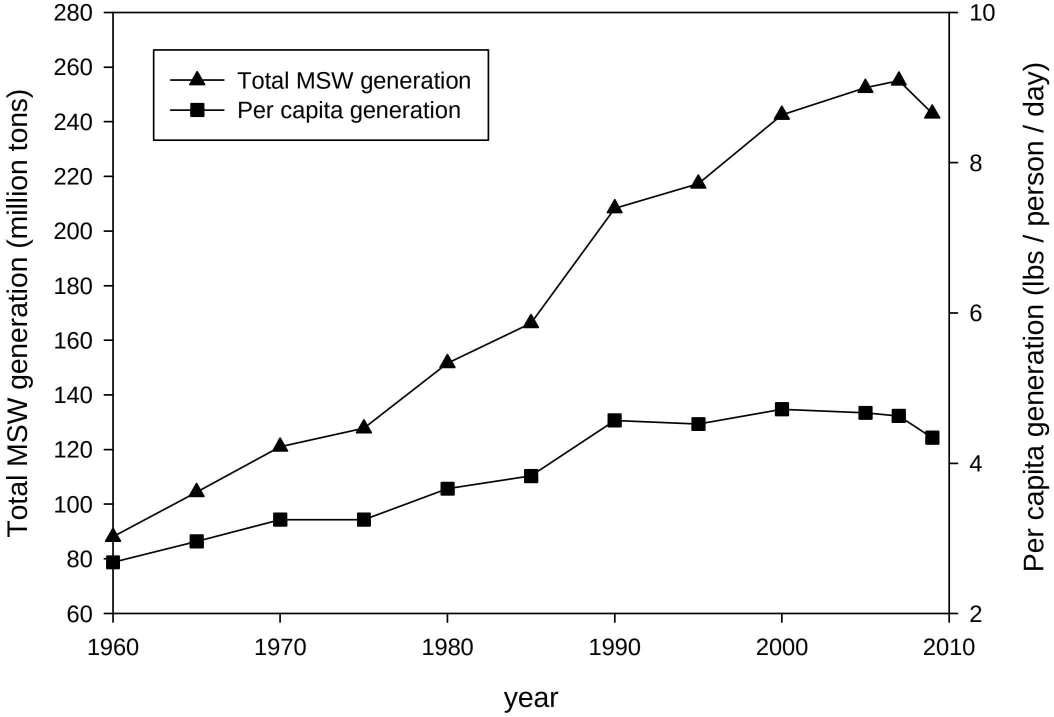


Figure 2-5: Total MSW generation and per capita rates from 1960 to 2009 adapted from [6]

Manufacturing

After sorting into common types, plastic wastes continue to pretreatment processes, which consist of size reduction, cleaning and drying, sorting and granulating. At the beginning of the pre-treatment process, the size of the materials is reduced by grinding to simplify further processing. Then, the plastic flakes go through a washing process to improve the purity of the material by separating dirt from the plastic flake and removing any contaminants such as printing ink. The materials are sorted according to their properties such as density, wettability, electrical properties, chemical properties, or optical properties. Then, the sorted plastic will be prepared for the next step of reprocessing. There are two common types of recycling process: chemical recycling and mechanical recycling.

Chemical recycling

The basis of plastic chemical recycling involves breaking down the polymer molecules by using chemical and/or thermal processes. The methods may cause main chain scission, degradation or de-polymerization of the polymer, and yield a basic structure (monomer). Then the materials will be able to be fed back to the polymerization process to produce new polymer [55-58]. The chemical recycling process may have an end product quality that is superior to mechanical recycling due to the chemical purification. However, it is considered more expensive, difficult and may produce more environmental burdens compared to mechanical recycling [58].

Chemical recycling for PLA can be done by hydrolysis to break the chain structure into lactic acid. Another procedure is depolymerizing of PLA to lactide (cyclic dimer of lactic acid). The end product of recycling can be lactic acid, lactide or PLA [15, 44]. Tsuji *et al.* reported an efficient way of recycling by hydrolyzing PLA at high temperature without a catalyst. This process required only a short time (10 – 20 min), and a high yield of lactic acid (90%) was obtained at 250°C [15].

Mechanical recycling

The process of mechanical recycling is less complicated than chemical recycling. After the plastic flake is cleaned in the pre-treatment process, it is extruded and pelletized. Then it will be prepared for further product processing. The concerns about this process are contaminants in the polymer and degradation of the polymer during manufacturing. Usually the processing equipment is equipped with a filtration system for screening the impurity particles. In some cases, impurities can damage the equipment and also reduce the quality and properties of the polymer [59]. Degradation during the reprocessing, such as hydrolysis and thermal degradation, can cause chain cleavage at ester groups. The degradation causes a reduction in molecular weight and changes polymer properties. These are the main drawbacks of the method [39, 59]. However, mechanical recycling is not as complicated as chemical recycling and is also inexpensive.

Market and Economics

As an individual, sorting PET or HDPE bottles at the recycling bin is not enough for helping recycle the wastes. Without using and buying recycled products, those bottles will be left in storage and will eventually be disposed as wastes again. The recycle loop will be completed when there are markets for recycled products. A high demand for recyclable products by customers may induce the manufacturers to pay more attention to this market niche and try to develop more recycled base products. The recycling of PLA may have not yet become successful. However, there is an opportunity for this business to grow. The Belgian lactic acid producer, Galactic, is building a 1,000 metric ton lactic acid production plant. Galactic is collaborating with Natureworks to collect both post consumer and post industrial PLA bottles as a feedstock for producing lactic acid. The chemical recycling process will be used to break down PLA back to lactic acid [14].

Response surface methodology

Experiments are part of the scientific method to obtain results and draw conclusions. Outputs of experiments are influenced by many variables. To have an economical and reasonable time frame for experiments, planning and designing of the experiments are needed.

RSM is a mathematical and statistical method used to determine the optimum conditions for the experiment. For example, the degradation of a plastic is affected by the level of exposure time (x_1) and temperature (x_2). The degree of degradation is the response value (y). The functions of level of x_1 and x_2 that yields the result y can be expressed by

$$y = f(x_1, x_2) + \epsilon$$

where ϵ is the experimental error in y. Usually, the relationship between y and x_1 and x_2 is unknown. The first step for RSM is to determine a proper approximation of the relationship between y and x_1 and x_2 by using a first-order model:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \cdots + \beta_k x_k + \epsilon$$

A higher degree polynomial is required for a response surface with curvature, such as the second-order model:

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum \sum_{i<j} \beta_{ij} x_i x_j + \epsilon$$

Usually, RSM uses one of these models, but sometimes it can also use both of them. After the data for the approximation of the polynomials is collected, the method of least squares is used to estimate the parameters of the model. The analysis of the response surface is done by a design for fitting the surface called the response surface design. After fitting the surface, the region with optimal response is identified [60].

CHAPTER 3
MATERIALS AND METHODS

Introduction

This study is divided in two main parts. The first part is the cleaning and preparation of the raw material to obtain the clean recycled flakes. The second part concentrates on the comparison between the properties of varying contents of posted-consumer and virgin PLA sheets as shown in Figure 3-1.

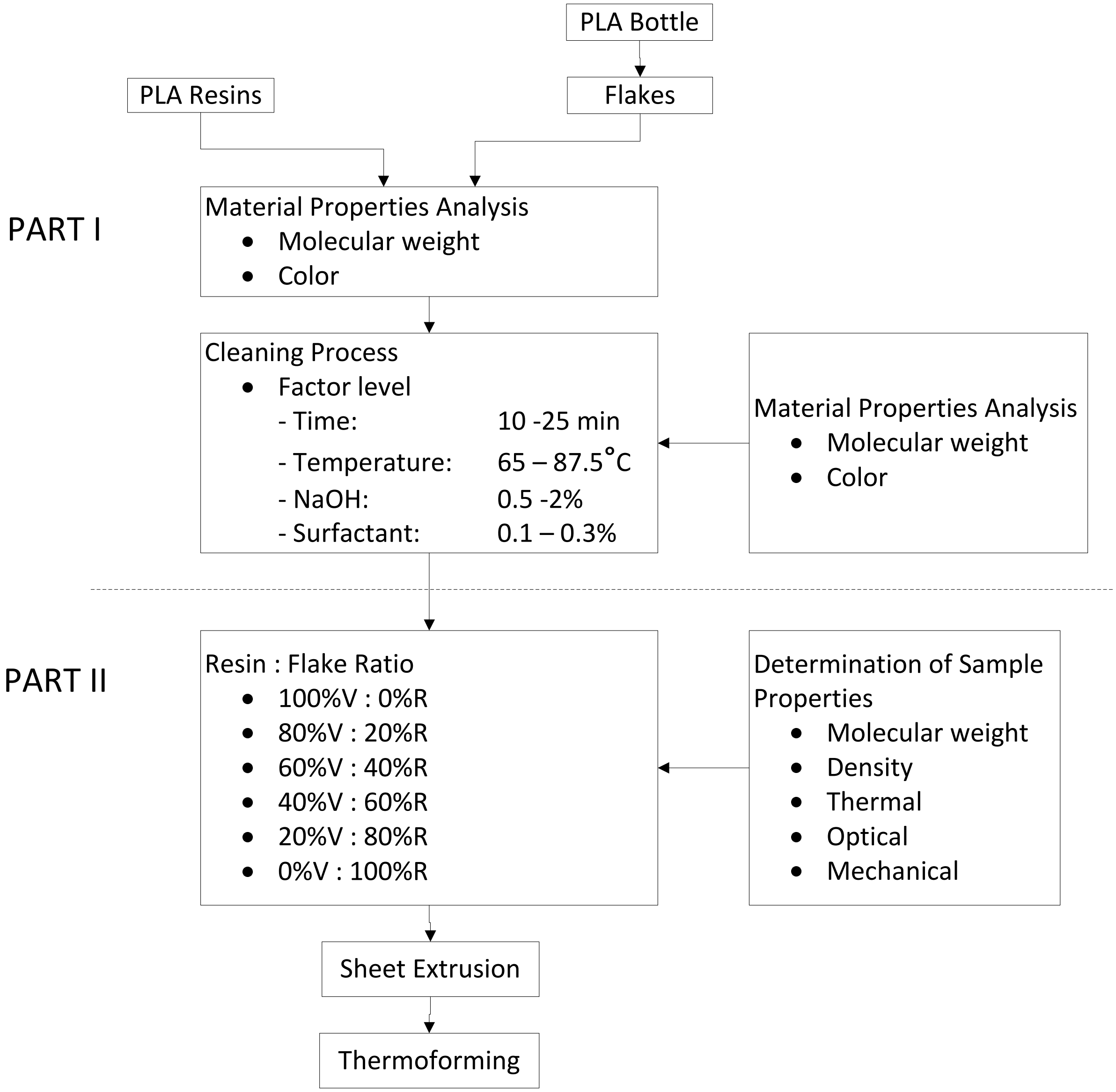


Figure 3-1: Project experimental flow chart

Materials

Post-consumer PLA 500 ml water bottles were provided by Primo Water Corporation (Winston Salem, NC). Virgin PLA resin (PLA 2002D) was obtained from NatureWorks®Ingeo™. Nonionic octylphenol biodegradable surface-active agent (Triton® X-100) and NaOH were procured from a local store.

Methods

Sample preparation - Flake preparation process

Bottle caps, rings and labels were removed by hand before grinding the post-consumer PLA water bottles. After that each bottle was cut into 3 large pieces and placed into the grinder, B.P.T. granulator machine from Polymer Machinery® (Berlin, CT). Bottles were ground into small pieces by two rotating steel blades inside the machine. The size was 3.35 to 4.7 mm [59].

Experimental design for the cleaning process of the PLA flake

The cleaning procedure was divided into two steps: cleaning with caustic solution (NaOH) and rinsing with water. Since there is no standard commercial cleaning condition for post consumer PLA plastic, the cleaning method used for PET recycled plastic was adapted to use in this process. To determine the optimal cleaning conditions for the flakes, an experimental design was conducted by using response surface methodology (RSM). Four main factors from the cleaning conditions used for recycling PET were selected: a) cleaning temperature, b) time, c) concentration of sodium hydroxide, and d) surfactant. The maximum and minimum values of each factor were assigned as indicated in Table 3-1. In order to construct a response surface, 30 cleaning condition treatments were selected as shown in Table 3-2.

The caustic solution for cleaning consisted of 0.5 to 2% sodium hydroxide (NaOH) solution with 0.1 to 0.3% surfactant. The cleaning solution was preheated to the desired temperature. The solution was stirred at approximately 800 rpm by a CompactDigital Stirrer BDC2002 agitato, (Caframo, Wiarton, Ontario, Canada). When the solution reached the temperature shown in Table 3-2, the flakes were introduced for the established period of time. At the end of the specified time, the NaOH and surfactant were drained off, and the flakes were rinsed with water at room temperature and stirred at 800 rpm for 5 min. Finally, the flakes were removed from the water and allowed to dry at 23°C and 50% relative humidity for 24 hours.

The cleaned flake from each treatment condition was vacuum dried at 90°C for four hours before the molecular weight and color properties were determined. The values of these properties were used in the RSM to determine the optimum cleaning condition. After the optimum cleaning condition was determined, all the remained flakes were cleaned under this condition.

Table 3-1: Factor levels for each cleaning parameter

Levels	**Time (min)**	**Temperature (°C)**	**NaOH (%)**	**Surfactant (%)**
Highest	25	95	2	1
Middle	15	85	1	0.3
Lowest	5	65	0.5	0.1

Table 3-2: Experimental design treatment conditions for PLA flake cleaning process

Treatment	**Time (min)**	**Temperature (°C)**	**NaOH (%)**	**Surfactant (%)**
1	10	72.5	2	0.2
2	10	72.5	0.5	0.4
3	25	72.5	0.5	0.2
4	25	72.5	2	0.4
5	10	87.5	0.5	0.2
6	10	87.5	2	0.4
7	25	87.5	2	0.2
8	25	87.5	0.5	0.4
9	17.5	80	1.25	0.3
10	17.5	80	1.25	0.3
11	10	72.5	0.5	0.2
12	10	72.5	2	0.4
13	25	72.5	2	0.2

Table 3-2 (continued)

14	25	72.5	0.5	0.4
15	10	87.5	2	0.2
16	10	87.5	0.5	0.4
17	25	87.5	0.5	0.2
18	25	87.5	2	0.4
19	17.5	80	1.25	0.3
20	17.5	80	1.25	0.3
21	17.5	65	1.25	0.3
22	17.5	95	1.25	0.3
23	10	80	1.25	0.3
24	25	80	1.25	0.3
25	17.5	80	1.25	0.1
26	17.5	80	1.25	0.5
27	17.5	80	0.5	0.3
28	17.5	80	2	0.3
29	17.5	80	1.25	0.3
30	17.5	80	1.25	0.3

PLA sheet extrusion process

PLA resin and flake were extruded by using a Microextruder model RCP-0625 (Randcastle Extrusion Systems, Inc., Cedar Grove, NJ). PLA virgin resin was combined with cleaned bottle flake in six combinations and mixing ratios as listed in Table 3-3. The processing temperature profile recommended from NatureWorks® for PLA resin 2002 and the actual processing temperature of the PLA and flake from the extruder are listed in Table 3-4.

Table 3-3: Ratios of PLA virgin resin and flake for sheet extrusion samples

Combination number	**Ratio (virgin resin: flake)**
1	100 : 0
2	80 : 20
3	60 : 40
4	40 : 60
5	20 : 80
6	0 : 100

Table 3-4: Standard and actual temperature profile for PLA extrusion

Section	**Standard Temperature Profile (°F)**	**Actual Temperature Profile (°F)**
Zone 1	355	375
Zone 2	375	390
Zone 3	390	400
Transfer tube	390	400
Die	375	385

Sample analysis

Molecular weight properties

Molecular weight properties (*i.e.*, weight average molecular weight (M_w), number average molecular weight (M_n) and molecular weight distribution or polydispersity index (PDI)) of the PLA resin and bottle flakes were analyzed by gel permeation chromatography (GPC) with equipment from Waters Inc. (Milford, MA). The system consisted of a Waters 1515 isocratic pump, a Waters 717 autosampler, a Waters 2414 refractive index detector, and a set of three columns (HR-2, HR-3 and HR-4 also from Waters) interfaced with Waters Breeze software, all from Waters, Inc. For each PLA specimen, three samples of 20 mg each were cut from the sheet and dissolved in 10 ml of HPLC grade tetrahydrofuran (THF). Then 100 µL from each sample was withdrawn and injected into the system with a flow rate of 1 cm^3-min^{-1} for 45 min at 25°C.

Physical properties

Densities of the extruded PLA sheets were determined by using a density gradient method in accordance with ASTM D 1505 Method C in section X 2.3 [61]. A solution of water and calcium nitrate was used to create a density-gradient scale between 0.90 and 1.3 g-cm^{-3}. Samples of 5 mm in diameter were cut and submerged in the density gradient column. Three samples were tested from each PLA sheet specimen.

Optical properties

UV light

Ultraviolet and visible light transmission of PLA sheet samples were measured by using a Perkin-Elmer Lambda 25 (Waltham, MA). Three samples from each PLA sheet were scanned over the range 190 to 800 nm at 480 nm min^{-1}.

Color

A LabScan XE from HunterLab (Reston, VA) was use to identify the color differences among PLA sheets. The result was reported in the CIE L*a*b* system. The 100% virgin PLA sheet was assigned as the control for color comparisons between 100% virgin samples and the samples with varying recycled contents. The color difference can be calculated from equation (3.1). Three samples for each PLA sheet condition were tested.

$$\Delta E = \left[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\right]^{\frac{1}{2}} \tag{3.1}$$

where

$$\Delta L^* = L^*_{standard} - L^*_{sample}$$

$$\Delta L^* = a^*_{standard} - a^*_{sample}$$

$$\Delta L^* = b^*_{standard} - b^*_{sample}$$

Infrared

Fourier transform infrared spectroscopy (FTIR) was used to determine any changes in functional groups in the PLA sheets. Three samples from each PLA sheet were scanned using a Shimadzu IR-Prestige 21 (Columbia, MD) from 4000 to 650 cm^{-1}.

Thermal properties

Glass transition temperature, melting temperature, enthalpy of fusion and crystallinity

The glass transition (T_g) and melting (T_m) temperatures were determined by a differential scanning calorimeter (DSC) Q100 from Thermal Analysis Inc (New Castle, DE) in accordance with ASTM D 3418 [62]. Three cycles of heat-cool-heat were performed: heating from 25 to 185°C, then isothermal for 5 minutes, cooling from 185 to 25°C, and heating back to 185°C, all at a ramping rate of 10°C min^{-1} under a nitrogen atmosphere. Three samples of 6 to 10 mg each were tested for each PLA specimen. The crystallinity (χ_c) was determined using equation (3.2):

$$\chi_C(wt\%) = 100 \times \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0} \tag{3.2}$$

where ΔH_m is the enthalpy of melting, ΔH_c is the enthalpy of crystallization and $\Delta H^0{}_m$ is the enthalpy of 100% crystalline PLA, which is 93 J g^{-1} [19].

Heat deflection temperature

The thermo mechanical properties of the PLA sheets were analyzed by using a dynamic mechanical analyzer (DMA) Q800 from Thermal Analysis Inc (New Castle, DE) in tension mode, with a clamp preload of 0.01 N. The tests were conducted in the temperature range of 0 to 140°C at 5°C min^{-1} heating rate under DMA-multi-frequency strain mode. Three samples of 5 mm width and 20 mm length were used for each PLA sheet.

Mechanical properties

Tensile strength, percentage of elongation at break, modulus of elasticity and tensile strength at yield were measured using a Universal Testing Machine 5560 series from Instron, Inc. (Norwood, MA) in accordance with ASTM D882 [63]. The initial grip separation was 125 mm (5 in) and the rate of grip separation was 12.5 mm min^{-1} (0.5 inch min^{-1}). Three samples for each specimen were tested.

Thermoforming

A Hydro Trim thermoformer model 1620 from Hydrotrim, (W. Nyack, NY) with aluminum thermoforming molds were used to thermoform virgin PLA sheet and PLA sheet with varying percentages of recycled content. The temperature for the top and bottom heaters was set at 110°C and the heating time and the forming time were set to 10 seconds. At least two PLA sheets from each specimen were thermoformed.

Statistical Analysis

Analysis of variance (ANOVA) with Fisher's least significant difference (LSD) or Tukey's honestly significant difference (HSD) were conducted to compare the samples at $\alpha=0.05$. The tests were conducted using the R program (http://www.r-project.org/).

CHAPTER 4

RESULTS AND DISCUSSION

Properties of virgin resin and flake before cleaning process

Thermal and molecular weight properties

Before the bottles were subjected to the recycle process, the thermal properties of the PLA resins and PLA bottle flakes were analyzed by DSC. The results indicated that the T_g, T_m and M_W of the resins and flake were statistically significantly different, which is expected since the PLA resin is PLA for thermoforming applications (PLA 2002D). There were no significant differences in the heat of fusion between the PLA resin and flakes. No significant differences were found in the M_n, PDI values of the PLA resin and bottle flakes; Table 4-1 and 4-2 show these values.

Table 4-1: Thermal properties of PLA resin and PLA bottle flakes before the cleaning process

PLA	**T_g (°C)**	**T_m (°C)**	**H_m (j/g)**	**X_c (%)**
Resin	61.3 ± 0.3^{a}	152.4 ± 0.2^{a}	28.8 ± 0.39^{a}	30.93 ± 0.42^{a}
Flake	59.8 ± 0.1^{b}	148.3 ± 0.7^{b}	27.5 ± 0.7^{a}	29.57 ± 1.10^{a}

Note: values are mean ± standard error; within the same column, means with different superscripts are statistically significantly different at $\alpha = 0.05$.

Table 4-2: Molecular weights of PLA resin and PLA bottle flakes before cleaning process

PLA	M_n (kDa)	M_w (kDa)	Polydispersity
Resin	79.36 ± 1.1^{a}	121.31 ± 0.45^{a}	1.53 ± 0.02^{a}
Flake	79.78 ± 1.4^{a}	117.44 ± 0.72^{b}	1.47 ± 0.02^{a}

Note: values are mean ± standard error; within the same column, means with different superscripts are statistically significantly different at $\alpha = 0.05$.

Experimental design of the cleaning process for the PLA flake

The raw data of the results of the RSM design are presented in Appendix A. Many RSM parameters such as M_n, *L*, a* and b** were used to determine surface responses as a function of the variation of cleaning time between 5 to 25 min, temperature between 65 and 85°C, NaOH concentration between 0.5 to 1 wt.-%, and surfactant concentration between 0.1 and 1 wt.-%. None of the parameters showed statistically significant differences. Table 4-3 shows an example of the response surface model run by using M_n as a response variable, showing a non-significant with *p-value* = 0.4742. These results indicated that the quadratic response surface model used to characterize the best parameters for the cleaning process was not significant, and therefore any of the factors in the model will also be not significant. Even though there were factors such as heat and water that could induce hydrolytic degradation of PLA during the cleaning process, the results of the experiment show that we cannot reject the null hypothesis that "the cleaning time between 5 to 25 min, temperatures between 65 and 85°C, concentration of NaOH between 0.5 to 1 wt.-%, surfactant between 0.1 and 1 wt.-% do not have an effect on the final color and physical properties of the cleaned PLA flakes." Since the maximum time of the treatment was 25 minutes at 95°C, the flake did not have enough exposure time to hydrolyze and degrade.

Since this experiment failed to show that these parameters have an effect on the final thermal properties of cleaned PLA flake, the middle point – time 15 min, temperature 85°C, NaOH concentration at 1 wt.-% and surfactant at 0.3 wt.-% - was used for the cleaning of all the PLA flake used in this study. These middle point values are the same as commonly used for cleaning postconsumer PET. Therefore, the MRF will not need to change the conditions when processing PLA.

Table 4-3: Overall response surface model looking at M_n as response value

Factor	**Value**
The treatment degree of freedom	14
The error degree of freedom	15
Sum of square between treatment	221.39
Sum of square within treatment	229.88
Mean square between treatment	15.81
Mean square within treatment	15.32
F-value	1.03
P-value	0.47

Extruded sample analysis

The thickness of PLA extruded sheets varied from 14 to 17 mil due to the rolling speed fluctuation of the roller.

Molecular weight properties

Table 4-4 displays the molecular weight of the extruded PLA samples. There were no statistically significant differences of M_n and PDI for the PLA resin, bottle flake and the six PLA extruded sheet samples at $\alpha < 0.05$. However, there were differences in M_w results among samples 100V, 80V and 60V and 20V and 100R. PLA extruded sheet samples 100V, 80V and 60V were not significantly different than the PLA resin since these three samples contained a high percentage of virgin material. However, sample 20V and 100R exhibited lower M_w compared with 100V, 80V and 60V, which can be attributed to the high amount of recycled content in the final PLA extruded sheets. PLA samples exposed to a recycling cycle were thermally abused twice; therefore, increased chain scission and degradation can be expected due to the second polymer extrusion process. PLA samples exposed to more than one extrusion cycle have shown lower M_w [39, 64, 65]

Table 4-4: M_n, M_w and PDI for PLA resin, flake and extruded sheet with varying percent of virgin and recycled PLA content

	M_n (kDa)	M_w (kDa)	Polydispersity
Resin	79.36 ± 1.13^{a}	121.31 ± 0.44^{a}	1.53 ± 0.02^{a}
100V	78.46 ± 4.29^{a}	$120.00 \pm 1.49^{a,b}$	1.54 ± 0.06^{a}
80V	77.21 ± 1.02^{a}	$119.19 \pm 0.37^{a,b,c}$	1.54 ± 0.01^{a}
60V	76.86 ± 0.56^{a}	$118.43 \pm 0.19^{a,b,c}$	1.54 ± 0.01^{a}
40V	76.81 ± 3.37^{a}	116.59 ± 1.54^{c}	1.52 ± 0.05^{a}
20V	74.39 ± 0.58^{a}	113.39 ± 0.21^{d}	1.52 ± 0.01^{a}
100R	74.31 ± 2.16^{a}	113.26 ± 1.87^{d}	1.52 ± 0.02^{a}
Flake	79.78 ± 1.40^{a}	$117.44 \pm 0.72^{b,c}$	1.47 ± 0.02^{a}

Note: values are mean ± standard error; within the same column, means with different superscripts are statistically significantly different at $\alpha = 0.05$.

Physical properties

Density

The densities of PLA extruded sheets are presented in Table 4-4. There was no significant difference in the results, and the average density for PLA sheet samples was approximately 1.24 g-cm^{-3} [2, 3].

Table 4-5: Density of PLA extruded sheets

	Density, g-cm^{-3}
PLA resin 2002D	1.24 [2]
100V	1.237±0.004^{a}
80V	1.238±0.002^{a}
60V	1.239±0.005^{a}
40V	1.237±0.001^{a}
20V	1.237±0.001^{a}
100R	1.236±0.001^{a}
PLA resin 7000D	1.24 [3]

Note: values are mean ± standard error; within the same column, means with different superscripts are statistically significantly different at α = 0.05.

Optical properties

UV light

Figure 4-1 shows the UV spectra of 100% virgin PLA sheet. Transmission of UV light through PLA sheet samples starts to decline from approximately 90% at 345 nm to 85% at 300 nm. Between 300 nm and 240 nm, UV light transmission drop dramatically, falling to 3.5% at 240 nm and then increasing again at lower wavelengths [5]. UV transmission in the range of 260 to 285 nm of the virgin PLA sheets and PLA with varying recycle contents is statistically significantly different as shown in Table 4-6 and Figure 4-2. In this range, UV light transmission was reduced as the recycled content of PLA increased. This reduction may cause by the UV-light absorption at 280 nm of the carboxylic chain end group which was the result of the chain scission of thermal degradation [66]. There was no significant difference in absorption in the visible light region (400 to 800 nm) within the samples.

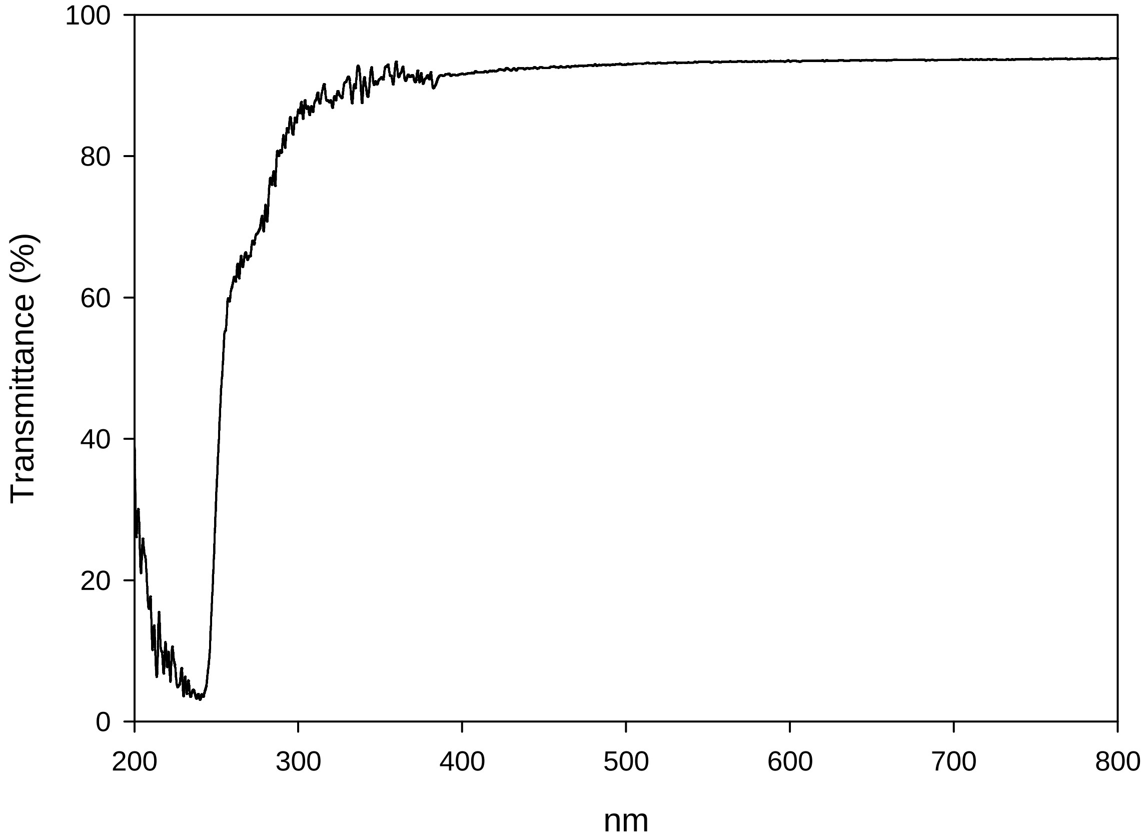


Figure 4-1: UV spectra of 100% virgin PLA sheet sample

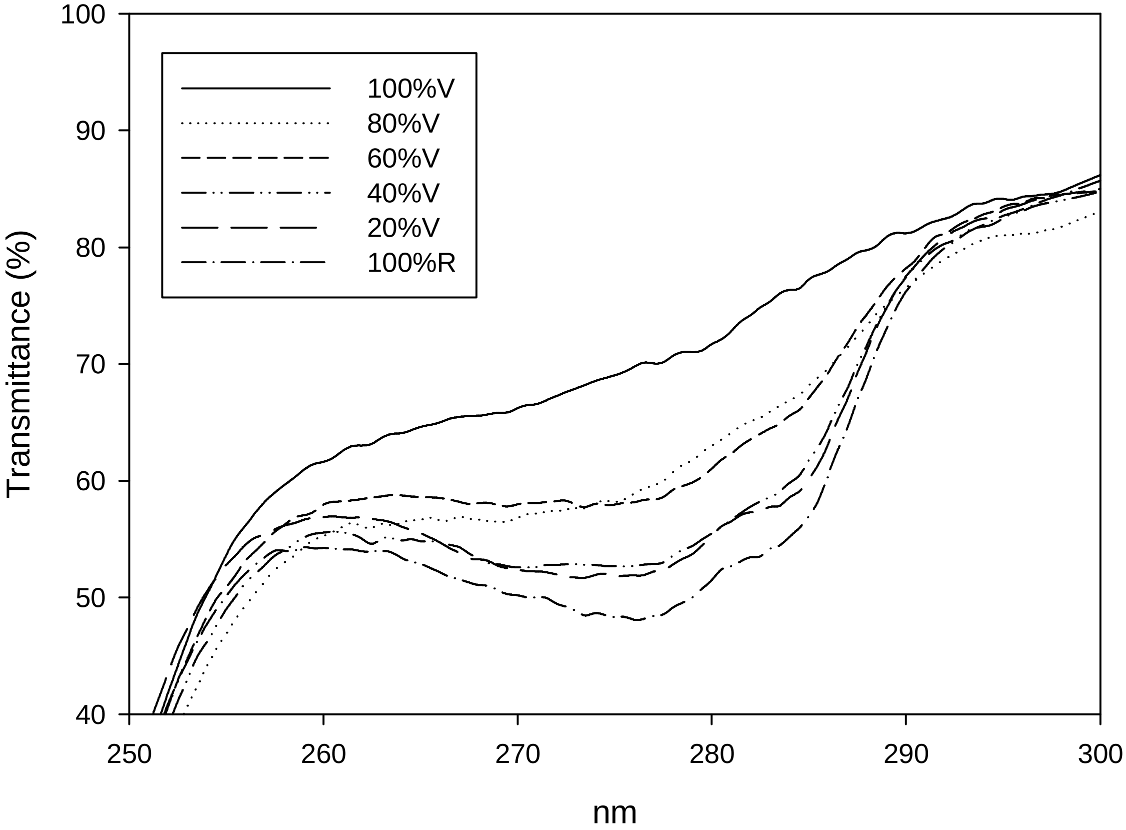


Figure 4-2: UV spectra of varying PLA sheets with varying amounts of recycled contents between 250 and 300 nm

Table 4-6: Percent transmittance of UV spectra at wavelength 260, 275, 285 and 290nm

	Transmission, % @			
	260 nm	**275 nm**	**285 nm**	**290 nm**
100V	61.92±1.23^{a}	69.08±0.74^{a}	77.87±1.93^{a}	80.63±0.84^{a}
80V	54.51±0.68^{b}	57.63±1.36^{b}	68.37±0.79^{b}	77.42±0.95^{a}
60V	58.13±2.19^{a}	56.31±1.97^{b}	66.12±2.85^{b,c}	78.12±1.24^{a}
40V	55.61±1.43^{b}	52.46±0.39^{b,c}	60.42±1.15^{b,c,d}	78.15±0.81^{a}
20V	56.79±0.62^{a}	53.04±0.91^{b,c}	58.68±0.60^{c,d}	78.83±0.45^{a}
100R	52.74±3.18^{c}	47.17±4.64^{c}	56.70±4.43^{d}	77.08±1.49^{a}

Note: values are mean ± standard error; within the same column, means with different superscripts are statistically significantly different at $\alpha = 0.05$.

Color

The colors of the PLA resin, flake and sheets were characterized by the CIELAB system. The *L** value represents the whiteness in percentage, 100% is white and 0% is black. The color range of red to green is indicated by *a** values; a positive *a** value indicates red and a negative *a** value indicates green. A positive *b** value indicates yellow and a negative *b** value indicates blue. The color values of PLA sheets extrusion with various recycled PLA content are shown in Table 4-4. PLA sheets became slightly darker (Figure 4-3), more reddish (Figure 4-4) and more bluish as recycled content increased (Figure 4-5). This dark color observed in the higher PLA recycled content samples may be due to the slight blue color of the bottle flake.

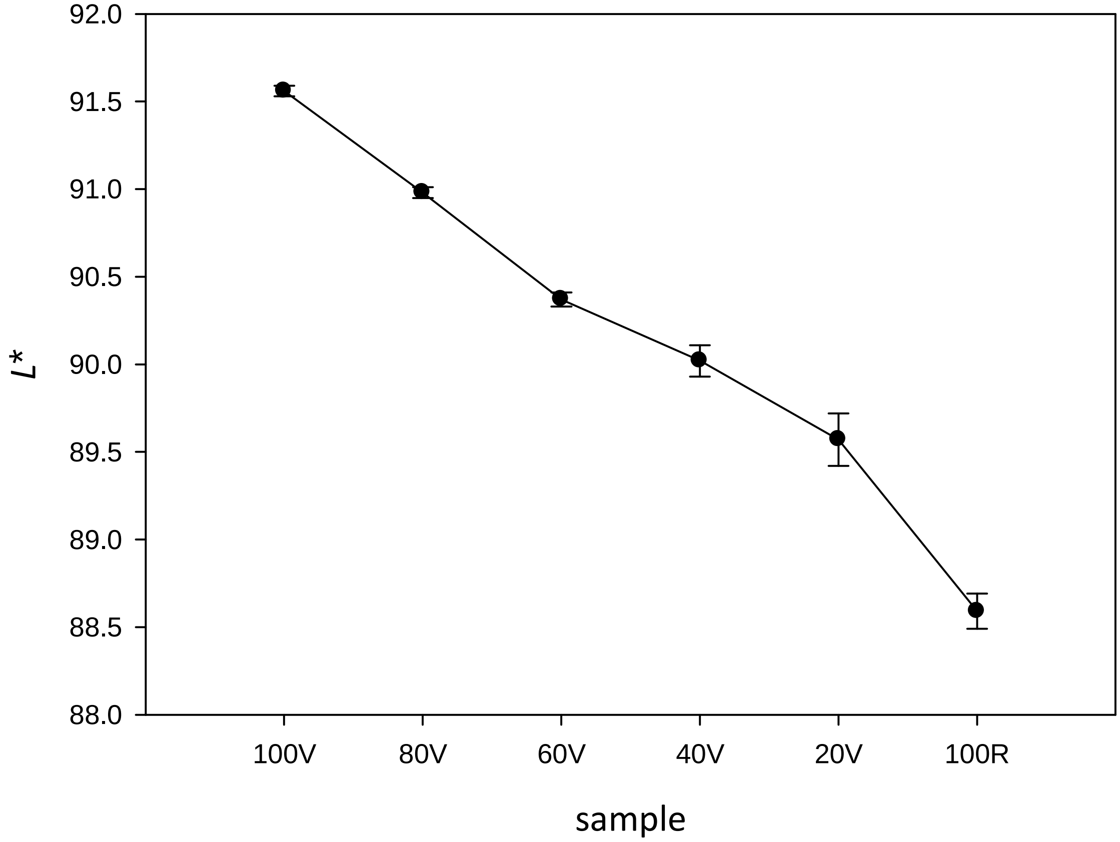


Figure 4-3: *L** value for the PLA sheet samples with different amounts of recycled PLA flakes.

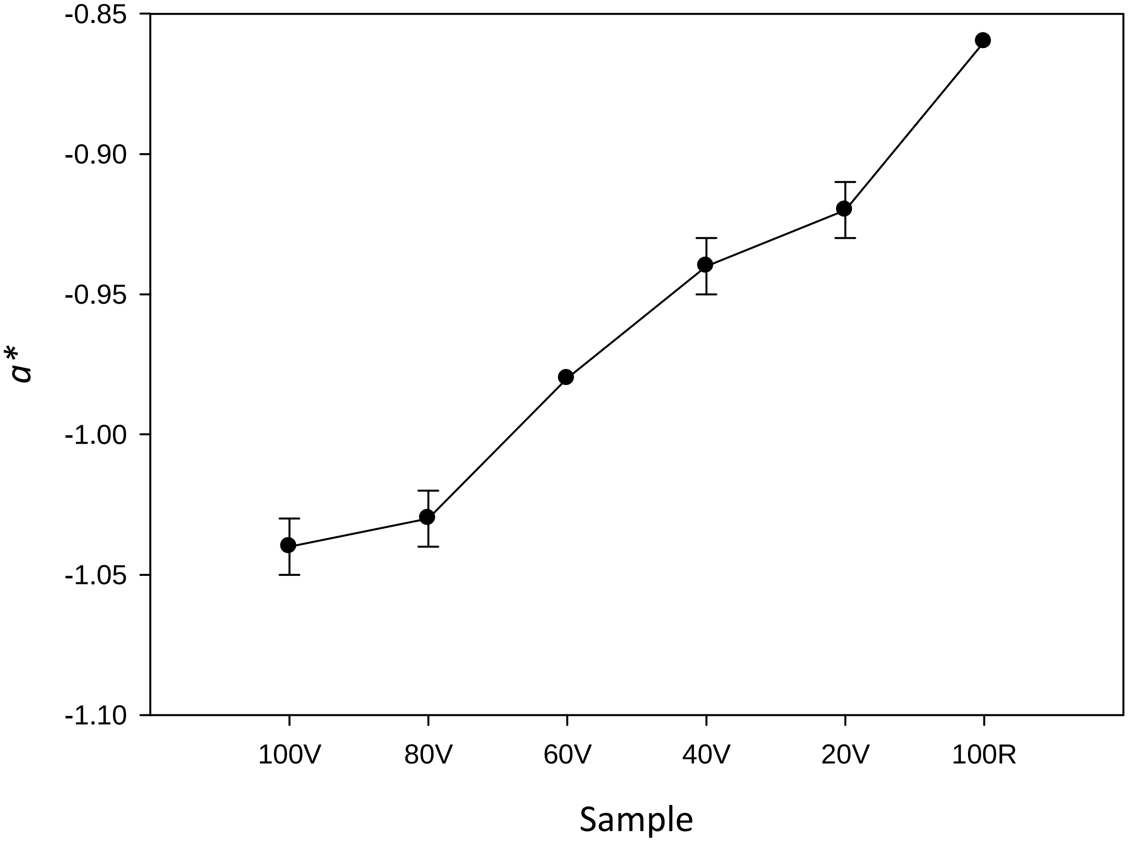


Figure 4-4: *a** value for the PLA sheet samples with different amounts of recycled PLA flakes.

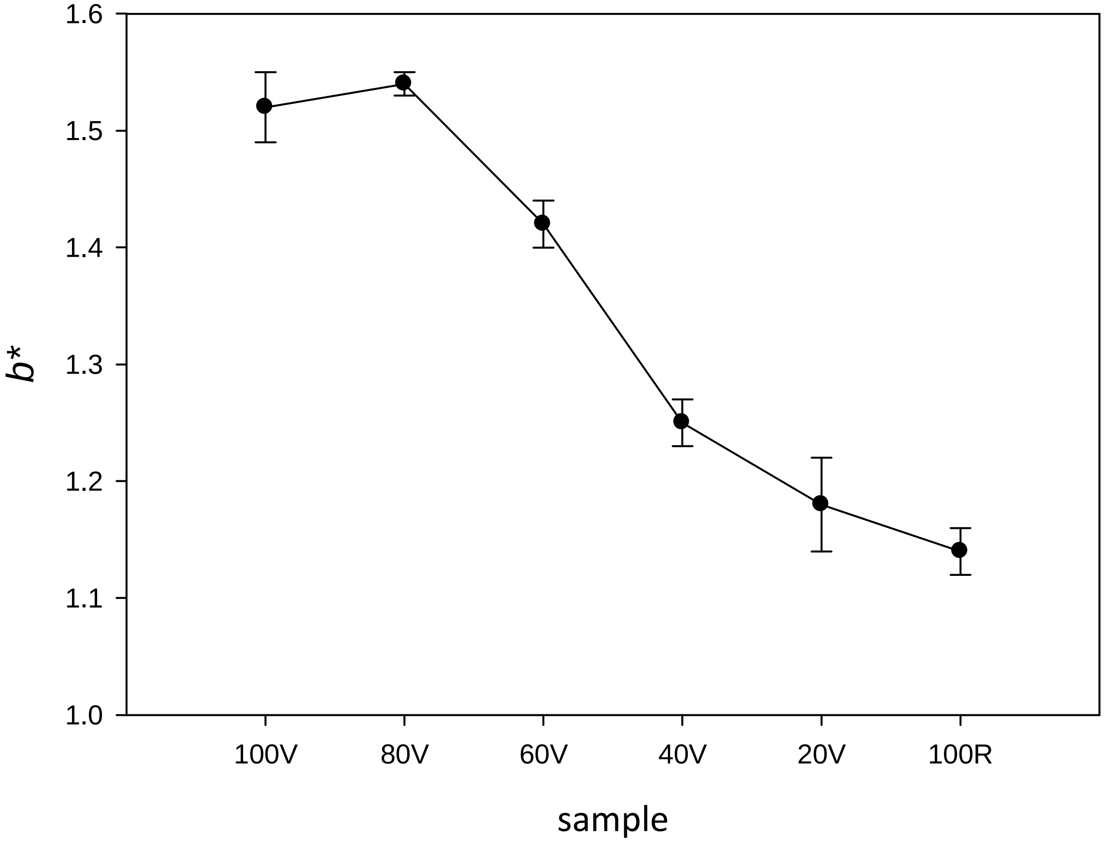


Figure4-5: *b** value for the PLA sheet samples with different amounts of recycled PLA flakes.

Table4-7: The *L*, *a** and *b** values for PLA sheets with varying degree of percent of virgin and recycled PLA contents

	L* (%)	***a****	***b****	**ΔE**
100V	91.56±0.03^{a}	-1.04±0.01^{a}	1.52±0.03^{a}	-
80V	90.98±0.03^{b}	-1.03±0.01^{a}	1.54±0.01^{a}	0.58
60V	90.37±0.04^{c}	-0.98±0.01^{b}	1.42±0.02^{b}	1.20
40V	90.02±0.09^{d}	-0.94±0.01^{c}	1.25±0.02^{c}	1.57
20V	89.57±0.15^{e}	-0.92±0.01^{d}	1.18±0.04^{c,d}	2.02
100R	88.59±0.1^{f}	-0.86±0.02^{e}	1.14±0.02^{d}	3.00

Note: values are mean ± standard error; within the same column, means with different superscripts are statistically significantly different at α = 0.05

Infrared properties

PLA shows FTIR peak intensities as shown in Table 4-8.To determine variation in the PLA functional groups, ATR-FTIR was obtained for each sample. An example of the 100V PLA FTIR spectrum is shown in Figure 4-5. During the flake cleaning process, hydrolytic degradation may occur due to the presence of water and heat; random chain scission in the back bone will increase the chain ends (-OH) in the polymer structure [5, 38]. Also during the extrusion, thermal degradation can generate various decomposition products such as lactic acid, lactide, carbon monoxide, carbon dioxide, acetaldehyde and ketene [39, 64, 67]. However, there are no visible new peaks appearing in the sample 60V and 100R spectra (Figure 4-6). Degradation in these samples may occur in such a small amount that the FTIR cannot detect the absorption from the degradation products. Also, the rough surface quality of the samples disrupts the infrared absorption and results in low peak intensity. There are some slight decreases of peak intensity between the 100V, 60V and 100R samples for the –C=O bond (Figure 4-7) and -C-O and -OH bending bonds (Figure 4-8). Further investigation would be required to determine whether these differences are significant.

Table 4-8: Infrared spectroscopy data with peak band assignments for PLA infrared spectra, adapted from Auras et al [5]

Assignment	**Peak position, cm^{-1}**
-OH stretch (free)	3571
-CH- stretch	2997 (asym), 2946 (sym), 2877
-C=O carbonyl stretch	1748
-CH_3 bend	1456
-CH- deformation including symmetric and asymmetric	1382, 1365
-C=O bend	1225
-C-O- stretch	1194, 1130, 1093
-OH bend	1047
-CH_3 rocking modes	956, 921
-C-C- stretch	926,868

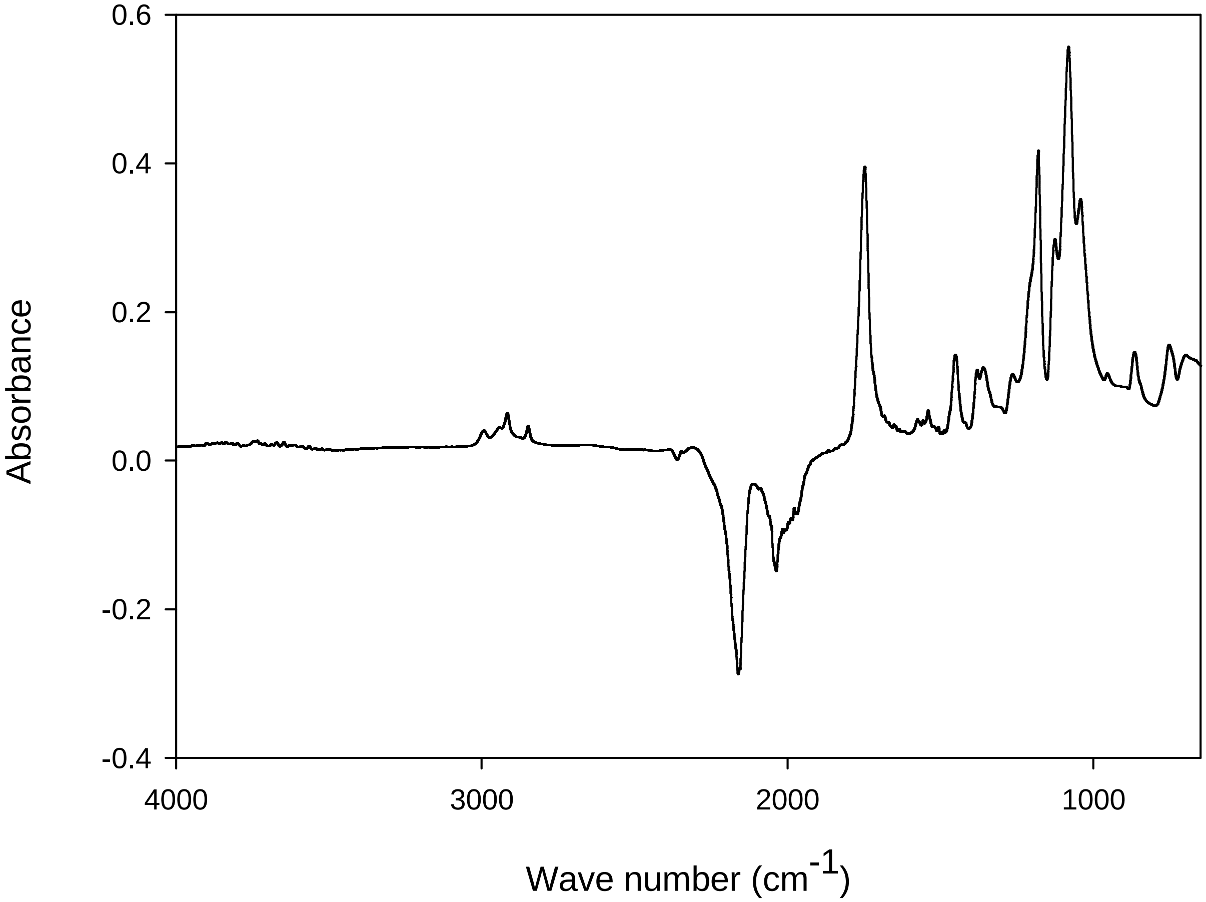


Figure 4-6: FTIR spectrum of 100% virgin PLA sheet samples

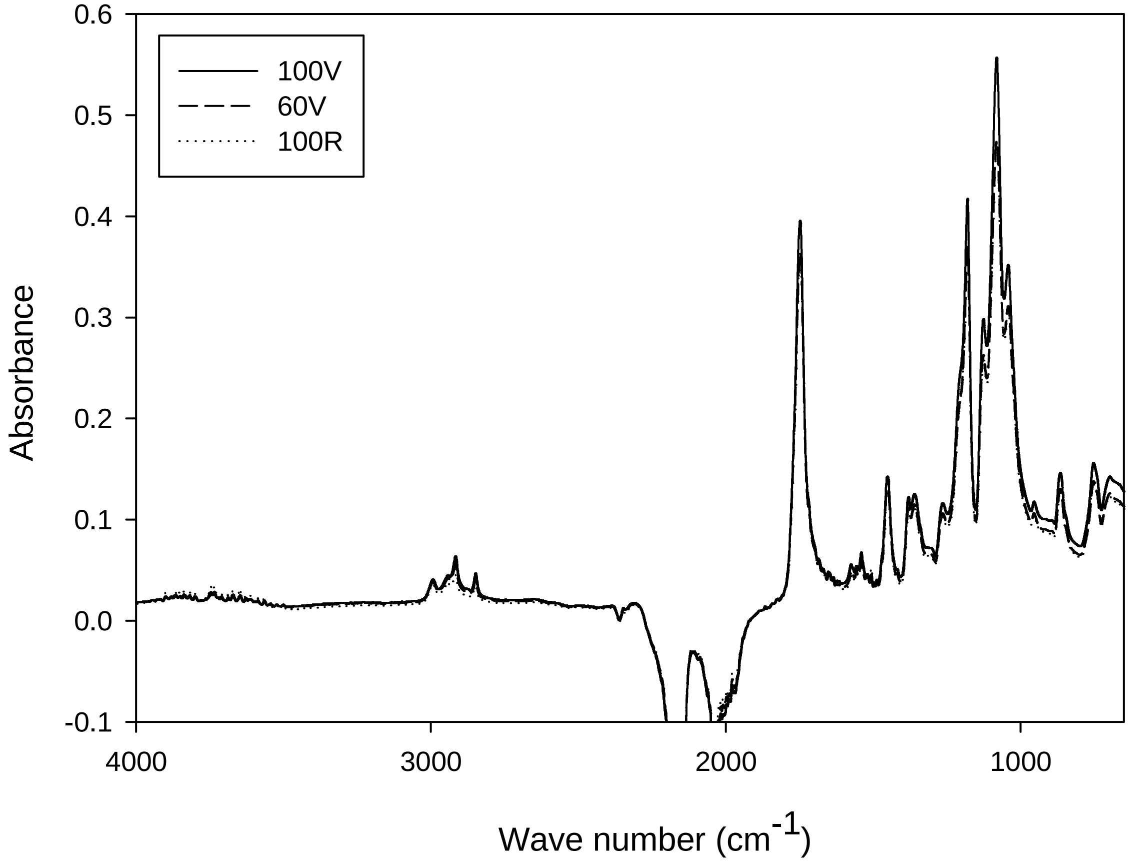


Figure 4-7: FTIR spectra of PLA sheet samples from 100V, 60V and 100R

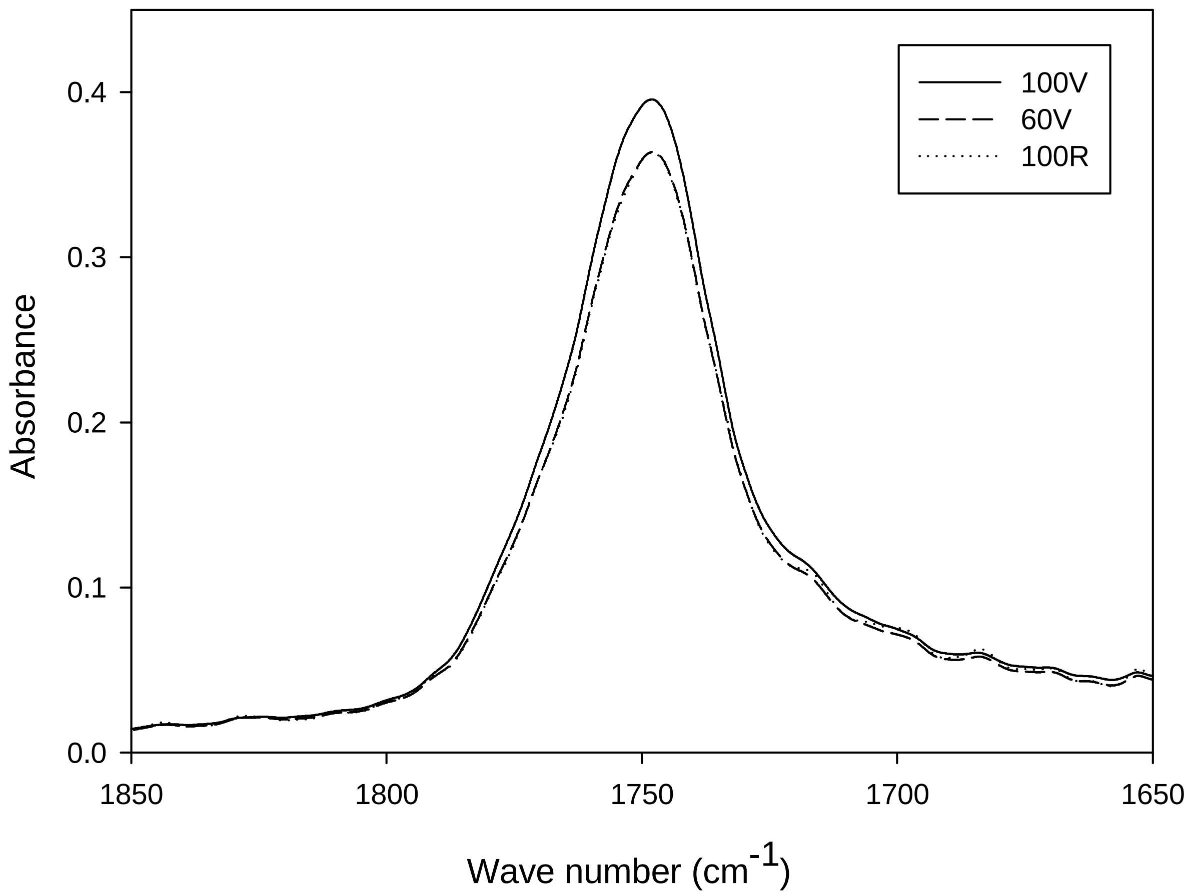


Figure 4-8: FTIR spectrum of 100V, 60V and 100R from 1850 to 1650 cm^{-1}, showing -C=O carbonyl stretch peak at 1748 cm^{-1}.

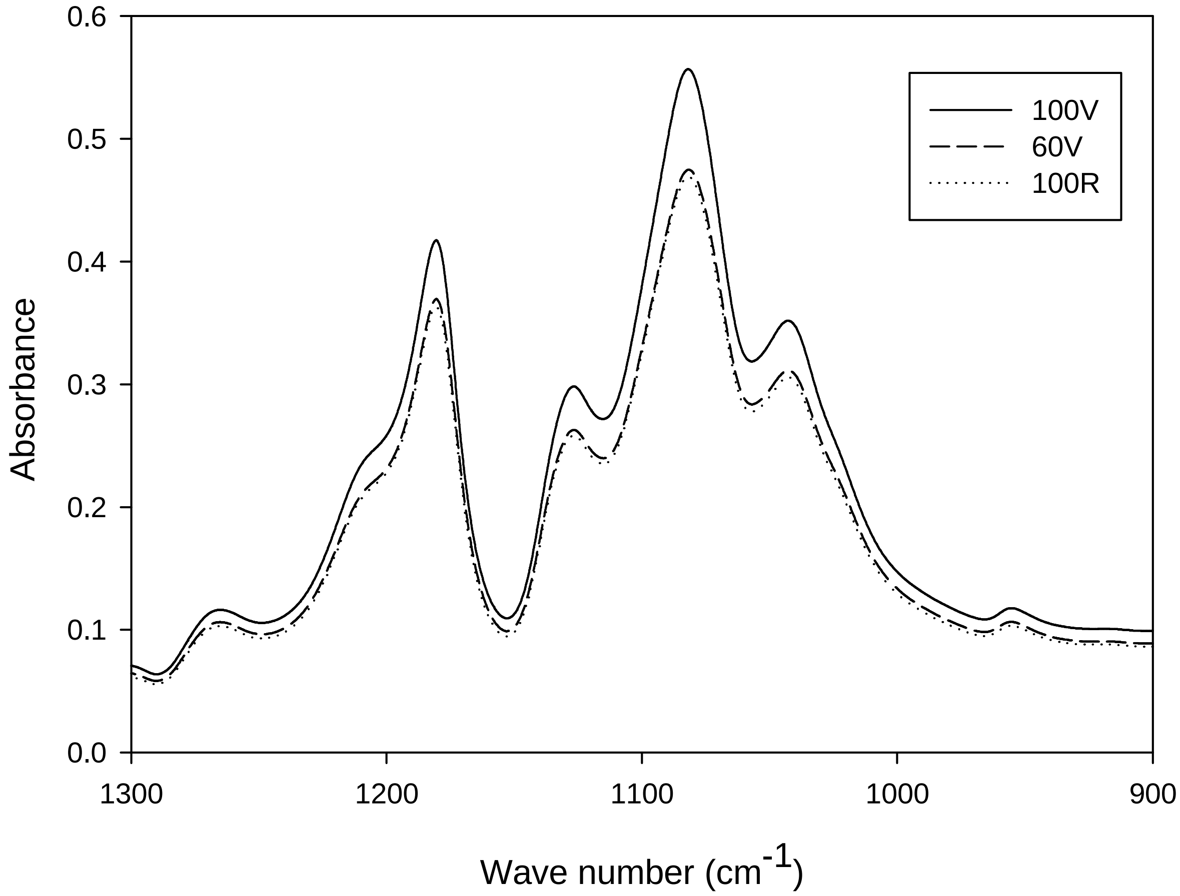


Figure 4-9: FTIR spectrum of 100V, 60V and 100R from 1300 to 900 cm^{-1}, showing -C-O- stretch peaks at 1194, 1130 and 1094 cm^{-1} and –OH bend peak at 1047 cm^{-1}

Thermal properties

Glass transition temperature, melting temperature, enthalpy of fusion and crystallinity

Glass transition temperatures were determined from the second heating cycle during the DSC run. The T_g for each sample is shown in Table 4-9. Statistically significant differences were found between 100R (lowest T_g = 59.6 °C) and 100V (highest T_g = 60.7 °C). A high amount of

PLA recycled flake content may reduce the T_g of the final extruded PLA sheets. The recycled PLA may introduce low molecular weight plasticizer or impurities, which lowers the final T_g of PLA sheets containing recycled PLA amounts. The melting point of the samples shows similar characteristics. The 100V samples showed the highest T_m (150.4 °C) and the lowest 100R (149.2 °C). Recycled PLA flakes may introduce irregularities in the highly ordered 100V samples. However, no statistically significant differences were found in the enthalpy of fusion and crystallinity of the samples.

Table 4-9: Thermal properties of PLA sheets with varying percent of virgin and recycled PLA content

	T_g (°C)	T_m (°C)	ΔH_c(j/g)	X_c (%)
100V	60.7 ± 0.0^{a}	150.4 ± 0.0^{a}	2.81 ± 0.08^{a}	3.01 ± 0.09^{a}
80V	60.5 ± 0.0^{a}	150.3 ± 0.1^{a}	2.74 ± 0.28^{a}	2.95 ± 0.30^{a}
60V	$60.3 \pm 0.1^{a,b}$	150.2 ± 0.1^{a}	1.92 ± 0.05^{a}	2.07 ± 0.06^{a}
40V	$60.1 \pm 0.0^{b,c}$	$150.1 \pm 0.3^{a,b}$	1.69 ± 0.65^{a}	1.82 ± 0.70^{a}
20V	60.0 ± 0.1^{c}	$149.8 \pm 0.1^{b,c}$	1.41 ± 0.06^{a}	1.51 ± 0.07^{a}
100R	59.6 ± 0.3^{c}	149.2 ± 0.3^{c}	2.01 ± 0.81^{a}	2.16 ± 0.83^{a}

Note: values are mean ± standard error; within the same column, means with different superscripts are statistically significantly different at $\alpha = 0.05$

Heat deflection temperature

An example of a DMA curve showing the storage modulus, loss modulus and tan delta for 100V PLA sheet is displayed in Figure 4-9. T_g is indicated between 55 and 65°C by the sudden change of tan delta. The DMA curves showed no significant difference of T_g among all the samples, in contract to the results from DSC (Table 4-10). The increased variability of the DMA results made this a less sensitive measure.

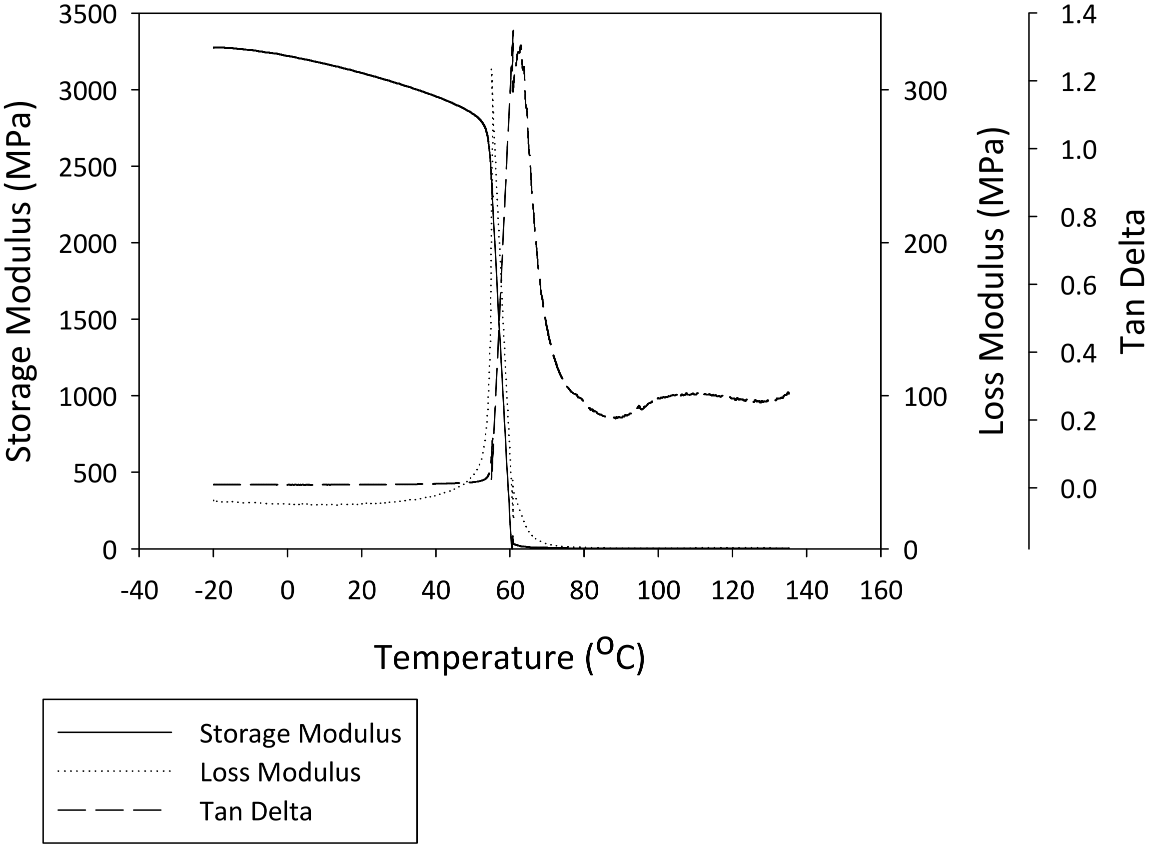


Figure 4-10: DMA curve of 100V PLA sheet sample shown storage modulus, loss modulus and tan delta as a function of temperature

Table 4-10: Loss modulus, tan delta and onset of rubbery plateau

	Loss modulus at 25°C (MPa)	Tan delta (°C)	Onset of Rubbery plateau (°C)
100V	29.79±11.35[a]	68.32±4.55[a]	58.06±4.88[a]
80V	36.53±6.95[a]	64.77±2.87[a]	54.10±1.00[a]
60V	39.88±1.13[a]	64.34±2.03[a]	52.83±0.28[a]
40V	40.22±3.08[a]	63.09±3.96[a]	52.63±0.33[a]
20V	28.59±3.95[a]	61.73±2.71[a]	51.89±0.10[a]
100R	31.22±6.00[a]	63.18±3.42[a]	53.09±0.93[a]

Note: values are mean ± standard error; within the same column, means with different superscripts are statistically significantly different at $\alpha = 0.05$.

Mechanical properties

Mechanical properties for PLA sheet samples in the machine direction (MD) and cross machine direction (CD) are shown in Tables 4-11 and 4-12, respectively. The tensile strength displayed a nonlinear relationship with the amount of recycled content. The tensile strength, modulus of elasticity and tensile strength at yield of samples 100V were significantly higher than 20V and 100R samples, in both MD and CD. The apparent increase of the tensile strength of 80V compared to 100V in the MD is likely a statistical fluke as the 80V and 60V samples had unusually high standard errors. A preliminary experiment (data not reported) did not show this anomalous increase.

Table4-11: Mechanical properties of PLA sheets with varying percent of virgin and recycled PLA contents in machine direction

	MD			
	Tensile Strength (MPa)	**Break Elongation (%)**	**Modulus of Elasticity (MPa)**	**Tensile Strength at Yield (MPa)**
100V	55.34±0.81^{a}	4.4±0.6^{a}	2875±13^{a,b}	53.02±0.61^{a}
80V	60.17±1.95^{b}	3.9±0.4^{a}	3125±79^{c}	55.45±1.57^{a}
60V	56.25±2.76^{a,b}	3.7±0.6^{a}	2948±87^{a}	51.50±2.21^{a}
40V	50.57±0.19^{c}	4.5±0.5^{a}	2744±33^{b,d}	46.37±0.20^{b}
20V	47.23±0.38^{c,d}	4.5±0.3^{a}	2687±39^{d}	42.85±0.43^{b,c}
100R	45.00±0.41^{d}	5.5±0.4^{a}	2610±15^{d}	40.667±0.55^{c}

Note: values are mean ± standard error; within the same column, means with different superscripts are statistically significantly different at $\alpha = 0.05$.

Table4-12: Mechanical properties of PLA sheets with varying percent of virgin and recycled PLA contents in cross machine direction

	CD			
	Tensile Strength (MPa)	**Break Elongation (%)**	**Modulus of Elasticity (MPa)**	**Tensile Strength at Yield (MPa)**
100V	59.10±1.74^{a}	2.43±0.03^{a}	2941±76^{a}	58.02±1.79^{a}
80V	60.83±0.66^{a}	2.43±0.03^{a}	3095±41^{a}	58.78±1.14^{a}
60V	52.23±3.25^{b}	2.27±0.03^{b}	2741±123^{b}	51.47±3.21^{b}
40V	49.50±1.09^{b}	2.17±0.03^{b}	2757±5.39^{b}	48.30±1.18^{b}
20V	48.70±1.10^{b}	2.23±0.09^{b}	2569±25^{b}	47.94±1.49^{b}
100R	39.70±0.91^{c}	1.83±0.03^{c}	2494±79^{c}	39.55±1.00^{c}

Note: values are mean ± standard error; within the same column, means with different superscripts are statistically significantly different at α = 0.05.

Thermoforming

A preheat temperature of 110°C was found to be suitable for thermoforming PLA sheets 100V, 80V, 60V and 40V. However, the 20V and 100R samples tended to stick slightly to the mold and it was difficult to remove the products from the mold. The problem was resolved by decreasing the preheating temperature by 5 to 10°C. The product thicknesses were measured and there were no statistically significant differences between the values.

Dimensions

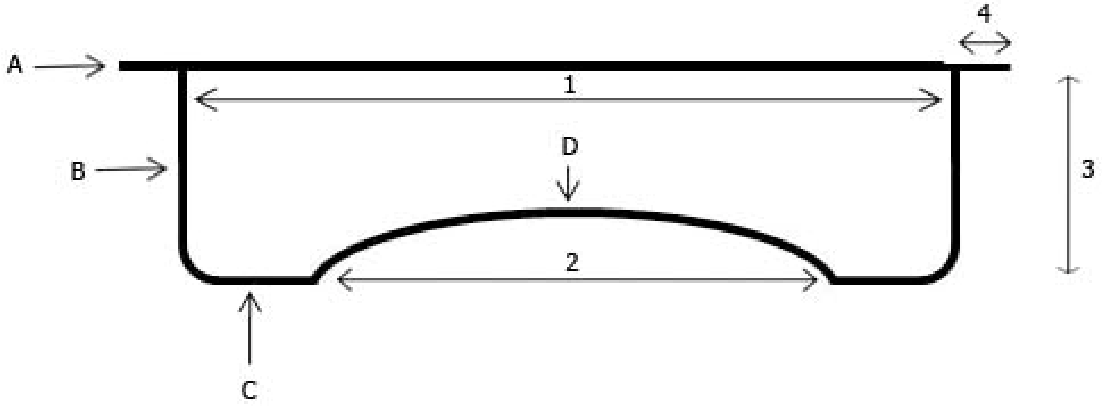


Figure 4-11: Sketch of a PLA thermoformed tray (not to scale)

Table 4-13: Thickness of PLA tray with varying percent of virgin and recycled PLA contents

	Thickness (mm)			
	Point A	**Point B**	**Point C**	**Point D**
100V	0.34±0.03 ^{a}	0.22±0.03 ^{a}	0.14±0.03 ^{a}	0.16±0.00 ^{a}
80V	0.34±0.01 ^{a}	0.22±0.01 ^{a}	0.12±0.01 ^{a}	0.16±0.01 ^{a}
60V	0.34±0.03 ^{a}	0.19±0.03 ^{a}	0.12±0.01 ^{a}	0.16±0.01 ^{a}
40V	0.35±0.02 ^{a}	0.20±0.03 ^{a}	0.12±0.01 ^{a}	0.17±0.01 ^{a}
20V	0.34±0.01 ^{a}	0.20±0.01 ^{a}	0.13±0.01 ^{a}	0.17±0.00 ^{a}
100R	0.35±0.01 ^{a}	0.19±0.01 ^{a}	0.13±0.01 ^{a}	0.16±0.00 ^{a}

Table 4-14: Dimensions of PLA tray with varying percent of virgin and recycled PLA contents

	Location			
	1 (mm)	**2 (mm)**	**3 (mm)**	**4 (mm)**
100V	75.96±0.27^{a}	60.55±0.41^{a}	25.18±0.28^{a}	7.92±0.04^{a}
80V	75.65±0.40^{a}	60.88±0.27^{a}	24.70±0.06^{a}	8.06±0.38^{a}
60V	76.14±0.1^{a}	60.34±0.46^{a}	24.99±0.23^{a}	7.84±0.11^{a}
40V	76.00±0.57^{a}	60.83±0.85^{a}	24.93±0.51^{a}	7.97±0.01^{a}
20V	76.21±0.18^{a}	60.91±0.85^{a}	24.67±0.19^{a}	7.81±0.18^{a}
100R	76.27±0.13^{a}	60.19±0.54^{a}	25.39±0.52^{a}	7.97±0.24^{a}

CHAPTER 5
CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Poly(lactide) PLA bottle flakes were subject to a mechanical recycling process, and later blended with virgin PLA resin to fabricate PLA sheet for thermoforming. The midpoint of recycled flake cleaning conditions with time of 15 min, temperature of 85 °C, NaOH concentration 1 wt.-% and surfactant 0.3 wt.-% (adapted from the typical cleaning process for recycling PET) was determined to be an appropriate cleaning condition for the PLA flakes. The thicknesses of the produced sheet varied from 0.35 to 0.41 mm. The properties of PLA sheet samples with various recycled contents were determined and compare with the properties of the 100% virgin PLA sheet.

No statistically significant differences ($\alpha = 0.05$) were found in density, M_n, PDI, ΔH_c, percentage of elongation at break and the T_g results from the DMA as a function of recycle content. However, at 20% or more recycled content, the PLA sheets became darker. The sheet generally absorbed more UV light in the 265 to 285 nm range. Further study is required to determine the cause of this absorption. At 40% recycled content or higher, the color of the PLA sheet became more bluish (b* decreased) and reddish (a* increased), but the color change for the blue tone was predominant. All of the mechanical properties in the cross-machine direction (tensile strength, percentage of elongation at break, modulus of elasticity and tensile strength at yield) decreased. Recycled content of 60% or more resulted in a reduction of M_w, T_g, tensile strength and tensile strength at yield in the MD direction. At 80% (sample 20V) recycled content the T_m and machine direction modulus of elasticity of the PLA sheets decreased.

There was not enough evidence to confirm hydrolytic and thermal degradation since peaks associated with degradation products were not visible in the FTIR spectra of 60V and 100R. The inferior properties of recycled samples indicated the existence of some degradation from the recycling process. Nevertheless, all sample sheets were successfully thermoformed into the trays without significant differences in the final dimensions.

Future work

This study provided information about the general properties and comparisons of the virgin and recycled PLA extruded sheet. However, there were some limitations, and further studies should be conducted in the future.

- Future study is needed to determine the properties of the thermoforming tray
- The biodegradability of the post-consumer recycled PLA.
- Other analysis techniques should be used to identify the mechanisms of degradation and formation of byproducts during the mechanical recycling process.
- Other manufacturing processes for producing recycled PLA products should be studied such as injection molding, blow molding, etc.
- Other aspects involving products with recycled PLA content should be studied such as the limitations of mechanical recycling for PLA, target audiences and potential markets for the products, comparative cost effectiveness of the use of recycled versus virgin PLA, and evaluation of environmental effects of using recycled PLA.

Appendix

Molecular weight data of RSM

Table A-1: Molecular weight for each cleaning condition of recycling PLA flakes

Treatment	Temp (°C)	Time (min)	Surface (%)	NaOH (%)	M_n (Da)	M_w (Da)	PDI
flake control					69992	115145	1.645116
					73750	116208	1.575697
					70491	115634	1.64039
trt01 sam1	72.5	10	0.2	2	73894	110270	1.492277
trt01 sam2					62651	111399	1.778084
trt01 sam3					58879	111262	1.889681
trt02 sam1	72.5	10	0.4	0.5	62110	112233	1.807
trt02 sam2					69136	114199	1.651812
trt02 sam3					58177	110117	1.892801
trt03 sam1	72.5	25	0.2	0.5	62354	110534	1.772696
trt03 sam2					63076	110751	1.755828
trt03 sam3					57794	108928	1.884758
trt04 sam1	72.5	25	0.4	2	68414	115635	1.690224
trt04 sam2					78085	117882	1.50966
trt04 sam3					71580	113203	1.581485
trt05 sam1	87.5	10	0.2	0.5	73596	115474	1.569032
trt05 sam2					68035	112854	1.658781
trt05 sam3					68871	113267	1.644638
trt06 sam1	87.5	10	0.4	2	69176	115299	1.66676
trt06 sam2					69133	114964	1.662929
trt06 sam3					67435	113743	1.6867
trt07 sam1	87.5	25	0.2	2	69484	111973	1.611496
trt07 sam2					70524	111999	1.588104
trt07 sam3					67660	112093	1.656704
trt08 sam1	87.5	25	0.4	0.5	74816	114552	1.531118
trt08 sam2					68980	112028	1.624053
trt08 sam3					70471	111845	1.587111
trt09 sam1	80	17.5	0.3	1.25	65764	112831	1.715692
trt09 sam2					70720	112563	1.59167
trt09 sam3					56778	110991	1.954834

Table A-1 (continued)

trt10 sam1	80	17.5	0.3	1.25	66011	112825	1.70919
trt10 sam2					75344	115500	1.532969
trt10 sam3					67217	108298	1.611169
trt11 sam1	72.5	10	0.2	0.5	64550	109660	1.698835
trt11 sam2					72634	113441	1.561803
trt11 sam3					71586	114573	1.600485
trt12 sam1	72.5	10	0.4	2	77956	117352	1.505354
trt12 sam2					72552	115639	1.593868
trt12 sam3					76486	117477	1.535929
trt13 sam1	72.5	25	0.2	2	72055	115679	1.605438
trt13 sam2					71612	116221	1.622925
trt13 sam3					71278	114619	1.608044
trt14 sam1	72.5	25	0.4	0.5	70165	115921	1.652126
trt14 sam2					67063	112378	1.675698
trt14 sam3					69887	113343	1.621814
trt15 sam1	87.5	10	0.2	2	61607	105909	1.719121
trt15 sam2					65745	108864	1.655863
trt15 sam3					73121	114840	1.570547
trt16 sam1	87.5	10	0.4	0.5	64954	114261	1.759094
trt16 sam2					67403	114870	1.704235
trt16 sam3					62096	112809	1.816702
trt17 sam1	87.5	25	0.2	0.5	66642	111929	1.679544
trt17 sam2					63504	109859	1.729964
trt17 sam3					61793	109584	1.773404
trt18 sam1	87.5	25	0.4	2	63914	110556	1.729769
trt18 sam2					55771	108908	1.952791
trt18 sam3					65650	112899	1.71971
trt19 sam1	80	17.5	0.3	1.25	68995	114538	1.660099
trt19 sam2					66222	114048	1.722209
trt19 sam3					53191	110289	2.073457
trt20 sam1	80	17.5	0.3	1.25	67982	112643	1.656941
trt20 sam2					60533	112085	1.85163
trt20 sam3					60429	111633	1.847341
trt21 sam1	65	17.5	0.3	1.25	68119	115127	1.690096
trt21 sam2					64547	113054	1.751493
trt21 sam3					68888	115055	1.670159
trt22 sam1	95	17.5	0.3	1.25	67385	113221	1.68022
trt22 sam2					61785	110945	1.795667
trt22 sam3					71097	114293	1.607568

Table A-1 (continued)

trt23 sam1	80	10	0.3	1.25	65924	113500	1.721672
trt23 sam2					71098	115376	1.622773
trt23 sam3					71619	115782	1.616654
trt24 sam1	80	25	0.3	1.25	73083	116294	1.591266
trt24 sam2					68320	114592	1.677295
trt24 sam3					66536	113100	1.69983
trt25 sam1	80	17.5	0.1	1.25	70845	115242	1.626674
trt25 sam2					66645	113672	1.705644
trt25 sam3					70657	114839	1.625307
trt26 sam1	80	17.5	0.5	1.25	67918	113480	1.67084
trt26 sam2					60398	110108	1.823032
trt26 sam3					62281	111063	1.783243
trt27 sam1	80	17.5	0.3	0.5	57023	109621	1.922409
trt27 sam2					62242	111014	1.783596
trt27 sam3					59527	109273	1.835672
trt28 sam1	80	17.5	0.3	2	61054	111342	1.823667
trt28 sam2					66271	112859	1.703
trt28 sam3					60917	111343	1.827794
trt29 sam1	80	17.5	0.3	1.25	64319	112118	1.743176
trt29 sam2					69997	114660	1.638072
trt29 sam3					65479	112697	1.721114
trt30 sam1	80	17.5	0.3	1.25	58927	109735	1.862229
trt30 sam2					63057	111138	1.762486
trt30 sam3					61731	110790	1.794741

Color properties for RSM

TableA-2: *L**,*a** and *b** values for each cleaning condition of recycling PLA flakes

Treatment	Temp C	Time(min)	Surface(%)	NaOH(%)	L*	a*	b*
flake control					72.84	-0.68	0.5
					71.94	-0.63	0.17
					68.84	-0.7	-0.17
trt01 sam1	72.5	10	0.2	2	71.39	-0.45	-0.45
trt01 sam2					70.99	-0.52	-1.62
trt01 sam3					69.08	-0.48	-1.03
trt02 sam1	72.5	10	0.4	0.5	73.19	-0.49	-0.61
trt02 sam2					70.27	-0.53	-1.21
trt02 sam3					68.21	-0.58	-1.24
trt03 sam1	72.5	25	0.2	0.5	72.63	-0.41	-1.46
trt03 sam2					70.42	-0.5	-1.41
trt03 sam3					71.38	-0.53	-0.31
trt04 sam1	72.5	25	0.4	2	71.56	-0.41	-1.28
trt04 sam2					73.07	-0.38	-1.25
trt04 sam3					73.67	-0.22	-1.69
trt05 sam1	87.5	10	0.2	0.5	73.12	-0.36	-2.36
trt05 sam2					74.61	-0.3	-1.23
trt05 sam3					74.13	-0.3	-0.67
trt06 sam1	87.5	10	0.4	2	72.76	-0.32	-1.09
trt06 sam2					73.61	-0.32	-1.16
trt06 sam3					75.16	-0.22	-1.63
trt07 sam1	87.5	25	0.2	2	73.88	-0.34	-1.72
trt07 sam2					73.33	-0.41	-0.67
trt07 sam3					72.46	-0.42	-1.05
trt08 sam1	87.5	25	0.4	0.5	72.64	-0.27	-0.69
trt08 sam2					76.92	-0.2	-0.61
trt08 sam3					76.89	-0.2	-0.85
trt09 sam1	80	17.5	0.3	1.25	74.15	-0.33	-1.43
trt09 sam2					73.39	-0.35	-1.32
trt09 sam3					71.87	-0.28	-0.36
trt10 sam1	80	17.5	0.3	1.25	72.82	-0.45	-0.58
trt10 sam2					69.41	-0.54	-0.39
trt10 sam3					69.79	-0.51	-1.07

Table A-2 (continued)

trt11 sam1	72.5	10	0.2	0.5	74.44	-0.31	-1.52
trt11 sam2					71.42	-0.22	-0.91
trt11 sam3					74.76	-0.28	-2.18
trt12 sam1	72.5	10	0.4	2	71.06	-0.44	-1.46
trt12 sam2					74.47	-0.36	-0.77
trt12 sam3					68.01	-0.44	-1.01
trt13 sam1	72.5	25	0.2	2	71.21	-0.37	-1.31
trt13 sam2					72.65	-0.28	-1.32
trt13 sam3					72.26	-0.36	-1.61
trt14 sam1	72.5	25	0.4	0.5	72.48	-0.4	-0.95
trt14 sam2					72.92	-0.41	-1.86
trt14 sam3					72.79	-0.35	-0.81
trt15 sam1	87.5	10	0.2	2	71.52	-0.36	-0.67
trt15 sam2					67.4	-0.5	-0.81
trt15 sam3					74.94	-0.34	-0.87
trt16 sam1	87.5	10	0.4	0.5	73.25	-0.39	-1.56
trt16 sam2					74.15	-0.34	-1
trt16 sam3					74.71	-0.29	-1.4
trt17 sam1	87.5	25	0.2	0.5	75.11	-0.17	-1.16
trt17 sam2					72.2	-0.36	-0.67
trt17 sam3					73.28	-0.25	-1.54
trt18 sam1	87.5	25	0.4	2	73.92	-0.27	-1.76
trt18 sam2					72.98	-0.35	-0.09
trt18 sam3					72.2	-0.38	-1.27
trt19 sam1	80	17.5	0.3	1.25	71.63	-0.39	-0.76
trt19 sam2					74.35	-0.36	-0.97
trt19 sam3					71.49	-0.39	-0.44
trt20 sam1	80	17.5	0.3	1.25	72.65	-0.35	-2.01
trt20 sam2					74.69	-0.31	-1.34
trt20 sam3					72.59	-0.42	-3.13
trt21 sam1	65	17.5	0.3	1.25	67.83	-0.68	-0.26
trt21 sam2					70.37	-0.49	-0.43
trt21 sam3					69.56	-0.39	-0.84
trt22 sam1	95	17.5	0.3	1.25	75.87	-0.3	-1.06
trt22 sam2					75.93	-0.18	-1.81
trt22 sam3					73.19	-0.24	-0.91

Table A-2 (continued)

trt23 sam1	80	10	0.3	1.25	72.73	-0.27	-0.88
trt23 sam2					71	-0.45	-2.4
trt23 sam3					71.82	-0.31	-0.83
trt24 sam1	80	25	0.3	1.25	71.17	-0.34	-1.48
trt24 sam2					74.88	-0.19	-1.57
trt24 sam3					73.06	-0.21	-1.97
trt25 sam1	80	17.5	0.1	1.25	74.65	-0.41	-1.53
trt25 sam2					74.23	-0.34	-1.5
trt25 sam3					73.48	-0.31	-1.02
trt26 sam1	80	17.5	0.5	1.25	70.63	-0.3	-0.36
trt26 sam2					75.59	-0.39	-2.37
trt26 sam3					71.3	-0.38	-2.2
trt27 sam1	80	17.5	0.3	0.5	73.91	-0.38	-0.59
trt27 sam2					71.36	-0.48	-1.14
trt27 sam3					72.17	-0.37	-0.41
trt28 sam1	80	17.5	0.3	2	71.28	-0.32	-0.72
trt28 sam2					72.3	-0.39	-0.89
trt28 sam3					67.86	-0.37	-0.4
trt29 sam1	80	17.5	0.3	1.25	73.32	-0.36	-0.82
trt29 sam2					70.72	-0.49	-1.56
trt29 sam3					70.32	-0.3	-1.27
trt30 sam1	80	17.5	0.3	1.25	71.59	-0.24	-1.01
trt30 sam2					72.13	-0.28	-1.18
trt30 sam3					72.91	-0.22	-0.74

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