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Formulation and Optimization of Algae-Filled Polylactic Acid Thermoplastic Compounds for Improved Biodegradation

by

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ABSTRACT

Conventional plastics derived from non-renewable petrochemicals – especially from fossil reserves – have become an integral part of human life because their structure can be chemically manipulated to obtain a wide range of properties and geometries necessary in nearly all industries. The volume and rate at which petroleum plastics are produced, used, and discarded has incited several significant issues related to human health, environmental conservation, and ecological biodiversity. To address these issues, many institutions have begun investigating solutions in both the development and end-of-life phases of plastic production and waste. In this thesis, a Chlorella-dominated algae mixture is dried and compounded at varying ratios with polylactic acid (PLA) at various particle sizes. The resulting blends were then characterized by thermal and mechanical analysis to examine processing and performance properties for injection molding. The blends were subject to weathering studies via standardized test methods and found that at 10, 20, and 30 wt.% algae, the blends are biodegradable with the rate of biodegradation directly correlated to the increasing concentration of algae.

Keywords: Thermoplastic compounding, algae, algal bioplastics, biodegradability, polylactic acid (PLA), injection molding

DEDICATION

To my mother, Jennifer Hartman, and my grandparents, Michael and Bushy Hartman, for their constant, unwavering love, support, and encouragement. Without you, I wouldn’t have had the courage to pursue my dreams. To my fiancé, Larry Byrd II., for his tireless cheering and reinforcement of my passions and goals. To Dr. Heather Broadhead, who fills too many roles to list, for her guidance, insight, creativity, and inspiration. I will carry with me all she has taught me and make the world a better place. To my senior design team member, Ethan Hanna, for having my back when I told him I want to spend my life playing with biomass. To the faculty of the USM School of Polymer Science and Engineering (SPSE) for the endless opportunities and “brain-stretching”. And finally, to the USM SPSE Class of 2023, together we have accomplished a number of great things, and this is only the beginning.

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LIST OF ABBREVIATIONS

CO_2	Carbon Dioxide
DSC	Differential Scanning Calorimetry
ERDC	U.S. Army Engineer Research and Development Center
PEG	Poly(ethylene glycol) diglycidyl ether
PHA	Polyhydroxyalkanoate
PLA	Polylactic Acid
RH	Relative Humidity
$T_{d5\%}$	5% Mass Loss Degradation Temperature
T_g	Glass Transition Temperature
TGA	Thermal Gravimetric Analysis
TSE	Twin-Screw Extrusion
USM	The University of Southern Mississippi
UV	Ultraviolet

CHAPTER I: INTRODUCTION

Conventional plastics derived from non-renewable petrochemicals – especially from fossil reserves – have become an integral part of human life because their structure can be chemically manipulated to obtain a wide range of properties and geometries necessary in nearly all industries. The volume and rate at which petroleum plastics are produced, used, and discarded has incited several significant issues related to human health, environmental conservation, and ecological biodiversity. To address these issues, many institutions have begun investigating solutions in both the development and end-of-life phases of plastic production and waste. Conventional plastics or petroleum-derived plastics (petro-plastics) are, as the name implies, derived from petroleum presenting a significant issue to the environment and sustainability. Global production, consumption, and discarding of petro-plastics presents a growing issue as the need for convenient, low cost materials and packaging grows. This issue is especially prevalent in a post-pandemic world that relied heavily on single-use commodities such as masks and gloves to limit the spread of disease for nearly two years. Plastics Europe reports that after the stagnation in production experienced globally due to the COVID-19 pandemic in 2020, global plastic production increased from 375.5 million tons to 390.7 million tons in 2022.[1] Of this 390.7 Mt only 8.3% accounted for post-consumer recycled plastics.[1] This 8.3% does not account for all plastic waste recycled globally, but rather the materials produced from the recycled material that successfully navigates the cleaning and reprocessing cycles to be produced into new products.

1.1 Recycling

Recycling itself faces a number of issues preventing the actualization of a wholly circular economy. Recycling on any scale is more expensive and requires more resources than producing virgin material. However, large scale recycling experiences many obstacles such as cleaning and sorting the waste appropriately and the vast difference in additives and processing agents in each soda bottle or plastic spork all being processed together greatly impacting the properties and quality of the polymer chains. Even in products that are composed of similar polymeric backbones, the variable of additives presents a significant barrier to the application of “regrind” or recycled polymer material for different products. Additionally, there are many different forms and stages of “recycling” such as mechanical recycling, feedstock recycling, energy recovery, and reuse.[2]

Mechanical recycling is the most conventional method in which materials are collected post-consumer and reincorporated into the material stream. This method faces many expense and quality related issues as many conventional polymers cannot be reprocessed indefinitely. Ultimately, these materials will experience significant material properties degradation over repeated cycles of processing normally consisting of shredding or grinding and then re-extruding the material into a secondary raw feedstock in the form of flakes, pellets, or granules that can be used for consumer goods manufacturing.[3] Repeated shear and heat trauma to the polymer chains renders the material unable to be reincorporated even into primarily virgin systems due to the necessary quality parameters of strength, purity, or durability the application requires.[2] Additionally, mechanical recycling methods tend to rely upon the consumer to clean and sort their waste appropriately when discarding it. A number of issues contribute to this constraint such as the lack of education surrounding what grades of materials are recyclable and the lack of incentive for performing extra labor domestically to decrease the expense of recycling materials industrially. A common issue in this regard is the discarding of thin films such as grocery bags or trash bags that are non-recyclable. A study conducted by the European Commission Joint Research Centre found that the quality of input waste material has a significant impact on sorting and recycling rates.[3] A shared issue among the participating plants is the presence of thin films in input material that, if not removed in the pre-sorting stage, entangle easily causing blockages.[3] Additionally, flexible post-consumer packaging often gets stuck in sensors along the line inhibiting the sorting process.[3] Ultimately, the overall end-of-life recycling rate equated a total of 14% when waste exported outside of the European Union was not considered. This presents another issue with regards to recycling, considering what becomes of the non-recyclable waste. Due to the significant technological and practical limitations on conventional recycling methods, in many cases, waste meant to be recycled is instead transported to landfills. Up to 80% of plastic waste is mismanaged and discarded into the environment in many countries such as China, Sri Lanka, Vietnam, and the Philippines.[4]

Feedstock recycling describes what is more commonly known as chemical recycling, where a polymer is returned to its oil or hydrocarbon components for use as a raw feedstock for polymer production. This method encompasses a broad classification of reactions such as glycolysis, alcoholysis, hydrolysis, methanolysis, gasification, and cracking.[5] This method is not commonly feasible for post-consumer materials due to the significant variance in additive content in plastic waste and higher degree of impurities.

Energy recovery describes the process of incinerating materials to recover inherent energy. This is a convenient method to dispose of materials that are unable to be reintroduced back into production. However, this method experiences drawbacks such as high greenhouse gas emissions and significant energy consumption. Reuse simply describes the repurposing of materials, often on the consumer end. Examples of this method include returning glass milk bottles or repurposing containers.[2] Plastic is generally more difficult to reuse compared to glass, metal, or ceramic products as plastic products generally do not exhibit the durability or longevity of alternative materials.[2]

Recycling is not yet efficient enough to instigate a wholly circular economy. Recycling is restricted by its high cost to maintain, the lack of knowledge surrounding recommended recycling practices, low control over purity, high variability of additive content, and limited reprocessability of conventional petro-plastics. Therefore, a shift in focus from reprocessing petro-plastics to designing similarly-performing materials that can be safely disposed of in the environment was made.

1.2 Bioplastics

As previously defined, petro-plastics describes a sector of materials derived from non-renewable fossil fuels. Alternatively, the term “bio-based plastics” can be used to describe the sector of materials derived from renewable materials. These materials are commonly referred to as bioplastics. However, the term bioplastics is also used to describe polymers in the medical sphere or biocompatible polymers. For the purpose of this thesis, the term bioplastics is assumed to refer to plastics derived from renewable feedstocks.

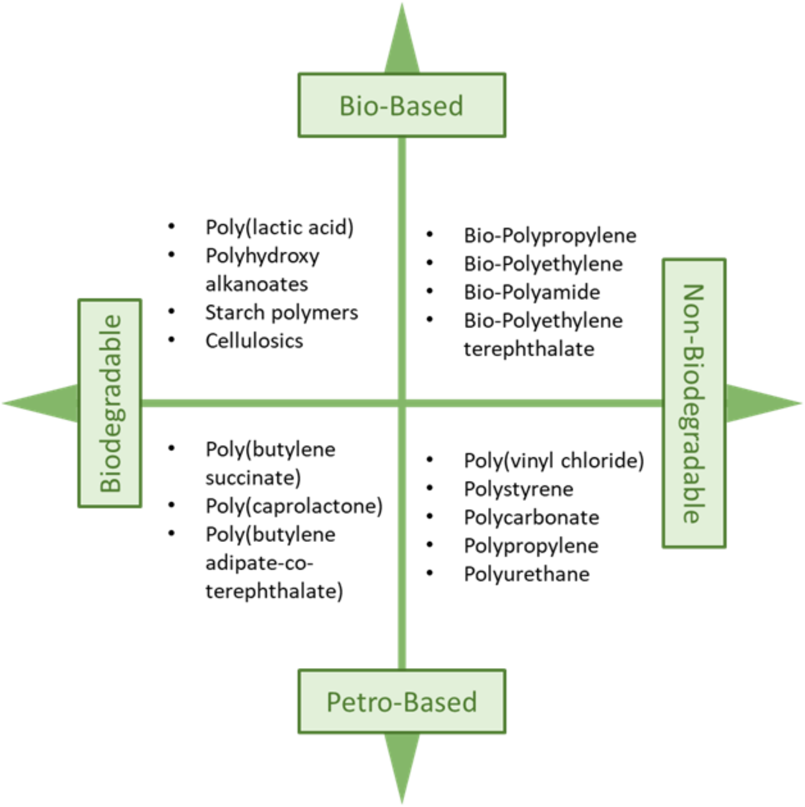


Figure 1. Classification of polymers.[6]

These plastics can be further classified by their ability to degrade into natural or non-toxic components. The classifications are described as biodegradable bioplastics, non-biodegradable bioplastics, biodegradable petro-plastics, and non-biodegradable petro-plastics, examples of which can be seen in Figure 1. Biodegradation describes the natural process by which organic chemicals in the environment are reduced to simpler compounds and redistributed through the biosphere via elemental cycles.[7]

Non-biodegradable petro-plastics experience degradation under a wide variety of conditions, however, these materials break down into micro-, and nano-plastic particles not capable of redistribution via elemental cycles. The plastic particles raise cause for concern as evidence of their integration into water, food, and airways has been discovered. Exposure to these plastic particulates has been linked with increased risk of cardiovascular and respiratory diseases furthering the need for biodegradable materials.[8]

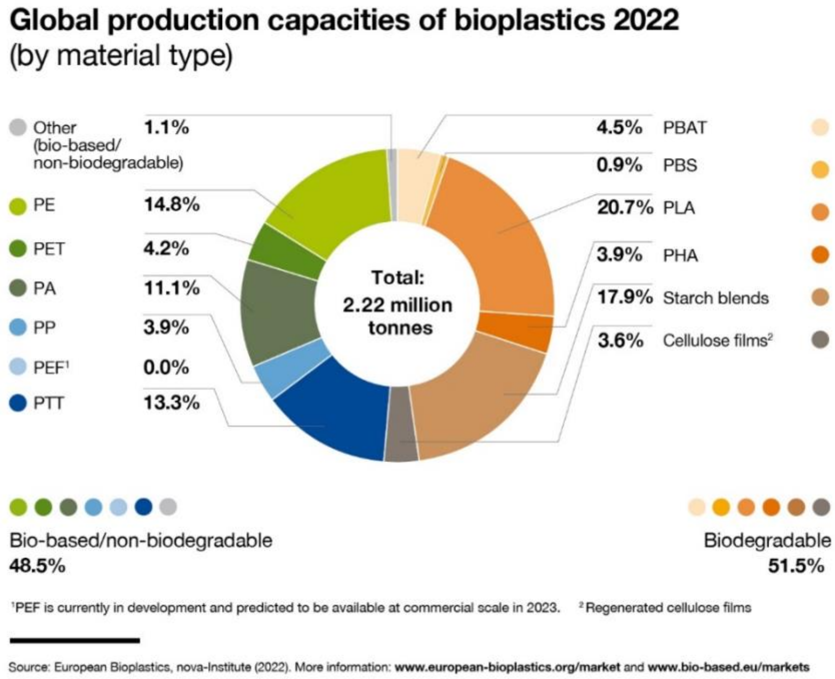


Figure 2. Global production capacities of bioplastics 2022 (by material type).[9]

An estimated 2.22 million tons of bioplastic was produced globally in 2022 as shown in Figure 2.[9] This figure is projected to rise to 6.3 Mt by 2027 as bioplastics begin to be incorporated in a variety of fields from packaging, consumer electronics, catering products, automotives, agriculture, toys, and textiles.[9] There are a number of different methods to develop and process bioplastics. Bioplastics can be derived from a number of renewable sources such as corn, potatoes, sugar cane, vegetable oil, hemp, henequen leaves, and banana stems.[10] Bioplastics can be derived through chemical treatment of these terrestrial crops, or they can be developed utilizing micro-organisms such as algae. Starch-based bioplastics currently dominate the bioplastic market as starches can be derived at low cost from common terrestrial crops previously mentioned such as corn, sugar cane, and potatoes. Algal autotrophic cultures are also utilized for the development of feedstocks as certain algal species such as Chlamydomonas are known to accumulate carbohydrates at higher metabolite ratios.[11] Utilizing micro-organisms, such as algae, as starch feedstocks have gathered attention due to the low cost, high production rate, and CO_2 mitigatory properties of utilizing algae rather than food crops. The current market leader for starch-based bioplastic is polylactic acid (PLA) as discussed in the following section.[1,12] Incorporation of biomass into plastics is also possible via processing rather than the previously discussed synthetic routes. Processing is an excellent method to utilize the waste streams from the synthetic routes of biorefining. Often for the micro-organism production of PLAs, PHAs, and other starch-derived bioplastics the carbohydrate metabolite portions are prioritized leaving residual protein. The protein metabolites of micro-organism feedstocks such as algae exhibit higher processing capacity than its lipid or carbohydrate components. This processing can occur in a number of ways, but the method utilized for this thesis is compounding.

The term compounding typically describes the combination of particulate fillers of varying properties into thermoplastic melts. The success of this process is determined by a combination of shear and heat parameters, ancillary equipment such as pre-blending equipment or additives, controlled feeding equipment into and out of the compounder, and downstream cooling and pelletizing of the compounded material.[13] The alteration of ancillary equipment and in turn, process design, is vital to material compounding. The geometry and dimensions of feeding equipment vary greatly and allow for the extruding of feedstocks of different compositions and geometries. Cooling configurations are vital to the ability to collect and pelletize the extrudate. Cooled water is preferred for simpler, cost-effective systems. The extrudate temperature typically must be below its glass transition temperature to be brittle enough to be fed through a pelletizer via grip wheels to be chopped into pellets via a high-speed rotary blade.

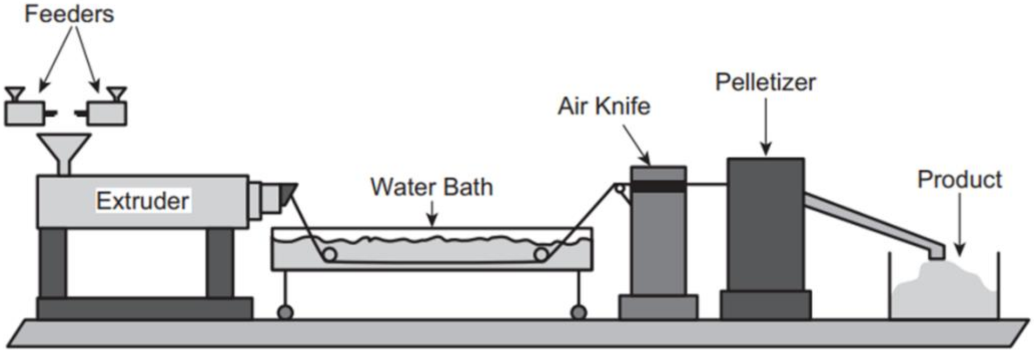


Figure 3. Diagram of the compounding process utilizing a water bath, air knife, and strand pelletizer.[14]

An understanding of the chemistry, particle size, bulk densities, and various other properties of materials is also key to successfully compounding materials with desirable properties.[13] For this thesis, Twin-Screw Extrusion (TSE) was utilized to compound the filler and thermoplastic materials. TSE, distinct from single-screw extrusion by the presence of dual screws enabling customizable rotatory parameters, is a solvent-free, continuous process utilizing dry polymers as reactive phases. TSE is used for a broad range of applications such as processing food, manufacturing thermoplastic materials, and early pharmaceutical applications.[15] To address thermoplastic compounding and modification, TSE is used to manufacture polymer blends to modify a vast range of polymeric and economic properties such as pigment, conductivity, impact strength, ductility, and cost. This process is illustrated with ancillary equipment in Figure 3. The quality and properties of a compounded blend can be attained by a number of different methods such as altering processing parameters or through the incorporation of additives. The goal for this project is to utilize these methods to successfully incorporate a critical load of algae into an algae-polylactic acid compound to improve the biodegradability of polylactic acid.

1.3 Polylactic acid

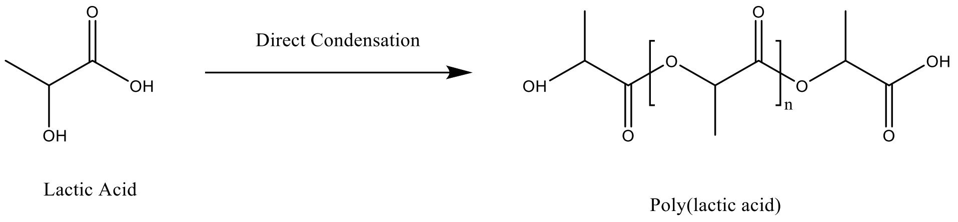


Figure 4. Direct condensation reaction of poly(lactic acid).

Polylactic acid (PLA) is a thermoplastic polyester derived from the direct condensation reaction of lactic acid in organic products such as corn and sugar cane as illustrated in Figure 4.[12] However, the use of terrestrial food crops for the development of bioplastics has been under review due to the adverse environmental effects associated with land use, cost, and competition with food crops. Micro-organism cultivation and harvesting provides an alternative feedstock for the production of starch for PLA synthesis. Algal species are a primary micro-organism studied for this purpose as the metabolite concentration production is highly tunable with the modification of their cultivation conditions allowing for the selective accumulation of carbohydrate metabolites over protein and lipids.[11]

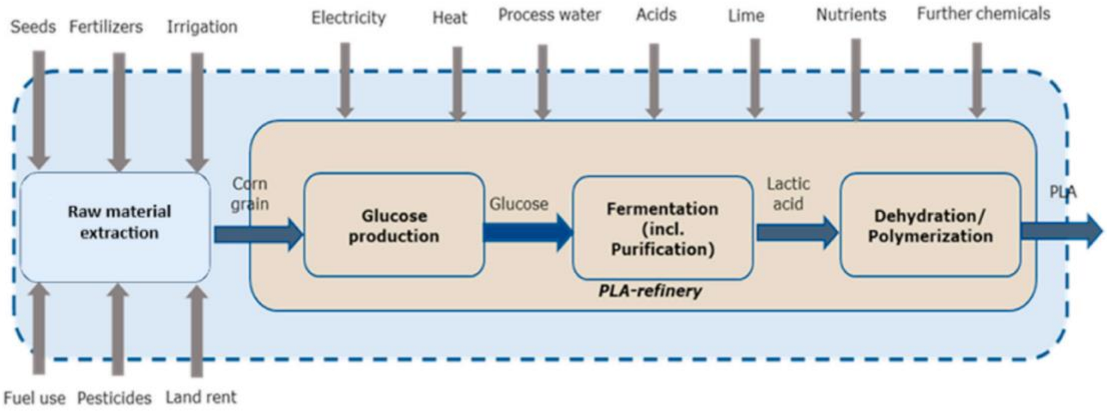


Figure 5. Production process of corn-based PLA.[12]

The production process of PLA is highly variable as each process is designed to the feedstock source. PLA is primarily derived from corn-starch, and typically involves the following: raw material extraction, glucose extraction, fermentation, and polymerization as seen in Figure 5. Corn-based PLA, while currently scaled to meet global need, is more expensive to produce than petro-based plastics. The production cost is strongly dependent on the selection of raw material and the technological progress in production of PLA. While corn is generally considered low cost to produce with the costs restricted to the cultivation and harvesting, the production of oil is significantly less expensive. The primary source of PLA's higher cost is associated with the fermentation and purification of corn-derived starch comprising approximately 50% of the total cost.[16] The production of PLA, while more expensive than petro-based plastics, requires 25-55 % less energy and is estimated to be further reduced to less than 10% of petro-based plastic energy production consumption in the future.[17]

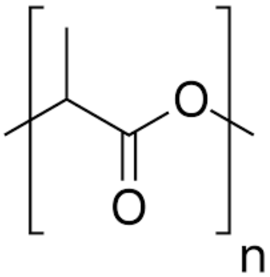


Figure 6. PLA structure.

PLA's simple chain structure illustrated in Figure 6 enables a significant degree of manipulation of its properties and performance. PLA can be processed by a number of conventional techniques such as injection molding, film extrusion, blow molding, thermoforming, fiber spinning, and film forming.[17] Currently, PLA is utilized for a number of applications such as food packaging, 3-D printing filament, and medical equipment due to its excellent biocompatibility.[17] PLA currently exhibits the most significant market share and guarantees the largest growth potential in comparison to other bio-based and biodegradable polymers on the market.[12] PLA is able to biodegrade by undergoing a process known as hydrolysis. This process occurs in two stages, initially featuring random non-enzymatic chain scission of the ester linkage in the polymer backbone upon exposure to high temperatures and moisture.[17] This reduces the molecular weight (Mw) of the polymer to lactic acid and low Mw oligomers that are able to engage with natural elemental cycles and metabolize into carbon dioxide and water.[17] The degradation rate of polymer systems is influenced by a number of variables such as particle size and shape, temperature, moisture, crystallinity, and potential additives.[17] PLA has been the subject of much debate as to the actual viability of its biodegradable properties. Variability in degradation testing conditions and environments has led to contradicting reports as to the biodegradability of PLA. UV radiation, moisture, temperature, micro-organism behavior, and sample geometry all greatly impact the degradation rate of PLA in different environments. Degradation of PLA has been reported to take anywhere from 12 weeks to 5 years in various conditions.[13,17] Additionally, samples in the form of thin films are expected to degrade at a much higher rate than larger or more thick samples resulting in data that may not be applicable to products typically made from PLA.

PLA's excellent biocompatibility, processability, flexibility, strength, and modulus, render it technically competitive with many conventional plastics currently on the market.[17] However, PLA exhibits poor toughness, generally slow biodegradation rate in environmental conditions, and exceeds the cost of petro-plastics to produce.[17]

1.4 Algae

"Algae", a term commonly used to encompass all marine macroalgae or seaweeds, describes a highly diverse class of aquatic photosynthetic organisms that consist of an estimated 30,000 – 1 million species.[18] In their natural environments, algae serve as oxygen producers and as a fundamental food source for nearly all marine ecosystems. Algae are biologically distinct from terrestrial and other aquatic vegetation by their extensive variety of photosynthetic pigments, lack of vascular system, and significant biodiversity.[19] The photosynthetic pigments they possess are significantly more varied than those of any known terrestrial plants.[20] In fact, some algal species have been observed to be 10% - 20% more photosynthetically efficient than conventional terrestrial plants making them an ideal resource for CO_2 mitigation.[20] Algal organisms are very hardy, they can thrive in nearly any marine environment and can withstand extreme temperatures, irradiation, drought, and salinity. Their hardiness enables them to be capable of not only growing in both freshwater and saltwater environments, but also in industrial wastewaters.[21,22] Algae experience a rapid reproduction rate, nearly doubling in mass in anywhere from 3.5 to 24 hour rates.[23] Algae are comprised of proteins, carbohydrates, lipids, nucleic acids, and free fatty acids (triglycerides, phospholipids, and glycolipids).[24] These components vary in concentration by species, but are the primary resource extracted from algae for a variety of applications. Algae classification is generally divided into three categories, macroalgae, microalgae, and cyanobacteria. Cyanobacteria are typically regarded as a subcategory of microalgae, distinguished only by their prokaryotic nature. The focus of this research will be narrowed to exclusively the scope of microalgae.

Microalgae or “microphytes” are microscopic, unicellular organisms that are typically broken down into the following categories: Diatoms (Bacillariophyceae), Green algae (Chlorophyceae) and Golden algae (Chrysophyceae). Microalgae range in size from a few micrometers to several hundred micrometers and are typically 1-30 µm in diameter.[25] Microalgae do not have roots, leaves, or stems like their macroscopic counterparts, instead they exist in the following ways: individually, unicellular chains, or groups.[19] Microalgae can function as autotrophs, heterotrophs, or mixotrophs. Autotrophic organisms use energy derived from photosynthesis, heterotrophic organisms use organic compounds as CO_2 and energy sources allowing them to grow even in the dark, and mixotrophic organisms can utilize a mixture of different sources of energy and carbon.[26] Higher metabolic yields can be obtained for a variety of microalgae under specific conditions. Chlorella and Spirulina species are the two most commonly reported algal species to be utilized as fillers in thermoplastic compounding due to their high protein content.[27,28] It is crucial to understand the initial composition of the strain in order to successfully maximize cultivation and conversion potential. For the purpose of compounding, algae species with higher contents of protein metabolites are preferred. The compounding process requires high degrees of heat and shear, under these conditions’ fatty acids, carbohydrates, and lipids tend to burn off more quickly than proteins.

Cultivating algae is a simple process that typically requires little upkeep varying on the method chosen. Cultivation occurs in low-cost mediums of fresh water, salt water, or even wastewater. For wastewaters that are unsafe for human consumption, algae can act as a natural bioremediator, removing the nutrients (nitrogen, carbon, phosphorus, etc.)

via biosorption removing harmful toxins and neutralizing acidic waters.[29] Essentially, the inorganic components residing in wastewater serve as a nutrient substrate for algal biomass generation. The successful cultivation of both micro- and macro- algae is primarily reliant on species and composition. Thus, the cultivation method is entirely dependent on the strain of algae and the desired primary metabolite. It has been determined that parameters such as pH, temperature, light intensity, salinity, CO_2, nutrients, culture density, and water circulation have significant effects on the cultivation yield.[19,25] It has been reported that by altering parameters such as light, temperature, and CO_2 access, algae metabolite yield can be improved. Algal cultivation methods are divided into two distinct methods, open-pond or raceway ponds, and photobioreactors. Raceway ponds are named for their distinct "racetrack" shape and for the presence of some form of pump or paddle that circulates the water.[24] This method is also referred to as "natural cultivation". These systems are typically shallow ponds, tanks, or circular ponds filled with water to create an outdoor cultivation system. While economically advantageous and simple to construct and operate, these systems consume large quantities of land, allow limited to no control over environmental conditions, experience rapid evaporation, and are susceptible to contamination.[24] Photo-bioreactors prioritize parameter control and sterilized apparatuses. There are many different configurations of this method, but they all share the same technique. Prepared algae samples are pumped through large acrylic or glass tubes and recirculated continuously to aid uniform photosynthesis and algae growth.[24] To improve biomass yield, light emitting diodes have been applied to incorporate more light into the system effectively increasing the rate of photosynthesis.[24] Additionally, having more control over parameters such as pH, temperature, light intensity, salinity, CO_2, nutrients, culture density, and water circulation enable the cultivation process to be specifically designed to each different strain of algae and thus optimize its metabolite yield. These fully sealed systems eliminate potential contamination, reduce evaporation, allow for better control over reaction parameters, and eliminate reliance on good weather or day-time cultivation as these systems can uniformly cultivate algal cultures even overnight.[24] The main disadvantages to this type of system are the large energy requirements, high expense, difficulties scaling up, difficulties cleaning some systems, cell damage from shear stress, and hinderance of environmental CO_2 mitigating effects.[24]

Algal feedstocks are currently applied in a number of fields such as absorbents, biofuels, cosmetics, pharmaceuticals, food dyes and additives, paints, electronics, and bioplastics. Algal biomass can be utilized to produce bioplastics by blending algal biomass with petro-based plastics, blending algal biomass with bioplastics, or utilizing algal biomass as a feedstock for starch production as previously discussed.[28] The incorporation of algae into bioplastics via compounding or blending has been reported to offer several advantages such as reducing carbon dioxide emissions, reducing food waste, and reducing energy consumption of processing. In the field of thermoplastic compounding, algae biomass as a filler has been reported to act as a plasticizer increasing the processability and melt flow properties of thermoplastics.[29] Additionally, the small particle size of algae biomass, typically in the 50 μm range, allows for improved mixing with thermoplastics.[30] Algae biomass, when used as a filler, has also been reported to improve biodegradability of PLA bioplastic.[31]

Algae as a biomass filler is especially advantageous in comparison to alternative biomass sources due to the lack of competition with terrestrial food crops, CO_2 mitigation capacity, highly manipulable metabolic contents, high speed and low cost cultivation, and microbial properties increasing the rate of biodegradation in environmental conditions.

1.5 Characterization Methods

1.5.1 Thermal Gravimetric Analysis (TGA)

Thermogravimetric Analysis is a quantitative analytical technique that is utilized to evaluate thermomechanical properties such as thermal stability, moisture content, volatile content, oxidative stability, thermal degradation, and estimated lifetime. TGA measures the mass lost from a given sample as a function of temperature. For this work, TGA was used to determine the 5 % degradation temperature of materials and blends. The degradation temperature ($T_{d5\%}$) describes the point at which the sample has lost 5% of its original mass due to thermal degradation. This value is useful for compounding to prevent destroying the feedstocks and is useful for further thermal characterization to prevent destroying thermal characterization equipment such as DSC.

1.5.2 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry is a thermal analysis technique that evaluates the relationship between a material's heat capacity and temperature in different environments. As a sample is subjected to thermal cycles, its heat capacity is measured as changes in heat flow allowing for the detection of glass transition, crystallinity, and melting. For this work, DSC was used to examine the crystallinity, melt behavior, and glass transition temperature (T_g) of materials and blends. The glass transition temperature describes the point at which amorphous or semi-crystalline polymers, such as PLA, transition from a glassy state to an amorphous state. This value is directly related to the physical and mechanical properties of materials.

1.5.3 Optical Microscopy

Optical microscopy was collected of the algae feedstock, PLA pellets, PLA Hammer-milled, PLA Cryo-milled, and pelletized PLA. The pelletized PLA is not a feedstock utilized for this project, optical microscopy was collected for this material to report the particle size and distribution of the compounds made during this study as they were all pelletized via the same system. It is important to note that the speed of pelletization has an effect on pellet size and that the pelletization speed changes for different materials as the various blends extruded at different torques. These variations are assumed to be negligible for this thesis. Scale bars are included for all PLA feedstocks at 1.00 mm. Microscopy of the algae feedstock has been included for the sole purpose of comparison to the other blends, for the purpose of illustrating particle size disparity without violating professional disclosure.

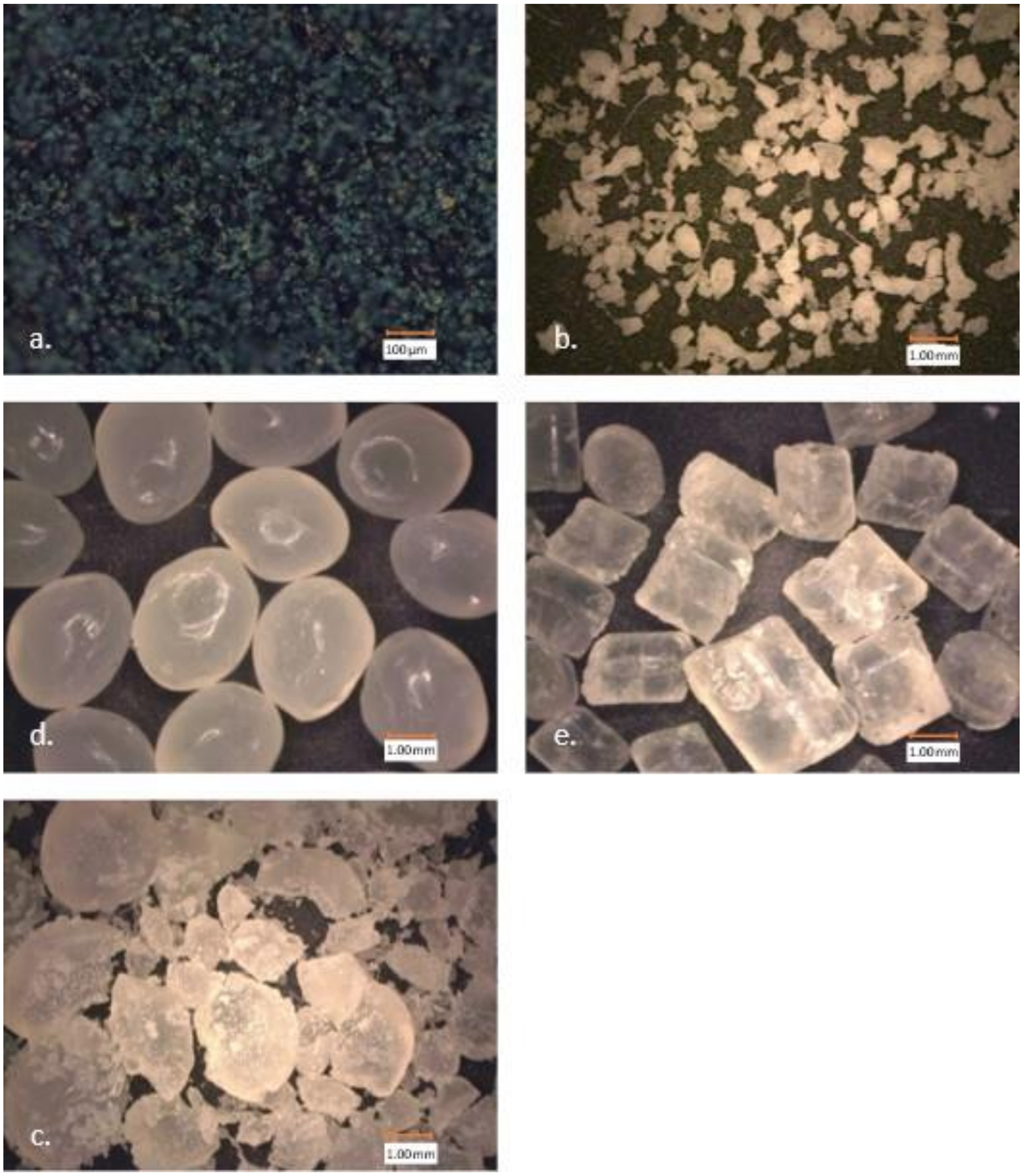


Figure 7. Optical Microscopy of a. algae, b. PLA-Cryo-Milled, c. PLApellets, d. PLApelletized, & e. PLA-Hammer-Milled.

Material	Particle Distribution (mm)	Avg. Particle Size (mm)	σ (± mm)
PLA Pellets	1.63	3.654	0.444
PLA Pelletized	3.35	2.842	0.782
PLA Hammer-milled	3.84	1.066	0.997
PLA Cryo-milled	0.92	0.440	0.258

Table 1. Particle Size.

CHAPTER II: EXPERIMENTAL

2.1 Materials

A Chlorella-rich blend of dried and ground algae was obtained from BLOOM. Binding agents, soybean oil and poly(ethylene glycol) diglycidyl ether (PEG) were obtained from The Chemical Company and Royce International, respectively. Poly lactic acid (PLA) pellets were Nature Works Igneo 4043D donated by ERDC. Hammer-milled PLA (PLAhm) samples were hammer-milled with a Micron Powder System Bantam Mill to a particle size of 1.066 mm ± 0.99. Cryo-milled PLA (PLAcm) samples were attrition milled under cryogenic conditions using a Micron Powder System Bantam Mill reducing to a particle size of 0.44 mm ± 0.26. All materials were dried in a Thermotron Environmental Chamber under 25 % relative humidity (% RH) and 60 °C prior to compounding.

2.2 Preparation of Blends

Algae (wt.%)	PLA (wt.%)	PLA Type	PEG (wt.%)	Soy Oil (wt.%)
9.5	89.5	Pellet	1	
9.5	89.5	Pellet		1
20	80	Pellet		
10	90	HM		
20	80	HM		
30	70	HM		
10	90	CM		
20	80	CM		
30	70	CM		

Table 2. Table of all compounds blended. (HM referring to “Hammer-milled” and CM referring to “Cryo-milled’)

Dried materials were weighed and blended manually via the weight ratios in Table 2. All blends were compounded on a Co-rotating Thermo Scientific PRISM Twin Screw Bench Top Extruder 16TC. The zone temperatures, screw speed, and torque are reported in Table 3. A volumetric feeder was used initially but was later substituted for a vibratory feeder due to feeding issues caused by the disparity in particle dispersion and use of powdered feedstocks. Blends were compounded at set parameters listed in Table 3.

Composition Ratios (wt.%)					Thermal Zones (°C)				Shear Parameters	
Algae	PLA	PLA Type	PEG	Soy Oil	T1	T2	T3	T4	Torque (Nm)	Screw Speed (rpm)
9.5	89.5	Pellet	1		210	210	210	195	-	200
9.5	89.5	Pellet		1	210	210	210	195	-	200
20	80	Pellet			210	210	210	195	-	200
10	90	HM			195	195	195	185	8.9-9.5	200
20	80	HM			195	195	195	185	9.2-9.8	200
30	70	HM			195	195	195	185	10.2-10.8	200
10	90	CM			195	195	195	185	9.5-10.2	200
20	80	CM			195	195	195	185	9.6-10.4	200
30	70	CM			195	195	195	185	9.7-10.5	200

Table 3. Processing parameters of all blends.

Feedstock:	ρ_{bulk} (g/mL)
PLA Pellet	0.731
PLA Hammer-Milled	0.655
Algae	0.542

Table 4. Bulk density calculations

CHAPTER III: COMPOUNDING

Compounding exclusively the PLA pellets and algae in a volumetric feeder resulted in a significant phase separation between the algae and the pellets due to the large disparity in particle size as illustrated in Table 1. Despite the material being mixed prior to pouring in the hopper, the algae particles sifted towards the bottom resulting in a primarily burnt algae gel-like material unable to be collected or pelletized. To remedy this phase separation, an identical blend was prepared with a 1 wt.% PEG binding agent to adhere to the algae to the pellets. This produced a gritty material that yielded a smoky odor while processing as if the material was burning in the barrel of the extruder. It was determined that the processing temperature for this blend was significantly higher than the degradation temperature of PEG and that the odor was in fact the PEG degrading in the barrel. A binding agent with a compatible processing temperature, soybean oil, was selected to replace the PEG binding agent. A 10 wt.% Algae-PLA-Soy blend was achieved. When attempting to increase the concentration of algae to achieve a 20 wt.% blend of Algae-PLA-Soy, the occurrence of "bridging" was observed. The algae and binding agent formed a tunnel along the auger preventing pellets from travelling along the screw and into the feed throat of the barrel effectively prohibiting material compounding.

To address these issues, a number of changes were made to the process. To reduce the possibility of bridging occurring, the volumetric feeder was replaced with a vibratory feeder. A vibratory feeder reduces the possibility of bridging by eliminating the auger-method of feeding material into the extruder. The auger-method of feeding functions by utilizing a large screw to catch and convey material through a cylinder casing housing the screw and into the barrel of the extruder. While this method provides a more consistent feed rate, it is not amenable for powder systems. A vibratory feeder utilizes high speed vibrations and gravity to convey material into the barrel of the extruder. This method is typically favored for small-particle or powder systems.

Figure 8. Hammer-mill screen after Hammer-milling session.

Despite the use of binding material to adhere the algae to the PLA pellets, significant phase dispersion was observed. To remedy this, binding agents were removed altogether in favor of particle size reduction of the PLA pellets. In reducing the particle size of the PLA, a higher dispersion was achieved and the disparity in bulk density was reduced. It is important to note that this issue could also have been addressed by processing and pelletizing the algae to increase its particle size to be comparable to the PLA pellets. However, this pathway runs the risk of destroying algae in the process due to the high heat and shear on a material that does not experience viscous flow in a ground and dried form. Particle size reduction of the PLA pellets initially was performed via hammer-milling. However, due to the amorphous nature of PLA, and the strong spherical geometry of the pellets the PLA quickly agglomerated in the instrument under the heat of friction and permeated the screen of the apparatus pictured in Figure 8. The hammer-mill screen acts as a control measure to ensure that the product is a specific particle size as typically the material must be small enough to exit out of the screen. The permeation of the screen resulted in the widest distribution of particle size among all feedstocks with a distribution of 3.84 mm. To attain a smaller, more consistent particle size, cryogenic attrition-milling was performed. Attrition-milling also known as “disk-milling” consists of two counter-rotating, metal disks that abrasively press material between them at high shear until the resulting particles are small enough to fall between the blades into an awaiting collection pan. The attrition-milling was conducted under cryogenic conditions to avoid agglomeration of PLA from the heat of friction and yielded a distribution value of 0.92 mm. The final adjustment was a reduction in processing temperature to reduce the likelihood of burning the algae at higher concentrations as illustrated in Table 3.

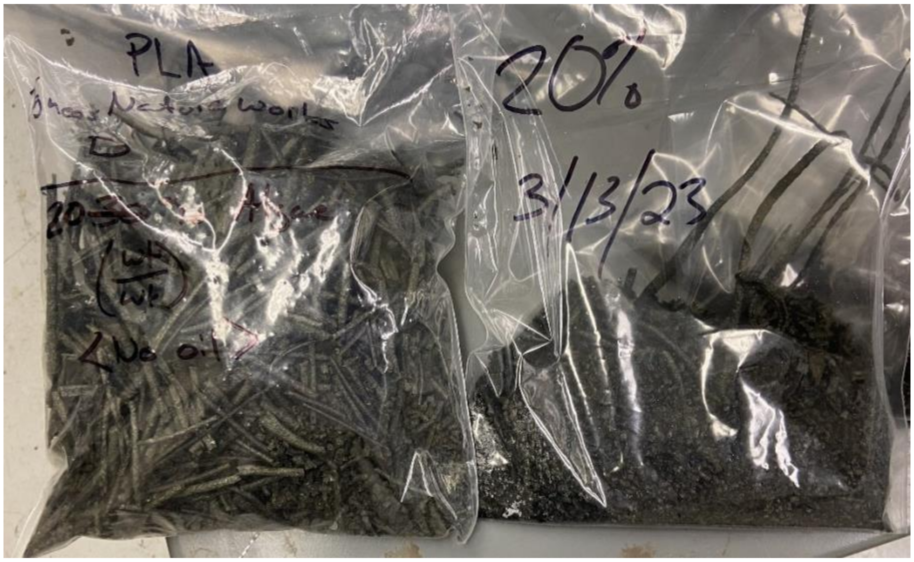


Figure 9. 20 wt.% Algae-PLAhm (left) and 20 wt.% Algae-PLAcm (right).

Under the adjusted conditions, 10, 20, and 30 wt.% Algae-PLAhm blends were processed via TSE. Material for each ratio was collected, but due to the grit-like consistency of the blends, they were unable to be pelletized and were instead ground up manually into a processable size for thermal and mechanical sample preparation. The consistency of the resulting blends is illustrated in Figure 9. The processing of the 10, 20, and 30 wt.% Algae-PLAcm, however, resulted in a smooth, pelletizable extrudate. The processing of the Algae-PLAcm blends were far less labor intensive than the Algae-PLAhm indicating potential for industrial production in the future.

CHAPTER IV: PROCESSING

30 wt.% algae is established to be the critical load of algae for this work. Compounding at 30 wt.% yielded several issues that prevented attempts to continue incorporating more algae biomass into the system such as off-gassing while extruding as the algae was being subjected to high temperatures and shear, the significant increase in brittleness of the blends making them difficult to work with and reducing their potential for higher strength applications, and ultimately time-constraints. Off-gassing during processing was more often observed with higher loads of algae. The odor produced while processing was exceedingly pungent and could potentially limit the scale up of these systems. Both Algae-PLAhm and Algae-PLAcm blends at all ratios were processed via melt-pressing and injection molding via hand-press similar to Figure 10.

Algae-PLAhm and Algae-PLAcm both exhibited improved processability in comparison to virgin PLA via melt-pressing and injection molding. Higher algal concentration of the blends decreased the quality of the processed product both by injection molding and melt-pressing. At higher loads of algae (20 and 30 wt.%), melt-pressing yielded panels that were brittle enough to break manually. Reduced particle size of PLA feedstocks, and thus higher dispersity of compounded blends exhibited a significant increase in brittleness. Blends of algae and hammier-milled feedstock yielded slightly higher flexibility and improved processability at higher loads of algae than the algae and cryo-milled feedstock blends. At 30 wt.% Algae-PLAcm, melt-pressed samples were unable to be harvested as they shattered in the panel mold upon extraction. Injection molding of 30 wt.% Algae-PLAcm was not attempted due to the observations from the melt-pressed samples. When melt-pressing 30 wt.% Algae-PLAhm, the panels were brittle but less so than the 30 wt.% Algae-PLAcm as the samples were able to be collected prior to melt-pressing with the hammer-milled blend.

Figure 10. Hand-press injection molder.

At 30 wt.% Algae-PLAcm, melt-pressed samples were unable to be harvested as they shattered in the panel mold upon extraction. Injection molding of 30 wt.% Algae-PLAcm was not attempted due to the observations from the melt-pressed samples. When melt-pressing 30 wt.% Algae-PLAhm, the panels were brittle but less so than the 30 wt.% Algae-PLAcm as the samples were able to be collected prior to melt-pressing with the hammer-milled blend. The slightly higher processability of the hammer-milled blends is attributed to a medium dispersion, between the cryo-milled and the PLA pellets, of the hammer-milled PLA allowing “pockets” of algae to form during processing increasing the material’s ability to absorb and sustain force.

Injection molding the 30 wt% Algae-PLAhm, resulted in the material experiencing off-gassing and swelling in the mold system. Both PLAhm and PLAcm exhibited swelling behavior within the mold among other processing and material issues. This is uncommon in thermoplastic materials as typically the blends shrink in the mold as they cool. Additionally, despite the use of mold-release agent prior to injecting, the 30 wt.% Algae-PLAhm blend cracked in a larger product mold cavity (golf-tee mold) leaving residual material that later could only be removed by dissolving in chloroform solvent. Injection molding of up to 20% was achieved, but it was agreed that currently, only the 10% Algae-PLAhm blends exhibit significant enough processability for commercialization of any kind.

CHAPTER V: VALIDATION DATA & DISCUSSION

5.1 Thermal Characterization

5.1.1. Thermal Gravimetric Analysis

TGA measurements were performed with a TA instruments Q550 equipped with an auto sampling carousel. The temperature range for all blends was 0-800 °C at a heating rate of 10 °C/min. in ambient conditions. Triplicate statistical repeatability was not able to be attained due to timing constraints. Representative TGA plots for each material are depicted in Figure 11. The degradation temperatures at 5 wt.% ($T_{d5\%}$) of the materials were determined using TA Instruments Trios software and reported in Table 6. TGA data for the 30 wt.% Algae-PLAcm does not include the ambient to 100 °C range. This is attributed to not allowing the furnace to cool completely before beginning another data collection period. Therefore the 30 wt.% Algae-PLAcm was unable to be determined or estimated. The curve for this data is still included for comparison to the behavior of the other blends.

TGA data was collected primarily to observe the rate of degradation to avoid degrading the materials in the extruder while compounding and in the DSC for further thermal characterization. The virgin PLA feedstock exhibited the highest degradation temperature indicating that the PLA requires the most energy to degrade allowing it to be processed at higher temperatures. The algae biomass exhibited the lowest $T_{d5\%}$ as expected due to its chemical makeup. The analysis of 5 % mass loss of the algae sample does not include the water loss experienced at 100 °C.

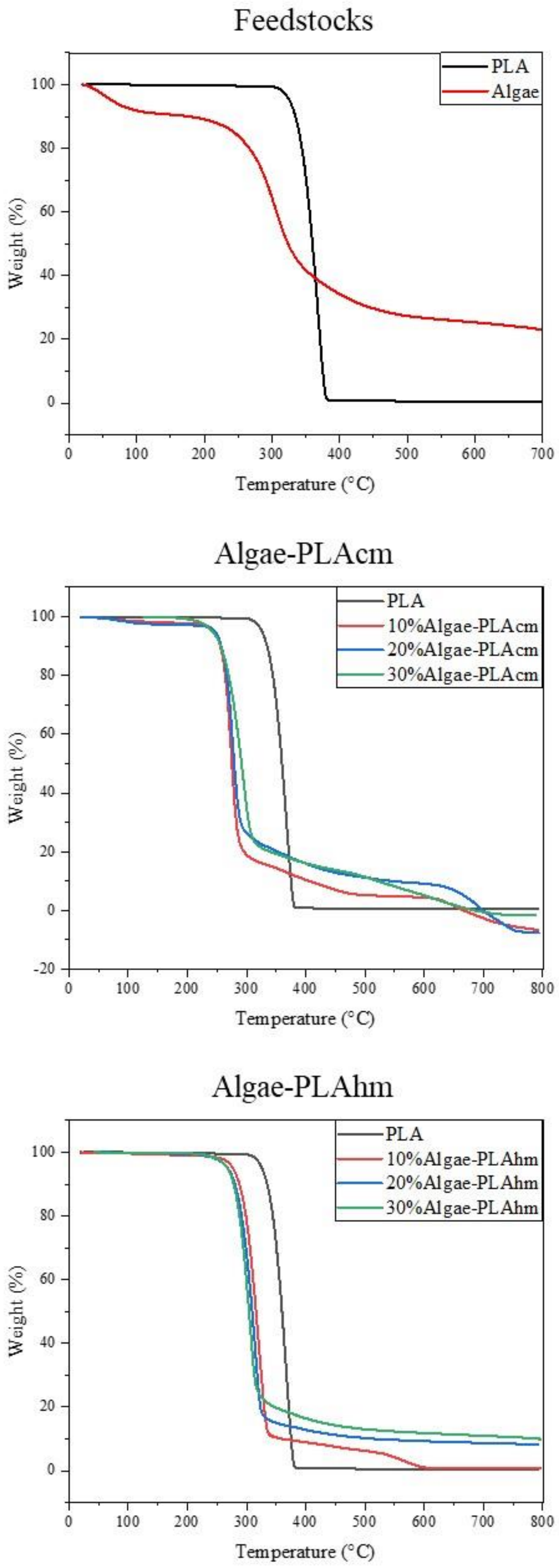


Figure 11. Representative TGA plots for all blends and feedstocks.

The increase in algae concentration increased the $T_{d5\%}$ of the cryo-milled feedstock blends (omitting the 30 wt.% of this variety) and decreased the $T_{d5\%}$ of the hammer-milled feedstock blends. The addition of the much lower $T_{d5\%}$ value algae biomass to the PLA is expected to decrease the $T_{d5\%}$ as the more readily degradable feedstock increases in the blends composition. The hammer-milled feedstock blends corroborate this expectation. The cryo-milled blends exhibit an increase despite the concentration of algae increasing (omitting the 30 wt.% Algae-PLAcm blend from consideration). This is hypothesized to be attributed to the high dispersion of the blend, where the algae filler, rather than acting wholly as a plasticizer and increasing flow volume, has slightly fortified the blends to thermal degradation by significant packing and chain alignment protecting the more degradable algae. Ultimately, the addition of algae decreased the degradation temperature overall as expected as a plasticizer.

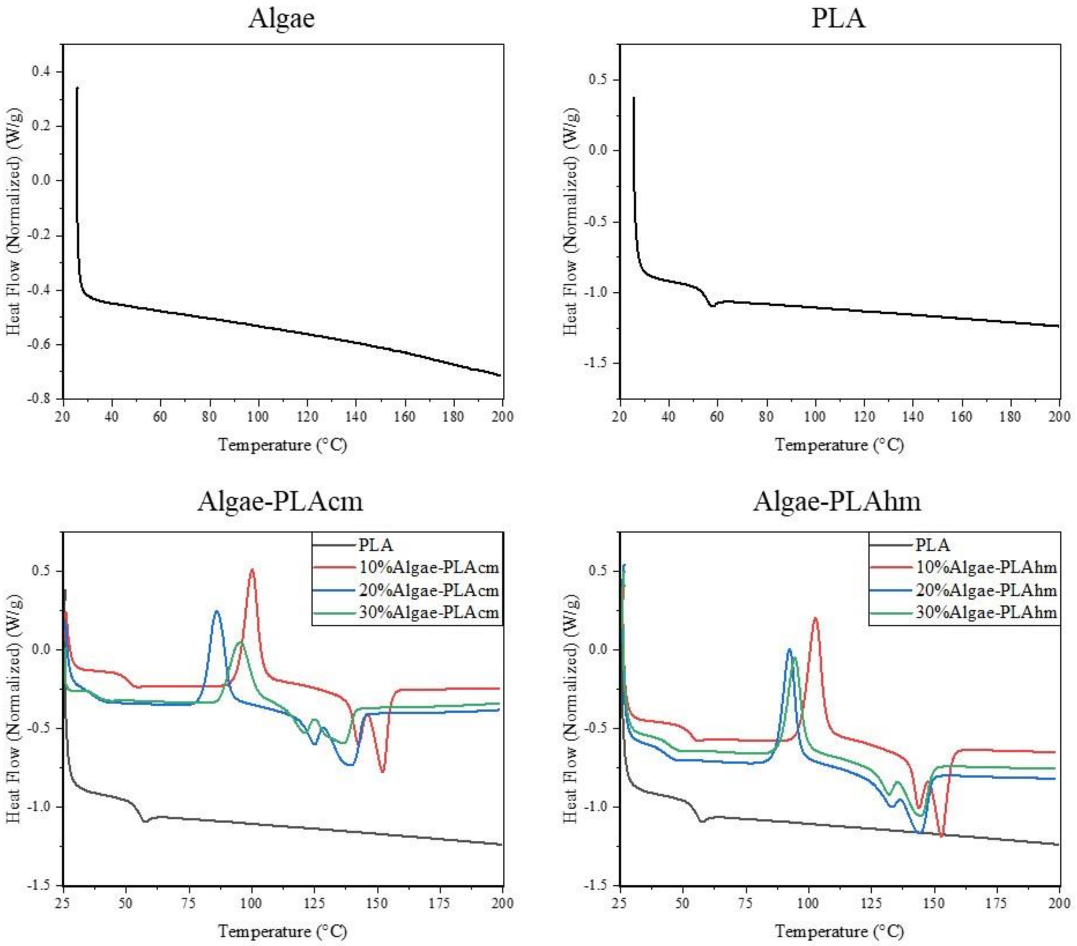
Sample	**$T_{d5\%}$ (°C)**
Algae	237.5
PLA	326.04
10 wt.% Algae-PLAcm	244.3
20 wt.% Algae-PLAcm	246.12
30 wt.% Algae-PLAcm	-
10 wt.% Algae-PLAhm	277.11
20 wt.% Algae-PLAhm	268.55
30 wt.% Algae-PLAhm	267.96

Table 6. $T_{d5\%}$ of the algae blends and the feedstocks.

5.1.2. Differential Scanning Calorimetry

DSC measurements were performed with a TA Instruments Q250 equipped with an auto sampling carousel. The reported temperature range evaluated for all blends was 25-200 °C at a heating and cooling rate of 10 °C/min. The weight of the samples was between 2.7 mg and 17.1 mg. The reported temperature range evaluated for the algae and virgin PLA feedstock was 25-200 °C at a heating and cooling rate of 5 °C/min. The weight of the samples was 5.3 mg and 6.9 mg. Triplicate statistical repeatability was not able to be attained due to timing constraints. Representative DSC plots for each material are depicted in Figure 12. The glass transition temperatures (T_g) of the materials were determined using TA Instruments Trios software and is listed in Table 5. DSC data for the 20 wt.% Algae-PLAcm blend does not exhibit a plateau prior to the onset of the glass transition curve requiring the value of T_g to be estimated from what was collected of the glass transition curve. This is attributed to not beginning the data analysis at a low enough temperature and in the future would be recommended to alter the testing parameters with this in mind.

The increase in algae concentration led to a decrease in T_g in both the cryo-milled feedstock and hammer-milled feedstock blends. This is attributed to the plasticizer effect of the algae biomass increasing the free volume between polymer chains. The T_g of the hammer-milled feedstock blends yielded higher T_g than the cryo-milled feedstock blends. This is attributed to the higher dispersion of the cryo-milled feedstock blends allowing the PLA polymer chains to more readily align with one another than the wider-dispersed hammer-milled feedstock blends. The 10 wt.% Algae-PLAhm performed more similarly to the virgin PLA than any of the other blends. The addition of algae filler to PLA feedstock resulted in a number of melt and crystallization peaks as seen in Figure 12 illustrating the effect algae filler has on the crystallization profile of the PLA feedstocks that indicated no such peaks.


Algae

PLA

Algae-PLAcm

Algae-PLAhm

Figure 12. Representative DSC plots for all blends and feedstocks.

Sample	Tg (°C)
Algae	-
PLA	54.96
10 wt.% Algae-PLAcm	50.1
20 wt.% Algae-PLAcm	37.71
30 wt.% Algae-PLAcm	37.83
10 wt.% Algae-PLAhm	52.85
20 wt.% Algae-PLAhm	47.12
30 wt.% Algae-PLAhm	44.16

Table 5. T_g of the algae blends and the feedstocks.

5.2 Tensile Characterization

Ultimate Tensile strength of injection molded dog bone tensile bars was conducted on an MTS Insight 10 kN using a modified ASTM: D638 method. At atmospheric conditions, a 2.5 kN load was employed for the measurement of the samples' tensile behaviors. Samples were carefully held under a load cell and subjected to force until the specimen reached its ultimate tensile strength and broke. The data collected was plotted as load vs. extension to express how the material responds to and absorbs force.

A correlation is seen between tensile strength and algae load. As expected, the increasing load of algae in the blends corresponds to a decrease in tensile strength. Additionally, a directly proportional relationship is observed between the dispersity of the blends and the tensile strength. This is attributed to the improved alignment of the chains when materials are more evenly dispersed.

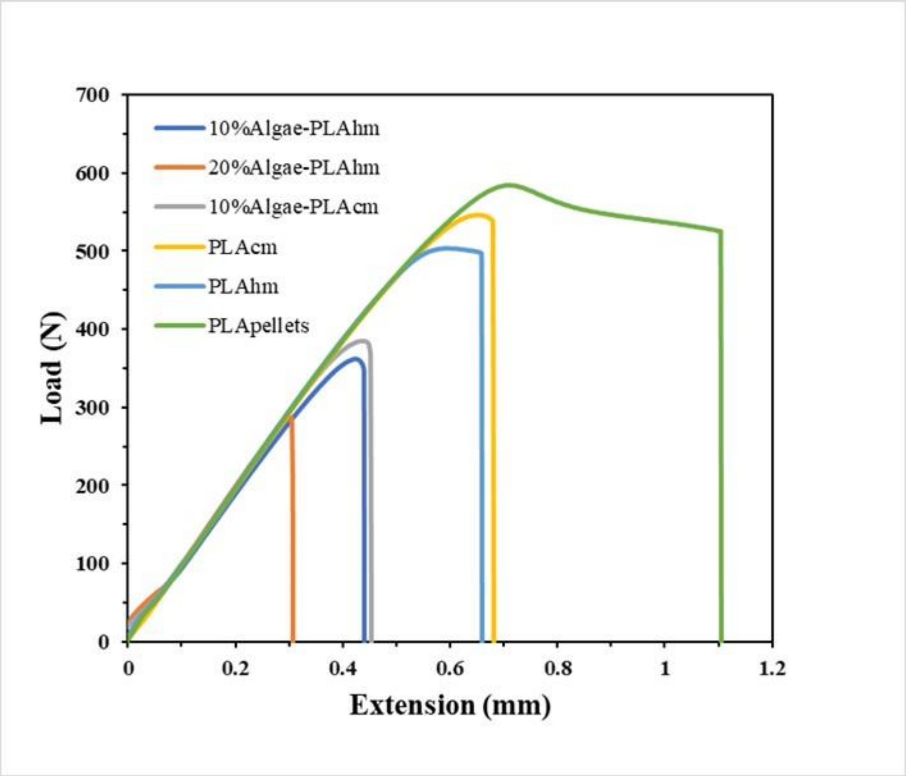


Figure 13. Representative Tensile plots for all blends and feedstocks.

5.3 Weathering Characterization

10, 20, and 30 wt.% Algae-PLAhm samples were aged in a xenon test chamber Q-SUN Xe-3 Xenon Test to simulate weathering phenomena. The samples were prepared by melt-pressing the environmental-chamber dried, pelletized blends to 1/8 ” thickness at 175 °C for 15 minutes and then fixturing them to aluminum Q-panels as illustrated in Figure 14. A modified ASTM G155 method was utilized to test the samples. A Daylight filter was used with an irradiation density of 0.35 W/(m^2*nm) at 340 nm. The air temperature in the chamber was set to 45 °C, the black panel temperature 63 °C, and the relative humidity was 45 °C. The exposure cycle consisted of 102 min. of light and 18 min. of light and water spray, and mass was collected for a total of five weeks at weekly intervals. The mass over time was collected, evaluated, and plotted as seen in Figure 15.

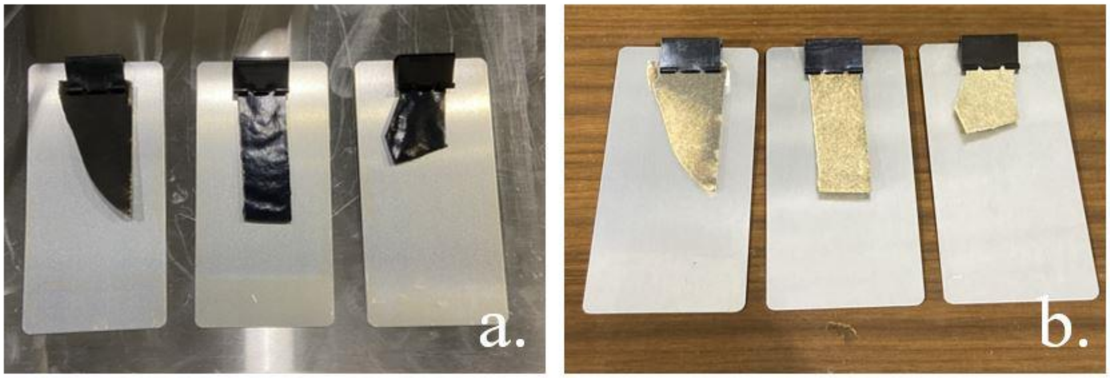


Figure 14. 10, 20, & 30 wt.% Algae-PLAhm (left to right) weathering samples before (a.) and after (b.) 5 weeks of weathering.

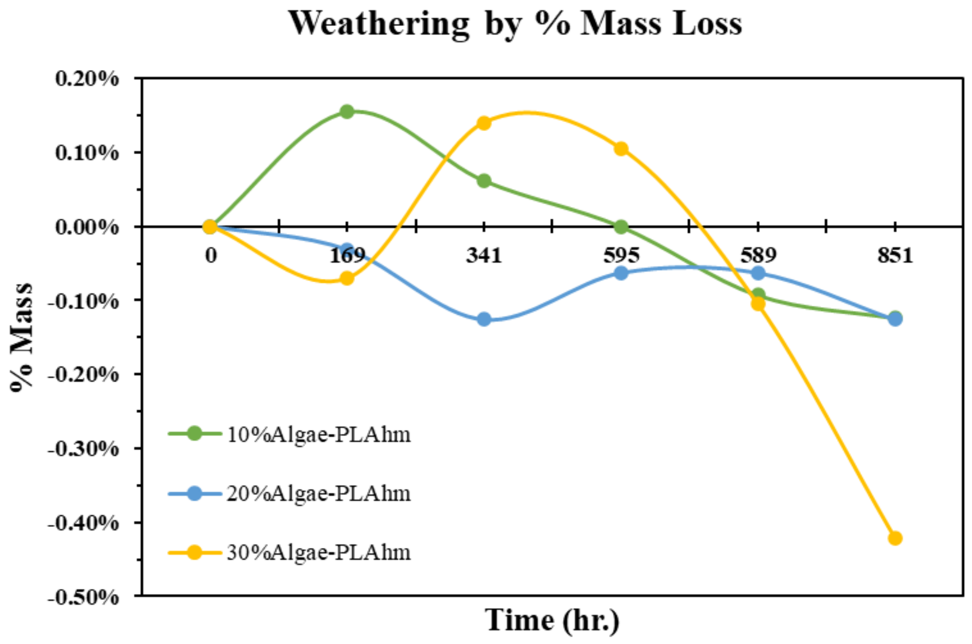


Figure 15. Weathering plot of % mass loss over time of the Algae-PLAhm blends.

Figure 14. illustrates the optical indicators of degradation in the form of bleaching due to the cycles of UV light from the Q-SUN chamber. A correlation between concentration of algae and rate of degradation is observed in Figure 15. The 20 wt.% and 30 wt.% blends exhibited an initial decrease in mass before beginning to gain mass from water absorption whereas the 10 wt.% blend experienced water absorption much earlier. By the end of the testing period, it appears graphically as though the 10 wt.% blend is leveling off and the 30 wt.% blend is degrading exponentially with the 20 wt.% falling in the middle. The observation is made regarding the 30 wt.% blend's "exponential" growth due to the more than doubling in mass loss between week four and week five of the evaluation period. All blends experienced a minimum of 0.10 % mass loss with the

highest being the 30 wt.% at 0.42 % mass loss and the lowest being the 10 wt.% with a 0.12 % mass loss.

Additionally, it is important to note that the samples were all 1/8 ” thick which is expected to slow the observed rate of degradation due to the sample consisting of more material to permeate as compared to typical thin films. Testing of this kind is necessary for applications and products that require a wall thickness larger than that of a thin film (~25 μm) but still require biodegradable properties.

CHAPTER VI: CONCLUSION

Compounding algae biomass in PLA blends was investigated via thermal, tensile, and weathering studies and confirmed to behave as a filler, plasticizer, and biodegradation agent. The impact of particle size disparity and dispersion on performance and processability was also investigated and discussed. A 10, 20 and 30 wt.% sample of the blends is illustrated in Figure 16.


10 wt.% Algae-PLAcm
20 wt.% Algae-PLAcm
30 wt.% Algae-PLAhm

Figure 16. Images of final blends at 10, 20, and 30 wt.%.

Algae-PLA blends were far easier to process than virgin PLA samples via injection molding. Little difference in melt-pressing between the algal blends and the virgin feedstock was observed aside from the plasticizer effect of the algae biomass. All algae-blends exhibited improved melt and flow properties, increased brittleness, decreased $T_{d5\%}$, decreased T_g, and decreased tensile strength in comparison to virgin PLA feedstock. Improved flow properties of the blends are attributed to the plasticizer effect of the algae filler increasing the free volume between polymer chains and the improved distribution of the blends with reduced particle size of the polymer feedstock.

As seen in Figure 13, the algae filler decreases the mechanical properties of the compounded blends. Upon greater loading of algae, the compounds experience failure at lower degrees of force indicating that algae filler increases brittleness in the materials. This is corroborated with observations noted while melt pressing the blends into panels At higher loads of algae (20 and 30 wt.%), melt pressing samples yielded panels that were brittle enough to break manually. The impact of particle dispersion was observed to have a greater impact on the brittleness of the blends than the algae load as while both the 30 wt.% Algae PLAcm and 30 wt.% Algae-PLAhm experienced difficulty while processing, the 30 wt.% Algae-PLAcm was too brittle to extract from the mold without damage via both melt-pressing and injection molding processing techniques. Overall, the hammer-milled blends yielded less durability and flexibility in injection molded products but not melt-pressed panels. Blends compounded with cryo-milled PLA yielded highly brittle melt-pressed panels and experienced significant issues with processing via injection molding.

Injection molding the 30 wt.% Algae-PLAhm, resulted in the material experiencing off-gassing and swelling in the mold system. Swelling is uncommon in thermoplastic materials as typically the blends shrink in the mold as they cool. Additionally, despite the use of mold-release agent prior to injecting, the 30 wt.% Algae-PLAcm blend cracked in the mold cavity leaving residual material that later could only be removed by dissolving in chloroform solvent. Injection molding of up to 20% Algae-

PLA was achieved, but it was agreed that currently, only the 10% Algae-PLAhm blends exhibit significant enough processability for commercialization of any kind.

The correlation between the algal concentration and decreased tensile properties is attributed to melt flow properties and polymer crystallinity observed in the DSC data. Figure 12 clearly indicates the occurrence of melt and crystalline regions within the thermoplastic material upon blending with algae. This analysis confirms that algae filler acts as a plasticizer increasing the melt-flow properties of the compounded blends. Additionally, this explains the difference observed in the 30 wt.% Algae-PLAhm product quality when melt-pressed rather than injection molded. When melt-pressed, the material chains are able to flow and align increasing the degree of crystalline regions, when the panels are removed from the melt-press they are cooled quickly effectively sealing the chains in their highly aligned configuration. When injection-molded, the material chains are exposed to a higher degree of shear and heat of friction, decreasing the possibility of alignment into crystalline regions. The process of injecting the material into the mold also does not typically encourage the settling and alignment of polymer chains.

A direct relationship between the concentration of algae and the rate of degradation was observed over five weeks via Q-SUN weathering monitored by mass loss. After five weeks of accelerated weathering all samples experienced a minimum of 0.10% mass loss by degradation with an indication that the 30 wt.% Algae-PLAhm was beginning to degrade exponentially. Utilizing alternate weathering test methods such as QUV accelerated weathering or aerobic/anaerobic composting studies are expected to yield significantly higher degrees of degradation quicker due to the algae filler's ability to enhance microbial activity.

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