Studies on the Blending of Poly(Lactic Acid) and Acrylonitrile Butadiene Styrene

by

Ryan Vadori

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The polymer materials industry is heavily dependent on the use of petroleum based plastics. This poses a problem, as the world is facing ongoing petroleum supply problems. A need exists for a bio-carbon based polymer material that has the performance and cost of currently used petroleum plastics. However, the overall performance of current bio-based plastics indicate that they must be somehow supplemented to achieve the properties of that of petroleum-based polymers. The low impact strength and thermal stability of poly(lactic acid), PLA are targets for improvement. One option is for development is through blending with acrylonitrile butadiene styrene (ABS). The viability and efficacy of using these two polymers as blending partners is investigated. The PLA used in these studies has unique and interesting crystallization properties. These have been examined and detailed in part 1. The second part of study includes neat polymer properties, miscibility analysis, and large scale process results. This results in an optimized blending ratio on which to go forward with development. The mechanical, thermal, and morphological properties are investigated in these studies. Significance of this research and development is widespread, as the material developed has the potential to reduce the use of petroleum-based carbon in plastics.
Acknowledgements

Grateful does not begin to describe my feelings for my advisors, Dr. Amar Mohanty and Dr. Manju Misra, who have welcomed me into their laboratory. They have taught and guided me through my attaining this degree in ways that go beyond their expected duties. I am indebted to them for guiding me to reach toward my potential as a young and aspiring scientist. I am also grateful to my committee advisor, Dr. Fantahun Defersha who has brought perspective to me work. I am thankful to my colleagues who I have had the privilege to share our workspace.

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### Selected Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ABS-1</td>
<td>Acrylonitrile Butadiene Styrene (high rubber grade)</td>
</tr>
<tr>
<td>ABS-2</td>
<td>Acrylonitrile Butadiene Styrene (standard grade)</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic mechanical analysis</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
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<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>LDPE</td>
<td>Low Density Polyethylene</td>
</tr>
<tr>
<td>PBAT</td>
<td>Poly(butylene adipate-co-terephthalate)</td>
</tr>
<tr>
<td>PCL</td>
<td>Poly(caprolactone)</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>PHBV</td>
<td>Poly(hydroxybutyrate-co-valerate)</td>
</tr>
<tr>
<td>PLA</td>
<td>Poly(lactic acid)</td>
</tr>
<tr>
<td>POM</td>
<td>Polarizing optical microscopy</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PVC</td>
<td>Poly(vinyl chloride)</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>$T_m$</td>
<td>Melting temperature</td>
</tr>
<tr>
<td>$T_c$</td>
<td>Crystallization temperature</td>
</tr>
<tr>
<td>$\Delta H_f$</td>
<td>Heat of fusion</td>
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1. Introduction

Since our early human ancestors started smelting ore and shaping it into tools, material choices have been the foundation for functionality in design. Materials are one of the most important aspects, dictating strength, weight, cost, and overall viability. The numerous materials that are available have penetrated so deeply into our daily lives that we are no longer attentive to them. Materials have undergone very significant advancements – especially in recent years. New classes have emerged, from aerogels to nanomaterials, each with special properties and applications.

The material industry underwent a large transformation with the advent of polymer materials. With strengths high enough for use in consumer goods, cost efficiency and low weight, polymers are a remarkable alternative to previously used metals and wood. Polymers come in two main forms, thermosets and thermoplastics. Thermosets are cured into their final state and cannot be melted and reused. They are generally rigid with low flexibility, a characteristic attributed to the amount of cross-linking in its molecular structure. Thermoplastics are generally more flexible, with higher fracture resistance and they can be remolded and recycled.

Polymers, which are mostly derived from petroleum reserves, are relatively inexpensive to produce. In addition, they are easily processed using methods perfected in the middle of the twentieth century.

According to the United Nations, sustainable development has three pillars on which it has foundation: economic, social, and environmental aspects must all be considered to ensure sustainable development. These aspects must be considered simultaneously, making progress in each, in contrast to an unbalanced approach. This sort of unbalanced approach has been taken increasingly frequently as industries increase in size, and are most concerned for their bottom
line. The petroleum industry is no exception, and during unprecedented growth in the later part of last century, it has neglected its social and environment responsibilities.

It is well documented that the world is currently using petroleum at a rate that will see reserves diminish in the near future. The nature of the source is that it takes thousands of years to produce; it is not in the population’s best interest to deplete it totally. The current rate at which it is consumed is not sustainable, and will surely lead to massive problems when it is consumed. Instead, the world would benefit greatly from a change in the industry. It is in its best interest to slowly dissuade use of oil by creating products that are either totally or partially not petroleum-based\(^2\).

Petroleum based plastic is cheap and easy to produce, has a wide range of properties that can be tailored to a specific application, and is moldable and easily shaped. The majority of applications allow the use of one of five major plastics: polypropylene (PP), polystyrene (PS), polyethylene (PE), poly(vinyl chloride) (PVC), and poly(ethylene terephthalate) (PET)\(^3\). Each of these polymeric materials is used for different applications, as each have different properties and cost.

These five polymers have the best performance to cost ratio of many of the currently available plastics. For this reason, they are considered commodity plastics – they do not have specialty performance (such as high thermal stability found in poly(ethylene terephthalate) (PET)), but their performance and cost allow them to be used for a majority of applications in the packaging industry\(^4\). These five polymers have properties that range from relatively low to high strength, poor to excellent barrier properties, and low to high heat capabilities, among others.

The fact that a plastic is petroleum-based refers to the carbon source of which it is obtained. If the carbon source that it is obtained is not from petro-chemicals, and instead from an agricultural
or other bio-feedstock, the plastic is considered bio-based. The second sustainable property that is considered is biodegradability. Landfilling is an issue, and biodegradability can be a solution to this problem.

As a result of the aforementioned economic and environmental shifts, there is an increasing importance in the use of bio-based materials to replace currently used petroleum-based materials.

2. Literature Review

2.1 Bioplastics

The real definition of bioplastics is somewhat obscured from society. Many equate the word bioplastic with biodegradable plastic, which is not the case entirely. A bioplastic may fall into one or more of several categories. If a polymer is bio-based, it is not necessarily biodegradable and if it is biodegradable, it is not necessarily bio-based. Polymers exist that are petroleum based, but still biodegrade, or that are biobased but do not biodegrade. Therefore the main categorization of bioplastics is as follows: Bio-based polymers, biodegradable polymers, and mixed source polymers. Mixed source polymers have a fundamental constituent which is bio-based, but also has petroleum based components. This categorization is shown in Figure 2.1.

Although bioplastics are currently available that are bio-based or biodegradable or both, they are not widely used in commercial situations. This is because there are barriers preventing them from regular use in commercial products. Many have insufficient performance in one or more properties such as toughness, heat stability or strength. From an economic standpoint, there is only one bioplastic that is currently truly cost competitive with petroleum based polymers, and
that is poly(lactic acid) (PLA). The main performance drawbacks for PLA are toughness and heat stability. It is a very brittle polymer, and begins to warp under relatively low temperatures, which prevents its widespread use.

Figure 2.1 - Bioplastic categorization chart
2.2 Poly(lactic acid)

Based upon various socio-political and economic issues, industries are searching for low cost greener materials to substitute their existing products. PLA is brittle and has low heat deflection temperature (HDT), however, it has excellent tensile strength and modulus. Current low scale production downsizes the utilization of PLA in many applications. This bioplastic alone cannot fulfill the property requirements for specific applications.

PLA is an aliphatic polyester thermoplastic that is biodegradable and non-toxic. It has a prominent role as one of the most appealing and practical biodegradable polyesters. Lactic acid is easily synthesized through a biotechnical process, usually involving lactobacillus. The raw materials required to form lactic acid are inexpensive and easily obtained. Its synthesis, as per patents by Dow Chemical®, is started through the fermentation of dextrose, obtained from biomass such as corn. A continuous condensation reaction produces low molecular weight PLA prepolymer. Low molecular weight oligomers are then converted into a mixture of lactide isomers. After a purification process, ring-opening polymerization (ROP) produces PLA high polymer as in Figure 2.2.

Figure 2.2 - Schematic of the polymerization of PLA. Redrawn after reference

\[\text{Lactic Acid} \rightarrow \text{PLA Pre-polymer} \rightarrow \text{PLA High Polymer} \rightarrow \text{Lactide Ring}\]
Lactic acid exists in two isomeric states, D- and L- enantiomers, which can be controlled during synthesis by modified strains of *lactobacillus*\textsuperscript{13,14}. The properties of PLA are what make it such an attractive polymer for biodegradable and renewable resource applications. It has good process ability, biocompatibility, and biodegradability\textsuperscript{6}. It has generally excellent mechanical properties, aside from its impact strength and heat deflection temperature (HDT). Its tensile strength and modulus surpass those of polypropylene\textsuperscript{15,16}. PLA is deficient in toughness, and several researchers have attempted to increase the toughness with varied success\textsuperscript{17}.

### 2.3 Review of Traditional Plastics with Special Focus on Acrylonitrile Butadiene Styrene (ABS)

Five main polymers dominate the current industry. It is a combination of cost and properties that has positioned them at the forefront of the industry. Their properties allow them to be used for most durable applications, aside from when extremely high strength or thermal stability are required. In addition to this, they are used extensively due to their very low cost. These polymers are: polyethylene, polypropylene, polystyrene, poly(vinyl chloride), and poly(ethylene terephthalate).\textsuperscript{3}

Polyethylene is has the simplest molecular formula and is the least costly of addition polymers.\textsuperscript{3} It can be separated into two categories, high-density and low-density. High-density polyethylene (HDPE) is strong, stiff, tough, resistant to chemicals and moisture, in addition to its being easily processed and formed. High-density polyethylene is a polymer that does not result in a transparent product. It is cost effective, and therefore used when clarity is not of great importance. Applications such as milk containers use HDPE for its strength\textsuperscript{18}.
Low-density polyethylene (LDPE) is fairly transparent, flexible, strong, tough, and moisture resistant.³ It is a good candidate for use in film applications. LDPE also has a high elongation in tensile loading. For this reason, along with the fact that it has good barrier properties, it is used for food storage bags. Polyethylene is also co extruded with other polymers, used as the adhesive layer, holding everything together¹⁸.

Polypropylene is harder, denser, and more transparent than polyethylene.³ It has a higher melting point (160°C) and can be used where thermal resistance is required. It is used more for rigid applications such as bottles, cups and bowls because of its high strength properties. It can be coupled with an oxygen barrier such as ethylene vinyl alcohol, which allows it to be used for condiments and salad dressing bottles¹⁹.

Polystyrene is an addition polymer of the styrene monomer. It is clear, strong, and brittle, but can undergo several processes such as mono or co-extrusion, injection molding and foaming, producing a wide range of products. Foamed polystyrene can be used for thermal insulation applications such as one-time use coolers or hot beverage cups. It is also used in meat and egg trays for its rigid form²⁰.

Another addition polymer, poly(vinyl chloride) PVC, is stiff yet ductile and has a medium strength. It is amorphous, transparent and has excellent resistance to chemicals and oils. When polymerized as polyvinylidene chloride (PVDC), it has excellent barrier properties and can be used as flexible packaging as a monolayer film²¹. In addition, plastic sheets require a polymer that has high tensile elongation abilities. PVC is used for this reason and also because it is inexpensive and easily extruded by cast film processes²².
Poly(ethylene terephthalate) has a glass-like transparency good gas barrier to carbonation, strong, lightweight and tough. It has excellent tensile strength, but low melting temperature, making it perfect for cold beverage applications which require great tensile strength in the axial and hoop directions\textsuperscript{23,24}.

Much of this plastic used in the automotive industry is in the form of acrylonitrile butadiene styrene (ABS). The structure of ABS is a matrix of styrene acrylonitrile copolymer (SAN) with a dispersion of rubbery polybutadiene (PB). ABS has been used as an additive to improve the toughness for engineering plastics\textsuperscript{25}.

Currently, polypropylene, polyvinyl chloride, polyurethane and acrylonitrile butadiene styrene (ABS) account for about 80\% of the plastics used in automotives\textsuperscript{26}. ABS finds applications in automotives, electronics and domestic appliances. Asian markets represent around 70\% of world ABS consumption. ABS can exhibit a wide range of properties due to the flexibility in composition and structure. ABS finds wide range of automotive interior applications including panels, consoles, radiator grills, headlight housings and interior trim parts\textsuperscript{26}.

ABS is an engineering thermoplastic with properties that surpass those of traditional commodity polymers (such as polystyrene). Traditionally, it has held a position in the marketplace between commodity polymers and high performance plastics such as nyons\textsuperscript{27,28}. Due to its flexibility of composition, ABS can exhibit a wide range of properties. In this research, high impact ABS (high polybutadiene content) has been chosen to toughen the PLA. ABS is petroleum-based and has high impact properties, good heat deflection temperature (above 80°C) and is easily available. ABS based synthetic polymer blends is reviewed by Greco et al\textsuperscript{29}.
ABS has been used as an additive to improve the toughness for engineering plastics. Blends of ABS (as a toughening agent) with nylon, poly(butylene terephthalate) (PBT), and polycarbonate (PC) have all been reported in literature.\textsuperscript{25,30-32} The blending of PC and ABS, especially, produce a competitive engineering polymer that results in a balance of toughness, thermal stability, ease of processing and cost.\textsuperscript{25} For this reason, ABS/PC blends are the dominant polymer used in the electronics industry.

\section*{2.4 Polymer Processing}

When considering the processing of a polymer to create a product, there are several very important properties to consider. The thermal properties dictate the processing temperature and possible the crystallinity. The melting point ($T_m$) and the glass-transition temperature ($T_g$) are the most important parameters in processing.\textsuperscript{33} For extrusion methods, the polymer must be heated above its melting temperature. For forming methods, the polymer must be heated above its glass-transition temperature, but not as high as its melting temperature. This ensures a pliable, rubbery material that is easily shaped and formed.

The moisture content of the polymer must be as low as possible, and certain polymers that undergo hydrolytic reactions will break down during processing. This results in a decrease in a molecular weight, and inevitably, the mechanical properties of the material. The melt stability/viscosity is the final important property to be considered in processing. Especially for injection molding, a good flowing polymer in the melt is crucial in order to fill the mold.\textsuperscript{33}

The most important polymer process is extrusion. Polymer blending and compounding is traditionally done using a twin-screw extruder. Not only is it the fundamental method for blending polymers, but it is also the preferred method of conveying molten polymers as part of
many other methods of polymer processing. Extrusion is used in injection molding, cast film, and blow molding, among others. The material is fed into a heated barrel containing rotating screws. These screws push the molten polymer through the barrel and a die at the final stage. There are three sections of the barrel, the feed, transition, and metering, as in Figure 2.3. The flights are deep in the feed section to allow material space to melt, they become smaller in the transition section, and are shallowest in the metering section. The compression ratio is the flight depth in the feed section over the depth in the metering section, and is an important parameter in controlling the shearing on the material. For poly(lactic acid), a compression ratio of 2-3 is recommended.

![Figure 2.3 - Schematic of the screw cross section in a twin screw extruder.](image-url)
Injection molding is used to produce parts that require a high dimensional precision. For many manufacturers, the cycle time is the most important aspect of the process. As expected, the faster the cycle time, the more parts are produced and therefore profit margins are higher. PLA has the ability to be injection molded, but some problems can arise. The low mold temperatures cause a lactide vapour (produced during processing) to condense on the tooling of the molder, forming a film. To combat this, mold temperatures may be increased, but this increases cycle time. In addition, a higher mold temperature can increase the crystallinity of the PLA, which will cause a decrease in its toughness. This is a difficult scale to balance and requires skill and experience.

PLA with a lactide content of 92-98% has been successfully extruded through the cast film process. As with injection molding, the PLA will leave a film of lactide from condensation on the tooling of the machine. To counteract this, higher roller temperatures are required (~25-50°C). By stretching the polymer and orienting it mechanically, the toughness may be increased.

Physical and thermal properties of polymers are extremely important and can dictate the final mechanical properties of the material. Physical properties are dependent on the crystallinity, crystalline thickness, spherulite size, morphology, and chain orientation. Poly(lactic acid) can be found in different stereo-chemical configurations including poly(L-lactide) and poly(D-lactide). Either configuration in purity or high percentage produces a semi-crystalline polymer, very high molecular weights produce an amorphous polymer. All of these configurations produce different mechanical and thermal properties.

The most important thermal characteristic of polymers is the glass transition temperature ($T_g$). Defined as the temperature at which the polymer undergoes a transformation from a rubbery material to a brittle material, it has several impacts on the use of the polymer. For PLA in
normal configurations (easily producible), the T<sub>g</sub> occurs at approximately 60°C. A table of glass transition temperatures as a function of the copolymer ratio is shown in Table 2.1. This causes a problem because as the polymer chains are mobile at this temperature, the material is softened and pliable, causing warping to occur. This is much too low a temperature for use in many applications, and must be raised in order to do so.

*Table 2.1 - Glass transition and melting temperatures for PLA. Adapted from 33*

<table>
<thead>
<tr>
<th>Poly(L-Lactide) to Poly(D-Lactide) Copolymer Ratio</th>
<th>Glass Transition Temperature (°C)</th>
<th>Melting Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0 (L/D,L)</td>
<td>63</td>
<td>178</td>
</tr>
<tr>
<td>95/5 (L/D,L)</td>
<td>59</td>
<td>164</td>
</tr>
<tr>
<td>90/10 (L/D,L)</td>
<td>56</td>
<td>150</td>
</tr>
<tr>
<td>85/15 (L/D,L)</td>
<td>56</td>
<td>140</td>
</tr>
<tr>
<td>80/20 (L/D,L)</td>
<td>56</td>
<td>125</td>
</tr>
</tbody>
</table>

Another important thermal property is the melting temperature, as it dictates the processing conditions of the polymer. PLA has a melting temperature around 170°C, which means it can be processed about 40°C above, around 200-210°C.

Mechanical properties of the polymers allow them to be used for each application as they allow. For example, poly(ethylene terephthalate), which has excellent tensile strength, is able to be used in applications such as cold beverages, especially carbonated which require the high strength for containment. The most important mechanical properties are the strength, stiffness and toughness. A material that has low strength but high toughness (elongation) can be used for
wraps or bags, as they stretch and do not easily develop holes. PLA has very low toughness, but
does have very high strength, which makes it similar to PS and PET in mechanical properties.\textsuperscript{35} However, its low $T_g$ stipulates that it is not able to replace these polymers, as it warps in relatively low temperatures, such as those found in a car during summertime.

\textbf{2.5 Crystallization and Polymer Properties}

Poly(lactic acid) (PLA) is a semi-crystalline polymer, meaning that it, like many polymers, has chains which are oriented in both the highly organized crystalline phase and random amorphous phase.\textsuperscript{34,36,37} The crystalline structure of the polymer is highly tied to its thermal conditioning. The mobility of the chains is dependent on the amount of energy that is accessible to them.\textsuperscript{38} When subjected to a higher heat, and therefore a higher energy, the chains are more free to move into more desirable states. The polymer may be heated for a prolonged time at a temperature below melting, but above the glass-transition temperature. In this range, the chains have the energy to be mobile, but are not yet in the molten state. This process is known as annealing, and causes the polymer chains to crystallize.\textsuperscript{39,40} The extent to which crystallization occurs is dependent on the temperature and the time of the process.\textsuperscript{41} The crystalline phase, in comparison to the amorphous phase, has a much more rigid structure, as well as less free volume for the chains to move into. Therefore, chains in the amorphous phase have more mobility. In addition, the amorphous phase undergoes a process known as relaxation which decreases the enthalpy over time as the chains find a lower energy state.\textsuperscript{42} This process causes an increase in the brittleness of the polymer over this time period and is seen as an aging process which is undesired.

It is well established that PLA has a very slow crystallization time.\textsuperscript{39} This leads to high amorphous content in the polymer as traditional processing such as injection molding does not
provide the time required for the PLA to crystallize to desired amounts. Increasing the time of processing is not a desired solution as longer cycle times decrease output for manufacturers. A higher crystallinity can have a positive influence on the performance of the polymer\textsuperscript{39,43-44}. In addition, with a lower amorphous content, there is less ability of the polymer to undergo the relaxation process, which for an already brittle polymer such as PLA is undesired. Several attempts have been made to increase the crystallization rate of PLA for viable use in injection molding\textsuperscript{14,24,45-47}. There are three main ways to try to increase the crystallization rate of a polymer: nucleation, plasticization and process engineering. Nucleation of the polymer utilizes additives to overcome surface free energy barrier, and thus initiates crystallization at a higher temperature\textsuperscript{48}. Plasticizer may be added to increase the mobility of chains, thus allowing the energy required to undergo the folding process of the chains to be less\textsuperscript{48}. Finally, process engineering can be done to optimize the molding conditions to provide the ideal temperature and time to promote crystallization. Crystallization is not always desired, however, and can lead to properties that are not suitable for a given application\textsuperscript{46}.

Polymer processing is an important consideration in plastics production. Its effects can be seen in the overall performance of the polymer. It can affect the crystal formation and their morphological structures, in addition to mechanical and thermal properties\textsuperscript{34}.

### 2.6 Polymer Blending Theory

Generally, polymer/polymer blended systems are not miscible, or are only miscible under certain condition ‘windows’.\textsuperscript{27} There is usually little compatibility between two polymers, and therefore one polymer amalgamates into spherical regions, while the other fills the rest of the space \textsuperscript{49}. To
increase interaction and adhesion between the two phases, a compatibilizer is required. This acts as an intermediary between phases, allowing each to bond to it. Not only does this aid in increasing the interaction surface area, but also allows each phase to better adhere to each other. This adhesion has a profound influence on the mechanical properties of the blended system.

A two-polymer system may be comprised of polymers with extremely high mechanical strength, but together, they are only as strong as the bond between them. Thus, final mechanical properties can be decreased from original.

While miscibility is limited to a specific set of conditions, generally, immiscibility is the dominant form; that is to say when blended, most polymer systems are immiscible. Generally, the polymers are not well matched for blending purposes. There is too much tension that exists between the phases of the polymers. If no compatibilization occurs to reduce this tension, the polymers will reduce the surface area between phases as much as possible, and the dispersion will be extremely coarse. At lower concentrations of either polymer, one polymer will form spherical regions inside the matrix of the other. At higher loading, the minor polymer will form different arrangements such as cylinders, fibers, and sheets. It is said that at both ends of the concentration scale, the blend is dispersed, and in the middle, it is co-continuous. There is normally poor adhesion between phases as well. This leads to poor strength of the polymer, as it is only as strong as the interfacial adhesion will allow. Once the interface between the polymers can no longer hold together, then the structural integrity is compromised. Thus, for a polymer system to exhibit satisfactory performance, compatibilization is required.

It has been shown in literature that blending acrylonitrile butadiene styrene and poly(lactic acid) results in an immiscible blend. However, compatibility can still be optimized. PLA has a solubility parameter, $\delta$, of 9.58 cal$^{1/2}$cm$^{3/2}$. According to blending theory, for best blending
results, ABS must have a solubility parameter within the range of $8.58 – 10.58 \text{cal}^{1/2} \text{cm}^{3/2}$ ($9.58 \pm 1 \text{cal}^{1/2} \text{cm}^{3/2}$). The closer these numbers are to each other, the more compatible the blend will be. Since the formulation of ABS has such a wide range of variance, its solubility parameter, too, has a wide variance. According to Tan et al.\textsuperscript{25}, for ABS to achieve a solubility parameter of $9.58 \text{cal}^{1/2} \text{cm}^{3/2}$, the polybutadiene content must be approximately $38\%$.\textsuperscript{25} Not only will this produce good blending between PLA and ABS, but also a high polybutadiene content will toughen the PLA. For these reasons, Styron’s Magnum\textsuperscript{TM} 1150 EM was chosen, with polyacrylonitrile content of $24\%$, polybutadiene content of $40\%$, and polystyrene content of $36\%$.

As stated previously, the toughness of PLA is always an issue. Naturework’s Ingeo\textsuperscript{TM} 3801X grade PLA was chosen for its already high toughness. Both polymers have acceptable impact strength, as well as all other mechanical properties. The goal of this project is to blend these polymers without reduction of these properties.

The final issue to be faced when blending ABS and PLA is their separate melting temperatures. PLA has a processing temperature of approximately $175^\circ C$, while ABS has a much higher processing temperature, at approximately $220^\circ C$. There will obstacles to overcome in order to melt blend the two polymers together at a high temperature. At $220^\circ C$, it is likely that PLA will undergo some small degradation, in the form of broken polymer chains. Additives or creative process engineering are needed to make this blending successful. This is part of the ongoing progress of the project, as there is still a great deal of research to be done.

As discussed, scientific problems with creating polymer blends include poor dispersion, high interfacial tension and low interphasial adhesion.\textsuperscript{49} The objective is to use polymer blending techniques along with chemical modifications to produce a high performance product that meets
all property requirements. These main problems will be dealt with in this manner to ensure a product that is commercially attractive.

In terms of a big picture project, the blending described in this investigation is only the beginning of developing materials that can replace those found in the automotive industry. To expand this project, the ABS + PLA blend (BioABS) may be used as the matrix in a biocomposite with agricultural residue as the reinforcing agent. To do this, several more steps need to be taken:

- Engineer the biomass.
- Green composite fabrication and performance evaluation.
- Zone process optimization.
- Reduced step processing.
- Environmental and economic assessment
- Outreach and commercialization pathway.

For this project to be successful, all elements mentioned in this section must be attended to carefully and closely.

### 2.8 Toughening and Compatibilization

When polymers that are blended together are miscible with each other and exhibit uniform physical properties macroscopically, the blend may be considered an alloy. An alloy’s performance is dependent not only on the constituents and their proportion, but on the morphology of the final blend.\(^53\) Thus, proper dispersion methods, such as mechanical mixing,
and compatibilization must be used appropriately. There are three goals that a compatibilizer must achieve:

- Reduce the interfacial tension between the polymers, and as a result, there will be finer dispersion.
- Stabilize the morphology of the blend. This protects against thermal or shear effects during processing.
- Produce adhesion between phases, especially required in the solid state.

To achieve these goals, there are several strategies to the method of compatibilization. The first is the addition of a co-solvent, which is miscible with both polymers. Adding a co-polymer to the system is another method of compatibilization. One part of the co-polymer must be miscible with one of the polymers, another part miscible with the other polymer. A coreshell co-polymer is the third method. By reactive extrusion, it is possible to modify the macromolecules to create localized miscibility regions between the phases. Finally, the last method is the use of mechano-chemical blending.

The addition of a co-polymer as a compatibilizer to the system was at one time the most common method of compatibilization. The co-polymer was either graft or block, making it also a very easy reaction to predict. For co-polymer compatibilization to be effective, there are several requirements that must be met:

- The co-polymer compatibilizer must have a maximum miscibility with both polymers in the blend. This ensures very good adhesion between phases.
• The molecular weight of each block in the chain should only be slightly higher than that of critical entanglement, \( M_c \). This is the molecular weight above which entanglement occurs.

• The concentration of compatibilizer must be just above the critical miscelle concentration. Time is important in processing; higher viscosity means slower processing times.

For reactive compatibilization, many of the same principles still hold true. Reactive compatibilization must create sufficient dispersive and distributive mixing for maximum surface area between phases. The reactant must be versatile enough to react across the interphase. As well, the rate of reaction must be fast enough to allow the reaction to take place while the blend is in the melt.

Toughening of poly(lactic acid) (PLA) has been attempted by many researchers, with varying success. There are several mechanisms that are thought to be able to effectively toughen the PLA polymer. Hassouna\(^{54}\) has attempted toughening through a plasticization reaction by using poly(ethylene glycol) (PEG) and maleic anhydride. This has led to a significant lowering of the glass transition temperature \( (T_g) \), signifying plasticization. As well, the ultimate strain was raised from 0.07% to 1.30%, showing the increase in ductility due to the reaction. Liu et al.\(^{55}\) have blended PLA with an ethyl-butyl acrylate and glycidyl methacrylate copolymer (EBA-GMA) and an ethylene methacrylic acid zinc ionomer (EMAA-Zn). The mechanisms of reaction are vulcanization and compatibilization, which occur simultaneously to toughen the blend. This has arguably been the best attempt at toughening PLA, with an increase in impact strength from 38 J/m to 770 J/m. Another notable toughening mechanism is through simple reactive blending. By choosing certain polymers, a synergistic effect can be seen. Oyama et al.\(^{56}\) has shown the value
in reactive blending PLA with ethylene-glycidyl methacrylate (EGMA). Through this reaction, the impact strength was increased from 3kJ/m$^2$ to more than 70kJ/m$^2$.

2.9 Bio-based and Biodegradable Plastic Blends

As mentioned throughout this report, there are performance barriers that are currently impeding the widespread use of bioplastics.\(^6\) To overcome these barriers, many industrial manufacturers are electing to blend the bioplastic with a petroleum-based supplement to balance the final properties. This is considered a step toward higher sustainability. PLA has been central in many of these blending experiments, but other bioplastics have been used as well.\(^{16,58-65}\) Generally, the sustainability of the final product is graded based on two criteria: bio-based content and biodegradability.\(^{66}\)

Blending a bio-based with a petroleum-based plastic can, in some cases, result in a biodegradable blend.\(^{58}\) This is only the case when the petroleum-based plastic is also biodegradable. Such instances of biodegradable petroleum based plastics are: Poly(butylene succinate), PBS; Poly(butylene adipate-co-terephthalate), PBAT; and Polycaprolactone, PCL. If the petroleum-based polymer is not biodegradable, then the main aim of the blend is to increase the bio-based content. This is done when biodegradation ability is not so much a concern as the bio-based content.

PLA has been blended with numerous polymers in the attempt to create a partially bio-based non-biodegradable blend with high toughness.\(^{60-62}\) In order to do this, the general school of thought is to blend the PLA with a very tough, low strength polymer to balance properties. PLA blended with petroleum based polymers such as low density polyethylene (LDPE)\(^{59}\), poly(methyl
methacrylate) (PMMA)\textsuperscript{60}, acrylonitrile butadiene styrene (ABS)\textsuperscript{61}, and polypropylene (PP)\textsuperscript{62}, have been studied.

A blend of PLA/LDPE was studied by Hillmyer et al.\textsuperscript{59}. It was found that the crystallinity of the blend had a large impact on the final properties, most notable the toughness. When blending LDPE with an amorphous form of PLA, the result was an incompatible blend with poor toughness. Compatibilization was implemented to rectify this, by way of a LDPE-PLA diblock copolymer. In contrast, when semi-crystalline PLA was blended, the result was a miscible blend, even in the absence of a compatibilizer. Indeed, this led to increased toughness with the dual polymer blend.\textsuperscript{59}

Recently, Natureworks LLC released a study of several commercial-grade toughening agents for PLA.\textsuperscript{61} They found that acrylonitrile butadiene styrene with a butadiene content of 70\% had the highest effect on toughness. Using Blendex\textsuperscript{TM} 338, they saw significant improvement in the impact strength and elongation at break of the PLA. They also found that a commercial polyurethane additive known as Pellethane\textsuperscript{TM} 2102-75S was successful in improving the impact strength and elongation at break.

Blends of PLA with biodegradable polymers have also been studied.\textsuperscript{16,63-65} Poly(butylene adipate-co-terephthalate) (PBAT) presents properties that contrast those of PLA. It is for this reason that they make suitable blending partners, providing toughness and flexibility to the very brittle PLA. Jiang et al.\textsuperscript{63} studied the blends of PLA/PBAT and found that a small amount of PBAT improved the ductility and reduced the viscosity of the melted blend. This results in high toughness and good process ability.
Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is another bio-based and biodegradable polymer.\textsuperscript{67,68} Blends of PLA/PHBV were studied by Nanda et al.\textsuperscript{16} and it was found that small improvements in some mechanical properties were found depending on processing conditions and ratio of each polymer component.

Poly(caprolactone) (PCL) is a petroleum based biodegradable polymer that is rubbery and has a low glass-transition temperature. Again, it provides the contrast in properties to PLA that make it a viable blending candidate. Blends of PLA/PCL were studied by Broz et al.\textsuperscript{64} and it was found that there is little compatibility, indicating that compatibilization is required. Use of a PLA-PCL-PLA triblock copolymer to PLA/PCL blends improved the ductility of the blend.\textsuperscript{65}

\section{3. Problem Statement}

Currently, industry utilizes plastics that are mainly derived from petroleum. This is a problem, as it is not a sustainable practice for the future. In addition, many plastics that are not petroleum based have some undesirable qualities. The aim of this research is to thoroughly study the effects of blending bio-based polylactic acid (PLA) with petroleum-based acrylonitrile butadiene styrene (ABS) to improve toughness and heat stability of PLA for suitable use in durable applications. The blend will be evaluated based on its mechanical, thermal, and morphological properties. The outcome of this research is important, as it has the potential to reduce the use of petroleum-based carbon in the automotive industry.

\section{4. Objectives and Hypotheses}

The aim of this research is to blend poly(lactic acid) (PLA) and acrylonitrile butadiene styrene (ABS) to improve the performance of PLA for suitable use in durable polymer applications.
Specifically, the goal for properties is that of currently used ABS, which is used extensively for this application. This is important, as it will reduce the use of petroleum-based carbon in the form of ABS. As a corollary, the cost of such a blended polymer has the potential to be less than that of neat ABS, as PLA is currently less expensive.

This research is divided into four main sections; each one requires the completion of the previous. The development of a viable material is dependent on the success of each stage, requiring proper chemistry and polymer blending theory. Performance evaluations and prototyping will finalize the development of the material.

4.1 Objective 1

The first objective of this research is to study the performance of the neat constituents to validate their use in these studies. Specifically, the materials must be characterized in search of properties that are dependent on processing conditions. This will aid the remainder of the research, as a fundamental understanding of each polymer is required. In particular, PLA seems to have a very slow crystallization time that affects its mechanical properties. Investigating these characteristics of the polymer is imperative as the knowledge of them dictates how they are handled during blending and processing in later stages of development. With slow crystallization like that of PLA, a higher mold temperature allows more crystallinity, it is expected that more crystallinity will decrease the toughness of the polymer.

4.2 Objective 2

The mechanical properties of the neat polymers must be compared in order to select which grade of each polymer (high impact etc.) is best for blending. Generally PLA is brittle with high strength and modulus, and ABS can be found in a wide range of properties as the terpolymer
constituents are changed. It is expected that a high impact grade of each polymer is required in order to enhance the impact strength as high as possible as this is the largest drawback of PLA.

4.3 Objective 3

Once the grades are selected, a miscibility analysis must ensue to investigate the relative affinity of the polymers for each other. This will include blending in a broad spectrum of ratios to see if there is a standout ratio that produces better properties. This is conceivable depending on the thermodynamics and surface energies of both polymers. According to literature, PLA and ABS blends are widely not compatible, or immiscible. This is expected, and to create better adhesion between the polymers, the use of additives is expected to be required further down the road.

4.4 Objective 4

Experimental processing of polymer blends usually involves the use of laboratory scale equipment. These machines are generally smaller than the processing machines found in industry in order to accommodate the fabrication of many differing formulations. With the change in scale from lab to industrial, there are also changes in conditions that are applied to the polymers. This can have an effect on the performance of the polymer blends. Semi-industrial (referred to as pilot) scale machines are expected to subject the polymers to higher shear energies. This can, in turn, affect the mechanical properties, which is to be studied.

It is expected that the outcome of all of this research is the fundamental groundwork on which to base the development of a new novel biomaterial. The conclusions found here will aid in this development and can be used for more general polymer blending research.
5. Experimental Part

5.1 Materials

Keeping in mind the goal of this research is to ultimately lead to the development of a materials that is suitable for use in durable applications, the polymers were chosen accordingly. The poly(lactic acid) (PLA) based biopolymer, which is referred to in this manuscript simply as PLA, was chosen for its already improved properties. It has a bio-based content of approximately 70% (71.1%) and is based on an injection moulding grade PLA that has been modified with nucleating agent, crystal accelerator and impact modifier, among other additives. Its properties are greatly improved from neat PLA. The main properties that have been improved are the impact strength and elongation at break, giving the polymer properties that are closer to those of acrylonitrile butadiene styrene (ABS). Developing a material with properties that are similar to ABS is the objective. The idea here is to blend this polymer with ABS to further increase the properties.

Two different grades of ABS were used in blend preparation. This was done for comparison purposes. One ABS grade is a simple injection-moulding grade (Chi Mei PA 747). This was chosen as a typical middle-of-the-pack grade polymer and no attempt was made to choose it for the purpose of blending. The other ABS grade (Styron Magnum 1150 EM) was chosen in order to increase compatibility of the polymers as well as produce the best properties through blending. This ABS is a high impact grade with approximately 40% polybutadiene content.
5.2 Experimental Design

In study 1, the experiments were designed to show the effect of mold temperature on the crystallinity of the PLA based bioplastic. In addition, the mechanical properties are linked to the crystallinity, and so the final effect of the mold temperature on these properties was investigated. The experiment compared mold temperatures, but also investigated time after molding as the crystallinity may be affected. There is also a well-known kinetic transformation that the chain can undergo over time known as physical aging. The study was designed to investigate all of these effects fully, and so samples mold at 30, 60 and 90°C were investigated at 2, 5, 15 and 45 days after molding.

In study 2, the experiments were designed to investigate the viability of blending ABS and PLA. In addition, the goal of the section is to provide detailed analysis of the properties and fundamental science of the blending. Therefore, the section begins with providing neat properties of the polymers, then proceeds to detail all viable ratios of the two polymers together to show if there is a certain ratio that creates better properties than the rest. To conclude, the effect of lab and pilot scale processing was examined. A statistical analysis was completed on the miscibility analysis to see if each ratio produced a significantly different result. This was done to identify which of the blend ratios are most viable going forward with compatibilization and further development.
5.3 Compounding of PLA and ABS

5.3.1 Drying

All polymers were obtained in pellet form (weighing approximately 0.1g per pellet). Before any polymer processing could occur, the moisture level in the polymer must be decreased below 100 ppm. This is especially crucial in polyesters such as PLA, which are known to undergo chain fission through hydrolysis at high temperatures. To decrease the moisture, the polymer pellets were dried in a convection oven for at least 4 hours at 80°C.

5.3.2 Processing for Study 2

Blends were mixed and processed with a DSM micro-compounder and micro-injection moulder. Leistritz twin screw extruder in conjunction with an Arburg injection-moulder were also used to process a few select formulations. The DSM machine is a lab-scale instrument where approximately 10 g are processed at one time in a batch-style processing procedure using a twin screw micro processing. This micro-compounder was used to create blends and samples for
testing on the lab scale. Unfortunately, this is not a true representation of the conditions that are found in industrial processing of polymers.

To study the effect of conditions that are closer to industrial, the Leistritz twin-screw extruder was used to prepare the blends. The Arburg injection-moulder was used to mould the blends into samples for testing. Both of these machines are considered pilot scale and they subject the polymers to conditions that are closer to what is found in industry. Therefore, this is a good indication of the efficacy of the blend.

5.4 Characterization

5.4.1 Mechanical properties

An Instron 3382 mechanical tester was utilized to measure the tensile and flexural strength of the samples. This was completed 48 hours after processing according to ASTM standards D638 and D790 for tensile and flexural, respectively. A crosshead speed of 5 mm min\(^{-1}\) was used for tensile testing, and 1.408 mm min\(^{-1}\) was used for flexural testing. The impact strength was investigated using a TMI 43-02 notched Izod impact tester, according to ASTM D256. Five samples were taken and averaged to ensure the tests were carried out correctly.

5.4.2 Differential Scanning Calorimetry (DSC)

The crystallization was measured and quantified using a DSC Q200 from TA Instruments. The test was done to a 10 mg sample under a nitrogen flow of 50 mL/min. Ramp rate of 10°C min\(^{-1}\) were used in heat/cool/heat mode. Two samples were taken to confirm the first was correct. Crystallization percent was calculated using\(^{70}\):
\[ X_c(\%) = \frac{(\Delta H_m + \Delta H_c + \Delta H_r)}{f \Delta H_f} \times 100 \]  

(1)

where \( \Delta H_m, \Delta H_c, \) and \( \Delta H_r \) are the enthalpies of melting, cold crystallization, and reordering of polymer chains, respectively. The weight fraction of PLA in the polymer (70%) is denoted by \( f \), which is the only crystalline content in the polymer. These values were obtained by integrating the melting, cold crystallization, and reordering peaks. The heat of fusion (\( \Delta H_f \)), or the melting enthalpy of 100% crystalline PLA, was taken as 93.7 J/g, as found in the literature\(^ {17} \).

5.4.3 Dynamic Mechanical Analysis (DMA)

The storage modulus as a function of temperature was measured using a DMA Q800 from TA Instruments according to ASTM standard D4065. These tests were carried out on a dual cantilever clamp, with a heat rate of 3°C min\(^{-1} \) from 30 to 150°C, and strain of 15 μm with 1 Hz frequency. Again, two tests were taken for each sample.

5.4.4 Optical Microscopy

A qualitative analysis of the crystallization was performed using a Nikon Polarizing microscope with a hot stage attachment. An initial test was done to allow maximal crystal growth. This was done for comparison to the crystalline structure created during molding conditions. The polymer was heated to 210°C until molten, then cooled to 145°C and held isothermal for 10 min. Pictures were taken at 0, 5, and 10 min after 145°C was reached. To simulate molding conditions, the polymers were again heated until molten, then transferred to the hot stage of the microscope set at 30, 60 and 90°C, and held isothermal for 10 min. This created a crystal structure that closely resembled those found after molding at each temperature.
6. Results and Discussion Study 1: PLA Crystallization

Process parameters can have a durastic impact on the mechanical properties of the polymer. Specifically, the molding temperature can influence the degree that a polymer crystallizes. In this section, this mechanism was investigated along with the impact of crystallization on the mechanical properties. To accomplish this, three molding temperatures were used: 30°C, 60°C, and 90°C, and samples were tested 2, 5, 15, and 45 days after molding to see the effect of time.

The following chapter (6) is an excerpt from the peer reviewed journal article of the same author (prior to peer reviewing). Vadori, R. Misra, M. Mohanty, A. The Effect of Mold Temperature on the Performance of Injection Molded Poly(lactic acid)-Based Bioplastic Journal of Macromolecular Materials and Engineering DOI: 10.1002/mame.201200274 2013.

6.1 DSC and Crystallization

The crystallization behavior of the poly(lactic acid) (PLA) was studied using differential scanning calorimetry (DSC) (Figure 6.1-6.4). From the DSC graph comparing the mold temperatures, several trends are immediately apparent. The 90°C molded samples have a much smaller cold crystallization peak ($\Delta H_c$) than the 30°C or 90°C molded samples. This is attributed to the fact that the polymer molded at 90°C has chains that have fewer tendencies to move into a crystallized form when being heated. This is an indication that the chains are already in a state of higher crystallinity, but this alone cannot be used to determine the crystallinity. In addition, the 90°C mold has the highest difference between the re-ordering peak and the melting peak. This indicates that the most energy is required to break the chains into the amorphous molten state. In terms of DSC, the 90°C molded sample most closely resembles an annealed specimen, which is essentially what molding at such a heightened temperature replicates. This heightened temperature provides the energy input necessary to allow more crystallization by holding at a
temperature that is below the recrystallization, but high enough not to cause the polymer chains to freeze in the amorphous state\textsuperscript{71,72}.

Crystallization, which was calculated according to equation (1), is presented in Table 6.1. The percent crystallinity increases as a function of mold temperature. As the mold temperature is increased from 30°C to 90°C, the crystallinity increased from 25 to 43%. The 90°C mold, as suggested by the DSC curve results, has the highest percentage of crystallinity. The margin is not a small one, however, as the 90°C molded samples have a crystallinity of 43% while the 30°C and 60°C molded samples have a crystallinity of 25% and 28% respectively.

It has been well known that the mold temperature can play a role in the crystallization, but perhaps not to this extent. Although a change in the crystallinity of the polymer was expected, this change is very large. Small differences in crystallinity do not produce much difference in terms of overall performance of the polymer. However, larger changes in crystallinity can have a dramatic effect on the mechanical properties\textsuperscript{34,39,73}. Harris and Lee\textsuperscript{39} found that by increasing the crystallinity of PLA via nucleating agents, the mechanical properties and moldability were improved. They saw a 25% increase in flexural strength and modulus from a near amorphous to high crystalline sample.
Figure 6.1 - DSC Curves of PLA molded at 30, 60, and 90°C at 2 days after molding.

Figure 6.2 - DSC Curves of PLA molded at 30, 60, and 90°C at 5 days after molding.
Figure 6.3 - DSC Curves of PLA molded at 30, 60, and 90°C at 15 days after molding.

Figure 6.4 - DSC Curves of PLA molded at 30, 60, and 90°C at 45 days after molding.
Table 6.1 - Crystallinity of PLA molded at 30, 60, and 90°C as a function of time.

<table>
<thead>
<tr>
<th>Days after Molding</th>
<th>30°C Mold</th>
<th>60°C Mold</th>
<th>90°C Mold</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>25</td>
<td>28</td>
<td>43</td>
</tr>
<tr>
<td>5</td>
<td>27</td>
<td>29</td>
<td>44</td>
</tr>
<tr>
<td>15</td>
<td>28</td>
<td>30</td>
<td>44</td>
</tr>
<tr>
<td>45</td>
<td>28</td>
<td>30</td>
<td>45</td>
</tr>
</tbody>
</table>

Figure 6.5 - Schematic of crystal structure of a semi crystalline polymer. With higher crystallinity, the crystalline regions become bigger and more frequent in occurrence.
The crystallinity can also be viewed as a function of 2, 5, 15, and 45 days after molding (Figure 6.6). Looking at the graph, all three samples are influenced by similar trends. The crystallinity increases at a much faster rate directly after molding, but eventually levels off to become more stable. The 30°C mold saw the biggest increase in crystallinity over time, going from 25% to 28% crystallinity, an increase of 3% over 45 days. The 60°C and 90°C samples saw the same increase of 2%. Hu et al.\textsuperscript{46} also noted an increase in crystallinity of PLA as the aging process occurs.

![Figure 6.6 Crystallinity (%) versus time of PLA measured after molding for 30°C, 60°C, and 90°C samples.](image)

By the 45-day mark, the crystallinity of the samples is no longer increasing. The increasing crystallinity is a process in which the polymer chains slowly reorder themselves over time into a
state of higher crystallinity\textsuperscript{74}. The amorphous region also undergoes a transition into a state of lower energy, a process considered physical aging\textsuperscript{36,38,42,74} Semi-crystalline polymers such as PLA are known for undergoing this process, and this result was expected. In accordance with this study, Shieh et al.\textsuperscript{36} found that a higher amorphous fraction also leads to more physical aging in the polymer. The change in crystallinity is relatively small (\leq 10\%) and with the change in the amorphous region is considered the cause for the increase in brittleness over time of many polymers\textsuperscript{42}. This effect, compounded by regular use and wear over time can cause the failure of polymer parts that have been injection molded.

6.2 Mechanical Properties as a Function of Mold Temperature

The mechanical properties of the samples were studied and given in Table 6.2. Again, the data may be divided into trends that run across the temperatures of the molds, and into trends that follow the course of time. The differences brought on by varying the mold temperature can be seen by comparing the data of each mold 48 hours after molding. Looking at the elongation at break of the samples, it is apparent that there is a decrease seen with an increase in mold temperature. This difference is comparably large, with the largest difference being an entire order of magnitude. The 30°C mold produced a sample with tensile elongation of 243\%, which is more than a ten-fold improvement over the 90°C mold (22.4\%). The 60°C mold produces a sample with an elongation that roughly splits the difference between the 30°C and 90°C mold, meaning that the relationship between the mold temperature and the tensile elongation at break is roughly linear.

The standard deviation of the percent elongations of the 30 and 90°C molds are small, signifying a fairly stable morphology. However, the 60°C mold has widely varying results, producing a large standard deviation. This can be attributed to the fact that the 60°C mold is very proximate
to the glass transition temperature (T_g). As such, the samples are held at a temperature in which the some of the polymer chains are mobile and some are not, making the final morphology much more sensitive and easily changed from sample to sample. This creates a high variance in the results.

Table 6.2 - Mechanical properties of PLA molded at 30°C, 60°C, and 90°C.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2 (48 hours)</td>
<td>30</td>
<td>23.4 ± 0.31</td>
<td>2.52 ± 0.04</td>
<td>243 ± 5.75</td>
<td>40.6 ± 0.52</td>
<td>2.67 ± 0.05</td>
<td>113.83 ± 5.93</td>
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<tr>
<td></td>
<td>60</td>
<td>25.4 ± 0.68</td>
<td>2.56 ± 0.02</td>
<td>142 ± 37.3</td>
<td>40.8 ± 1.57</td>
<td>2.70 ± 0.08</td>
<td>103.32 ± 4.15</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>25.8 ± 0.25</td>
<td>2.50 ± 0.03</td>
<td>22.4 ± 4.21</td>
<td>45.8 ± 2.47</td>
<td>2.71 ± 0.08</td>
<td>67.68 ± 5.55</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>25.4 ± 0.82</td>
<td>2.63 ± 0.02</td>
<td>201 ± 12.34</td>
<td>43.1 ± 0.51</td>
<td>3.21 ± 0.07</td>
<td>108.23 ± 5.86</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>27.4 ± 0.98</td>
<td>2.56 ± 0.01</td>
<td>136 ± 41.21</td>
<td>41.9 ± 3.14</td>
<td>3.23 ± 0.04</td>
<td>117.43 ± 3.93</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>26.0 ± 1.16</td>
<td>2.39 ± 0.09</td>
<td>9.67 ± 2.42</td>
<td>47.1 ± 1.49</td>
<td>3.07 ± 0.10</td>
<td>70.96 ± 1.47</td>
</tr>
<tr>
<td>15</td>
<td>30</td>
<td>25.9 ± 0.34</td>
<td>2.61 ± 0.02</td>
<td>157 ± 30.42</td>
<td>43.9 ± 0.21</td>
<td>3.16 ± 0.05</td>
<td>99.05 ± 11.26</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>26.6 ± 0.50</td>
<td>2.58 ± 0.04</td>
<td>122 ± 35.07</td>
<td>46.1 ± 2.44</td>
<td>3.25 ± 0.10</td>
<td>120.03 ± 5.82</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>26.8 ± 0.69</td>
<td>2.54 ± 0.04</td>
<td>18.1 ± 2.36</td>
<td>44.6 ± 3.10</td>
<td>3.01 ± 0.05</td>
<td>66.98 ± 1.84</td>
</tr>
<tr>
<td>45</td>
<td>30</td>
<td>28.0 ± 0.72</td>
<td>2.69 ± 0.01</td>
<td>155 ± 12.62</td>
<td>45.1 ± 2.62</td>
<td>3.28 ± 0.05</td>
<td>112.81 ± 10.3</td>
</tr>
<tr>
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<td>60</td>
<td>27.5 ± 0.20</td>
<td>2.60 ± 0.03</td>
<td>135 ± 19.91</td>
<td>46.0 ± 2.55</td>
<td>3.30 ± 0.10</td>
<td>114.47 ± 6.05</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>28.2 ± 0.37</td>
<td>2.52 ± 0.04</td>
<td>12.4 ± 1.76</td>
<td>43.3 ± 1.67</td>
<td>3.12 ± 0.10</td>
<td>67.41 ± 2.22</td>
</tr>
</tbody>
</table>
Similar trends can be seen in the impact strength of the PLA. When molded at 30°C, the samples had an impact strength of 113.83 J/m while the samples molded at 90°C had an impact strength of only 67.68 J/m. The 60°C mold produced samples that again fell between the values of the other two (103 J/m), although it is closer in value to the 30°C molded samples than the 90°C molded samples. Again, the trend is that with increasing mold temperature, there is a decrease seen in properties. This trend is not a small one, as the difference between the 90°C and the 30°C molds are large, increasing the impact strength close to 70%. Studies conducted on pure PLA previously done differ from this result. Perego et al. 34 found that with pure PLA, as the crystallization increases, a decrease in the elongation and an increase in the impact strength is seen. In addition, they saw an increase in the modulus with an increase in crystallinity. The cause for the apparent difference is the presence of the additives to this grade of PLA. The impact modifier, nucleating agent, and crystal accelerant play a role in the determining properties.

The tensile and flexural strength do not produce large variance between the molds, as is found with elongation and impact strength. The slight trend that can be inferred is an increase in the strength as the mold temperature increases. This is, however, a trivial result in comparison to the increases in impact strength and elongation. The increase is very small, (tensile increases from 23.4 to 25.8 MPa, while flexural increases from 40.6 to 45.8 MPa). The modulus initially does not have any significant trends. However, as time goes by, there is a slight decrease in modulus as the mold temperature increases. This is, again, very slight and not a meaningful result in comparison to the difference seen in elongation and impact strength.
Figure 6.7 - Elongation at break versus time of PLA after molding at 30°C, 60°C, and 90°C.

Figure 6.8 - Impact strength versus time of PLA after molding at 30°C, 60°C, and 90°C.
The increase in impact strength and elongation as the mold temperature decreases is attributed to the crystallinity of the samples as well as the impact modified phase interacting with the PLA.\textsuperscript{34} As seen from the results of the DSC scans, the 90°C molded sample had a much higher crystalline content. A more crystalline polymer has more chains that are arranged in this tight configuration, and less in the loosely arranged amorphous region. When loading in the tensile and impact conditions, the toughness is increased because the chains configured in the amorphous region have slightly more freedom to move than the crystalline chains.\textsuperscript{36} Perego et al.\textsuperscript{34} also studied the effect of PLA crystallinity on the mechanical properties. They found that with pure PLA, as the crystallization increases, a decrease in the elongation and an increase in the impact strength is seen. In addition, they saw an increase in the modulus with an increase in crystallinity. With the impact modified PLA, both elongation and impact strength increased, which is due to the interaction of the rubbery additive phase with the semi-crystalline PLA. With a higher amorphous content in the PLA, the rubbery phase is more able to absorb the energy. When the PLA phase is more crystalline and therefore rigid, it does not allow the modifier to absorb as much of the energy, and therefore the impact and elongation properties are less. The difference in mechanical properties can also be attributed to the mechanism of crystalline growth. With a higher mold temperature, there is less nucleation, but the crystallites are allowed to grow to a larger size\textsuperscript{75}. This nucleation versus crystallite size can have an effect on mechanical properties as well as the amount of crystallinity of the polymer.\textsuperscript{75} Suryanegara et al.\textsuperscript{32} also found the elongation at break of amorphous PLA to be much greater than that of crystalline.

These differences that are dependent on mold temperature are seen as an increase in the toughness of the material. It is especially important in the eyes of the molder. Not only does mold temperature have an effect on properties, but also on the energy input and cycle time.
Heating a mold to 90°C all day has a large energy requirement, which costs the molding company money. With a higher temperature mold, the cycle time is also increased, as the part requires more time to set up in the mold. This has a negative effect on the amount of output of parts from the injection molder.

### 6.3 Mechanical Properties as a Function of Time

The mechanical properties of the samples molded at different temperatures may be studied as a function of time after molding. This gives insight into the stability of the material in terms of crystalline morphology. In terms of elongation at break, changes are seen in the properties over time. The 30°C molded samples decrease in elongation drastically immediately after molding, dropping from 243% to 201% between 2 and 5 days after molding. This deterioration slows, but a large decrease is still seen between 5 and 15 days, from 201% to 157%. This is where stabilization of the elongation takes place, and maintains the 155% value even after 45 days. The 60°C molded sample does decrease in its elongation nearly as much as the 30°C samples. The standard deviation is high, and all results fall into the same value range. No real trends can be excerpted from these results, thus deterioration is not seen. Unlike the 30°C samples, the 90°C molded samples shows stabilization from the beginning, staying fairly steady at approximately 20%. This is due to the crystallinity of the polymer. While the 90°C mold temperature allows more crystallization, there is less amorphous phase of the polymer. With less amorphous phase, the polymer is less prone to physical aging.

The impact strength shows some similarities to the elongation, but the change is not as dramatic. The 30°C and 60°C samples show relatively wide variance in their values, and if standard
deviation is considered, no real trends can be asserted. Although they have values that remain much higher than the 90°C molded samples, their properties fluctuate. The 90°C molded samples are much more stable in their impact strength, there is not much variance over time, and even less variance between the samples themselves (small standard deviation). There are slight increases in the tensile and flexural strength and modulus over time. This is attributed to the increase in crystallinity seen over time.

The amorphous phase of PLA is actually a dual phase consisting of a free and constrained amorphous region. The free amorphous region behaves as one would expect, but the constrained amorphous chains are situated closely to the crystalline phase which constrains their mobility to a higher degree. As time goes by, the amorphous phase of a polymer will tend to move toward a configuration of lower energy. This slow reorganization of chains is known as the physical aging of the polymer. As this occurs, the polymer becomes more brittle, which is seen in the decrease in impact strength and elongation, as well as the slight increase in modulus over time. These effects are drastic for the 30°C molded samples because they have the lowest initial crystallinity. The lower mold temperature does not allow the polymer chains to reorder themselves into a higher crystallinity. Instead, they are essentially frozen into the amorphous state, producing a highly amorphous polymer. With a higher number of chains in the free amorphous orientation, the polymer is much more susceptible to physical aging and relaxation, which is compounded by the fact that there is less crystallized region to inhibit the movement of the chains.

This equilibrium point can be seen as a configuration with a high degree of stability. In this way, the properties of the 90°C molded samples can be explained. If the 90°C molded samples are closer to the equilibrium point, the higher their stability. In accordance, the properties will have
low variance, both between the samples in a sample set (small standard deviation) and as time goes by. In contrast, the 30°C molded samples vary more both from sample to sample in the same batch of processing and as time progresses. Both of these cases are true with the 90°C molded samples, so it is then said to be more stable than the 30°C or 60°C molded samples. These results produce a practical conundrum in terms of what the molder wants. If the specifications of the part are tight and do not allow much variance, the 90°C mold should be used as it produces more stability. However, if some variance is allowed, and the overall properties, namely toughness, are important, than the 30°C mold should be used. The 60°C is never recommended as it produces slightly lower properties than the 30°C mold, and even more variance. Hu et al. also found a decrease in elongation of PLA/PEG (70%/30% by weight) blends as a function of time and crystallization.

6.4 Dynamic Mechanical Analysis

The dynamic mechanical analysis was studied and storage modulus versus temperature is given (Figure 6.9-6.12). Looking at these graphs, the DSC results are verified. Considering the 30°C and 60°C molded samples, the storage modulus decreases to zero as the temperature passes the glass transition temperature. This is because the large amount of amorphous region becomes too rubbery for the material to store energy above the glass transition temperature. After recrystallization, the ability of the material to store energy returns slightly, and thus an increase is seen to the modulus value that the 90°C mold has at that temperature. At this point (above ~90°C), the polymer is recrystallized and has a similar crystallization percent to the 90°C molded sample. The fact that the 90°C molded sample does not increase with temperature (deteriorates
through the range of temperatures) reaffirms the fact that there is very little recrystallization in the 90°C sample, and that it is already in a stable crystalline state.75

Figure 6.9 - Storage modulus versus temperature of PLA for molding at 30°C, 60°C, and 90°C at 2 days after molding
Figure 6.10 - Storage modulus versus temperature of PLA for molding at 30°C, 60°C, and 90°C at 5 days after molding

Figure 6.11 - Storage modulus versus temperature of PLA for molding at 30°C, 60°C, and 90°C at 15 days after molding
Figure 6.12 - Storage modulus versus temperature of PLA for molding at 30°C, 60°C, and 90°C at 45 days after molding.

6.5 Optical Microscopy

Studying the morphology of the crystalline phase provides a qualitative view of the mechanisms at play in this study (Figure 6.13). First looking at a sample in which the crystallites have been allowed to grow unrestricted allows comparison between large, fully-grown crystals and those made in the injection molding conditions (30, 60, 90°C). The unrestricted growth is basically an annealed sample. Studying it with a polarized optical microscope, large, clearly visible crystallites are formed. The growth is slow, as after 10 min of being held isothermal, there is still propagation. There is a fair amount of nucleation, but, more importantly, the crystals grow to a relatively large size. Looking at the 30 and 60°C samples, almost no crystallization is seen, whereas the 90°C sample has extremely faint crystals which are also very small. These figures
show the difference in crystallinity between the molded samples and also show the amount that this PLA can crystallize by investigating the crystal morphology of an annealed sample.
6.6 Study 1 Conclusions

In this study, the effect of molding temperature on the mechanical properties was investigated for Poly(lactic acid) (PLA) based bioplastic. It was found that the 90°C mold temperature produced a polymer sample with an increased crystallinity over the samples molded at the 30°C and 60°C mold temperatures. Calculated from DSC curves, the crystallinity of the 90°C molded sample was 42% versus 25% and 27% for the 30 and 60°C molded samples, respectively. As a result,
the 30°C samples had higher elongation at break and the impact strength than that of the 90°C samples. The 30°C sample had a elongation and impact strength of 243% and 113 J/m, while the 90°C sample had a elongation and impact strength of 22% and 67 J/m, respectively. This is a result of the higher amorphous region, which is able to reorder its constituent chains in order to absorb some of the stresses acting on the material. The 30 and 60°C mold temperatures produced samples with wider relative variance in properties from sample to sample, suggesting a lower stability. Over time, the toughness of the polymer molded at 30°C decreased whereas the 90°C molding produced a sample which was relatively stable over time. Even when taking into account the decrease in toughness, the 30°C molding had much higher toughness than that of the 90°C molding, producing a 10 times increase in elongation and nearly a 2 times increase in impact strength.

The method of crystallizing the polymer discussed in this study is to mold at a higher temperature, annealing the material and allowing the crystal structure to form. Alternatively, nucleating agents may be used to crystallize the polymer at lower molding temperatures\textsuperscript{47}. As shown in the study, higher molding leads to higher crystallinity, but some properties, such as impact strength and elongation, are decreased using this method. With this compromise in mind, solutions may be found dependent on the application but not as a wide-use solution for the material. This presents a practical compromise for the molder. If a polymer with very low variance sample to sample and over time is required, then the polymer should be molded at the higher temperature, which produces a more stable material. If the molder is only concerned with properties, namely toughness, than the lower mold temperature should be used. In addition, the higher mold temperature requires more energy input as well as reduces cycle time. Both cost the molder financially.
7. Results and Discussion Part 2: Polymer Blending

The following sections outline the second phase of research completed. With the final goal being to develop a bio-based polymer blend that has properties comparable to acrylonitrile butadiene styrene (ABS), the two constituent polymers must be chosen. Furthermore, their viability as blending candidates must be discerned, and then blending may ensue. The final properties that are most crucial to the success of this material are its impact strength, heat deflection temperature, and overall strength.

7.1 Viability of Blending PLA/ABS

The polymers that were chosen as candidates for blending are acrylonitrile butadiene styrene (ABS) and poly(lactic acid) (PLA). Having many desirable properties for use in durable applications, PLA was chosen as the bio-based constituent. Recently, Natureworks LLC has released a PLA based product that takes the first step toward the properties of ABS. Noted as an impact modified grade, it has improved elongation and impact strength to that of neat PLA. In addition, bio-content is in excess of 70%/wt. This particular grade was chosen to blend with ABS as properties are better matched.

To choose the grade of ABS that is best suited for blending, several effects were taken into consideration. First, from Huggins-Flory polymer blending theory, solubility parameters can be used to predict the compatibility of polymers. From literature, the solubility parameter of PLA is 9.58 cal$^{1/2}$cm$^{3/2}$. For best results, the grade of ABS that should be used to blend with PLA has a solubility parameter as close as possible to 9.58 cal$^{1/2}$cm$^{3/2}$. Taken from literature, the solubility parameter of ABS changes as a function of its rubber content. It was found that ABS with butadiene content around 40%/wt. has a solubility parameter close to 9.58 cal$^{1/2}$cm$^{3/2}$. This
allows the high impact grade of ABS to toughen the PLA to the highest possible degree. The final properties were also carefully considered based on the properties of the ABS. Along with the high impact ABS, a general injection grade ABS is tested and compared. From heretoforeward, the high butadiene content ABS will be denoted as ABS-1 and the general grade ABS as ABS-2.

![DSC curves for neat PLA, ABS-1 and ABS-2](image)

*Figure 7.1 - DSC curves for neat PLA, ABS-1 and ABS-2*

The mechanical properties of the aforementioned polymers are presented in Table 7.1, in addition to the properties of an ABS sample taken from a commercially available product. The properties of this sample serve as a goal for which the blend can aspire. ABS-1 is the high impact
grade that was chosen based on its compatibility with PLA. ABS-2 is the general injection-moulding grade with which to compare.

Comparing the two ABS grades, ABS-1, which has higher rubber content, also has higher elongation at break at 42.4% compared to 11.6%. As well, the rubber provides higher impact strength of 499 J/m compared to only 245 J/m. Generally, ABS-1 is much tougher of a material. Other properties are comparable, although ABS-2 has higher stiffness, as its polyacrylonitrile and polystyrene content are higher.

In contrast to ABS, PLA is generally known to have an inferior toughness, but high tensile strength\(^5\). However, in this high impact grade PLA, some of the strength has been sacrificed to improve the toughness.

*Table 7.1 - Mechanical properties of neat PLA, ABS-1, ABS-2 and an ABS sample from industry.*

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Tensile Strength</th>
<th>Tensile Modulus</th>
<th>Elongation at Break</th>
<th>Flexural Strength</th>
<th>Flexural Modulus</th>
<th>Impact Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[MPa]</td>
<td>[GPa]</td>
<td>[%]</td>
<td>[MPa]</td>
<td>[GPa]</td>
<td>[J/m]</td>
</tr>
<tr>
<td>ABS 1 (Magnum 1150)</td>
<td>44.4 ± 0.96</td>
<td>1.66 ± 0.02</td>
<td>42.4 ± 22.8</td>
<td>65.6 ± 2.27</td>
<td>2.18 ± 0.10</td>
<td>499.39 ± 16.2</td>
</tr>
<tr>
<td>ABS 2 (PA 747)</td>
<td>39.3 ± 0.28</td>
<td>1.92 ± 0.08</td>
<td>11.6 ± 4.67</td>
<td>67.92 ± 0.62</td>
<td>2.37 ± 0.02</td>
<td>244.95 ± 13.9</td>
</tr>
<tr>
<td>PLA (3801X)</td>
<td>30.4 ± 0.56</td>
<td>2.69 ± 0.03</td>
<td>131 ± 97.7</td>
<td>42.3 ± 0.47</td>
<td>2.95± 0.06</td>
<td>135.4 ± 7.19</td>
</tr>
</tbody>
</table>
As mentioned in previous chapters, the rule of mixtures is a general rule that can be applied to polymer blending to predict the final properties given that the polymers are miscible with each other. A rule of mixtures analysis was applied to the prospective polymer blends. Assuming equal mixing ratios, a miscible blend of PLA and each ABS grade are presented in Table 7.2. From this, it is easy to see that ABS-1 is the better candidate to generate the desired properties when blended with PLA. Both impact strength and elongation, which are crucial parameters, are expected to be better with ABS-1. Of course, as mentioned, the blend is not expected to be miscible. However, a future consideration is to compatibilize the blend, rendering it miscible. This analysis is then important for the future of this development.

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<tr>
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</thead>
<tbody>
<tr>
<td>PLA: ABS-1</td>
<td>37.4</td>
<td>2.18</td>
<td>86.7</td>
<td>53.95</td>
<td>2.57</td>
<td>317.39</td>
</tr>
<tr>
<td>(50:50)</td>
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<tr>
<td>PLA: ABS-2</td>
<td>34.85</td>
<td>2.31</td>
<td>71.3</td>
<td>55.11</td>
<td>2.66</td>
<td>190.17</td>
</tr>
<tr>
<td>(50:50)</td>
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</table>

The final consideration is the processing of the blends. To create these blended polymer materials, a twin-screw extruder was used along with an injection moulder. The basis of these
machines is to heat the polymer into a viscous melt in order to blend and shape it as desired. Thermal properties of the materials are important to these processes, and are given in Table 7.3.

The melting temperature is the most important consideration of processing. Both polymers need to be heated past their melting point. However, ABS has a generally higher melting point of PLA, which can pose a problem if the temperature required is too high. By TGA analysis, the onset of degradation was determined for each polymer. Degradation of PLA occurs 123°C higher than the melting temperature of ABS, suggesting that properties of PLA will not decrease during processing at required temperatures.

Table 7.3 - Thermal properties of neat PLA, ABS-1 and ABS-2

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Melting Temperature (°C)</th>
<th>Onset of Degradation (°C)</th>
<th>Heat Deflection Temperature (°C)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS 1 (Magnum 1150)</td>
<td>218 *</td>
<td>403 ± 3</td>
<td>96.10 ± 2.3</td>
<td>-</td>
</tr>
<tr>
<td>ABS 2 (PA 747)</td>
<td>190 *</td>
<td>406 ± 6</td>
<td>86*</td>
<td>-</td>
</tr>
<tr>
<td>PLA (3801X)</td>
<td>161 ± 1.56</td>
<td>341 ± 5</td>
<td>45.93 ± 1.5</td>
<td>38.8 ± 3.1</td>
</tr>
</tbody>
</table>

*Values have been taken from technical data sheets provided by respective companies.

7.3 Blend Optimization and Miscibility Analysis

As mentioned in previous sections, the miscibility of many polymer blends is limited to certain ‘windows’ of blending. In other words, a polymer blend may only be miscible in certain
blending ratios. Depending on the surface energy and thermodynamics of mixing of the constituents, the morphology is highly dependent on the polymer ratios. Generally, blends find themselves in a co-continuous state at equal volumes, and become dispersed/continuous as the volume of one is increased.

These changes in morphology can lead to very different properties as a compounded effect along with the constituent properties of the blend. If a blend moves from co-continuous to dispersed/continuous, there is much less volume of interphase between the polymers. In addition, increasing the volume fraction of one of the polymers will cause the properties of that polymer to increasingly dominate the properties of the final blend. It is for this reason that miscibility analysis must be conducted – to see which ratio is the most viable for blending.

Presented in Table 7.4, mechanical properties of PLA/ABS-1 blends with decreasing volume fractions of PLA. Statistical analysis was completed on this data using the Tukey method of one-way ANOVA. This statistical analysis was completed on the three most important properties in this development, elongation at break, impact strength and heat deflection temperature. Given with the values in the table are alphabetical representations of the statistical results. In a given column (separating each property), each different letter represents a value that falls into its own statistical range and is significantly different than all values of dissimilar letters. The letter ‘A’ represents the highest value range, and it descends alphabetically. For the elongation at break, there is only two significantly different ranges which the values fall into. The highest range holds the values of ratios 10:90 and 90:10. This simply indicates that the lack of interphase that occurs when one of the phases is below 10-15% allows the major polymer to apply its own properties to the entire sample. Both the impact strength and elongation at break have five different ranges that occur for six values, indicating that a difference occurs with each different formulation ratio.
Impact strength decreases as the ratio tends toward 1, again signifying that the interphase impedes the performance of the polymer blend. On the other hand, the heat deflection temperature increases with increasing ABS-1 content, showing that regardless of the phase configuration, the ABS-1 is still able to lend its heat absorbing capabilities to the blend. This is again discussed in following sections.

For all blending ratios, the final properties fall outside the rule of mixtures, always being lower. This indicates that the blends are not miscible in any ratio. This result is expected, as immiscibility generally dominates. Since all PLA/ABS-1 blend ratios are immiscible, the best option is to choose the blend with the best balance of potential properties and bio-content.

Table 7.4 - Mechanical properties of PLA:ABS-1 blends with decreasing PLA content.

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<thead>
<tr>
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<tbody>
<tr>
<td>90:10</td>
<td>30.5 ± 1.74</td>
<td>2.45 ± 0.04</td>
<td>41.7 ± 35.7</td>
<td>44.4 ± 0.56</td>
<td>3.04 ± 0.01</td>
<td>93.36 ± 7.34</td>
<td>47.19 ± 0.7</td>
</tr>
<tr>
<td></td>
<td>(A)</td>
<td></td>
<td></td>
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<tr>
<td>80:20</td>
<td>27.0 ± 0.68</td>
<td>2.23 ± 0.04</td>
<td>10.9 ± 4.87</td>
<td>43.9 ± 0.38</td>
<td>2.90 ± 0.06</td>
<td>63.55 ± 10.9</td>
<td>48.62 ± 1.2</td>
</tr>
<tr>
<td></td>
<td>(B)</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70:30</td>
<td>27.2 ± 0.85</td>
<td>2.10 ± 0.03</td>
<td>5.73 ± 0.82</td>
<td>46.9 ± 0.61</td>
<td>2.71 ± 0.05</td>
<td>44.76 ± 4.92</td>
<td>52.49 ± 0.9</td>
</tr>
<tr>
<td></td>
<td>(B)</td>
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<tr>
<td>Proportion</td>
<td>Elongation at Break (B)</td>
<td>Impact Strength (E)</td>
<td>Heat Deflection Temperature (C)</td>
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<tr>
<td>50:50</td>
<td>28.2 ± 0.52</td>
<td>5.61 ± 2.59</td>
<td>47.7 ± 0.47</td>
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<tr>
<td></td>
<td>2.03 ± 0.02</td>
<td>4.6 ± 0.02</td>
<td>41.13 ± 8.94</td>
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<tr>
<td></td>
<td>65.93 ± 1.5</td>
<td>2.46 ± 0.02</td>
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</tr>
<tr>
<td>30:70</td>
<td>31.9 ± 0.39</td>
<td>15.9 ± 7.27</td>
<td>55.0 ± 0.08</td>
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<tr>
<td></td>
<td>1.83 ± 0.01</td>
<td>2.31 ± 0.01</td>
<td>76.15 ± 5.79</td>
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<td>84.13 ± 1.0</td>
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<td>10:90</td>
<td>37.3 ± 1.02</td>
<td>43.9 ± 7.59</td>
<td>61.0 ± 0.43</td>
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<td></td>
<td>1.71 ± 0.03</td>
<td>2.15 ± 0.02</td>
<td>363.0 ± 61.55</td>
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<td>94.87 ± 2.1</td>
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Figures 7.2, 7.3, and 7.4 demonstrate the progression of key properties with increasing proportion of ABS-1. Elongation at break is a result of the immiscibility seen in these blends. As the volume of the interphase increases to the highest point (50:50 blend) the state of the blend is co-continuous. With a higher volume of the interphase (higher interaction between polymers), if there is poor compatibility, then the properties will be greatly affected. This is exactly the case in this instance. There is poor adhesion between the polymers, and as they are constrained to interact in great amounts, the properties decrease greatly.

The impact strength follows the same trend, although there is a great disparity between the impact strength for PLA and ABS-1. When the ABS-1 dominates the blend (90% or more), then its properties lend greatly to the final properties, and it causes the graph to appear one-sided. The heat deflection temperature (HDT) follows a different trend. As the volume of ABS-1 increases, the HDT increases steadily. This is due to the heat absorption ability of ABS-1.
incompatibility of the phases has a smaller effect on the HDT than on mechanical properties because although the sample is being stressed and strained mechanically, the property is dependent on the ability of the material to absorb the heat energy. The ABS-1 volume in the blend allows this absorption to occur, minimizing the deflection of the sample. Therefore, the higher the ABS-1 content, the higher the final HDT of the sample.

The low compatibility of the blend is a challenge, but is can be overcome through compatibilization. This involves the use of additives to increase the adhesion between phases, or to act as a buffer that both polymers are compatible with. Taking into account the potential properties of the blend after compatibilization, the 70:30 PLA:ABS-1 blend is the most viable ratio to continue development of the material. It has the best balance of potential properties and bio-content.

![Elongation at Break](image)

**Figure 7.2** - Elongation at break of blends of PLA:ABS-1 with increasing ABS-1 (Magnum 1150) content.
Figure 7.3 - Impact strength of blend of PLA:ABS-1 with increasing ABS-1 (Magnum 1150) content.

Figure 7.4 - Heat deflection temperature of blend of PLA:ABS-1 with increasing ABS-1 (Magnum 1150) content.
Figure 7.4 - Heat deflection temperature of blends of PLA:ABS11 with increasing ABS-1 (Magnum 1150) content.

7.4 Large Scale Extrusion and Injection Molding

Lab scale processing of polymer blends is an excellent method to determine the viability of that blend in terms of compatibility and overall properties. However, lab scale processing as done to this point does not subject the polymer melt to the same conditions as seen in industry. Industrial scale processing applies greater energies to the polymer\textsuperscript{79}. This energy is mostly conducted into the polymer through the shearing action of the screws in the extruder. Thus, it is important to measure the effects of large scale versus lab scale processing especially when dealing with polymers that are known to undergo chain size reduction when exposed to high temperatures and energies for periods of time\textsuperscript{80}. Poly(lactic acid) (PLA) has been well known to display this kind of behaviour.

Miscibility analysis was completed on PLA/acrylonitrile butadiene styrene-1 (ABS-1) blends to verify if there is a ratio of PLA to ABS-1 that blends particularly well. Polymer blending theory suggests that some miscible blends are only miscible in certain windows, but in the case of PLA/ABS-1, no such window exists. There is little or no adhesion between the phases in all ratios, and so the more interface that is present, the lower the overall properties will be. Thus, 70:30 PLA:ABS-1 ratio was chosen as the most viable as it has the best balance of bio-based content and potential properties (according to the rule of mixtures).
Table 7.6 - Mechanical properties of neat PLA, ABS-1 and PLA:ABS-1 blend after processing in large scale machinery.

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<tr>
<td>Pilot Scale</td>
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<tr>
<td>PLA</td>
<td>23.4 ± 0.31</td>
<td>2.52 ± 0.04</td>
<td>243 ± 5.75</td>
<td>40.6 ± 0.52</td>
<td>2.67 ± 0.05</td>
<td>113.83 ± 5.93</td>
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<td>ABS</td>
<td>39.2 ± 0.59</td>
<td>1.60 ± 0.01</td>
<td>34.1 ± 18.9</td>
<td>62.5 ± 1.16</td>
<td>1.98 ± 0.04</td>
<td>429.70 ± 11.0</td>
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<td>70:30</td>
<td>27.2 ± 0.85</td>
<td>2.10 ± 0.03</td>
<td>5.73 ± 0.82</td>
<td>46.9 ± 0.61</td>
<td>2.71 ± 0.05</td>
<td>44.76 ± 4.92</td>
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<tr>
<td>Lab Scale</td>
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<tr>
<td>PLA</td>
<td>30.4 ± 0.56</td>
<td>2.69 ± 0.03</td>
<td>131 ± 97.7</td>
<td>42.3 ± 0.47</td>
<td>2.95 ± 0.06</td>
<td>135.4 ± 7.19</td>
</tr>
<tr>
<td>ABS</td>
<td>44.4 ± 0.96</td>
<td>1.66 ± 0.02</td>
<td>42.4 ± 22.8</td>
<td>65.6 ± 2.27</td>
<td>2.18 ± 0.10</td>
<td>499.39 ± 16.2</td>
</tr>
<tr>
<td>70:30</td>
<td>27.9 ± 1.34</td>
<td>2.34 ± 0.01</td>
<td>4.92 ± 1.31</td>
<td>44.4 ± 0.89</td>
<td>2.56 ± 0.06</td>
<td>43.43 ± 12.74</td>
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</tbody>
</table>

Table 7.6 presents the properties of PLA, ABS-1 and a 70:30 blend (PLA:ABS-1) after extrusion and injection moulding in semi-industrial scale processing equipment. For comparison, the properties of PLA, ABS, and the blend are given after processing in lab scale equipment. The retention time in each machine is similar, allowing for direct comparison between the two processes.

Figures 7.5 and 7.6 give the large scale and lab scale data side by side for PLA for comparison reasons. The large-scale data is inferior to the lab scale in all areas except for the elongation at
break for PLA. The reason that it is decreased from lab to large scale is the polymers have been subjected to higher shearing energies and have likely gone through a reduction in molecular weight\textsuperscript{55}, causing properties to decrease.

The elongation at break on the other hand is increased from lab to large scale processing. This is likely because of the crystallization of the PLA polymer\textsuperscript{48}. As was demonstrated in the first section of the results, the elongation at break is highly dependent on the crystal structure of the PLA. In the large-scale process, the moulding occurs into a large mould that acts as a heat sink at the temperature required. In this case, the polymer was cooled instantly to a temperature of 30°C upon injection. This causes a highly amorphous polymer because adequate time is not given for crystallites to form. Therefore, as explained in section 1 of the results, a higher elongation at break is achieved. When moulding in the lab-scale processing equipment, the smaller mould cannot act as a heat sink, allowing the polymer more time to cool. This creates a polymer that is slightly more crystalline than if processed with large-scale equipment.

For ABS-1, all properties are decreased from lab to large-scale processing. The effect is not as severe, but the underlying principles remain the same. The higher shearing and energy input into the polymer melt ultimately causes a reduction in properties. Comparing the data obtained from blending ABS-1 and PLA both on the lab and large scale, the properties remain very close. This indicates that the effect of the higher shearing effect is dominated by the fact that there is little adhesion between phases, causing the properties to remain.
Figure 7.5 - Mechanical properties of PLA when processed in large scale versus lab scale equipment.

Figure 7.6 - Mechanical properties of PLA when processed in large scale versus lab scale equipment.
Figure 7.7 - Mechanical properties of ABS-1 when processed in large scale versus lab scale equipment.

Figure 7.8 - Mechanical properties of ABS-1 when processed in large scale versus lab scale equipment.
Considering the dynamic mechanical analysis (DMA) data presented in Figure 7.9, several important parameters can be seen. Firstly, the glass transition temperature of PLA and ABS-1 are 60°C and 122°C respectively. When blended, the resulting polymer displays two distinct glass transition temperatures. Each one is representative of the constituent polymers although slightly shifted from original. The glass transition peak found at 62°C corresponds to PLA and the peak found at 102°C corresponds to ABS-1. The fact that there are two separate and distinct glass transition is a good indication and further proof that the two polymers are not compatible. As compatibilization occurs, the blended polymer will display glass transition peaks that move close together, and eventually become a single peak – indicating adhesion between phases.

Figure 7.9 - Tan delta of PLA, ABS-1, and PLA:ABS-1 blended 70:30.
Storage modulus of PLA, ABS-1 and the 70:30 blend are presented in Figure 7.10. As expected, ABS-1 holds its stiffness in the presence of a heat ramp. It holds much of its mechanical integrity until after reaching 100°C. The PLA, on the other hand, is heated up only to its glass transition before becoming rubbery. After this temperature is reached, the PLA loses ability to store energy input mechanically. At approximately 80°C, the polymer undergoes recrystallization when enough heat is given to the polymer chains to allow them mobility, and therefore recrystallization. This allows the modulus to return to the polymer, showing an increase in the graph. The blend shows the same behaviour as PLA, though is slightly less affected by the heat. This is due to the presence of ABS-1 and its ability to absorb the heat without much reduction in ability to store mechanical energy.

*Figure 7.10* - Storage modulus of PLA when processed in large scale versus lab scale equipment.
As far as the morphology is concerned, there is very little discernable difference between the neat polymers and the blends. This is due to the fact that the PLA has been modified with several additives. The morphology (Figure 7.11-7.13) of the ABS-1 is somewhat rough looking with the fracture surface showing some signs of brittle fracture. This is mostly due to the fact that the sample was cryogenically frozen and therefore the rubber was in a brittle stage during fracture. In addition, since ABS-1 is a compatible terpolymer, there are three constituents in its structure. All three of these phases are present in the morphology, showing a complex structure rather than a smooth, clean break. The PLA shows a similar fracture as does the blend of the two polymers. It is clear, however, from the morphology of the fracture surface of the blend that there is little compatibility between the phases. There are striations in the direction of fracture, indicating that a smaller amount of energy was required to break the sample.

![SEM micrographs of ABS-1 morphology at 2000X (A) and 6000X (B)](image)

*Figure 7.11 - SEM micrographs of ABS-1 morphology at 2000X (A) and 6000X (B)*
Figure 7.12 - SEM micrographs of PLA morphology at 2000X (A) and 6000X (B)

Figure 7.13 - SEM micrographs of PLA:ABS-1 70:30 morphology at 2000X (A) and 6000X (B)
7.5 Study 2 Conclusion

This study was done in several sections and spans a breadth of areas of polymer and blend development. First, the viability analysis was completed on blending poly(lactic acid) (PLA) and acrylonitrile butadiene styrene (ABS). In this investigation, the properties of PLA as well as two grades of ABS were measured to show the potential properties of blending PLA and ABS. In addition, two ABS grades were used, the one selected solely for the purpose of blending proved to be a much better blending candidate. It showed better compatibility as well as potential ability according to the rule of mixtures.

To investigate the vulnerability of the material properties to larger scale processing, a semi-industrial scale twin-screw extruder and pilot scale injection moulder were utilized. As expected, the properties decreased when processing in the semi-industrial machines in comparison to the lab scale machines. This was due to the higher shear energies experienced in the larger equipment. The outcome of this study was that the high impact grade ABS (ABS-1) was a decidedly better candidate than the general purpose injection grade ABS (ABS-2). In addition, through the miscibility analysis, it was found that the blending ratio of PLA:ABS-1 was best at 70:30 for further development.

8. Economic Assessment and Significance

Advantages of many bioplastics include biodegradability, renewability, low energy input and less carbon dioxide (CO₂) emission. Use of renewable plastics can help in reducing CO₂ content
in the atmosphere by CO$_2$ sequestration. Through life cycle analysis (LCA), it has been shown that bioplastics have a smaller impact on the environment$^{82,83}$.

Polymer materials are newcomers to the bulk material market. Their use only extends into the previous century, while materials such as metals, wood, cement have been used for centuries, if not millennia. Between 1971 and 2006 the plastics production in the European Union grew by an annual increase of 4.6%, while other bulk materials only grew by 0.7% in approximately the same time.$^{84}$ To the same end, only 15% of the world’s population account for 50% of the total world production of plastics.$^{84}$ This indicates that there is still room enough for sustained growth in the market, most notable among developing countries.

Recently, a shift has been generated as the world concern has brought environmental issues, climate change, and non-renewable resources (i.e. fossil fuels) into the forefront. Bioplastics are currently viewed as a potential substitute for some non-renewable materials. As such, and considering the aforementioned potential of polymers in general, it is likely that bioplastics will continue to grow. They only require a small meaningful share of the polymer industry to be able to substantially diminish the current industry’s environmental impact.$^{84}$

Previously, the high price of poly(lactic acid) (PLA) was a restriction for its use. This restriction narrowed its applications to medical and specialty areas. Breakthroughs have come in lactide and polymerization technology that have created production possibilities for PLA in higher bulk volumes. Since 2002, when PLA was first produced on a large scale, it has been gradually penetrating the market. Its application range extends into packaging, textiles, nonwovens, electronics, agriculture in addition to several domestic and durable uses. Companies see future potential in transport as well as electric appliances and electronics.$^{84}$.
PLA is (as of 2009) offered at $1.20/lb and has since been reduced in price.\textsuperscript{84} NatureWorks is the first to produce PLA on the large scale. The largest producer of lactic acid and lactides is PURAC, its Thailand plant has a capacity of 100,000 t.p.a. Several emerging companies are also seeing potential for PLA\textsuperscript{84}. Sulzer and Synbra are producing foamed PLA, similar to expanded polystyrene. The price of PLA is expected to drop below $1.00.\textsuperscript{84}

The cost of ABS is tied to the price of petroleum, as it is a petroleum-based polymer. It currently stands just above the price of commodity plastics such as polypropylene, at approximately $1.20 per pound.

9. Conclusion

Each individual study was concluded in sections 6.6 and 7.5 respectively. This section serves as a summarization of the significance and scope of the project to date.

The research completed in the different sections of these studies serves as the fundamental understanding that is required as the first step toward developing a successful polymer blend. The unique properties of the bio-based impact modified poly(lactic acid) (PLA) were investigated with special attention to its crystallinity as a function of processing. The crystallinity, as it was found, impacts the mechanical properties of the material to a great degree. The mechanical properties of ABS and PLA were then given with several experiments designed to show the true blending nature of the two polymers. It was found that they do not form a miscible blend alone, but with the help of a compatibilizer, a viable material may be found.

This investigated information has been empirically obtained and observed through careful experiment and it lays the groundwork for the development of a new novel material. By
developing materials that incorporate bio-carbon and still maintain performance of the material, we are looking to nature as a source of inspiration. This is without a doubt a more sustainable method for material design and development. In addition we are curbing our dependence on a non-renewable based resource. This research done here is part of a growing foundation of research and development towards developing a bio-based material of certain desirable performance for some practical uses. With further research, our target is in engineering a new bio-based material with high bio-carbon content for real world applications.

10. **Future Recommendations**

The research that has been done to date is leading toward the goal of developing a material that is partially bio-based and has the performance properties to replace currently used acrylonitrile butadiene styrene (ABS) plastic. This would create more sustainable manufacturing in various industries including electronics and automotive. An investigation has been completed providing information necessary to complete this material development. This includes viability analysis, compatibility analysis, a study of the effect of mold temperatures on mechanical properties, and a study of the effect of scale of processing on the mechanical properties.

The required next steps in this development are to find an efficient compatibilizer that allows adhesion between the poly(lactic acid) (PLA) and ABS phases of the material. With this done, mechanical and thermal properties are expected to increase dramatically. A suitable biofibre must be reengineered on the surface to allow to bonding to the polymer matrix. Once the biofibre is also compatible, a complete investigation of all underlying fundamental processes leading to the properties can ensue.
11. References


76. Menczel JD, Prime RB. *Thermal analysis of polymers*. Wiley Online Library; 2009.


