New Engineered Materials from Biobased Plastics and Lignin

by

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NEW ENGINEERED MATERIALS FROM BIOBASED PLASTICS AND LIGNIN

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The blending of lignin as a component in a thermoplastic blend poses a challenge in the form of dispersion and compatibility. Polyesters such as poly(lactic acid) and poly(butylene adipate-co-terephthalate) offer the best opportunity of compatibility in melt blending with lignin due to their ability to form hydrogen bonds. The fractionation of lignin into more homogeneous fractions offers better dispersion and more consistent properties, retaining the toughness of the original polymer in addition to bridging stress transfer between PLA and PBAT. Functionalization of lignin was done by lactic acid grafting. The resulting blend of PLA/PBAT/modified fractionated lignin showed improved interaction between lignin and PLA, but reduced compatibility between lignin and PBAT.

This thesis provides a deeper understanding on the effect of lignin heterogeneity, its fractions, and the functionalization of lignin on lignin and bioplastic blends to further the use of a largely produced industrial by-product in high value applications.
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Glossary:

COOH – Carboxylic acid
DMA – Dynamic mechanical analysis
DMF – Dimethyl formamide
DMSO – Dimethyl sulfoxide
DSC – Differential scanning calorimeter
dTGA – Derivative thermogravimetric analysis
FTIR – Fourier transform infrared
GMA – Glycidyl methacrylate
GPC – Gel permeation chromatography
HKL – Hardwood Kraft lignin
HPL – Hydroxypropylated Kraft lignin
KL – Kraft lignin
LLDPE – Linear low density polyethylene
M_n – Number average molecular weight
M_w – Weight average molecular weight
M-KL – Modified Kraft lignin
M-MSL – Modified methanol soluble lignin
MIL – Methanol insoluble lignin
MSL – Methanol soluble lignin
OH - Hydroxyl
PBAT – Poly(butylene adipate-co-terephthalate)
PBS – Poly(butylene succinate)
PBSA – Poly(butylene succinate-co-adipate)
PBSL – Poly(butylene succinate-co-lactate)
PCL – Poly-ε-caprolactone
PE – Polyethylene
PEO – Poly(ethylene oxide)
PET – Poly(ethylene terephthalate)
PDLA – Poly(dexorotary-lactic acid)
PDLLA – Poly(dexorotary-co-laxorotary-lactic acid)
PHA – Polyhydroxylalkanoate
PHB – Polyhydroxylbutyrate
PLA – Poly(lactic acid)
PLLA – Poly(Lexorotary-lactic acid)
PMMA – Poly(methyl methacrylate)
PP – Polypropylene
PS – Polystyrene
PVAc – Poly(vinyl acetate)
ROP – Ring opening polymerization
SEC – Size exclusion chromatography
SEM – Scanning electron microscope
SKL – Softwood Kraft lignin
\( T_c \) – Crystallization temperature
\( T_g \) – Glass transition temperature
\( T_m \) – Melting Temperature
\( \text{Tan} \delta \) – Tan delta
TGA – Thermogravimetric analysis
THF - Tetrahydrofuran
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1.0 Introduction
One of the observable trends in the field of plastics in recent years is the possible shift from fossil fuel based resources to that of renewable origins. Some of the factors causing this shift include: rising oil prices, the unsustainable practice of using materials derived from fossil fuel, and increased amount of materials being landfilled. The growing realization that this process is unsustainable triggered initiatives such as the three ‘R’s: reduce, reuse, and recycle. However, these initiatives still do not create the closed-loop cycle that creates sustainability because it is still dependent on petroleum resources [1]. The solution: bioplastics.

Plastics are consistently seeing increased numbers of applications globally. As a result, the global plastics production increased by 10 million tonnes in 2011, a relatively modest growth of 3.7% (in comparison to the 5% average annual growth in the past 20 years), resulting in global annual production of 280 million tonnes [2]. This staggering number requires vast amounts of fossil fuel derived chemicals to fulfill the global demand. This dependency on fossil fuel is highly sensitive to the volatile oil prices, affecting the price of commodity plastics such as polyethylene and polypropylene [3].

In addition to the unstable feedstock prices, non-biodegradable polymers also face the problem related to its end of life issues. Although some recycling does take place, the majority of end of life plastic products end up in landfills, incinerated, or simply left in the environment [4]. The option of landfilling of non-biodegradable plastics allow for contained allocation of plastic wastes, but is slowly becoming an unviable option due to the staggering amount of material being produced and disposed annually [1]. Combustion is the most used
alternative to landfilling in order to completely disintegrate waste plastic products. However, the burning of these plastic products would mean releasing additional carbon in the form of carbon dioxide into the atmosphere, a major greenhouse gas contributing to global warming [1]. The last and least attractive scenario is uncontained disposal of plastic wastes. This scenario leads to the destruction of habitat and wildlife [5].

The use of renewable resourced and/or biodegradable bioplastics remedies most of these problems. The use of renewable resources to produce these plastics creates a more sustainable approach since these resources are ultimately derived from carbon dioxide present in the atmosphere, thereby reducing the effect of global warming [1]. Additionally, the use of biodegradable plastic reduces the amount of material that has to be landfilled, while plastic that does happen to escape into the environment would eventually degrade through a combination of hydrolytic degradation, photodegradation, and microbial degradation [6].

The largest issue preventing renewable resourced bioplastics to be widely adopted is associated with the cost of production of commercial synthetic bioplastics from raw materials such as sugars and starches [7]. To overcome this, an approach to reduce the material cost by adding low cost additives like talc and calcium carbonate [6]. A more sustainable alternative to common commercial fillers is by utilizing agro-residues and industrial by-products such as natural fibre, protein isolates, and lignin [8]. In addition to lowering the costs of the resulting material, this approach also adds value to the by-products, thereby creating a more sustainable end product.
Lignin is a naturally occurring polymer that is synthesized by most plants to act as a binder for cellulose and hemicellulose in the plant structure [9]; hence it is one of the most abundant renewable biomaterial available. Industrially, lignin is a by-product of the paper industry and the second generation biofuel industry [10]. The amount of lignin in woody materials used for these processes can vary between 15-30%, which totals to 70 million tons of lignin produced annually from the paper industry alone. Currently, almost all the lignin produced is used as an inefficient source of boiler fuel, producing less energy per unit mass compared to other sources such as coal [9]. Due to its natural abundance, availability in the commercial market, and naturally occurring form, lignin has a great potential to be utilized as low cost filler for bioplastics, possibly even adding to material properties.

1.1 Research Problem
Addition of lignin into a synthetic bioplastic such as PLA would further reduce the market price of the resulting blend to be competitive with that of conventional petroleum based polymers. The challenge regarding the mixing of these two components comes in the compatibilization of the two materials [10]. The compatibility of the two materials would create a more continuous and homogeneous structure which would dictate the ability of the composite to absorb and dissipate stresses applied. Additionally, lignin has a unique chemical structure which could be taken advantage of in more specialized applications [11].

Although lignin has hydroxyl groups that could form hydrogen bonding with the carbonyl groups of the PLA structure, the compatibility of the two components are still nowhere near optimal [12]. However, these hydroxyl groups are highly reactive functional groups which could be exploited to add new functionalities onto the lignin molecule. The method that will
be studied in this project is the grafting of lactic acid onto lignin to produce branched arms of poly(lactic acid) on the lignin structure. Based on the concept of “like dissolves like”, the grafting of lactic acid on lignin would potentially increase its compatibility with PLA and improve its tensile, flexural, impact, and thermal properties compared to the uncompatibilized composite.

Lignin is also a heterogeneous material, in that it is highly varied in constituent, structure, and molecular weight even in a single plant [11]. Issues in reproducibility and ability to study the interactions between lignin and polymer have stemmed from this heterogeneity. As such, lignin needs to be homogenized prior to polymer blending in order to better understand the properties of each lignin fractions in the polymer matrix in addition to attaining better and reproducible results.

This project consists of two parts.

In the first part, lignin was fractionated by methanol extraction to separate it by differences in chemical structure and molecular weight. The fractionated lignin will then be blended with PLA and PBAT to achieve a balance of properties to study the interaction between lignin and the polymer matrix.

The second part consists of functionalizing lignin by the polycondensation of lactic acid onto lignin hydroxyl groups, which will be characterized by thermal and infrared spectroscopy techniques to confirm grafting and analyze the structure of PLA grafted lignin. After, functionalization, the modified and unmodified lignin will be blended with PLA and PBAT matrices at various weight percentages, where it’s mechanical and thermal properties will be investigated to evaluate the compatibilization level on the blend properties.
1.2 Literature Review

1.2.1 Lignin

Lignin is one of the most abundant renewable resources available. Being a constituent of most plants, lignin acts as a binder which holds together cellulose, hemicelluloses, and other plant cellular materials, giving strength and flexibility to the plant structures [13]. Figure 1 shows the schematic of a mature cell wall [14]. Sections 1-4 indicate the cell wall of a plant while section 5 is the interstitial lamella between each cell. Lignin exists in both the cell wall sections and the middle lamella. In the middle lamella, lignin exists at a very high concentration compared to the other components as a three dimensional polymer network with lamella thickness of more than 100 nm [13]. Lignin in the cell walls exists as two dimensional network polymer sheets of with a thickness of approximately 2 nm which is chemically bound to hemicellulose by benzyl ether linkages. The hemicellulose in turn sheathes the crystalline cellulose fibre bundles known as microfibrils, which can be observed in sections 1-4 as lines spanning out around the cell wall. As a result, the two dimensional lignin matrix holds the microfibrils together in the cell wall layers with the help of hemicellulose. Lignin itself has no direct adhesion with cellulose due to their compatibility [13]. Layer number 1, the primary wall is the first layer created during the growth process and starts out as a pectin-rich layer which later turns into a lignin rich layer. As observed in the Figure 1, the arrangement of microfibril in the primary wall is random whereas the subsequent layers are much more organized. The middle layer, which is the thickest, has a lateral organization which provides mechanical properties characteristic of wood. Additionally, the lignin content from the outer cell wall to the inner cell wall gradually decreases while cellulose and hemicellulose increases. Apart from providing structure in the plant, lignin has also been known to reduce dimensional changes in wood due to changes in
moisture content, and increase toxicity to reduce damages that may be caused by decay and most insect attacks.

**Figure 1. Schematic of a plant cell wall.** Redrawn after reference [14].

Although much is still unknown about the biosynthesis of lignin, its structure has been extensively studied. Lignin is a polyphenol produced from three monomers as shown in figure 2: para-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol [9,15], which are converted into para-hydroxyphenyl, guaiacyl, and syringyl residues upon polymerization. The chemical structures of lignin differs from plant to plant, even differs in parts of the plant. For example, softwood lignin is composed mainly of guaiacyl structures; hardwood lignin is composed of almost equal parts guaiacyl and syringyl; while grass lignin is composed of all guaiacyl, syringyl, and para-hydroxyphenyl structures [9,15]. An example of proposed
chemical structure of softwood lignin can be seen in figure 3. These phenolic structures are polymerized through various linkages to produce complex three dimensional structures characteristic of lignin [9,16]. As a result, different structures of lignin have slightly differing properties, such as the more condensed structure of softwood lignin with higher number of inter- and intramolecular bonds, causing lower mobility which increases the $T_g$ of softwood lignin when compared to hardwood.

Figure 2. Chemical structure of lignin monomers. Redrawn after reference [15].

Currently, lignin is produced from two large industrial processes: the paper industry, and the second generation bioethanol industry utilizing lignocellulosic from agricultural residues [9]. This thesis mainly focuses on lignin produced from the paper industry through the Kraft process. The Kraft process breaks down the lignocellulosic structure by dissolving the lignin and hemicelluloses phase at high pressure and temperature in sodium hydroxide and sodium
The resulting insoluble pulp is bleached and formed into paper while the lignin phase is combusted to recover the inorganics. The lignin produced by the Kraft process is deemed relatively pure of cellulose; however it may still contain hemicelluloses. Additionally, the treatment at high temperature and pressure under basic medium hydrolyzes the bonds that connect lignin and cellulose, producing hydroxyl groups on the lignin structure [8]. Both aliphatic and phenolic hydroxyls are exposed from this process. New functionalities could be introduced to lignin through reaction pathways that utilize these hydroxyl groups.

Although relatively free of cellulose and hemicellulose, the lignin molecule resulting from the Kraft pulping process is highly heterogeneous in structure, molecular weight, and co-monomer ratios, affecting various material properties such as its solubility and glass transition temperatures. The heterogeneity of lignin largely comes from the previously

![Proposed model softwood lignin chemical structure. Redrawn after reference [8].](image-url)
mentioned differences in the lamella and wall structures [11,13]. The molecular weight distribution of lignin taken from Organosolv and chemical pulping shows bimodal behavior in its molecular weight distribution consistent with the two types of lignin structures [11]. It has also been suggested that the higher degree of phenylpropane group arrangement in the cell wall structure is aligned tangential to the secondary wall due to the orientation of cellulose microfibrils in the secondary wall [11].

A number of lignin fractionation and solvent extraction studies has been conducted to further understand the heterogeneity of lignin. Both aqueous and a number of organic solvents have been used to fractionate lignin, along with ultrafiltration processes [11,17-29].

One of the most commonly used compounds to fractionate lignin is dichloromethane (CH$_2$Cl$_2$). It has been shown that Lignin compounds extracted by solvent with weak or moderate hydrogen bonding capability such as dichloromethane [17-19], ethyl ether [20], and ethyl acetate [21] tend to be much lower in molecular weight. Gel permeation chromatography (GPC) study of these compounds show that they have a relatively low polydispersity (1.4-2.1), while the number average molecular weight (M$_n$) of these fractions tend to range between 200-1500 depending on the source and extraction process employed, however softwood Kraft lignin are most often below 800 [17]. Based on the molecular weight, it has been concluded that these fractions are monomers and oligomers of the phenyl propane molecule that make up lignin[20]. Additionally, in most cases these lignin only represent a small weight percentage of most commercial lignin unless the lignin has been severely damaged by the methods employed. Acidic functional groups found in this fraction are also higher than the higher molecular weight compounds, along with a higher carbon and lower oxygen content [17]. It has also been found that lower molecular weight compounds
tend to have a higher ratio of phenolic hydroxyl group and lower aliphatic hydroxyl groups consistent with values obtained from elemental analysis [17,19].

Other commonly used solvents are propanol and iso-propanol [27,28]. Propanol extractions of lignin that have been treated with dichloromethane are generally one step above those obtainable by dichloromethane in size, with $M_n$ ranging from 1050 to 2700 (softwood Kraft lignin are generally <1500) also having relatively low polydispersity ranging from 1.4 to 2.7. The resulting lignin has a higher number of hydroxyl groups than its lower molecular weight fraction, with an average of 1.34 OH group for each phenyl propane monomer as opposed to 1.07 for the dichloromethane fraction. Acid functionality saw a decrease when compared to the dichloromethane counterpart from 2.3 to 1.1 mmol/g. This fraction accounts for 20-40% weight of the overall lignin [28].

The use of methanol as a fractionating solvent extracts lignin molecules with similar average molecular weights as those that can be extracted by propanol ($M_n$ range of 440-3300); however they have a much higher polydispersity index (1.7-7.2), hence a higher yield of 33-53%. The resulting material is more heterogeneous than the propanol fraction. General observable trends include: lower phenolic OH content, lower sulfur content, lower methoxy content, and lower acid content. No change is observed with regards to aliphatic hydroxyl content between propanol and methanol fractions [17-19].

Solvents that could dissolve larger molecular weight compounds generally could also dissolve the lower molecular weight fractions. Well documented solvents include: Alkali solutions, dimethyl formamide (DMF), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), and pyridine [11]. Solvent mixtures can also dissolve a majority of the undissolve
components. Solvent mixtures that have been studied include: isopropanol/water mixture and 60:40, and methanol/dichloromethane mixture at 70:30 by weight [27]. These solvent and solvent mixtures generally dissolve the remaining lignin molecules, which mean the resulting lignin has a higher $M_n$ and high polydispersity index depending on the original lignin’s heterogeneity [27]. This fraction has a low phenolic hydroxyl content, lower overall hydroxyl content, lower methoxy content, higher ether groups, and lower acid content, along with unsaturated hydrocarbons. Aliphatic hydroxyl groups however, do not see much change between propanol, methanol, and high molecular weight fractions [17].

The lignin fractions insoluble to the solvents listed generally still contain hemicelluloses and cellulose fragments. Hemicellulose and cellulose fragments do not dissolve in the same solvents as lignin [20], hence fragments containing lignin attached by a covalent bond to hemicelluloses and cellulose are not soluble in any solvent.

### 1.2.2 Bioplastics

The simplest definition of bioplastic is: a form of plastics that are derived from renewable resources, or plastics that are able to biodegrade within a relatively short period of time as defined by ASTM D6400. The classifications of bioplastics are outlined in figure 4 below. Among all the categories, the one not included under the term bioplastics is the non-biodegradable and non-renewable resource based plastics such as fossil fuel based polyethylene (PE), polypropylene (PP), poly(ethylene terephthalate) (PET), and polystyrene (PS).
The bioplastics placed under the renewable column are made from renewable resources derived directly or indirectly from carbon dioxide present in the atmosphere. An example of a material directly derived from carbon dioxide is poly(propylene carbonate) (PPC) which is produced by polymerizing propylene oxide and carbon dioxide [30]. On the other hand, carbon dioxide can be indirectly made into bioplastics through plants and microbes. Plants take carbon dioxide in the atmosphere and convert it into sugar molecules which can be converted into cellulose and starches within the plant, or used as a feedstock for microbial fermentation, converting them into usable monomers such as lactic acid which can be polymerized into poly(lactic acid) (PLA) [31].

Mixed resource polymers are partially derived from renewable resources and partially derived from fossil fuel. An example is poly(trimethylene terephthalate) (PTT). PTT is made of polymerizing 1,3-propanediol which is fermented from sugars, and terephthalic acid which is derived from petroleum based resources [7]. Although they have more impact on the
environment due to the presence of fossil fuel derived material, they are still nevertheless a shift from 100% non-renewable based plastics.

Materials that fall under the non-renewable column are derived from petroleum based resources. These materials are generally derived from chemicals collected from the crude oil refineries, which are chemically converted into usable monomers to be polymerized into the resulting polymer [3].

All biodegradable plastics fall under the bioplastic umbrella simply due to the fact that they prevent waste accumulation. For a material to be biodegradable, it has to be able to break down into smaller molecules through the help of water hydrolysis, enzymatic hydrolysis, or photodegradation, where the smaller molecules can then be metabolized by microbes into carbon dioxide [31]. Plastics such as PLA and PHA are produced from carbon dioxide from the atmosphere, and breaks down back into carbon dioxide after biodegradation, creating a closed loop cycle [1]. On the other hand, the non-renewable, biodegradable plastic is a much more unsustainable alternative since it contributes to the net increase of carbon dioxide into the atmosphere. Some examples of petroleum based biodegradable plastics include poly(butylene adipate-co-terephthalate) (PBAT), poly-ε-caprolactone (PCL), and poly(vinyl alcohol) (PVOH).

Plastics that fall under the non-biodegradable, but are fully or partially derived from renewable resources are also numerous in numbers. For Example, Braskem (Brazil) has produced a method of converting bio-ethanol into ethylene, which can then be polymerized into bio-polyethylene [7]. Such non-biodegradable but renewable resource based plastics
converts the plastic into a carbon sink, capturing carbon dioxide from the atmosphere and storing them for indefinite period of time.

In prior decades, bioplastics were only found in specialty applications such as degradable medical devices [16]. This is due to the high cost of production and instability for long term applications. The advent of modern technology has allowed for large scale productions of alternatives to petroleum based plastics by using feedstock derived from renewable resources [6]. As a result, the manufacturing of plastic does not contribute to the emission of greenhouse gases. Additionally, newly commercialized methods to produce renewable resource based, non-biodegradable plastics will also help the shift to bioplastics.

The market for bioplastics is rapidly increasing. The largest and oldest commercially produced bioplastics, starches and cellulose esters, are predicted to reach an annual production of 668 million kg by the year 2013, which doubles the production capacity in a time span of only 4 years [7]. On the other hand, the annual production of poly(lactic acid) (PLA) was 229 million kg in the year 2009 and predicted to reach an annual production of nearly half a billion kg in the near future allowing the price of PLA and other bioplastics to compete with conventional petroleum based polymers such as polypropylene and polyethylene [7]. These increased production capacities are made possible by the combination of economy of scale and technological advances. Increased demand for renewable and sustainable products has triggered the increase in demand for biobased plastics.

While the problems associated with high production costs have been largely reduced, the aforementioned instability that causes the degradation of these products still remains;
however, these instabilities have become a characteristic desired in a large number of applications [31]. Pollution, increased costs associated with waste disposal, and the decreasing areas for land filling are the main cause of this need. As a result, degradable plastics have begun to fill in its niche in applications where waste disposal is a concern.

1.2.3 Poly(Lactic Acid)

Figure 5. Chemical structure of PLA.

The monomer of poly(lactic acid), lactic acid was discovered in 1780 by a Swedish chemist named Carl Wilhelm Scheele in sour milk, which was later determined by Louis Pasteur to be a fermentation metabolite of certain micro-organism [32]. Additionally, lactic acid was thought to be an impure form of acetic acid due to its low volatility, and the isomers were thought to be two different chemicals due to difference in solubility. The industrial production of lactic acid was first established in 1881 by fermentation of starch and sugars by lactic acid producing bacteria, which can be controlled to produce optically pure isomer of lactic acid whereas production through chemical synthesis would produce a racemic mixture of the isomers [32].

Figure 6. Condensation reaction of two lactic acid monomers into its dimer.
Lactic acid is the simplest form of chiral alpha hydroxy acid, as shown in figure 5 above, which means it contains a carboxylic acid group and an alcohol group on the adjacent carbon, giving it two reactive functionalities (figure 6) in addition to two optical isomers (figure 7), the dexorotary lactic acid (d-lactic acid) and the lexorotary lactic acid (l-lactic acid) [32]. Lactic acid also easily reacts with another lactic acid molecule to produce a dimer by esterification reactions, where the carboxylic acid group condenses with the hydroxyl group to form an ester bond, and releases water. This reaction can easily be reversed through the hydrolysis of the ester bond by water. As a result, a solution of lactic acid under normal storage condition would never be 100% pure due to the presence of water, oligomers, and even its cyclic dimer: lactide. The polymerization of PLA will be covered in section 1.2.6.

![Lactic acid optical isomers and its cyclic dimer.](image)

The physical and mechanical properties of PLA are highly dictated by the optical purity and the placement of the optical isomers [6]. Properties obtained from poly(l-lactic acid) (PLLA) or poly(d-lactic acid) (PDLA), random copolymers of poly(d,l-lactic acid) (PDLLA), and block copolymers of PDLLA differ from each other [6]. Additional parameters affecting PLA properties include: molecular weight, polymerization conditions, thermal history, and purity.

PLLA and PDLA polymers are semi-crystalline due to their stereoregularity, which is similar to isotactic polypropylene. On the other hand, the random copolymer of PDLLA is completely amorphous, and is analogous to atactic polypropylene [6]. As a result, PDLLA does not show any crystallization or melting enthalpies under differential scanning
calorimetry (DSC) tests, while PLLA have melt crystallization, cold crystallization, and melting enthalpies due to formation and deformation of crystals. Typical values for glass transition temperature of PLLA are between 50 and 70 °C with a peak melting temperature located between 170°C and 190°C [6,16,33]. Past its glass transition temperature, a polymer shifts from brittle, glassy state to its rubbery state where polymer chains have more mobility.

Crystallization of PLA occurs during the cooling of molten PLA where the formation of crystals creates a more thermodynamically stable conformation [6]. This crystallization is heavily affected by cooling rate, where fast cooling rate would create lower crystallinity due to the rapid removal of energy, preventing chain movements to create crystals, resulting in small and imperfect crystals. Slow cooling rate, energy is dissipated slowly, providing enough energy for the crystals to grow. On the other hand, the cold crystallization, which occurs between $T_g$ and $T_m$, is caused by movement of amorphous polymer chains to produce a more thermodynamically stable arrangement. PLA can also be annealed at its crystallization temperature to achieve higher crystallinity [6,33].

The mechanical properties of PLA is comparable to that of polystyrene with tensile modulus of 3000-4000 MPa, tensile strength of 50-70 MPa, flexural modulus of 4000-5000 MPa, and flexural strength of approximately 100 MPa. However, since PLA is in its glassy state at room temperature, it is generally brittle with elongation of 2-10% and low impact resistance [6].

The properties of PLLA and PDLLA also have a few differences due to their stereoregularities and the inability of PDLLA to crystallize. For example, the tensile strength
of PDLLA is 10-20 MPa lower than that of PLLA, in addition to lower flexural strength, impact strength, heat deflection temperature, and Rockwell hardness [16,33].

Molecular weight also plays a significant role in the properties of PLA. Flexural strength of a PLA with molecular weight of 23000 Da was found to be 64 MPa; at 58000 Da, the flexural strength was found to be 100 MPa; while at 67000 Da, the flexural strength was 106 MPa [6].

Another factor affecting the mechanical properties of PLA is crystallinity. The effect of crystallinity can easily be observed by the comparison of annealed and non-annealed samples [6]. Due to larger crystal size and domains, increase in modulus and strength is common. Although change in elongation is generally not observed with change in crystallinity, impact resistance is generally improved. Low crystallinity PLA (3-9%) with notched Izod impact resistance of 2-3 kJ/m² was increased to 3-7 kJ/m² at crystallinities of (45-70%) [6]. This improvement was even more significant for unnotched Izod impact which increased from 14-20 kJ/m² to 18-35 kJ/m² [6].

Methods to increase the toughness of PLA have seen some success. Such methods include blending with a tough polymer, copolymerization, grafting, plasticization, and the addition of branched polymers [6]. This project studies a combination of the first and last method: the blend of PLA/PBAT and branched polymer with lignin core [6].
1.2.4 Poly(Butylene Adipate-co-Terephthalate)

![Chemical structure of PBAT](image.png)

**Poly(Butylene Adipate-co-Terephthalate)**

Figure 8. Chemical structure of PBAT.

Compared to PLA, studies that have been conducted on the aliphatic-aromatic copolyester poly(butylene adipate-co-terephthalate) (PBAT) are lower in number and much more recent [34-37]. Biodegradable aliphatic polyesters such as PLA, PHB, and PCL have existed prior to the development of PBAT, however they lack properties that can be provided by aromatic polyesters such as poly(ethylene terephthalate) (PET). The development of aliphatic-aromatic copolyesters provided biodegradability and good tensile properties [35].

PBAT is a class of biodegradable petro-based biopolymer currently commercialized by a few companies including BASF (Ecoflex) and Xinfu Pharmaceuticals (Biocosafe 2003) [7]. The properties of PBAT have been compared to that of low density polyethylene with regards to its elongation, tensile strength, melting temperature. Commercial PBAT is known to be a toughening material for PLA since it has an elongation of more than 500% and extremely high impact strength in addition to biodegradability [38]. Poly-\(\varepsilon\)-caprolactone (PCL) has also been used as a toughening material for PLA, however its low melting point of 60°C prevents it from being a lucrative toughening material with the already temperature sensitive PLA; PBAT on the other hand has a melting temperature of around 110°C which makes it far more desirable than PCL as an impact modifier [6].
Synthesis of PBAT is done with the monomers (figure 9) 1,4-butanediol, adipic acid, and terephthalic acid through a one-step bulk polycondensation of the monomers with an acidic catalyst [34]. Properties of the resulting polymer have been found to be dependent on the molar ratio of adipic acid to terephthalic acid [34,35]. Tensile strength of PBAT films were found to improve from 8 MPa for 31 mol% terephthalic acid to 12 MPa for 39 mol% terephthalic acid at which optimum molar ratio for tensile strength is observed [34]. The elongation at break of the same films saw a decreasing trend with increased aromatic content while melt temperature and hydrophobicity increased with increasing terephthalic acid content. Additionally, increasing terephthalic acid content showed reduced biodegradability [39].

Currently, commercial PBAT is being produced from petrochemical resources which creates an even larger environmental impact compared to non-degradable polymers due to its ability to breakdown into carbon dioxide, contributing to the increase in greenhouse gasses. However, this fact may change in the very near future with commercial production of partially biobased PBAT.
1,4-butanediol is currently being commercially produced by BioAmber, with Genomatica planning for production in 2013 [40,41]. The production process employed by BioAmber involves converting its bio-succininc acid fermented from sugars into 1,4-butanediol through catalytic conversion process [41]. Advances in the field of metabolic engineering has also successfully produced bio-1,4-butanediol from the fermentation of renewable carbohydrate feedstocks by the bacteria *E. coli*. A simple substitution from petro-based 1,4-butanediol to biobased 1,4-butanediol would constitute between 35-40% biobased content, a substitution currently planned by Novamont to improve PBAT’s environmental footprint and lower production costs [42]. The production of bio-adipic acid, which is currently produced from petrochemical based cyclohexane, is also being developed by a number of companies including DSM, Verdezyne, Rennovia, and BioAmber will be in commercial production as soon as 2015 [43]. Similarly, biobased terephthalic acid has also been developed by Toray using bio-paraxylene produced by Gevo [44]. Based on the current development, it is possible that we might have a fully renewable PBAT by the middle of the decade.

### 1.2.5 Blends of Poly(Butylene Adipate-co-Terephthalate) and Poly(Lactic Acid)

One of the most studied blends of PBAT is with PLA due to their complementary properties and the resulting biodegradability of the blend [38,45-53]. PLA has high tensile and flexural strength and modulus; however it is brittle in comparison with many commercial polymers. As such, the most common study done on PLA blending is to blend it with a tough polymer to improve its toughness. PLA/polyolefin and other non-biodegradable polymer blends have been extensively studied and the addition of LLDPE was found to improve PLA’s impact
resistance to up to 350 J/m compared to the 20 J/m of neat PLA [6]. However, to retain its compostability and improve its toughness, a biodegradable and tough polymer must be added. Possible polymers include: poly-ε-caprolactone (PCL), poly(vinyl alcohol) (PVOH), poly(butylene succinate) (PBS), poly(butylene succinate-co-adipate) (PBSA), poly(butylene succinate-co-lactate) (PBSL), and of course PBAT [6].

PBAT and PCL have relatively similar mechanical properties with extremely high toughness and flexibility (elongation of >500%), which means a small quantity of either material would impart significant toughness to PLA, retaining high biobased content [6]. However, PBAT is superior to PCL with regards to its thermal properties. PCL has a T_m of ~60°C making it unsuitable in certain environmental conditions, whereas PBAT has a T_m of ~110°C. Additionally, a T_g of ~ -60°C for PCL and ~ -35°C for PBAT indicate that PBAT would have better miscibility with PLA which has a T_g of ~60°C due to the lower T_g difference [6].

A study of the thermal properties of a PLA/PBAT blend with up to 20% PBAT content showed no change in the glass transition temperature profiles [38]. Through dynamic mechanical analysis (DMA), the tan δ plot showed a peak for each polymer, one at -30°C for PBAT and one at 60°C for PLA indicating their glass transition temperatures. The resulting blends showed two peaks contributed by each component which remain unchanged indicating lack of significant molecular interactions between the two polymers [38]. This lack of change in the T_g of the blends was confirmed by values obtained from differential scanning calorimetry (DSC) curves done at 5 and 10°C/min. On the other hand, the cold crystallization temperature that is attributed for PLA showed a 10°C reduction from 117.8°C and a narrower peak width for all PLA/PBAT blends indicating enhanced crystallization of PLA. This is confirmed by the increased number of crystals in PLA/PBAT blends when
observed through the polarized optical microscope. However, similar values observed with crystallization enthalpy and melting enthalpies for neat PLA and the blends indicate no significant change in final crystallinity [38]. DSC curves also showed separation of PLA melting peak into 2 melting peaks where one has a maxima corresponding to neat PLA and the other has a maxima that is 3°C lower which indicate presence of a new crystalline structure induced by PBAT. This effect however was not observed at higher heating rates. Another DSC study of PLA/PBAT blends showed done at 40°C/min showed a reduction in PLA $T_g$ when PBAT content is increased from 0% to 2.5% followed by a gradual increase in $T_g$ from PBAT content of 2.5% to 20% [45]. This result indicates the miscibility of PLA/PBAT blends up to 2.5% PBAT content where $T_g$ decrease was observed, followed by a reduced miscibility as PBAT content was increased. The same study attributed the reduction of cold crystallization temperature to the anti-nucleating effect of PBAT due to the molten state of PBAT at PLA cold crystallization temperature. As a result of this anti-nucleating effect, cold crystallization temperature, crystallinity, and melting temperatures were all reduced as PBAT content was increased [45].

Studies done on the mechanical properties of PLA/PBAT blends found that the blend toughness behaved as predicted [46]. Tensile strength were found to gradually decrease along with modulus with increased PBAT content while elongation and impact strengths were improved significantly even with only 5% PBAT content. Typically, PLA undergoes brittle fracture where fracture takes place without any visible plastic deformation. On the other hand, PBAT undergoes ductile fracture, where yield occurs, followed by cold drawing and stress induced crystallization before the occurrence of fracture. The resulting PLA/PBAT blends showed ductile fracture even at 5 weight% PBAT in the PLA matrix [46]. Percentage
Tensile properties of the neat PLA and the PLA/PBAT blends are reported in Table 1. Elongation at yield remains at approximately 2% for neat PLA and all the PLA/PBAT blends while elongation at break undergoes a significant increase at 5 weight% PBAT and a gradual increase in elongation with increasing PBAT content. The decrease in tensile strength and modulus were also as expected due to the lower strength of PBAT [46].

SEM Micrographs of the cryo-fractured surfaces of the PLA/PBAT blends showed the blend morphology [45]. The surface of neat PLA (100% PLA) showed no necking and elongation, producing a smooth fracture surface. On the other hand, the fracture surface of neat PBAT polymer showed significant plastic deformation, creating a coarse surface. At 2.5 weight% of PBAT, the fracture surface showed almost no signs of plastic deformation and no phase separation creating an almost smooth surface, which is uniform with the large T_g shift [45]. At 5 or more weight% of PBAT however, phase separation becomes visible where PBAT is formed as droplets in the PLA matrix [47]. The size of the droplets increased with increasing PBAT content. This phase separation effect is consistent with the debonding effect of rubber toughened system. Studies conducted at PBAT contents of higher than 20% showed different behavior compared to those with lower PBAT content. At 30 weight% PBAT, a number of thin and short PBAT fibril could be observed while the PLA phase showed discreet elongated structures. At 50 weight% PBAT, the PLA and PBAT phases are banded and connected with each other indicating a co-continuous structure [47]. At even higher PBAT content (70% and 80%), PBAT matrix can be observed with PLA inclusions. As such, it can be concluded that the phase inversion of the PLA/PBAT blend begin to occur at 30 weight% PBAT [47].

Compatibilization of the blend has a potential to improve some of the properties. The addition of a free-radical would induce reactive compatibilization within the polymer structures [48]. The addition of a peroxide, 2,5-dimethyl-2,5-di(tert-butyl peroxy) hexane, of
up to 0.2 weight% for a 25 weight% PBAT blend showed improved elongation. Further addition of peroxide caused the blend to become brittle due to extensive crosslinking and degradation of the polymers confirmed by size exclusion chromatography (SEC). This is observed with the blend morphology, where the size of PBAT inclusions were observed to gradually decrease with increasing peroxide content of up to 0.2%, upon which further addition of peroxide caused the blend to have large domains with irregular size and shape. A study of the T_g through tan δ curves showed decreasing gap between the T_g of PLA and PBAT with increasing peroxide content [48].

Another study used a random ternary block co-polymer of ethylene, acrylic ester, and GMA (T-GMA) (M_w: 240,000 g/mol), which is made up of 24% acrylic ester, 8% glycidyl methacrylate (GMA), and 68% ethylene, in a reactive extrusion process [49]. The glycidyl groups on the copolymer is responsible of forming ether bonds with PLA or PBAT hydroxyl groups creating a larger copolymer with PLA and PBAT structures to compatibilize the two polymer phase. At 10% PBAT content, elongation at break was improved with addition of 2 and 5 weight% T-GMA, but was reduced at 10 weight% T-GMA; impact strength was improved for PLA/PBAT blends with up to 30% PBAT content and reached maximum impact strength at 4% T-GMA content; while tensile strength was mostly unaffected. Morphology of 70/30 PLA blend with and without 5% T-GMA showed reduced amount of debonding with more shear yielding upon the addition of T-GMA [49].

Another compatibilized blend of PLA/PBAT involves inducing transesterification of PLA and PBAT to produce a compatibilizing block co-polymer by the addition of terbutyl titanate (TBT) during melt extrusion [50]. Tensile strength was improved on the addition of 0.1% TBT and continues to increase until it reaches a plateau at 0.5% TBT. Elongation was
improved from 50 to nearly 300% at 0.4% TBT while impact strength increased from 5 to 9 kJ/m². Tensile fracture surface showed a nearly smooth surface when no TBT was added, whereas the blend with 0.5% TBT showed short oriented fibrils. Impact fracture samples showed cavitation and debonding for blends uncompatibilized blends and a smooth surface for 0.5% TBT samples indicating highly improved dispersion [50].

Methods employing ultrasound to improve dispersion of PBAT in the PLA matrix have also seen success [51]. The polymer blends were melt mixed in the presence of a sonicator and then compression molded. For a blend with 50/50 PLA/PBAT content, the T_g of the PLA phase as indicated by tan δ curve showed a reduction of 3°C with 10 second sonication time whereas the T_g of the PBAT phase showed a minor increase. With longer sonication time, the T_g was seen to move further apart [51]. Similar results were observed with the mechanical properties where 10 second sonication time showed improved Young’s modulus, and 20 second sonication time showed the best tensile strength upon which longer sonication time would cause the tensile properties to revert back to the original or even worsen. SEM morphological study of unsonicated blends showed an average domain size of approximately 8.8 µm, which was reduced to 4.7 µm at 30 second sonication. The behavior of the PLA/PBAT blends was observed to be similar to an emulsion system. At less than 30 second sonication time, enough acoustical energy was added to the system to reduce interfacial tension and improve dispersion, whereas at sonication times longer than 30 seconds, the energy added assisted in the flocculation of the dispersed PBAT to increase domain size [51].
1.2.6 Thermoplastic Blends of Lignin

Studies have been conducted to utilize lignin as a component in polymer blend systems, especially with polymers that are polar in nature due to their ability to form hydrogen bonds with lignin hydroxyl groups [9,11,12,22-24,26,28,29,54-77]. Most bioplastics have the proper functional groups to form hydrogen bonds with hydroxyl groups. Poly(L-lactic acid) (PLLA) have been blended with lignin without any addition of compatibilizers [12,54]. The existence of intermolecular interactions between PLLA and lignin were confirmed by DSC and FTIR studies, however tensile strength, elongation, and modulus all were reduced with increasing lignin content. It was shown that the addition of lignin reduced the molecular weight of PLLA molecules, and that the addition of lignin adds two factors that contribute to the reduction in mechanical properties: disruption of PLLA continuous phase and accelerated thermal degradation with increasing lignin contents [12]. Similar trends were observed with blends of lignin and polyhydroxybutyrate (PHB) where DSC curves showed gradual shifts in the T_g of PHB as the content of lignin is increased [56,57]. FTIR analysis of the lignin/PHB blend also showed shifts in carbonyl and hydroxyl peaks, indicating the presence of interaction, while SEM showed miscibility of the blend up to 30% lignin content. Lignin and polycaprolactone (PCL) blending showed no significant changes in the DSC curves, however strength and elongation were found to gradually decrease while modulus was improved with increasing lignin content [58]. Blending of lignin and polybutylene succinate (PBS) showed a reduction in tensile strength at low lignin content followed by gradual increase with increasing lignin content; increases in tensile modulus, flexural strength, and flexural modulus; and reduction in elongation and impact strength as the amount of lignin in the blend is increased [59].
The chemical modifications of lignin through its hydroxyl groups for polymer applications have been extensively studied since 1980s [11,22,23,60-62,78,79]. Ghosh et al [23] reacted the hydroxyl group of lignin with simple acid anhydrides to produce lignin-acetate, lignin-butyrate, lignin-hexanoate, and lignin-laurate, which add increasing lengths of linear carbon chains (n = 2, 4, 6, 12) to the lignin structure. The lignin esters were then blended with polyhydroxybutyrate (PHB) [23]. By fitting the glass transition temperatures of 0 to 100% PHB/lignin blends with the Fox equation, which approximates the theoretical value for glass transition temperatures, the extent of compatibility can be seen based on how much the experimental deviates from the theoretical. PHB/lignin blends showed slight shifts in the glass transition temperature of the lignin, indicating some interaction. It was also shown that the addition of lignin and modified lignin retards PHB crystallization.

Another study on lignin ester blends combines PCL with lignin-acetate, lignin-propionate, lignin-butyrate, and lignin-valerate (n = 2, 3, 4, 5) [58]. DSC study showed a shift in $T_g$ for blends containing low weight percentage of lignin esters, but began to deviate from theoretical approximation line at 20-80% lignin content. It was also shown that lignin butyrate and valerate has better compatibility to the PCL matrix compared to lignin acetate and propionate. This is due to the fact that the lignin derivatives containing butyrate and valerate have similarities to the structure of caprolactone, therefore better compatibility. Although no improvement in mechanical properties was seen compared to neat PCL, the observable trend shows that tensile strengths and elongation of the blends increase in increasing carbon chain length, while modulus is reduced with increasing carbon chain length, showing the effect of increased compatibility between the lignin and PCL phase.
The blend of lignin and polyethylene oxide (PEO) has been extensively studied for the purpose of melt spinning into lignin based carbon fibres [63,64]. The trend produced by the \( T_g \) of lignin/PEO blends followed the Kwei equation closely indicating the compatibility of the blend. FTIR of the blend showed gradual shift in the hydroxyl peak indicating presence of hydrogen bonding. The melt spinning of hardwood kraft lignin (HKL)/PEO blends were continuous for all ranges while softwood kraft lignin (SKL)/PEO blends only formed continuous fibres with lignin content of less than 75%. For HKL/PEO and organosolv/PEO blends, it was observed that strength and modulus was increased at 95% lignin/5% PEO content due to the disruption of intermolecular interaction of lignin macromolecules, while elongation was improved at 25% lignin/75% PEO content due to the elimination of supramolecular lignin complexes and formation of miscible blend system.

One of the earliest graft copolymerization of lignin was conducted in the early 1980s. Hydroxyalkylation of lignin was conducted as a route to reduce the brittleness of lignin derived polymers and improve the viscoelastic properties of such polymer by combining the high modulus lignin structure with lower modulus aliphatic ether [65,78]. The hydroxypropyl arms were created by reacting the carboxylic acid and hydroxyl groups of lignin with propylene oxide with KOH as the catalyst. It was found through a reaction rate study of model compounds, that the reaction rate of copolymer formation increases with increasing nucleophilicity, meaning the reaction rate is highest with aliphatic hydroxyl groups, followed by aromatic hydroxyl groups, and carboxylic acid groups. Analysis of the hydroxypropylated lignin (HPL) showed reduction in \( T_g \) and increased solubility in organic solvents, but no significant difference observed in the molecular weight or molecular weight distributions.
The resulting HPL have been blended with a number of polymer matrices to observe differences in properties of compatibilized and uncompatibilized blends. Blends of the HPL with polymethylmethacrylate (PMMA) produced a two-phase system which showed shifts in $T_g$ of PMMA to a higher temperature, increase in modulus with increasing HPL content, but reduced tensile strength [61]. The study also observed the effect of HPL molecular weight on the properties of the blend, to which no significant effects were observed. A comparison of blending method showed that tensile properties of the blend are better when the samples are injection moulded as opposed to solution cast moulded. Another study on the blend of HPL with polyvinyl alcohol (PVOH) showed that for PVOH with 0% hydrolyzed content, the blend showed distinct phase separation; however, at higher hydrolyzed content, the blend showed no sign of phase separation indicating highly compatibilized blends due to the presence of hydrogen bonding [79]. Blend of HPL with polycaprolactone (PCL) showed that the crystallization of the PCL matrix is highly dependent on the $T_g$ of the HPL core, hence the molecular weight and the length of the hydroxypropyl chain. It was found that the degree of crystallinity increases with the length of hydroxypropyl chain length.
1.2.7 Synthesis and Properties of Branched PLA Structures

The polymerization pathways of lactic acid into PLA (figure 10) can be classified into three general types: formation of high molecular weight linear PLA (red), branched PLA (blue), and telechelic PLA (green). The pathway to form high molecular weight linear PLA can further be broken down into direct condensation method, azeotropic dehydration method, and ring opening polymerization.

In the direct condensation method (top red arrow), lactic acid is heated at temperatures above its boiling point in the presence of catalyst. Water in the reactor needs to be continuously removed as it can hydrolize the ester groups formed, and reverse the equilibrium. During the conversion from monomer to low molecular weight oligomer, water can easily be evaporated due to the low viscosity of the reaction mixture; however, at higher molecular weights, removal of water becomes much more difficult due to lack of mass transfer caused by high
viscosity of the mixture [6]. The presence of water at this stage can cause reaction to reach equilibrium, and cause transesterification reactions to occur, which would reduce molecular weight and broaden the molecular weight distribution. The direct polycondensation generally produces PLA of low molecular weight due to the mass transfer limitations. A possible method to further increase the molecular weight can be done by conducting a solid-state polycondensation where the end groups located in the amorphous phases are further reacted at low temperature with a metal catalyst under vacuum conditions to remove water formed. General attainable molecular weight by melt polycondensation method is 2,000-10,000 g/mol while solid-state polycondensation allows for PLA of molecular weights of up to 100,000 g/mol.

An alternative method that has been adopted in place of melt polycondensation is the azeotropic dehydration method to overcome the viscosity problem is by the addition of a non-polar solvent which solubilises PLA. Due to the similar boiling points of water (100 °C) and lactic acid (122 °C), the mixture creates an azeotrope adding to the difficulty in water removal [32]. In addition to solubilising PLA, the addition of non-polar solvent breaks the azeotrope of water and lactic acid, easing the removal of water. Since the removal of water is not an obstacle, one of the largest advantages is the achievable range of molecular weight of well above 300,000 g/mol [6]. The monomer used for the azeotropic dehydration method is lactic acid, which is lower in cost compared to lactide used in the ring opening polymerization, which requires an additional preconditioning step to produce. Additionally, due to the addition of solvent, lower reaction temperatures could be adopted which allows for retention of optical purity. The disadvantages of this method are mainly associated with the solvent. The addition of solvent would add additional costs and environmental concerns as
the polymer would need to be collected from the solvent in addition to complete removal of the solvent from the final product.

The reaction mechanism of the ring opening polymerization (ROP) method is shown in figure 11. Lactide, the cyclic dimer of lactic acid is initiated by a molecule containing hydroxyl group which opens the ring by breaking an ester bond to form a new ester bond with the initiating molecule, attaching a lactic acid dimer onto the molecule. The resulting reaction leaves a hydroxyl group at the end of the lactic acid dimer to further initiate another lactide molecule. One of the largest advantages of the ROP method is the lack of water formation, allowing for high molecular weight structures to be attained [16]. The ROP method however requires for lactide to be manufactured from low molecular weight pre-polymer from polycondensation process, making the ROP method a 2 step process. Typically, lactide can be manufactured by heating PLA to induce backbiting reactions which form lactides, and vacuum atmosphere to distill off lactide molecules that are formed. The produced lactide could be a racemic mixture (a combination of D and L-lactides) or optically pure (only D or L-lactides) which can be easily separated based on the different melting points of each isomeric structure. As such, ROP is typically the preferred method to produce high molecular weight PLA due to its high degree of controllability [33].

![Figure 11. Reaction mechanism of ring opening polymerization (ROP) of PLA [32].](image)

The telechelic and branched PLA structures are generally copolymer systems which take advantage of an existing polymer with hydroxyl functionality to allow for lactide to be
grafted on the molecule. The telechelic PLA produces a linear PLA molecule. However, due to the symmetric nature of the co-monomer, the functionality of the end groups are not the same as the typical PLA molecule. For example, polymerization of PLA in the presence of diisocyanates would produce telechelic PLA with two carboxylic acid end groups instead of a hydroxyl tail and a carboxylic acid head [6]. On the other hand, branched PLA structures make use of structural co-monomers with more than 2 functionalities, capable of producing unique structures. The structures produced by branched PLA have been shown to improve various properties of PLA, improve compatibility of PLA with another polymer in a blend system, add different functionalities to PLA, and even control diffusion of material for applications such as controlled release of nutrients [80].

By carefully controlling the steps taken, precise complex structures can be obtained which would yield unique properties and functionalities. Higher structures can also be obtained by creating molecules with “lock and key” structures or micelle-like structures which have the ability to self-assemble.

A 3-arm star PLLA was synthesized through ROP of lactide with stannous octoate as catalyst, in the presence of glycerol as initiator [36]. Additionally, a parallel reaction is conducted to produce a linear chain initiated by lauryl alcohol. It was shown that 3-armed PLLA structure with a molecular weight of 36,000 g/mol had comparable T_g and higher T_{cc} (cold crystallization) to that of a linear PLLA with molecular weight of 420,000 g/mol. It was shown that branching reduces chain mobility of PLLA, and longer induction period for spherulite growth causing increased T_{cc} and reduced T_m. Another study which synthesized branched polymeric PLA structure in the presence of pyromellitic dianhydride (PMDA) and triglycidyl isocyanurate (TGIC) produced a blend of linear, 3-armed, and tree-like chains
with varied ratio of each component [81]. Measurement of mechanical properties of the branched polymer blends showed improved impact strength, tensile strength, and reduced melt index. A number of 4-armed star PLLA has also been successfully synthesized with erythritol and pentaerythritol catalyzed by calcium hydride [82].

A copolymer of PLLA containing 2, 4, and 6 armed chains were compared [83,84]. The cores used were succinic acid, 1,2,3,4-butanetetracarboxylic acid (BTCA) and 1,2,3,4,5,6-cyclohexanetetraacarboxylic acid (HCA) respectively, all of which contains carboxylic functional end groups. The reaction was further crosslinked by the addition of isosorbide (ISB), which also is used to increase Tg when used as a co-monomer due to its rigid cyclic structure. It was observed that with 4 and 6 armed stars, glass transition temperatures exceeding 80°C could be obtained. Crosslinking could also be controlled by optimizing reaction time and temperature [83].

More complex star structures could be obtained by creating dendritic star structures [85,86]. The steps can be divided into generations which double the amount of arms with increasing generation. The multi-functional core is a hexa-hydroxyfunctional dendrimer created from the reaction of 2,2-bis(hydroxymethyl) propionic acid (bis-MPA) which has one carboxylic acid group and two hydroxyl groups; and 1,1,1-tris(4’-hydroxyphenyl) ethane (THPE) which has three hydroxyl groups. The hexa-hydroxyfunctional, as it name states, has 6 hydroxyl groups that could react with the lactide molecule. After the first round of lactide has been polymerized on the multifunctional monomer, the first generation molecule is then functionalized with bis-MPA producing double the amount of available hydroxyl groups from 6 to 12, to be polymerized again with lactide to produce the second generation molecule. It was found that for the dendritic PLLA copolymer, Tg and Tm were reduced at
higher generations [85]. This molecule however has been found to have better diffusion properties for drug-release mechanism due to high porosity [86].

As opposed to star structures, combed structures were shown to provide different functionalities and properties [87]. The molecule, synthesized by copolymerization of PLLA with 3,4-dihydroxycinnamic acid (DHCA) and 3,4-diacetoxyccinnamic acid (DACA) where the number of DACA represents the number of extending branches from the DHCA-PLLA backbone. It was shown that the molecule containing the highest number of DACA showed high $T_g$ and degradation temperature, while the molecule with less DACA and longer DHCA/PLLA backbone showed better mechanical properties. Additionally, higher PLLA amount showed reduction in hydrolysis speed of the polymer.

Combed structures using polysaccharide backbones such as chitosan and dextran have also been studied [88-92]. Due to the hydrophilic nature of the backbone, water absorption is significantly increased, and consequently the hydrolysis rate. It was also shown that the comb structures with dextran backbone reduced the crystallinity of the resulting PLLA films with increasing PLLA weight ratio; however storage modulus was found to improve with the addition of dextran grafted PLLA.

The grafting of PLA structures on macromolecules has also been successfully conducted. PLLA was grafted onto wood flour surface by vapour assisted surface polymerization (VASP) method of lactide [93]. It was found that the wood flour surface assisted in improving the crystallinity of the grafted PLLA structure due to crystallization during in-situ polymerization and improved $T_m$. Blends of PLLA with PLLA grafted starch showed reduced mechanical properties, however improved compatibility was achieved compared to
blend containing PLLA and ungrafted starch [72]. The grafting of PLLA onto cellulose nanowhiskers showed large improvements in PLLA heat deflection temperature [94].

1.3 Objectives and Hypothesis
It could be seen from the literature review that the properties and structures of lignin have been extensively studied, however its commercial application is still lacking. Although the application of lignin as thermoplastic filler has been explored since the late 70s, successful blends of lignin and biopolymers targeted for advanced applications have yet to be observed. The addition of lignin into a polymer matrix generally causes the resulting blend to lose its strength and become brittle. Although some polymers do see a natural affinity to lignin due to the presence of functional groups that can form hydrogen bonds, one of the reasons for the reduction in properties of blends containing lignin is due to incompatibility, negating proper stress transfer form matrix to filler and increasing agglomeration. Increasing compatibility of lignin to the polymer matrix could also improve the properties of the resulting blend. Polymer grafted lignin has the advantage of both increasing compatibility by introducing new functionalities, and plasticization due to the polymer chain extensions. Grafting of lactic acid onto lignin adds ester functionality, which should create a better compatibility with other esters especially PLA. Additionally, the grafting of lactic acid would retain biodegradability and environmentally friendliness.

Another possible reason for the weaknesses associated with lignin blends is lignin heterogeneity. Theoretically, assuming both fractions have the same functionalities, the three dimensional and two dimensional lignin structures would impart different properties to the blend. Since the three dimensional structure has less surface area to volume ratio, it will have
less interaction with the matrix compared to the two dimensional structure. Although it is not yet confirmed whether lignin fractionation methods could separate the two geometries, it has been observed that the lower molecular weight fractions have better dispersion within the polymer matrix. The molecular structure of methanol soluble and insoluble lignin has been well studied, however the studies of its blend with biopolymers so far have been limited to the thermal and interaction study on PHB. Hence, lignin fractions separated by methanol will be studied in a blend system with aliphatic polyester (PLA) and aliphatic-aromatic copolyester (PBAT) in this project.

The objectives of this project are as follows:

1. Lignin will be fractionated by methanol followed by characterization of its thermal properties and molecular structure. The fractionated and un-fractionated lignin will then be blended with PLA and PBAT matrices to determine any effects of the lignin fraction on lignin-polymer interactions. Characterization of the blends will be done by testing its mechanical and thermal properties, observe its phase morphology, and study the molecular interactions within the blend.

2. The fractionated and un-fractionated lignin will then be functionalized by lactic acid grafting to improve its compatibility with the bioplastic matrices through polycondensation process, where grafting will be confirmed by studying its molecular structure and thermal properties.

3. Grafted lignin will then be blended with the biopolymer matrices to study the effect of the grafted PLA structures onto lignin surface on the interaction with the biopolymer
matrices. The modified lignin blends will be studied through the same mechanical, thermal, morphological, and molecular interaction studies.

2 Materials and Methods

2.1 Materials
Injection grade poly(lactic acid) (PLA) Ingeo 3251D (specific gravity 1.24, melt flow rate 35g/10min at 190°C and 2.16kg loading, and a relative viscosity of 2.5) resin was purchased from Natureworks LLC, Minnetonka, Minnesota, USA. Poly(butylene adipate-co-terephthalate) with a grade name of Biocosafe 2003 (specific gravity 1.26, melt flow rate of ≤20g/10 min) was purchased from Xinfu Pharmaceuticals, China. Softwood Kraft lignin Indulin AT was generously donated by MeadwestVaco, Richmond, Virginia, USA. The remaining solvents and reagents were purchased from Sigma-Aldrich Co.

2.2 Lignin Fractionation
Lignin fractionation was conducted by mixing 300g of lignin with 500mL of methanol at room temperature, filtered, and then rewashed with another 500mL methanol. The insoluble fraction was washed with water, and dried. The soluble fraction was collected and mixed with 1L HCl solution at pH 2.0 to precipitate the methanol soluble lignin, followed by water washing to remove excess HCl. Both fractions were dried in a vacuum oven at 80°C overnight to remove moisture and stored in a desiccator.

2.3 Lactic Acid Grafting of Lignin
Grafting of lignin is conducted by the method of azeotropic condensation polymerization. Toluene was chosen as the solvent due to its ability to dissolve high molecular weight PLA,
thereby reducing solution viscosity, and its high boiling temperature. The reaction setup is shown in figure 12 below. The reaction flask is placed in a temperature feedback controlled heating jacket with a stirrer attachment. One entry port of the flask is attached to the Dean Stark trap, which is attached to a condenser. Lactic acid is added with toluene into the reaction vessel and heated to 110°C to remove excess water. Lignin is then added at a certain ratio to lactic acid, followed by the catalyst, SnCl₂ at a weight ratio of 0.25% of the lactic acid, and the temperature is increased to 140°C and allowed to proceed for 24h. After 24h, the reaction is allowed to cool to approximately 80°C and removed to a beaker in an ice bath. Amyl acetate is then added to the cooled reaction mixture to extract toluene and homopolymer, followed by the addition of iced HCl solution at pH 2.0 to precipitate lignin from its gel phase. The precipitated lignin is then filtered to remove water, solvent, unreacted lactic acid, and SnCl₂, and dried in vacuum oven at 100°C to remove remaining solvent.

For analytical purposes, the precipitated lignin derivative was inserted in a Soxhlet apparatus with toluene to remove any remaining homopolymer for 24h and re-dried in vacuum oven prior to any tests to remove excess solvent.
2.4 Blend Preparation
Prior to processing, PLA, PBAT, and lignin were dried in a convection oven at 80°C for 6 hours to remove excess moisture from the resin. Compounding and injection moulding of the composite was conducted using DSM Xplore 15 mL Micro-Compounder and 12 mL Injection Moulding Machine. Compounding of the blend was done with co-rotating twin screw extruder with processing temperature of 170°C for all three processing zones, and a screw speed of 100 rpm. For all blends, PBAT and lignin were added and allowed to mix for 1 minute, followed by PLA feeding for 2 more minutes, giving a total of 3 minute extrusion time. For PLA/lignin blends, extrusion time was kept at 2 minutes whereas PBAT/lignin blends were mixed for 3 minutes. Injection moulding was done with a holding temperature of 170°C, mould temperature of 30°C, injection pressure of 6 bars for 6 seconds, and holding and packing pressures of 6 bars for 6 seconds each.
2.5 Mechanical Properties
Conditioning of the samples was done for 48 hours following injection moulding at temperature of 23°C and 50% relative humidity. Tensile and Flexural information were obtained using Instron Instrument Model 3382. The tensile and flexural tests were conducted according to ASTM D638 and D790 respectively. Due to the brittleness of PLA, crosshead speeds of 5 mm/min for tensile tests and 1.40 mm/min for flexural tests were used as recommended by the respective standards. Notched Izod Impact strength of the composite was measured based on ASTM D256 using TMI 43-02 Impact tester using a 5 ft-lb pendulum.

2.6 Thermal Properties
2.6.1 Differential Scanning Calorimetry
Melt temperature (T_m), crystallization temperature (T_c), glass transition temperature (T_g), melting enthalpy (ΔH_m), and crystallization enthalpy (ΔH_c) of the composites were determined using TA Instrument DSC Q200. The samples were prepared by placing 5-10 mg of composite sample in an aluminum pan. The DSC sample then undergoes a heat/cool/heat cycle at a ramp rate of 10°C/min from -50°C to 200°C under a nitrogen flow rate of 50 mL/min. Analysis of data obtained from the unit was done using TA Universal software.

2.6.2 Thermogravimetric Analysis
Thermogravimetric analysis is conducted using TA Instrument TGA Q500. This analysis allows for the study of thermal stability of the lignin and polymer samples in inert atmosphere. Prior to loading any sample, the pan is cleaned and loaded onto the device for calibration. Then, 5-10 mg of sample is loaded onto the pan and loaded onto the
thermogravimetric analyzer and heated at a rate of 20°C/min up to 800°C where lignin would have turned into carbon, and polymers have degraded. The weight of the sample is continuously measured throughout the run and plotted against temperature.

For modified lignin sample, since lactic acid/lactic acid oligomers do not undergo carbonization, TGA is used to determine the grafting percentage. The resulting derivative TGA curve (dTGA) of grafted lignin is compared with ungrafted lignin to determine the appearance of any new peaks. The resulting dTGA curve is then deconvoluted to determine the mass of the new peak.

2.7 Blend Morphology
A scanning electron microscope, HITACHI S-570, Japan, was utilized to examine the fracture surfaces of tensile and impact samples to observe the interaction between lignin and the polymer matrix. The tensile and impact samples were prepared by sputtering gold particles in order to increase electron conductivity on the surface of the sample. Furthermore, due to the sensitivity of PLA to heat, the electron beam was shot at an intensity of 10 kV to reduce the deformation on the sample surface.

For samples containing PBAT, due to the ductility a cryo-fracture method have been adopted. The samples are notched and left inside liquid nitrogen for at least 30 minutes to reduce temperature to below PBAT T_g, followed by fracturing on the notched site.

To observe the dispersion and particle size distribution within the blend, selective solvent etching of the fracture surface was conducted. To remove lignin particles the fracture surface was exposed to an aqueous NaOH solution at pH 10 overnight.
2.8 Fourier Transform Infrared Spectroscopy

FTIR provides an easy method to determine any changes in chemical groups within the molecule based on the vibrations of each bond. As the low frequency infrared beam is emitted on the sample, energy is absorbed by molecules resulting in rotational or vibrational movements. The frequency of energy absorbed is characteristic to the chemical groups present in the sample. As a result, the beam that has passed through the sample would have energy vibrating at different frequencies than the original beam. The difference in the spectra of the beam can be analyzed to determine which frequencies have changed, hence the presence of functional groups.

The Fourier transform infrared spectroscopy was conducted on a Thermo Scientific Nicolet 6700 FT-IR with a Smart Orbit attachment. Calibration is conducted with no sample loaded on the beam path, and the spectra recorded and averaged over 36 readings. Analysis of sample is conducted by loading a fine powder or liquid form of the sample onto the platform, and the spectra is taken and averaged over 36 readings.
3 Blends of Fractionated Lignin, Poly(Butylene Adipate-co-Terephthalate) and Poly(Lactic Acid)

3.1 Results and Discussions

3.1.1 Fractionation of Lignin

The extraction process separates the Kraft lignin into two fractions: the methanol soluble lignin (MSL) and the methanol insoluble lignin (MIL) and shown in figure 13. Upon extraction, the yield of the methanol soluble fraction was found to be consistently at 29.6-34.2 weight% of the overall initial lignin weight, a methanol insoluble fraction of 56.8-61.4 weight%, and a weight loss of approximately 9%. These yield values are similar to values obtained by previous studies done on the fractionation of Kraft lignin, where the methanol soluble fractions make up roughly 30-50% of the overall weight, and the remaining insoluble fragments are composed of higher molecular weight components that can be dissolved through a combination of dichloromethane and methanol as have been found my Morck et al [17]. However, since the two components will be blended with the polymers as a solid powder, the high molecular weight fraction was not further extracted once the low molecular weight have been extracted, and the low molecular weight precipitated with dilute HCl solution. The resulting fractions showed distinctive characteristics that could be observed.
qualitatively. The low molecular weight fraction was yellowish-brown in color and much finer in size, whereas the high molecular weight fraction is much darker in color and coarser in size.

### 3.1.2 Analysis of Lignin Fractions
The TGA and dTGA analysis of the lignin fractions are presented in figure 14 in the following page. From the TGA curve, it can be seen that below 300°C, MIL is the most thermally stable, followed by KL and then MSL. MSL saw a slight weight loss under 100°C which may be attributed to water, however since all three samples were dried prior to testing, this may indicate that the MSL fraction is more hydrophilic than the MIL fraction. The final carbon content was also found to be higher for MIL compared to MSL, likely due to the low molecular weight of the MSL fraction, which makes it more volatile and susceptible to degradation [17]. The KL fragment however showed a slightly higher final carbon content, which may be caused by fusing of lignin molecules during heating, leading to more thermally stable structure [95]. The dTGA curve shows a single degradation peak for all three lignin at 380°C which is the degradation of the lignin structure [57]. The maximum degradation rate is highest for MSL, followed by MSL, and KL which is again the effect of molecular weight differences. The small degradation peaks at temperatures under 200°C can be attributed to water, traces of methanol, along with sugar residue and lignin monomers [95].
Since lignin behaves much more similar to a thermoset than a thermoplastic due to its high degree of crosslinking, a DSC analysis generally only presents a single glass transition temperature which is a function of molecular weight, chemical structure, degree of crosslinking, and intermolecular interactions[11]. As seen in figure 15 below, each lignin exhibits a single glass transition temperature. The methanol insoluble fraction shows a $T_g$ of 186.7°C, while the soluble fraction shows a $T_g$ of 128°C. The difference in $T_g$ of the two fractions have been shown to be an effect of molecular weight differences.[17,29,57] The
original lignin shows a $T_g$ intermediate of the two fractions. However, the $T_g$ of KL occurs at a relatively narrow range for a material consisting of 2 different fragments with $T_g$ difference of more than 60°C, indicates that the lignin fractions form intermolecular bonds typical of two miscible polymer system[57]. The fact that the fragments form intermolecular bonds will ultimately affect the ability of lignin to disperse and the method of interaction with the polymer matrix during melt processing. [28].

Figure 15. Differential scanning calorimetry curves of Kraft lignin and its fractions

The FTIR analysis shown in figure 16 below shows the differences in the chemical structures of KL, MSL, and MIL. The reference spectra were taken from Kubo et al [96]. Starting from the higher wavelength, the band occupying the wavelength range of 3100-3600 cm$^{-1}$ is produced by O-H stretching. The MSL band closely follows that of the original KL structure, however the ML band is broader towards the higher wavelength, which has been found to correlate with higher concentrations of aliphatic hydroxyl groups. The band at ~1704 cm$^{-1}$ corresponds to the unconjugated stretching of the C=O bond. The intensity of the carbonyl
peak is much higher for MSL compared to MIL which is likely responsible for the solubility of MSL in methanol due to the formation of hydrogen bonds between carbonyl and alcohol. The band at ~1590 cm\(^{-1}\) which is caused by the aromatic skeletal vibration, is much narrow in the MSL fraction and much wider and intense in the MIL fraction. The second aromatic skeletal vibration peak at ~1510 cm\(^{-1}\) is reduced in the MIL which also corresponds to the reduction of the band at ~1265 cm\(^{-1}\), which is attributed to guaiacyl ring breathing with C-O stretching, which indicate a lower concentration of guaiacyl monomer in the MIL structure. On the other hand, the strong peak at wavelength ~1125 cm\(^{-1}\) for MIL, caused by aromatic C-H deformation of syringyl, may suggest the higher concentration of syringyl in the MIL component. Such heterogeneity in the chemical structure may have a large influence degree of interaction between the lignin molecule and the thermoplastic matrix. Additionally, since the MIL fraction has a higher concentration of hydroxyl and the MSL has a higher concentration of carbonyl, the combination of the two in the unfractionated lignin may form intermolecular bonds, as reflected in the DSC curve in figure 15.

![Figure 16. Fourier transform infrared spectroscopy analysis of Kraft lignin (KL), methanol insoluble lignin (MIL), and methanol soluble lignin (MSL).](image-url)
3.1.3 Thermal Properties of Lignin Blends

The differential scanning calorimetry curves of neat PBAT and PLA, binary blends of PBAT/PLA, PLA/MSL, PBAT/MSL, and the ternary blends of MSL can be seen in figure 17 below. PLA has a $T_g$ of 61.6°C, a melting temperature approximately 170.0°C, and undergoes crystallization during cooling and cold crystallization during heating at a temperature of 102.0°C as observed in figure 5 [6]. On the other hand, PBAT shows a low $T_g$ of -34.0°C, and a melting temperature of 117.5°C, but no crystallization. The resulting blend of PLA and PBAT behaves as expected, with PBAT $T_g$ remaining relatively the same at -34.8°C, PLA $T_g$ at 60.7°C and a slight reduction in cold crystallization temperature of PLA due to the solid PBAT as has been previously reported in literature [38].

The PLA/MSL lignin showed a slightly different behavior compared to neat PLA. Minor changes in $T_g$ can be seen from 61.6°C to 59.5°C, a behavior which persists in the ternary MSL blend, which may indicate a plasticization effect of the low molecular weight lignin fraction towards PLA [6]. The increase in cold crystallization temperature from 102°C to 109°C and the reduced melting temperatures from 170.0°C to 167.9°C indicates that MSL is anti-nucleating PLA, retarding the crystallization of PLA [6]. Additionally, the addition of MSL caused PLA melting endotherm to start at a lower temperature, whereas neat PLA and PLA/PBAT blends showed a recrystallization exotherm prior to melting [45]. This behavior is not observed with the MIL fraction, which may indicate that the lower softening temperature of MSL causes mobility of MSL between PLA chains.
PBAT/MSL binary blend also showed a different behavior compared to both neat PBAT and PLA/PBAT blend. \( T_g \) of PBAT was increased from -33.9\(^\circ\)C to -11.4\(^\circ\)C which may indicate miscibility between PBAT and MSL phase. In addition to the increased \( T_g \), a reduction of PBAT melting temperature of 5\(^\circ\)C was also observed [57]. The \( T_g \) of MSL is not observed.
here which may be because PBAT/MSL is exhibiting a single glass transition due to complete miscibility, or similar to the other blends, the change in heat flow from the glass transition of MSL is too subtle to be observed [57].

It can further be observed that the resulting behavior of the MSL binary blends is translatable to the ternary blends, i.e. the MSL ternary blend showed an increase in PBAT $T_g$ that is similar to the PBAT/MSL blend and PLA $T_g$, $T_c$, and $T_m$ that are similar to the PLA/MSL blend. The PBAT phase showed further increase in $T_g$ from -34°C to -1°C which may be caused by different weight ratio of PBAT to lignin in the ternary blend (62/38) compared to the PBAT/MSL binary blend (70/30). The melting temperature of PBAT cannot be determined due to the fact that it occurs almost simultaneously with PLA cold crystallization, and is overwhelmed by the exotherm released during the cold crystallization due to the low crystallinity of PBAT [38].

Thermal properties of the ternary blends of the remaining two lignin showed different behavior compared to the MSL. The shift in $T_g$ of PBAT phase in the KL (-26.0°C) and MIL (-30.9°C) blends are less prominent compared to the MSL, suggesting that there is little compatibility between MIL and PBAT, and that the shift in the KL blend is attributed to the MSL component [57]. Another prominent difference in the lignin fractions can be seen with the crystallization characteristics. As observed the KL and MIL fractions reduced the cold crystallization temperature of PLA from 102°C to 95.1°C for KL blend and 96.8°C for MIL blend, which suggests the effect of nucleation [6]. As seen in figure 15, the MIL fraction has a $T_g$ of 187°C, which means that it is still in solid state at the temperature range, acting as a nucleation site for PLA crystals.
3.1.4 Mechanical Properties of Lignin Blends

Table 1. Summary of mechanical properties of PBAT and lignin binary blends, and PLA, PBAT, and lignin ternary blends. NB = non-breaking, P = partial break, H = hinging.

<table>
<thead>
<tr>
<th></th>
<th>PBAT</th>
<th>PBAT/KL 70/30</th>
<th>PBAT/MSL 70/30</th>
<th>PBAT 70/PLA 30</th>
<th>PLA 21/PBAT 49/KL 30</th>
<th>PLA 21/PBAT 49/MIL 30</th>
<th>PLA 21/PBAT 49/MSL 30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength (MPa)</td>
<td>21.7 ± 3.16</td>
<td>13.0 ± 0.39</td>
<td>14.6 ± 0.97</td>
<td>23.3 ± 1.07</td>
<td>14.4 ± 0.28</td>
<td>14.2 ± 0.26</td>
<td>18.9 ± 0.75</td>
</tr>
<tr>
<td>Tensile Modulus (MPa)</td>
<td>59 ± 6.8</td>
<td>148 ± 6.3</td>
<td>82 ± 11.1</td>
<td>751 ± 53.8</td>
<td>515 ± 16.4</td>
<td>588 ± 34.6</td>
<td>636 ± 36.9</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>597 ± 137.5</td>
<td>285 ± 26.2</td>
<td>583 ± 90.9</td>
<td>279 ± 79.3</td>
<td>36 ± 5.4</td>
<td>42 ± 25.6</td>
<td>300 ± 19.7</td>
</tr>
<tr>
<td>Impact Resistance (J/m)</td>
<td>(NB) 266 ± 34.3</td>
<td>(P) 14.1 ± 0.29</td>
<td>(NB) 47 ± 12.1</td>
<td>(NB) 46 ± 2.5</td>
<td>(H) 83 ± 20.1</td>
<td>(NB) 14.1 ± 0.29</td>
<td>(NB) 47 ± 12.1</td>
</tr>
<tr>
<td>Flexural Strength (MPa)</td>
<td>4.1 ± 0.16</td>
<td>6.6 ± 0.27</td>
<td>4.1 ± 0.29</td>
<td>25.8 ± 0.65</td>
<td>19.4 ± 0.76</td>
<td>19.0 ± 0.51</td>
<td>17.3 ± 1.49</td>
</tr>
<tr>
<td>Flexural Modulus (MPa)</td>
<td>82 ± 4.0</td>
<td>154 ± 8.9</td>
<td>80 ± 8.6</td>
<td>949 ± 29.9</td>
<td>653 ± 35.4</td>
<td>645 ± 21.1</td>
<td>566 ± 44.5</td>
</tr>
</tbody>
</table>

Table 1 above provides a summary of the mechanical properties of the blends. As observed, PBAT is an extremely tough polymer, with an elongation of nearly 600% and non-breaking under notched Izod impact test. The relatively higher tensile strength of PBAT stems from the fact that at higher elongations, the PBAT chains can reorganize to become highly oriented through stress induced crystallization, thereby increasing the force required to break [37] as observed in the stress-strain curves in figure 18 in the following page. Additionally, due to this fact, since the flexural test was only conducted up to 5% strain, the chains are unable to undergo stress induced crystallization, hence the lower flexural strength [25]. Although PBAT has high toughness, its stiffness is lacking, with a tensile modulus of 59 MPa and a flexural modulus of 82 MPa.
The PBAT/lignin binary blends retain some of the behavior of the PBAT matrix in that there are not much improvement with regards to strength. The PBAT/KL blend fares much better with regards to modulus, due to the addition of solid filler which prevents polymer chains from slipping, thereby reducing movement and making the blend stiffer. Additionally, since PBAT is still a major phase, the impact resistance and elongation of PBAT/KL blend is still highly influenced by it. The addition of lignin creates a propagation site that reduces the impact resistance, from non-breaking to a partial break at 266 J/m. Additionally, since lignin restricts movement of polymer chain, chain entanglement and slippage is reduced, along with the ability to form a highly oriented structure, hence the reducing elongation and tensile strength, similar to the behavior observed by Nitz et al [25] and Li et al [97]. The increase in flexural strength and flexural modulus is typical of a filler system due to the increase in stiffness. The yield strength was improved by the addition of KL as seen in the stress-strain curves; however the ability of the blend to achieve higher ultimate tensile strength from
stress induced crystallization has been impacted by the reduction in elongation and the strength of the highly ordered structure. Previous studies on blending of PBAT with Alcell, sisal, and abaca lignin showed the same increase in yield stress, modulus, and retention of toughness up to 40 and 50% of lignin by weight [25].

The PBAT/MSL blends on the other hand shows a slightly different behavior. Minor changes in both tensile and flexural modulus coupled with retention of elongation and impact resistance might indicate that the combination is acting as a homogeneous blend system rather than a filler composite system [74]. The retention of elongation, since lignin itself is brittle in nature, points to the fact that lignin is well dispersed within the PBAT matrix. However, the tensile strength listed in table 1, which is the tensile strength at break of the blend, shows a lower value compared to neat PBAT at relatively similar elongations as shown in the stress-strain curves. This means that ability of the blend to undergo stress-induced crystallization is affected by the addition of lignin in that there may be a plasticization effect due to the low molecular weight nature of the MSL component [28].

The addition of PLA to PBAT improves the yield strength of the blend as seen in the stress-strain curves (figure 19), whereas the stress at break and the effect of stress induced crystallization remained relatively similar. The yield effect is due to the movement of PLA chains[38]. However, since PBAT is still the dominant component in the PLA/PBAT blend, its properties is still highly influenced by the properties of PBAT, which results in drawing, followed by stress induced crystallization, and a retention of most of PBAT’s toughness as reflected by the impact strength and elongation. The behavior of the PLA/PBAT is consistent with reported results where phase separation and incompatibility of the PLA/PBAT phases caused reduction in mechanical properties from predicted theoretical values [49].
The KL and MIL ternary blends with PLA and PBAT showed very similar mechanical properties with tensile strengths of 14.4 and 14.2 MPa, tensile moduli of 515 and 588 MPa, elongations of 36 and 42%, impact strengths of 47 and 46 J/m, flexural strengths of 19.4 and 19 MPa, and flexural modulus of 653 and 645 MPa respectively. This difference between the KL and MIL blends with the MSL blend, indicate that the mechanical property of the KL blend is highly influenced by the MIL component of the lignin. As observed in the DSC curves, though the KL lignin is highly heterogeneous, it still only shows one $T_g$ which is located somewhere inbetween the $T_g$s of MSL and MIL. The $T_g$ of the MIL component, as observed is 186.7 °C, which is higher than the processing temperature of 170°C shows that the MIL component is not softened during the processing temperature, hence affecting dispersion and interaction with the polymer matrix. The yield observed in the stress-strain curve of the KL, MIL, and even MSL blends are not as abrupt as the PLA/PBAT binary blend, which may suggest that lignin is bridging the stress transfer between the two incompatible phases. The impact strength showed a large reduction which can be partly...
attributed to the reduction in PBAT content; however, the more significant cause seems to stem from the degree of interaction of PLA and lignin which has been found to be weak and brittle [12,54,66].

Upon separation of the high molecular weight MIL component, the MSL ternary blend exhibits elongation similar to that of the original PLA/PBAT blend, with the yield strength of the KL and MIL blends. It is observed that the yield strength for all ternary lignin blends, which is approximately 2/3 of its original value, is similar to the reduction in overall PLA content. This lack of change suggests that the lignin fractions have little effect on the properties of the PLA phase, which is further supported by the DSC thermograms showing minute changes in the thermal properties of the PLA phase. Similar to the PLA/PBAT blend, the MSL blend showed stress induced crystallization characteristic of the continuous PBAT phase. Similarly, the impact resistance is highly affected by the PLA/lignin combination, since high impact was observed by the PBAT/PLA and PBAT/MSL blends.

The lack of change with the tensile properties associated with the PLA phase suggests that in the ternary blends, lignin does not have much effect on the PLA domains. On the other hand, the changes observed with the PBAT/lignin binary blends suggest interaction between PBAT and lignin. However, the significant reduction in impact strengths and the smooth transition between the yield of PLA and drawing of PBAT on the ternary blends show that there is an interface where PLA and lignin interacts as observed in the SEM images. The lignin particulates are well dispersed within the PBAT matrix, but see very little dispersion in the PLA domain, reflecting the differences in solubility of lignin in PLA and PBAT [38]. However, some hydrogen bonding do occur with the hydroxyl group of lignin and the
carbonyl groups of PLA [54], which forms an interface that bridges the PLA and PBAT domains.

### 3.1.5 Blend Morphology

The Scanning electron microscope images of the PBAT/lignin blends can be seen in figure 20 in the following page. The impact fracture surface of the PBAT/KL blend in figure 20A shows the existence of highly heterogeneous lignin particle size distribution. The larger lignin particles are likely agglomerates created by the formation of intermolecular bonds in lignin structures, which are weaker than covalent bonds [78], hence causing areas of weakness in the blend infrastructure, affecting its toughness and strength. Figure 20A shows a lignin particle with a crack through the center of the particle, formed during the application of stress, breaking the intermolecular forces binding lignin molecules in the agglomerates [11]. The cryo-fractured sample which has been treated with sodium hydroxide solution shows the space previously occupied by lignin. As expected, the particle size distribution of the PBAT/KL blend shown in figure 20B has is large, with particle sizes ranging from <1 μm to 50 μm due to the large MIL particles and the formation of agglomerates. The large lignin macromolecules indicate that the surface area of contact between lignin and PBAT is reduced, thereby reducing the stress-transfer, leading to reduced performance. The cavity left by the large particulate in image B, shows evidence of wetting, which suggests the presence of interaction between lignin and PBAT in the interface.
Images C and D were both taken from cryo-fractured samples of the PBAT/MSL blends, due to the non-breaking behavior towards impact stress of the MSL blend. The unextracted surface shown in image C shows a much smoother break, without any evidence of delamination or pullout between PBAT and MSL, or even presence of visible lignin particles. This homogeneity of course confirms the compatibility between PBAT and MSL shown by the DSC analysis. The extracted cryo-fracture surface shows the dispersion of lignin within the PBAT matrix. Most of the MSL particles dispersed within the PBAT matrix are less than
2 µm to as low as approximately 100 nm, which is the smallest observable cavity by the microscope at 8000 times magnification.

The PLA/PBAT binary and PLA/PBAT/lignin ternary blends are shown in figure 21 in the following page. Figures A and B are of a cryo-fractured surface where figure A is composed of 70% PBAT and 30% PLA by weight, while figure B is of the same composition, but with 1% by weight of MSL added into the system during compounding, followed by NaOH solution extraction prior to SEM imaging. The neat PBAT/PLA blend showed a typical blend with low compatibility, producing separation between the two phases where PLA is the discontinuous phase of beads with particle size ranging between 1-2 µm while PBAT is the continuous phase. The PLA/PBAT/1% MSL blend, showed more or less similar PLA particle sizes of approximately 1 µm; however, it can be seen that some of the PLA particles are elongated and wetted into the continuous PBAT matrix, which suggest some compatibilization effect by MSL.

Figures C and D are SEM images of the 49% PBAT, 21% PLA, and 30% KL blend. Unlike the PLA/PBAT binary blend or even the PBAT/KL blend, the unextracted fracture surface of the KL ternary blend showed a very rough terrain, but shows no distinct phase separation. Other than a small amount of beads which represent the PLA phase, the differences between PLA, PBAT, and Kraft lignin cannot be distinguished. However, upon extraction by NaOH solution the difference in phases become much clearer. The lignin particle distribution that becomes apparent upon solvent extraction remained relatively unchanged when compared to the PBAT/KL blend. The interfacial feature that indicates wetting of PBAT and lignin is also evident, however the phase structure of PLA has changed from the neat PLA/PBAT binary blend. As observed in figure D, the PLA phase now appears as phase separated discontinuous
domains instead of spherical beads with particle sizes of approximately 1-2 μm. The appearance of gaps between the PLA and PBAT phase which were not observed in figure 21C, indicate that the gaps may have been previously occupied by lignin, confirming the behavior observed with mechanical properties of lignin bridging the two PBAT and PLA phases.

Figure 21. Scanning electron images of cryo-fractured surfaces of PLA/PBAT binary blend and PLA/PBAT/lignin ternary blends. A: PLA/PBAT blend, B: PLA/PBAT with 1% MSL solvent extracted, C: PLA/PBAT/KL ternary blend, D: solvent extracted PLA/PBAT/KL ternary blend, E: PLA/PBAT/MSL ternary blend, F: solvent extracted PLA/PBAT/MSL ternary blend.
The last two images, figures 21E and F, show the lignin unextracted and extracted fracture surfaces of the PBAT 49%, PLA 21%, and MSL 30% ternary blends. As with the binary blend, the phase between PBAT and lignin is less obvious in the unextracted surface, and the PLA are much more visible in the form of small beads with 1-2 µm particle size. However, it can be seen that the PLA beads are not as prominent as the PLA/PBAT binary blend, and with some particles partly incorporated into the PBAT matrix. The extracted sample of the MSL ternary blend shows a much more intricate and detailed morphology. As seen in figure 21F, the apart from the beads, the PLA is actually present in the PBAT matrix as elongated domains. This suggest that the blend of PBAT and PLA with the addition of MSL is closer to the ratio of phase inversion as observed by Li et al [47] with PLA/PBAT blends at 30/70 ratio where one polymer is transitioned from a continuous phase to discontinuous, which is highly dependent in the viscosities of the two polymers. However, since there are differences in the material properties, this behavior was not observed with the neat PLA/PBAT 30/70 blend used in this project, but is observed upon the addition of MSL which means that the 30/70 PLA/PBAT is farther form the phase inversion ratio. Since MSL is highly dispersed in PBAT, it may suggest that MSL lowers the viscosity of the PBAT phase causing it to be closer to the phase inversion ratio, producing the highly elongated phases. This behavior of MSL which affects the viscosity of PBAT is consistent with the idea that MSL is plasticizing PBAT [47].

3.2 Conclusions

The blends of lignin and its methanol fractionated components showed the effect of heterogeneity on the ability of lignin to be blended into a thermoplastic matrix. Fractionation
of Kraft lignin in methanol showed that the two fractions have pretty extensive differences thermally, chemically, and physically as far as lignin goes. The methanol soluble fraction of Kraft lignin has a lower softening temperature and is much more hydrophilic based on its ability to retain moisture from the atmosphere and also based on the larger presence of polar carbonyl functional group, which is also likely the root of its solubility in methanol. FTIR study also showed a higher concentration of guaiacyl monomer making up the MSL, while the MIL has very little guaiacyl but much more syringyl monomers. Conversely, the MIL lignin has a higher glass transition temperature, and is much more hydrophobic due to the low concentration of carbonyl groups as observed in the FTIR and low weight loss attributed to water based on TGA analysis. The original Kraft lignin of course retains properties that are intermediate of both fractions except for the higher thermal stability based on the TGA, which is likely due to the formation of lignin complexes composed of MIL and MSL fractions.

The PBAT/lignin binary blends showed the stark differences in dispersion and compatibility of the two lignin fractions with PBAT. Fractures within the KL particle inside the blend showed the weakness of the lignin agglomerates, which affected the mechanical properties of the resulting PBAT/KL blends, lowering its elongation, and the ability of PBAT to undergo stress induced crystallization. On the other hand the PBAT/MSL blends showed a homogeneous morphology with complete wetting of the lignin particles by PBAT in addition to high dispersion with particles measuring in the nano scale. DSC studies also showed significant changes in the glass transition temperature of the PBAT phase, pointing to compatibility of PBAT and MSL, which is reflected in the mechanical properties showing retention of elongation and toughness, with improvements in yield strength.
The addition of PLA to the PBAT/lignin blend showed improvements in strength and modulus as expected. Additionally, compared to the neat PLA/PBAT blend, the ternary blends showed more continuous behavior under tensile test, indicating lignin is bridging the two incompatible PLA/PBAT phase, which was confirmed by the SEM images. The KL and MIL blends showed significant reduction in toughness, while the MSL blend showed similar elongation values but reduced impact strength, indicating that while there is some interaction between lignin and PLA, such interaction is very weak and brittle. DSC images showed an even higher shift to the glass transition temperature of PBAT by the addition of MSL in the PLA/PBAT/MSL ternary blend, which may likely be due to the slightly higher ratio of MSL to PBAT. The KL and MIL blends showed a nucleation of PLA phase, while the MSL blends showed an anti-nucleating behavior, but the changes to PLA glass transition temperature, were too minor to indicate any significant interaction between PLA and lignin. The effect of MSL on PBAT however, is consistent with most of the results showing the plasticization of PBAT by the MSL compounds.
4 Synthesis of Lactic Acid Grafted Lignin

4.1 Results and Discussions

4.1.1 Synthesis of Grafted Lignin

The schematic representing the grafting of lactic acid onto lignin can be seen in figure 22. Lignin with its aliphatic and aromatic hydroxyl groups undergoes condensation reaction with the carboxylic acid group of lactic acid to create an ester. The resulting compound gains a polar ester compound, but retains its hydroxyl functionality, allowing for more intermolecular interactions such as dipole-dipole and hydrogen bonding. The hydroxyl functionality of lactic acid can further react with another lactic acid through the same condensation reaction route to produce an extended PLA “arm” from the lignin core. Since these hydroxyl groups are numerous across the entire lignin molecule, the formation of these PLA arms are limited by the accessibility of lignin hydroxyl groups and the concentration of the lactic acid monomers. However, the formation of homopolymer can be assumed to be more prominent than that of lignin grafting [72], therefore excess lactic acid is added into the reaction mixture to encourage grafting.

As previously mentioned, the azeotropic condensation method of PLA polymerization has the advantage of lower cost monomer and less demanding reaction setup compared to the
more common grafting method of ring opening polymerization, and a higher achievable molecular weight range and lower temperature requirement compared to melt polycondensation [6]. However, a solvent is required in order to break the azeotrope between water and lactic acid and solubilize the higher molecular weight polymers to reduce the reaction viscosity. Toluene is a commonly used option for azeotropic dehydration of PLA due to its ability to dissolve high molecular weight PLA to reduce viscosity; its inability to solubilize lactic acid and its low molecular weight oligomers; and its ability to break the azeotrope between lactic acid and water, which allow continuous removal of water from the reaction vessel [72]. Additionally, lignin and its PLA grafted derivatives were not found to be soluble in toluene, which maximizes its exposure in the lactic acid monomer and oligomer, thereby increasing the grafting efficiency of lactic acid.

It was found that upon the addition of lignin into the mixture of lactic acid and toluene, lignin turned from its powder form into a viscous gel with the lactic acid phase. This result was unexpected because lignin is insoluble in either lactic acid or toluene separately. Based on their Hansen solubility parameters, lignin was expected to be more miscible with lactic acid than toluene due to the closer proximity of lignin to the lactic acid solubility parameter [98]. However, this partial solubility indicate that the lignin-lactic acid phase would produce a reaction with characteristics similar to a homogeneous reaction mixture rather than a heterogeneous one.

Lactic acid was added into the reaction mixture at a concentration of 10, 5, and 1 mL/g lignin to observe the differences in the grafting efficiency of differing amounts of monomer concentration. The resulting grafted compounds are labeled as MLignin-10mL, MLignin-5mL, and MLignin-1mL.
When the reaction has been allowed to proceed for 24h, the reaction mixture was poured into a beaker in an ice bath and allowed to cool to low temperature. Amyl acetate and ice water were added in order to separate the toluene and homopolymer phase, and the lignin phase. Upon addition of water with constant stirring, lignin began to coagulate and settle on the bottom of the beaker, where the remaining liquid can be decanted and filtered for remaining solids. The extracted liquid phase however, was still brown in colour, indicating incomplete removal of lignin from the toluene-amyl acetate phase. Due to this fact, the yield and grafting efficiency could not be determined based on the weight gain. An alternative method was used to determine the grafting efficiency.

4.1.2 Thermal Degradation of Grafted Lignin

The thermal degradation of lignin and grafted lignin compounds were studied through thermogravimetric analysis equipment, which determines the remaining weight of the lignin at any given temperature. Figure 23 in the following page depicts the thermogravimetric (left) and derivative thermogravimetric (right) curves of the lignin and grafted lignin derivatives. The degradation curve of lignin, shown in the blue line follows a typical lignin degradation curve [99], where a minor weight loss was observed between 100-200°C due to the remaining hemicellulose fragments still covalently bonded to the lignin molecule. After the cellulosics have been degraded, the lignin molecule begins to degrade where the increase in enthalpy causes more volatile compounds to reach the required activation energy for the destruction of chemical bonds which is referred to as bond dissociation energy [100]. The carbon-oxygen bond has a bond dissociation energy ~7 kcal/mol less than that of carbon-carbon bond, which makes it much less stable, therefore easier to degrade. The breaking of C-O bonds result in
the formation of free radicals, which further encourage the formation of the more stable C-C bonds. This occurrence is called the carbonization process. As a result of carbonization, at temperatures exceeding 500°C, the molecular structure of lignin is composed of mostly carbon, with the carbon content continuing to increase with further increase in temperature [100].

![Figure 23. Thermogravimetric analysis (TGA) (left) and derivative thermogravimetric (dTGA) analysis (right) of lignin and modified lignin (MLignin) with reacted with different monomer concentrations.](image)

The degradation curves of the grafted lignin compounds can be seen from the remaining red, green, and purple curves. As a result of grafting, the overall thermal stability of the molecule has been reduced as observed from the TGA curve. The onset degradation temperature has been reduced by approximately ~100°C from ~200 to ~300°C. This reduced thermal stability is due to the less thermally stable grafted PLA structures. This is reflected clearly in the derivative TGA curve on the right which shows the peak degradation temperature of lignin, which has not shifted much from its original temperature of ~380°C, and the peak degradation temperature attributed to the grafted PLA structures between 200-300°C.

Some differences can be observed between the MLignin-1mL and the MLignin-10mL such as the peak degradation temperature and the maximum rate of weight loss. For MLignin-1mL, a PLA peak degradation temperature of 252.8°C was observed as shown in table 2 along with
a maximum degradation rate of 0.409 wt. %/min. On the other hand, MLignin-10mL had a PLA peak degradation temperature of 273.2°C and a maximum degradation rate of 0.318 wt. %/min. The lower peak degradation temperature of the 1mL lignin most likely indicates the shorter chain length of the grafted PLA structure, which is much easier to degrade than the longer chain length observed with the MLignin-5mL and MLignin-10mL. However, it can be seen that the 1mL lignin has a narrower curve in addition to a higher peak indicating the uniformity of the grafted PLA structure, while the 5 and 10mL lignin have a shorter broader curve. One possible reason for the broadness of the 5 and 10mL lignin could be the presence of transesterification reactions by lactic acid monomer and oligomers [101]. The transesterification reaction commonly occurs in a typical PLA condensation polymerization at high monomer concentration and at high temperatures, causing cleavage of the grafted PLA chains, creating a broader molecular weight distribution. The small peak at ~150°C which appeared for the 5 and 10mL lignins can be attributed to the fractions that have undergone transesterification, leaving smaller, less thermally stable oligomer. Also, as a result of the less thermally stable PLA structures which doesn’t carbonize, the final weight percentage is reduced from 48.6% to 34-39% after grafting.

Table 2. Summary of thermogravimetric analysis of modified lignin.

<table>
<thead>
<tr>
<th>Lignin</th>
<th>PLA Deg. Temp. (C)</th>
<th>Weight of Residue at 700°C (%)</th>
<th>PLA Grafting (%)</th>
<th>Normalized Lignin Residue (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normalized Lignin</td>
<td>252.8</td>
<td>33.9</td>
<td>0</td>
<td>48.6</td>
</tr>
<tr>
<td>MLignin-1mL</td>
<td>273.8</td>
<td>34.5</td>
<td>30.5</td>
<td>49.6</td>
</tr>
<tr>
<td>MLignin-5mL</td>
<td>273.2</td>
<td>38.8</td>
<td>26.5</td>
<td>52.8</td>
</tr>
<tr>
<td>MLignin-10mL</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.1.3 Study of Grafting Efficiency

Since yield could not be determined by the weight increase, the grafting efficiency could not be determined gravimetrically, hence another method was adopted for this purpose. PLA is known to completely thermally degrade, and has a degradation temperature relatively far apart from that of lignin [6], the thermogravimetric analysis can also be used to determine the grafting percentage. As observed in figure 23 on page 68, the peaks between 250-275°C is present due to the PLA structure, while the peak at 380°C is attributed to lignin. The degradation of PLA much like most commercial synthetic polymers follows a Gaussian distribution [6], deconvolution of the dTGA curve with a Gaussian approximation allowed for the determination of the weight percentage of the grafted PLA structure. However, due to the complex degradation of the lignin molecule, the accuracy of the method is affected to a certain degree.

![Deconvolution of derivative TGA of modified lignin reacted with 10 mL Lactic Acid/g Lignin (Left) and 1 mL Lactic Acid/g Lignin(right). Green discontinuous lines represent the deconvoluted peaks.](image)

The peak deconvolution of the dTGA curves of 1 and 10mL lignin can be seen in figure 24 above. Generally, 3-4 distinct peaks can be obtained from the deconvolution of the dTGA curve. The first peak at ~150°C as observed in the 10mL dTGA curve, is relatively low in intensity and has a large width. At high monomer concentration and high reaction
temperatures, transesterification reactions tend to occur, causing the cleavage of longer PLA chains [6]. The chains degraded at these temperatures are likely only composed of a few lactic acid molecule in length, but are still largely varied in length. This peak is almost non-existent for the MLignin-1mL due to the low concentration of monomer, therefore less occurrence of transesterification reactions. The second peak between 250 and 275°C as previously mentioned is due to the PLA structure, while the third and fourth peak are largely attributed to the thermal degradation of the lignin molecule.

Table 2 also shows the weight percentage of grafted PLA listed in the third column. The weight percentage of the grafted PLA is relatively consistent between monomer concentrations of 1 to 5 mL/g lignin and showed a reduction in the grafted percentage at 10mL/g lignin due to occurrence of transesterification reactions, indicating non-optimal reaction conditions at 10mL monomer concentration. However, the increase in peak degradation temperature would suggest the 10mL lignin on average has longer extensions.

The last column provides a measure of accuracy of this method of determining the grafting percentage, by comparing the normalized weight of lignin. Since PLA is very thermally unstable compared to lignin, the degradation of PLA should pose almost no effect to the degradation of lignin. Additionally, since PLA completely degrades at high temperatures, means that it has no contribution to the final sample weight at 700°C. The equation to determine the normalized weight of lignin residue was done as follows:

\[
\text{Normalized Lignin Residue} = \frac{\text{Weight of Residue}}{100 - \text{Grafted PLA}} \times 100\%
\]

The unmodified lignin had a residue of 48.6% which is composed of mostly carbon. The resulting normalized weights of the grafted lignin saw no major discrepancy for all lignin
derivatives, indicating that the method to determine the grafting percentage by thermal degradation has a relatively good accuracy.

4.1.4 Characterization of Molecular Structure
The FTIR of the lignin and PLA-lignin graft copolymer is shown in figure 25 in the following page. A number of changes are visible, some of which are marked by the vertical dotted lines. Starting from the left, the peak at 3300-3600 cm\(^{-1}\) is attributed to hydroxyl groups [96]. Lignin hydroxyl groups are in the form of aliphatic and phenolic hydroxyl, in addition to carboxylic acids. Overall, the intensity of the hydroxyl peak has not changed much, indicating the extremely low or non-existence of water and lactic acid monomer and oligomers. There is also an observable shift in the maxima of the hydroxyl peak from \(~3350\) cm\(^{-1}\) for unmodified lignin, to \(~3500\) cm\(^{-1}\) for all the modified compounds. This shift to higher wavelengths has been attributed to the higher concentration of aliphatic hydroxyl groups as opposed to phenolic hydroxyl groups. The result pointing to higher aliphatic hydroxyl is consistent with the idea that upon reaction with lactic acid, both existing aliphatic and phenolic hydroxyl groups on lignin, turns into aliphatic due to the linear nature of PLA. Another indicator of the increase in aliphatic PLA groups is the methyl bands occurring at \(~3000\) cm\(^{-1}\) and methylene at \(~2940\) cm\(^{-1}\) which indicates the C-H stretching in methyl and methylene. It can be seen that for unmodified lignin, the methyl group is almost nonexistent, whereas for all three modified lignin, the methyl group from the lactic acid showed a minor but prominent shoulder. The relative intensity attributed to the methylene group can also be seen to increase with the addition of PLA chains. Going down the spectra, the most prominent change is caused by the addition of carbonyl functional groups which are typically present between 1700 and 1750 cm\(^{-1}\) from the unconjugated C=O stretching. Initially, the
carbonyl group of lignin is present as a shoulder at ~1705 cm\(^{-1}\). After grafting, the carbonyl group of lignin is shadowed by the peak at ~1730 cm\(^{-1}\), due to the addition of ester groups. The peaks ~1590, ~1510, and ~1420 cm\(^{-1}\) are attributed to aromatic skeletal vibrations of lignin benzene rings, which can be seen to have undergone no change, which is as expected since the grafting process is not destructive to the lignin structure. Additional peaks related to the C-H groups include C-H deformation of methyl and methylene at ~1450 cm\(^{-1}\) and symmetric C-H bending at 1360 cm\(^{-1}\) also indicate the addition of the PLA chains [72]. Since homopolymer has been removed from the lignin samples, the high intensity peak contributed by the ester groups and no significant change in the intensity of hydroxyl band confirms the grafting of PLA chains on the lignin molecule.

![Figure 25. Fourier transform infrared spectroscopy of modified lignins with reacted at different monomer concentrations.](image)
4.2 Conclusions

Synthesis of PLA grafted lignin by non-conventional azeotropic dehydration method was able to produce a material, which upon further purification yielded lignin grafted with between 26-30% by weight of lactic acid. Grafting was confirmed by FTIR analysis of the purified lignin compound which indicated the presence of functionalities common with the structure of PLA. TGA was also used to determine the thermal stability of the grafted lignin and the grafting percentage of PLA on lignin by deconvoluting the derivative TGA curve. This method showed a relatively good accuracy of determining the yield of the grafted compound, provided there is a distinct difference between the thermal stability of the copolymers.
5  Blends of Modified Lignin, Poly(Butylene Adipate-co-Terephthalate), and Poly(Lactic Acid)

5.1 Results and Discussions

5.1.1 Mechanical Properties

The mechanical properties of the modified and unmodified ternary blends are summarized in table 3 in the following page. Comparing the modified blends and the unmodified blends, reduction in strength and modulus, both flexural and tensile can be observed, while elongation is slightly improved. The tensile strength was reduced from 14.4 to 12.3 MPa for the unmodified and modified kraft lignins, while the methanol soluble version saw a reduction of tensile strength from 18.9 to 15.8 MPa. Likewise, the flexural strengths were also reduced from 19.4 to 14.0 MPa for the KL blends and from 17.3 to 16.4 MPa for the MSL blends. The tensile moduli were also reduced, however the flexural moduli only decreased for the KL blends and not for the MSL blend, which showed an unexpected increase of more than 120 MPa after lignin modification. Elongation for the KL blend saw an improvement from 36 to 48%, while the MSL blend remained relatively the same, considering their standard deviations. On the other hand, the impact strengths remain unchanged, which shows that the interaction between PLA and lignin even after grafting of PLA arms does not have any effect on the impact strength of the blend. These changes in mechanical properties may indicate a plasticization effect stemming from the addition of grafted lignin, as has been shown for PLA blended with multi-branched structure [80].
Table 3. Summary of mechanical properties of PBAT/PLA binary blend and PLA/PBAT/modified lignin ternary blends.

<table>
<thead>
<tr>
<th></th>
<th>PBAT 70/ PLA 30</th>
<th>PLA 21/ PBAT 49/ KL 30</th>
<th>PLA 21/ PBAT 49/ MKL 30</th>
<th>PLA 21/ PBAT 49/ MSL 30</th>
<th>PLA 21/ PBAT 49/ M-MSL 30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength (MPa)</td>
<td>23.3 ± 1.07</td>
<td>14.4 ± 0.28</td>
<td>12.3 ± 0.21</td>
<td>18.9 ± 0.75</td>
<td>15.8 ± 0.66</td>
</tr>
<tr>
<td>Tensile Modulus (MPa)</td>
<td>751 ± 53.8</td>
<td>515 ± 16.4</td>
<td>481 ± 20.2</td>
<td>636 ± 36.9</td>
<td>508 ± 34.0</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>279 ± 79.3</td>
<td>36 ± 5.4</td>
<td>48 ± 6.4</td>
<td>300 ± 19.7</td>
<td>271 ± 25.1</td>
</tr>
<tr>
<td>Impact Resistance (J/m)</td>
<td>(NB)</td>
<td>47 ± 12.1</td>
<td>42 ± 4.3</td>
<td>83 ± 20.1</td>
<td>84 ± 10.6</td>
</tr>
<tr>
<td>Flexural Strength (MPa)</td>
<td>25.8 ± 0.65</td>
<td>19.4 ± 0.76</td>
<td>14.0 ± 0.74</td>
<td>17.3 ± 1.49</td>
<td>16.4 ± 1.97</td>
</tr>
<tr>
<td>Flexural Modulus (MPa)</td>
<td>949 ± 29.9</td>
<td>653 ± 35.4</td>
<td>486 ± 41.1</td>
<td>566 ± 44.5</td>
<td>687 ± 68.3</td>
</tr>
</tbody>
</table>

The stress-strain curve (figure 26) shows reduced stress for both modified lignin blends during the yield and elongation. The modified KL blend showed a reduced strength, however elongation was improved, consistent with the proposed plasticization effect of the multi-branched lignin molecule. On the other hand, the modified MSL blend showed reduced strength but not much improvement in elongation. The stress-strain curve does show that not much improvement can be observed with regards to the interaction between PLA, PBAT, and lignin. The ability of the PBAT phase to undergo stress-induced crystallization has not been affected much, since it shows a similar elongation profile as the unmodified MSL blend at a lower strength.
One possibility that might cause the lack of improvements in the mechanical properties may be due to the insufficient interaction between the grafted chains and the PLA/PBAT phase. Since it has been shown through the DSC curves in section 3 that there is compatibility and interaction between PBAT and MSL, while the PLA and PBAT has little compatibility, the reduction in strength may be caused by reduced interaction between PBAT and MSL due to the grafted PLA chains causing less adhesion, hence weakened stress-transfer from PBAT to lignin. However, the mechanical properties also showed no indication of improvements in compatibility between the lignin and PLA by the grafted PLA chains likely due to the insufficient grafting to allow for any chain-chain interaction such as entanglement that is crucial for the elastic behavior of a typical polymer blend [72].

5.1.2 Thermal Properties

The DSC curves of the modified and unmodified ternary lignin blends are shown in figure 27. One of the largest change that can be observed is the shift in the $T_g$ of the modified lignin, compared to the unmodified ones. The $T_g$ of PBAT in the KL blend shifted from -34.0 to -26.0 °C while the MSL blend moved the PBAT $T_g$ to -1.5 °C in the ternary blends. Both
shifts were observed due to the compatibility of the MSL component with the PBAT phase, which is commonly observed with compatible polymer-lignin blends [102]. However, the grafting of PLA onto lignin caused reduction in compatibility of lignin with PBAT, causing the T_g to shift back to its original positions. This reduced compatibility is likely due to the inherent incompatibility between PBAT and PLA as observed with the PLA/PBAT binary blend [38]. As a result, the T_g of PBAT in the M-KL blend was reduced from -26.0 to -34.5 °C, while the M-MSL blend was reduced from -1.5 to -18.1 °C. One peculiar phenomenon was observed in the DSC curves, which is the presence of a slight exothermic peak located at 29.6 °C, which was only visible in only one other blend, which is the PBAT/MSL blend shown in figure 17 occurring at 41.0 °C. These peaks occur at temperatures very similar to the exothermic peak found in the cooling curves attributed to the crystallization of the PBAT structure, which indicates that this exothermic occurring during heating may be due to the cold crystallization of PBAT [34].

Figure 27. Differential scanning calorimetry analysis of PLA/PBAT/modified lignin ternary blends.
A few minor changes can be noted to the PLA phase. The M-KL doesn’t seem to show any significant effects on the PLA phase compared to KL. On the other hand, the modified MSL compound seems to have a rather drastic effect on the crystallization of PLA. The unmodified MSL shows an anti-nucleating effect towards PLA whereas the binary PLA/PBAT blend would cause nucleation of PLA, which indicates that the interaction between MSL and PLA is more favorable than PLA and PBAT. As a result of MSL blending, the crystallization temperature of PLA increased by 10°C from 99 to 109°C as discussed in section 3. However, the modification of the MSL molecules by attaching PLA chains onto lignin reverted the crystallization temperature nearly back to its original value. One possible explanation that could describe this behavior is the interaction between PLA and the grafted PLA chain is even more prominent than the direct PLA/lignin interaction, which changed the crystallization behavior back to its original behavior.

5.1.3 Blend Morphology
The extracted fracture surface of the PBAT/PLA/M-KL (figure 28B) blend showed more distinct lignin particles compared to the KL ternary blend (figure 21D page 61) in addition to larger average particle size as shown in image A of figure 28. The PLA molecules are also more evident in the M-KL blend and much more varied in size. Another significant change in the M-KL blend is the presence of PLA within the lignin agglomerate, which is shown as white specks, which seems to be completely wetted, showing the improved interaction between PLA and lignin after modification. The extracted image of the M-KL blend showed a similar morphology to the unmodified KL blend with heterogeneous particle size.
The unextracted M-MSL blends showed a similar morphology to the MSL blend. However, upon extraction the differences between the two blends are more obvious. As observed, the elongated structures that were created in the MSL ternary blend due to the effect of MSL on PBAT viscosity is not observed in the M-MSL blend as observed in figure 28D. Although the particle size distribution of lignin hasn’t changed in both MSL and M-MSL blends, the behavior of PLA shows that it has reverted into the individual bead structure which was observed in the PLA/PBAT binary blend, but based on the gap in between the PLA and PBAT phase left behind by the extracted lignin, lignin still acts as a bridge between PLA and PBAT. This further shows the reduction in compatibility between PBAT and MSL due to the
grafting of PLA; however, the fact that the PLA particles are largely varied in size for both M-KL and M-MSL, show that the slightly improved compatibility between PLA and the modified lignin produced a much smaller PLA inclusions.

5.2 Conclusions

The grafting of PLA onto lignin shows a slight reduction in strength for the ternary blends of PLA, PBAT, and lignin, but retention of elongation and impact strength of the original ternary blends. This behavior is consistent with the reduction in compatibility between both lignin and PBAT as shown in the DSC study. The weakened interface results in the reduction of stress transfer between PBAT and lignin, causing reduced strength. On the other hand, the SEM images showed the presence of PLA inside lignin agglomerates, which may suggest improved interaction between modified lignin and PLA. However, the lack of improved properties in the blend may be due to weak interactions between PLA and modified lignin. This weak interaction may be caused by the inefficient grafting process which needs to be optimized to yield higher grafting.
Conclusions and Future Research

6.1 Conclusions

6.1.1 Blends of Fractionated Lignin

Lignin was successfully fractionated with methanol to create a more homogeneous material for melt blending with thermoplastics. The resulting methanol soluble and insoluble fractions of lignin showed distinct differences in thermal behavior and chemical structure. DSC thermograms indicated the methanol soluble lignin has lower glass transition temperature of approximately 120°C, the insoluble fraction has a glass transition at 187°C. The original Kraft lignin exhibited a narrow glass transition temperature at 154°C which is located between the glass transitions of the two fractions. This indicates that the mixture of lignin fraction acts as one homogeneous compound due to the possible formation of complexes based on the chemical functionalities of the lignin fractions. The PBAT/lignin binary blends showed that the mechanical behavior of the Kraft lignin blend is largely dictated by the behavior of the methanol insoluble particles, which contain large lignin agglomerates acting as weak fillers in a polymer composite system. This weakness resulted in reduced elongation, impact, and tensile strength. On the other hand, the methanol soluble lignin/PBAT blend showed excellent toughness and retention of the ability of PBAT to undergo stress-induced crystallization. This is likely due to the highly dispersed lignin particles as indicated by the SEM study, and the improved compatibility as suggested by the shift of PBAT glass transition temperature.

The PLA/PBAT ternary blends showed similar behavior where the KL and MIL blends were much more brittle compared to the MSL blend, which showed retention of the PLA/PBAT binary blend elongation, with 30% lignin by weight. However, the discontinuity in the phase behavior was reduced from the PLA/PBAT blend to all three of the lignin blends as observed
in the stress-strain curves. This reveals the occurrence of stress transfer between PBAT and PLA bridged by lignin, which was confirmed by the presence of lignin particles in the PBAT/PLA interface on the SEM morphological study. The DSC study however, indicated no improvement in the compatibility between PLA and the fractionated lignins which uniform with the lack of change in the yield strength of the ternary blend, a property mainly attributed to the stiff PLA phase. The DSC thermograms however, showed that the KL and MIL blends induced crystallization in PLA, whereas the MSL blend showed the opposite behavior, which is anti-nucleating PLA crystallization. The impact strength showed showed the highest reduction for the KL and MIL blends due to the formation of agglomerates and complexes, however the MSL blend also showed a relatively significant reduction, which may stem from the insufficient interaction between lignin and PLA for both MSL and MIL, creating a weak interface which leads to the formation of micro cracks within the blend, therefore weakening its impact strength.

6.1.2 Impact of Lactic Acid Grafted Lignin on Thermoplastic/Lignin Blends

The aim of lactic acid grafting of lignin was to improve compatibility and contact between lignin, which is made up of highly cross-linked benzyl propane based monomers with bioplastics in the form of aliphatic-aromatic copolyester (PBAT) and aliphatic polyester (PLA). The condensation polymerization of lactic acid onto lignin would produce multiple extended PLA arms which would interact with the linear polymers through dipole-dipole interaction and chain entanglement, thereby improving the compatibility and dispersion of the modified lignin in the polymer matrix. Azeotropic dehydration of lactic acid, which is currently a less conventional method for lactic acid grafting, has shown to successfully graft lactic acid onto lignin by up to 30% PLA by weight as measured by thermo gravimetric
analysis. The resulting compounds which were purified of homopolymer, monomer, and oligomer, showed both lignin and PLA chemical groups under Fourier transform infrared spectroscopy.

The resulting ternary blend containing either modified Kraft lignin and modified methanol soluble lignin showed reduced mechanical strength due to reduction in the compatibility between lignin and PBAT. On the other hand, morphological studies indicated slight improvement in compatibility between modified lignin and PLA. However, since lignin bridges the void between the incompatible combination of PBAT and PLA as seen in the lignin fraction study, the blend with lignin containing higher amount of grafted PLA would suffer from the lack of interaction with PBAT. Therefore, the tradeoff granted from PLA grafting would require some optimization with regards to the amount of grafting required or ingenuity to engineer a lignin molecule that could retain both the grafted PLA chain and its base chemical functional groups to produce the best adhesion between the three components in order to maximize the properties of the PLA/PBAT blend.

As seen in the studies conducted in this thesis, fractionated lignin can stand alone as reinforcing filler in PBAT due to its high compatibility. However, the interaction between the fractionated and modified lignin with PLA is still lacking. As a result, the ternary blend between PLA, PBAT, and lignin is also less than optimum for high value commercial applications. This lack of interaction between modified lignin and PLA is likely due to the insufficient grafting. By optimizing the reaction conditions or perhaps modifying the reaction method, much higher amount of grafting should be attainable which should produce maximum interaction with PLA.
6.2 Future Research

6.2.1 Ring Opening Polymerized Lactic Acid Grafted Lignin Blends

Based on the discussion proposed in this thesis, one of the largest problems that affect the performance of a PLA/lignin blend is the compatibility between the two materials. The grafting of PLA onto compounds which previously has little to no compatibility with PLA showed improved adhesion, hence improved mechanical, thermal, and even optical properties. The grafting of lignin through the azeotropic dehydration allows for the advantage of reduced steps and much less rigorous procedure to be adopted in addition to limitations in available laboratory infrastructure. However, it has been commonly known that the grafting of PLA by ring opening polymerization method offers a highly pure grafted compound, high grafting efficiency and yield, and optically pure grafted PLLA chains [72,94]. With longer grafted chains, the modified lignin compound should find further improvement in interaction with the PLA phase.

A pretreatment step prior to PLA grafting could also be adopted to block some of the hydroxyl groups in order to limit the increase in size of lignin [94]. Since one molecule of lignin has numerous hydroxyl groups, grafting a lignin chain on each would suffer from the density of the grafted polymer chains, which may prevent interaction with outside polymer chains. Additionally, if the entire lignin surface was covered with PLA chains, the functional groups on lignin responsible for its compatibility with PBAT may be blocked as observed with the ternary blends observed in section 5. One method to block the hydroxyl group is by reacting with limiting amounts of acetic anhydride, which would leave some hydroxyl functional groups intact, while blocking others, therefore controlling the average number of PLA chains that can be grafted onto one molecule of lignin [94]. As such, the lignin-PLA
copolymers would be able to bridge PBAT and PLA effectively to create maximum interaction.

6.2.2 Auxiliary Properties of Lignin in Blends

The direct applications of the blends produced in this project have yet to be fully explored. However, based on the dispersion and compatibility of the MSL with PBAT and even PBAT/PLA matrix, it is likely that the inherent property of lignin can be exploited in applications that require more than just structural properties. One example is the antioxidant properties in lignin. A study on the radical scavenging ability of lignin in polypropylene matrix showed that lignin has approximately half of the radical scavenging ability of a commercial antioxidant [69, 75, 103]. However, at a much lower cost, lignin could become a very attractive alternative to increase the shelf-life of plastics that are exposed to the environments. Another possible application uses the natural ability of lignin which acts as an antimicrobial agent and protection against chemical damages [13], which makes lignin a good material for the application of a protective film in packaging.
7 References


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