university of groningen

faculty of science and engineering

Synthesis and properties of novel lignin-PLA biocomposites

An MSc. Research Project for the Degree of
Chemical Engineering - Bio-based Products

Main supervisor: prof. dr. H.J. Heeres
Second supervisor: dr. P.J. Deuss
Daily supervisor: D. Santosa

Author: **Andreea G. Sachelaru** (S3164780)
Contact: a.sachelaru@student.rug.nl
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Abstract

One of the most influential industries is the petroleum-based plastics industry, which has created devastating environmental problems, which need to be addressed urgently. This research project focuses on the issues of plastic pollution by investigating alternative bio-based materials. The aim of this research is to synthesize novel biocomposites from lignin and polylactic acid (PLA), to improve PLA's properties with regards to food packaging applications. First, graft polymerization reaction was carried out to synthesize PLA-lignin copolymers using a non-toxic organocatalyst, named 1,4,7-Triazabicyclodec-5-ene (TBD). Next, the copolymers were blended with commercial PLA to produce the lignin-PLA biocomposites. The materials contained 1 wt % lignin, in accordance to the literature, which indicates that the addition of a higher amount of lignin (> 5 wt%) is detrimental for the mechanical properties of PLA. Lastly, the lignin-PLA materials were shaped via solvent casting and the resulting films were tested for their mechanical and optical properties. The PLA-lignin biocomposites containing the grafted copolymers were compared with the PLA-lignin biocomposites containing unmodified lignin. This was done in order to identify the effect of the graft copolymerization before blending with PLA. In addition to previous literature research, where the focus stands on one type of lignin, this project employed different types of lignins: Kraft softwood lignins (Indulin and Lignoboost), organosolv hardwood lignin (Fabiola) and pyrolytic softwood lignin. All of them were compared for their chemical structures, biomass source and extraction processes, in order to determine their reinforcing effect on PLA. The grafting occurrence was proved by ^{1}H-NMR analysis of the copolymers, clearly showing the presence of both lignin and PLA in the samples. In addition, the obtained lignin-g-PLA/PLA biocomposites revealed improved mechanical and UV-Vis properties, which further demonstrate that grafting took place and it covalently-bonded the lignin to the PLA matrix. The mechanical testing of the grafted biocomposite films indicated that, while the addition of lignin via grafting slightly reduced the tensile strength, it also increased the elongation at break significantly for some samples. The best mechanical behavior was shown by samples grafted with grafted Kraft lignins, with a slight reduction in tensile strength (16-18 MPa) and considerable increase in elongation at break (3.4-3.6 %). This can be explained by their structure owing to the source of biomass and the extraction process. In addition, it was found that acetylation before grafting was not necessary as it did not generate notably better properties. Finally, the UV-vis analysis indicated that the addition of a small amount of well-dispersed lignin improved the UV-light barrier of PLA, in agreement with literature. A lignin-PLA biocomposite manages to block most of the detrimental light spectra e.g. UV-C and UV-B, which contribute to faster food spoilage and waste. Thus, lignin-PLA biocomposites are potential alternatives to conventional packaging materials, provided that further optimization of the production process is performed.

1 Introduction

Nowadays, one of the most urgent environmental problems is plastic pollution. The exponential increase in the production of disposable plastics, made from fossil fuels, overwhelmed the world's ability to manage them. This is leading to numerous issues for both wildlife and human populations. It is approximated that worldwide polymer production in 2050 will reach around 300 million tons [1]. Most of the plastic waste stems from the food packaging industry. Such plastic materials, however, have a crucial role in reducing food waste by maintaining the quality of foods and increasing their shelf-life. Currently, owing to their good properties and availability, petroleum-based plastics lead the packaging market. However, recent actions to mitigate climate change, as well as the increase in consumer awareness with regards to environmental issues, have created a great demand for sustainable alternatives for plastics [2].

Made from renewable sources, bio-based plastics can display an alternative to conventional plastics, provided that they meet certain criteria such as economic feasibility, facile processability and good mechanical properties. Bio-based polymers can be classified based on their biomass origin or synthesis method as: extracted from biomass, synthesized from bio-based derived monomers and produced from microorganisms. Examples of bio-based materials currently employed in packaging applications are poly(ε-caprolactone) (PCL), poly(hydroxyl alkanoates) (PHAs), poly(ethylene glycol) (PEG) and the most promising, poly(lactic acid) (PLA) [3].

While the bio-based origin of these materials is important, their end-of-life options are crucial. Thus, the perfect candidate material for the packaging industry should preferably allow for recyclability and, after the end of life, be compostable in industrial composting facilities.

1.1 Polylactic acid

Already commercially available, with a production capacity estimated as of 2019 to 29 kton/year [4], polylactic acid is a biodegradable aliphatic polyester, derived from renewable sources, such as corn starch or sugar cane. PLA can be synthesized via different mechanisms, such as ring-opening polymerization (ROP) of lactides or via condensation polymerization of lactic acid monomers (Figure 1). ROP is the most common mechanism, and it involves reacting lactic acid to cyclic lactides prior to polymerization to high molecular weight PLA. The lactides can be formed in three stereoisomers: l-lactide, d-lactide and meso-lactide (Figure 2). However, the amounts of each of the stereoisomers vary depending on the process, and it highly influences the crystallinity and thus, the mechanical properties of PLA. For instance, PLA containing at least 93% of the l-lactide is semicrystalline, whilst a PLA content of more d-lactide is in amorphous form [5].

PLA is a biomaterial with high potential to replace petroleum-based plastics. It has already achieved a great deal of attention and applicability in the packaging sector due to its inherently good mechanical properties. Currently, PLA exists in different grades and it was approved by the U.S. Food and Drug Administration (FDA) to ensure safety for food packaging [6] [7]. Nonetheless, PLA still has several drawbacks such as high brittleness, low UV light resistance and low oxygen and water barrier [6], which are further addressed in this investigation.
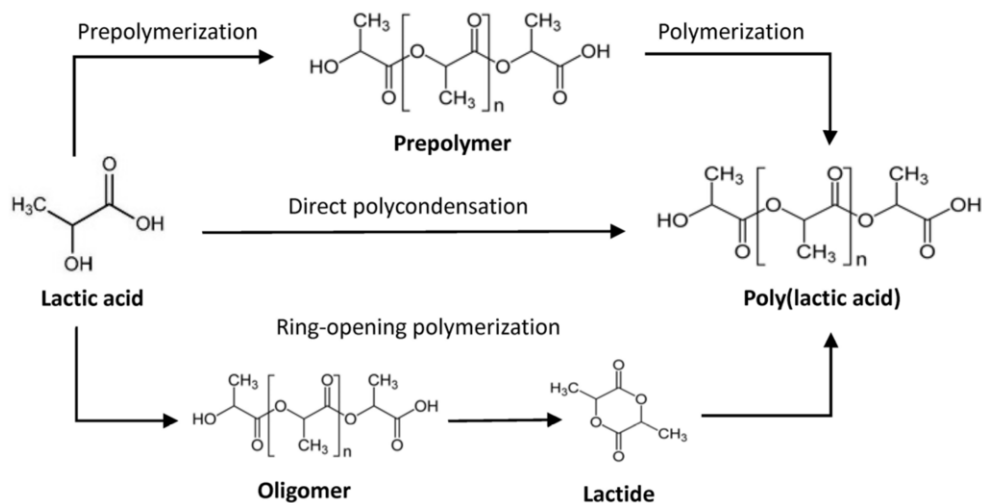
Figure 1 - Synthesis mechanisms of PLA [52].
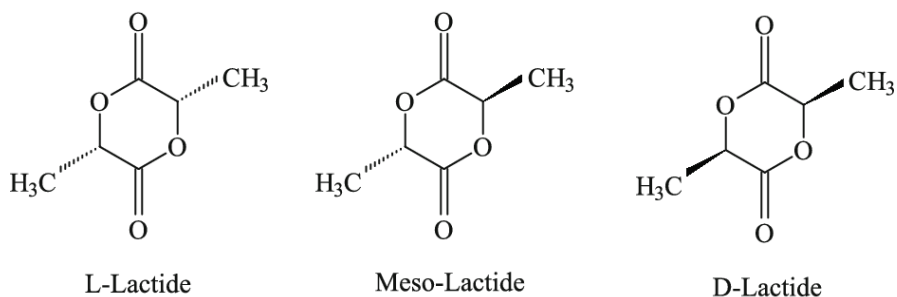
Figure 2 - Different stereoisomers of PLA [8]

Depending on its molecular weight and stereochemistry, the mechanical properties of PLA vary. In general, semicrystalline PLA is preferred over the amorphous one, with semicrystalline PLA having an approximate tensile modulus of 3 GPa, a tensile strength of 50-70 MPa and elongation at break of 4 % [9]. The glass transition temperature of PLA is around 60 ℃, with a melting temperature of 160 ℃ [10].

Regarding the biodegradability of PLA, similar with to other materials, is highly dependent on its structure and environmental conditions. Upon exposure to certain conditions (such as composting environment), at a temperature of 50-60 ℃, for 45-60 days, PLA is degraded in smaller molecules (oligomers, dimers and monomers), which are further broken down into H_2O and CO_2, by microorganisms [11]. The presence of different additives or fillers can slow down the degradation rate. Figure 3 shows the life cycle of PLA [12].

With a regard to food packaging applications, PLA has already been in use and in the current food packaging market, PLA is used in the form of packaging containers i.e., water, yoghurt, juice bottles for supermarket products. In addition, it has uses in service ware, composting bags and controlled release models for pesticides and fertilizers, adopted by environmentalists around the world [13].

The global market size for PLA packaging materials is estimated to reach USD 1 billion by 2027 [14]. This is due to changing lifestyle preferences of consumers and retail traders, which are fueling the growth in demand for such packaging. Nonetheless, it is necessary to improve specific properties of PLA in order to provide a smooth transition to alternative green packaging. Besides the significantly higher cost of PLA, one of its major hindrances is the high brittleness. This is because PLA has low deformation at break and high modulus, which greatly limits its applications as packaging materials. Using lignin as a cheap filler could overcome drawbacks, such as high cost. The lignin price varies, depending on the isolation process, between $70 and $150 per ton [15], while PLA is one of the most expensive plastics on the market: $1910 per ton [1]. Furthermore, integrating lignin can have a positive effect on PLA's mechanical properties. The reason for this is that lignin can act as a compatibilizer, due to its supramolecular structure and functionality. Moreover, lignin is a natural antioxidant, which can be used as additive in food packaging to prevent food spoiling and waste [16].
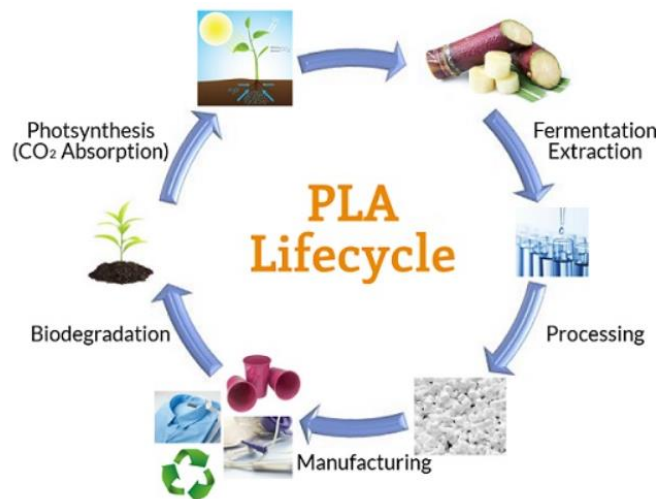

Figure 3 - Schematic representation of PLA's lifecycle, adopted from [12]

1.2 Lignin

Highly abundant in nature and accounting for nearly 10-30% weight of lignocellulosic biomass, lignin is a three-dimensional macromolecule present in all vascular plants with a role in providing structure and support to the plant, while also being a means of internal transport for water and nutrients [17], [18] (Figure 4). Lignin is present in varying amounts, depending on the type of plant. For example, softwoods (e.g., pine, cedar) comprise about 30 % of lignin, while hardwoods (e.g., oak, maple) slightly lower, 10-25 % lignin. With several exceptions, grasses contain less than 15 % lignin [19].
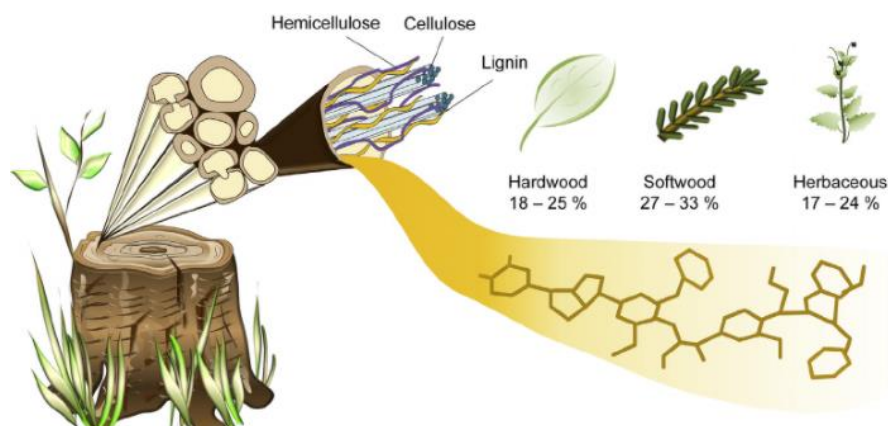
Figure 4 - Lignin's position in natural plants and the amounts on each type of plant [20].

Lignin's chemical structure is very complex and varies by the biomass sources and isolation process. In general, it is a macromolecule composed of amorphous polyphenols with a large amount of polar functional groups [17], [18]. The chemical structure of lignin stems from the dehydrogenating polymerization of the three monolignols (hydroxycinnamoyl alcohols), named: p-coumaryl alcohol (H-unit), coniferyl alcohol (G-unit) and sinapyl alcohol (S-unit) (Figure 5). These structures differentiate themselves by the degree of methoxylation at the aromatic ring positions: C3 and C5. Figure 5 shows their structures and it can be seen that the H-unit does not have any methoxy group attached to C3 and C5, the G-unit has a methoxy group at C3, while the S-unit has methoxy groups in both C3 and C5 positions [21].
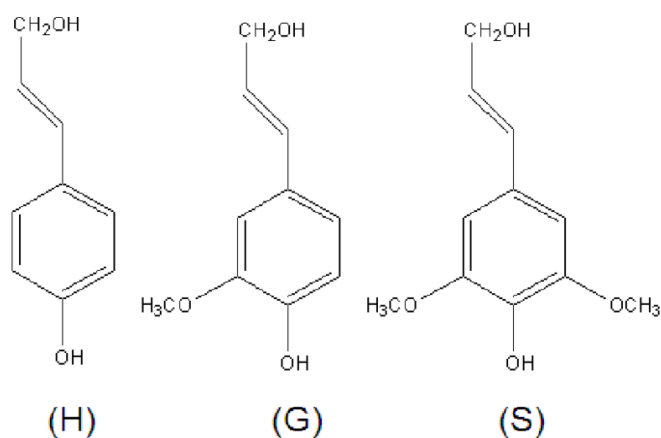
Lignin's structure shows high complexity owing to the precursor alcohols, which form the phenolic structures, which are linked together. This generates a 3D structure with a diversity of inter-unit linkages i.e. β-aryl ether, β-O-4, β-5, resinol, biphenyl, 4-O-5, etc. [22], the main one being the β-O-4 ether bond (Figure 6).

Figure 5 - Monolignols units in lignin [53].

However, the structure of lignin varies greatly, depending on the plant species and environment. For instance, hardwood lignin consists mainly of S-units and G-units, with few H-units. As another example, coniferous softwood lignin consists of high levels of G-units and very few H-units, while grasses contain all three monolignols [23]. Table 1 summarizes the amounts of different monolignols in lignin for the three main plant categories.
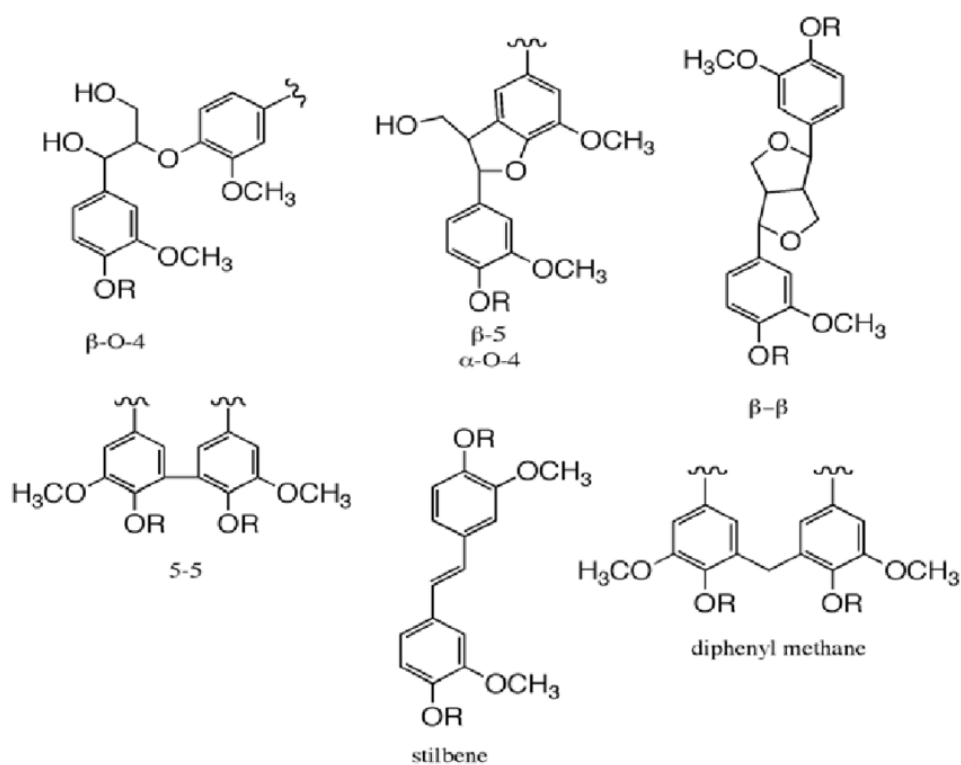

Figure 6 - Different linkages in lignin's structure [57].

Table 1 - Amounts of monolignols in different kinds of lignin [19].

Type of plant	H-unit (%)	G-unit (%)	S-unit (%)
Softwoods	< 5	> 95	-
Hardwoods	0-8	25-50	45-75
Grasses	5-35	35-80	20-55

In the context of integrating lignin in bio-composite production, several determinants, such as the number of specific functional groups, the molecular weight, different types of linkages and the amount and types of impurities, all influence the miscibility between lignin and a polymer matrix. However, the molecular structure of lignin is significantly modified, according to the type of isolation process it undergoes [15]. The separation of lignin from the other biomass components yields the so-called technical lignins. These lignins are the subjects of this research.

Technical lignin

In an industrial context, lignin is a by-product of the pulp and paper industry. Nonetheless its potential, lignin is either considered waste, or it is burned to be utilized as low energy fuel. This makes lignin cheap and abundant, while its natural origin and biodegradability are benefits worth considering when looking for potential applications.

Industrial lignin can be categorized into two groups: sulfur-free lignin and sulfur-containing lignin. The sulfur-free lignin is derived from biomass conversion employed in biofuel production, organosolv process and soda pulping process. The sulfur-containing lignin originates from both Kraft process and sulfite pulping processes and comprises the biggest category on the market as the moment [24].

Compared to native lignins, the structure of technical lignin is considerably degraded and condensed, due to the pulping process. Literature also reveals that there are lower amounts of β-ether linkages and high amounts of impurities [59].

In the Kraft process, the separation of lignin occurs at 170 ℃ with a solution of sodium hydroxide and sodium sulfide. The obtained lignin is solubilized and precipitated with a lower pH. Due to the usage of sodium sulfide, Kraft lignin also contains some amount of sulfur i.e. 2-3 % [19], [25]. Kraft lignin has a number average molecular weight of 2000-3000 g/mol and polydispersity in the range of 2-3 [24]. Based on literature, Kraft lignin has relatively low molecular weights owing to the harshness of the industrial Kraft process [26].

Another industrial process to isolate lignin is soda pulping. It is similar to the Kraft process, only that sodium sulfide is not used. It, thus, generates a lignin without sulfur content, which

is more similar to the native lignin. In addition, soda lignin has comparable average molecular weights with the kraft lignin [19].

Initially employed as a green replacement of the paper pulping industrial process, the organosolv process is also attractive for its capacity to efficiently separate the three biomass components: cellulose, hemicellulose and lignin in only one step. The organosolv process occurs by cooking the biomass using a mixture of water and an organic solvent, leading to the dissolution of the lignin in the cooking liquor. Furthermore, the lignin is precipitated via dilution with water. This process does not only result in high quality cellulose-rich pulp and a lignin-rich precipitate but also allows for the organic solvent to be recycled back effectively, as the amount of hazardous chemicals is reduced [27]. However, despite its sustainability and green approach, the organosolv process is more expensive and it currently exists only at pilot scale, leading to a high price for the resulting lignin [25].

Pyrolytic lignin

The fast pyrolysis of lignin is a process aiming at forming valuable chemicals or fuels. The resulting product is a dark-colored pyrolysis oil (PO), which contains a large number of functional groups containing oxygen. Pyrolytic lignin (PL) is the major constituent and it boosts the complexity and viscosity of the liquid mixture. Pyrolytic lignin is extracted via water fractioning of the pyrolytic oil [22]. PL is a highly cross-linked polymer with a matrix of phenolic derivatives and a broad molecular weight distribution. It contains various non-saturated derivatives, with ring positions vacant for various reactions such as crosslinking or condensation [28].

1.3 Biocomposites

Composites are materials consisting of two or more distinct parts or phases that, when combined together, lead to a material with different properties compared to those of the individual components. Generally, to form a composite, a strong reinforcement material is ingrained in a usually weaker matrix phase. The benefits of such composite materials are that the mechanical properties can be significantly improved.

Bio-composites are composites having both phases stemming from a biological origin. For instance, the reinforcement phase material can be plant fibers such as cotton, hemp, wood or recycled wastepaper, while the matrix phase could be a polymer, preferably also derived from renewable sources. The reinforcing natural fibers can be classified as wood (softwood and hardwood) or non-wood fibers (bast, leaf, seed-hair fibers) [29]. With regards to the specific application in food packaging, the biocomposite should be shaped into films. Nonetheless, if natural fibers are used as filler, proper packaging films cannot be obtained, due to the fibers' large size and density. However, all-natural fibers, no matter their origin, are composed of three main cell wall natural polymers: cellulose, hemicellulose and lignin. The latter can be isolated and constitutes the subject of this investigation by integration into PLA's matrix phase. It is important to note that lignin competes with other cheap additives and plasticizers, however one of the objectives of this project is to also valorize the lignin waste from the pulping industry.

1.4 The state of the art: lignin-PLA biocomposites

Recently, there is a significant interest in the integration of lignin with synthetic polymers via copolymerization or simple blending. Table 2 on the next page shows an overview of the literature research carried out recently regarding lignin/PLA biocomposites.

Most commonly, lignin is added as a filler in thermoplastics, thermoset polymers and even rubber, however with both positive and negative results. On the positive side, being a hyperbranched chemical structure with numerous functional groups (phenolic and ketones groups), which are UV-absorbing chromophores, gives lignin the ability to block natural broad-spectrum UV [30]. As this property is highly desired in food packaging materials, it is worth investigating lignin's effect in biocomposite integration. Furthermore, some studies have shown that blending lignin with polylactic acid leads to an increase in the thermal stability and processability of lignin. The graft polymerization of lignin with lactic acid led to an increase in the glass transition temperature and an improvement of UV absorbance [31], [32], [31]. On the negative side, factors such as lignin's molecular size, the distribution of the functional groups and others might limit its applicability [24]. One major obstacle in achieving a PLA-lignin bio-composite with improved properties might be the poor dispersion of lignin on the PLA matrix, leading to self-aggregation and a decline in mechanical properties [31]. This is because the structure of lignin is highly irregular with high amounts of hydroxyl groups, which can form hydrogen bonds with the other functional groups present in lignin's structure and yield great intermolecular associations. Nevertheless, modification of lignin can be carried out prior to blending with the PLA, to improve its dispersibility with the polymeric matrix [31]. Among these modifications, graft polymerization and acetylation are two attractive approaches to covalently alter the structure of lignin.

Table 2 - Overview of literature studies on lignin/PLA materials, adopted from [25]

Lignin type	Biomass source	Lignin treatment	Mixing technique	Shaping technique	Source
Kraft	Softwood	Acetylation + PLA grafting	Solvent mixing	Hot press	[31]
		Acetylation		Solvent casting	[30]
		Plasticizers	Extrusion	-	[18]
				Hot press	[24]
		-			[33]
	Hardwood	Plasticizers			[34]
		Acetylation			[26]
Organosolv	Hardwood	Fatty acid esterification	Solvent mixing	Solvent casting	[35]
		Acetylation	Extrusion	-	[18]
		-		Hot press	[33]
	Softwood	Fatty acid esterification	Solvent mixing	Solvent casting	[34]
	-	Rubber+lactide grafting			[36]

It can be seen from Table 2 that each of the research previously done focuses on either one type of lignin (Kraft or Organosolv) or one biomass source of lignin (hardwood or softwood). Therefore, in addition to the state of the art, this investigation aims at analyzing the influence of both aspects: extraction processes and biomass sources. Moreover, lignin is integrated into the PLA matrix via a novel grafting reaction, as well as a simple blending, in order to obtain a comparison between the two synthesis methods. Lastly, the necessity of acetylation pre-treatment combined with grafting is also evaluated.

Graft polymerization

Graft polymerization is a technique used to modify the characteristics of polymers, involving the covalent bonding of monomers into the chain. It was shown that, for the production of lignin-based materials, grafting is one of the most effective methods to modify the properties of polymers [32]. With the aim of improving the distribution of lignin in PLA, lignin-g-PLA graft copolymers can be synthesized and blended with PLA. Other investigations demonstrate that producing different composites, such as PLA-talc [37], via grafting polymerization, successfully leads to the introduction of the well-dispersed graft into PLA, thus improving its properties. It is then expected that introducing lignin in this approach would yield similar results. While lignin's structure includes a mixture of aliphatic and phenolic hydroxyl functional groups, this can introduce some selectivity challenges. Literature indicates that organocatalytic ring opening polymerization is efficient with aliphatic hydroxyl groups,

however there is few research on phenolic groups. It is only shown that phenolic alcohols partly act as initiators in the polymerization, however they are slower compared to aliphatic groups [31]. Thus, more investigations should be conducted to determine the influence of the structural properties of lignin with regards to PLA modification.

In this project, the graft polymerization of PLA on lignin (10 wt%) was carried out via an organocatalytic ring-opening polymerization of lactide (ROP), which was facilitated by a metal-free organo-catalyst (see reaction scheme in Figure 8 [31]). TBD is a non-toxic, metal-free organo-catalyst and it was used in the view of employing a green synthesis process. Only 10 wt % of the lignin species was added because this is the amount which was found in literature to be the most appropriate for a reinforcing effect. The addition of higher percentages of lignin can lead to the formation of large lignin aggregation, which interfere with the PLA matrix phase [25].
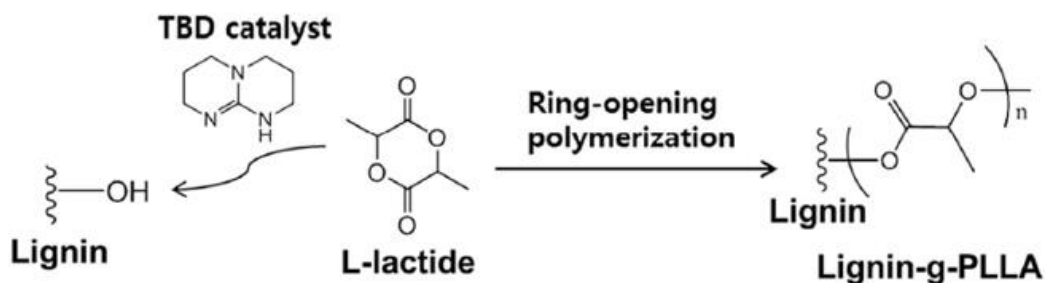

Figure 8 - Reaction scheme of the organocatalytic ROP of lactide with lignin, adapted from [31] [49].

Acetylation

The abundant hydroxyl groups present on the surface of the lignin's structure tend to interact with each other via hydrogen bonding, which leads to aggregation and a reduction in the reinforcement of non-polar polymers [31]. Thus, a surface modification was needed, to reduce such effects and increase the dispersibility of lignin molecules, resulting in an increase in the reinforcement. Among others, acetylation is proven to be a very efficient mechanism to decrease the polarity of lignin, increasing the interfacial adhesion between the lignin molecules and PLA's matrix [38]. In this investigation, the acetylation of lignin was performed prior to grafting and its outcome was compared with the non-acetylated grafts. The goal was to determine whether or not a lignin pre-treatment is necessary and it leads to significant improvements. Generally, pre-treatments are not advantageous as they are time-consuming and generate more waste.

Processing methods, shaping and compatibilizers

The two phases in bio-composites can be mixed together via different methods such extrusion or solvent mixing. Furthermore, shaping the bio-composites can be done via different techniques, such as injection molding, hot press molding, solvent casting, electrospinning or compression molding [39]. Industrially, extrusion is advantageous due to reduction of processing time and decrease in usage and waste of (toxic) solvents. There are different types of extruders that can be used, depending on the desired application of the product. For processing PLA, twin-screw extrusion is most commonly used at industrial level [39].

Solvent casting is the simplest and most commonly used method to produce bio-composites. In this process, the blend is dissolved in an appropriate solvent, which is further evaporated, allowing the formation of the bio-composite films. Since it uses high amounts of toxic solvents and it takes a long time to complete, this method is most suitable for lab-scale or small production processes. Depending on the solvent, the evaporation rate and the duration might vary and the distribution of the constituent elements throughout the film depends on the ratio in the solution [39]. In addition, in the case that there is no pre-treatment requirement, the solvent mixing step can be skipped, and the two phases can be directly mixed in the cast solution. Research on PLA suggests that the preparation of biocomposites by solvent casting leads to slightly better mechanical properties compared to extruded PLA. This is most significant for elongation at break. However, the potential solvent leftovers in the sample can influence these properties and should, thus, be considered [25].

It is shown in literature that the usage of compatibilizers can improve bonding between the PLA matrix and the filler. For instance, Wang et al. used a silane coupling agent of (2,3-epoxypropoxy)propyl-trimethoxysilane, via a one-step solvent-free modification procedure [40].

In this project, the bio-composites containing the PLA polymeric matrix and lignin as filler, are produced via solvent mixing and shaped through a solvent casting method[1], as it will be further disclosed. Furthermore, no compatibilizers were added, in the view of minimizing the complexity of the process.

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[1] Unfortunately, at the time of conducting this project, the extruder was not available and experiments could not be performed to eventually compare the results with the solvent casting method. This would be interesting to see in the future.
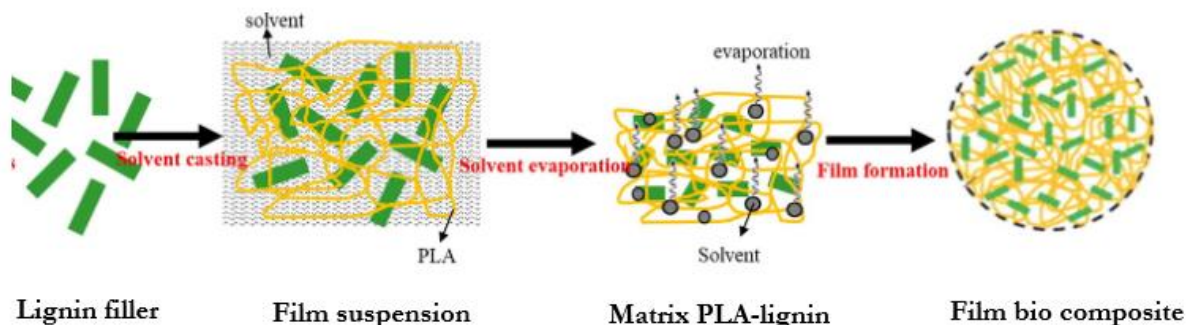
Figure 7 - Schematic representation of lignin/PLA biocomposite film formation via solvent casting, adapted from [41].

1.5 PLA as food packaging plastics

Owing to its composability and non-toxicity, the poly(lactic acid) material has been generally recognized as safe by the Food and Drug Administration (FDA). PLA is suitable for use in food and beverages packaging applications [42].

PLA is a versatile biopolymer and represents a promising alternative to synthetic polymers. However, its inherent structural drawbacks, such as high brittleness and weak barrier properties limit its applications. For instance, a conventional plastic such as PET shows a high tensile strength of $150 - 180$ MPa and an elongation at break of $150 - 180$ %. In contrast, PLA shows a tensile strength of 60 MPa and a low elongation at break of 4 -6 % [22].

Table 3 comprises an overview of the mechanical and barrier properties of PLA, compared to conventional packaging materials.

Table 3 - Overview of the properties of packaging plastics compared to PLA [25].

Material	Tensile modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)	P_{O2} (10^{-7} ml m/ m²day Pa)	WCA (˚)	Price (€/kg)
HDPE	0.98	20-30	600	7.13	96	0.9
LDPE	0.15-0.34	7-25	300-900	44.76	96	0.9
PP	1.18	27-98	200-1000	4.9-9.9	102.1	0.9-1.0
PET	3.5	150-180	70	0.1-0.5	72.5	0.72
PS	2.7-3.4	30-50	2	9.9-14.8	87.4	1.1-1.2
PLA	3.5	60	4-6	2.7	71	2

UV-vis barrier

A crucial parameter to be considered regarding polymeric films for packaging applications is the barrier to UV light. The absorption of UV light by the polymers is one of the major determinants influencing the quality of food. More specifically, light-sensitive products, such

as dairy, juices, vitamins and edible oils require protection from UV radiation, as it has been demonstrated that light affects the flavor and nutritional content of such products [5].

The light wavelengths of interest for packaging applications are those in the range 200-2200 nm. They can be classified into three categories: UV (Ultraviolet) band: 100-400 nm; the visible spectrum (400-700 nm) and near infrared band (700-2200 nm). The UV-light spectrum, accounting for 3% of the total radiation entering the Earth, is responsible for chemical reactions and damage of certain polymers. This band can be divided into UV-A (400-315 nm), UV-B (315-280 nm), which determines the most photochemical degradation of polymers, and UV-C (280-100 nm), usually created by artificial sources [5].

Although PLA is extensively used in packaging, it lacks good barrier properties and thus, it has decreased value compared to conventional packaging materials. This is examined by looking at the transmittance of specific light wavelengths. PLA has almost no transmission in the lowest range (UV-C), though at 230 nm, its light transmission expands considerably. At 300 nm, almost all the UV-light is transmitted. Therefore, UV-C is completely blocked by PLA, however almost all UV-B and UV-A light penetrates the PLA films. Figure 10 shows an overview of light transmission of PLA compared to other conventional plastics. It can be seen that less UV-C light passes through PLA compared to LDPE. The others i.e., PET, PS, cellophane, however, transmit less of all types of UV. The highest UV-light barrier is displayed by PET, which blocks all UV-C and UV-B spectrums, which are the most detrimental for food products [5].

The addition of lignin to PLA is expected to improve the UV-vis light barrier of PLA film, in accordance to the type of lignin and its pre-treatment [31]. This is analyzed further in this project.
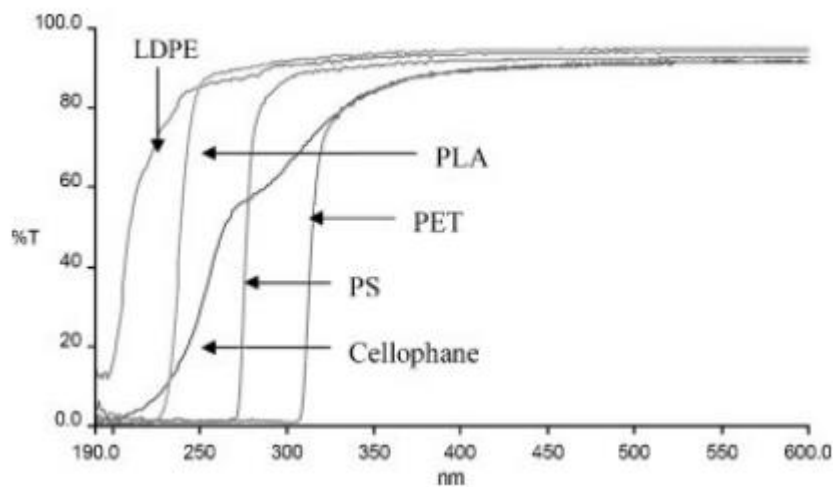

Figure 10 - Light transmission of PLA compared to conventional plastics [5].

Oxygen and water barrier

Extended storage can negatively affect most foods because of the penetration of oxygen through the material which oxidates the proteins, leading to undesirable flavors, colors and textures of the foods. Thus, in order to avoid such effects, the packaging material must have good oxygen barrier properties. This can extend the shelf-life of foods, also reducing food waste.

Previous studies show that PLA packaging films themselves have relatively good barrier properties, with a behavior intermediate between that of PET and PS. For this research, it is relevant to evaluate the effect of lignin's presence in PLA on the oxygen barrier. Since lignin bears functional groups which form a polyphenolic structure, it is known to naturally exhibit antioxidant activity [43]. Thus, it is expected that the addition of lignin to PLA leads to an enhancement of the oxygen barrier properties of packaging film, for both acetylated and non-acetylated samples.

In addition, water permeability is another important property for packaging materials. Preventing the water to pass through the material is crucial to maintaining the desired level of moisture so that the food does not spoil. The water barrier can be inspected via measuring the water contact angle. A small angle indicates a hydrophilic material i.e., the material interacts with water. Whereas a large angle suggests hydrophobicity, thus the material does not have interactions with water. Research indicates that the water contact angle of PLA is around 71 °, compared to PET: 72.5°. Polypropylene shows the largest water contact angle: 102.1°, followed by LDPE and HDPE: 96 ° (Table 3) [25]. The addition of lignin to PLA could improve hydrophobicity, as previous research shows that the addition of up to 5 wt % lignin has increased the water contact angle [30].

Price

A comparison between the prices of different packing materials is shown in Table 2. It can be seen that PLA has a significantly higher price per kilogram (2 €/kg) than the next most expensive alternative[2] (1.2 €/kg). Nevertheless, increasing the production of PLA can result in economies of scale, reducing the price per kg and making PLA a more affordable alternative to the oil-based plastics. More importantly, the addition of a cheap filler, such as lignin, can decrease the price of PLA packaging, if its production process is efficiently optimized.

2 Research objectives

Given the background information presented in the previous section, it is understandable that besides its advantages, PLA has several setbacks which need to be addressed. Apart from a

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[2] It is important, however, to realize that the prices for conventional plastics vary, according to the oil prices. Currently (2021), there is a substantial collapse in oil prices, thus in petroleum-based plastics prices.

high cost, PLA also exhibits high brittleness and low barrier properties, limiting its application in the packaging industry. Concerning this, filler materials or compatibilizers can be used to both decrease the cost and improve the properties. One possibility is using lignin as a filler, which is cheap, abundant and most importantly, a biopolymer. The incorporation of lignin with the PLA polymer matrix leads to the development of lignin-PLA biocomposites.

Thus, the main objectives of this project is to produce lignin-PLA biomaterials and determine which synthesis method is most appropriate to yield materials with improved properties and minimized costs. Furthermore, because lignin exhibits a very complex structure, another goal for this project is to determine which of lignin's structural characteristics play a role in effective integration into the PLA matrix. In addition, the necessity of a lignin pre-treatment was examined. Therefore, the following research questions are imposed:

1. Is grafting of lignin to PLA a more efficient technique compared to solvent blending with unmodified lignin, to yield materials with improved properties?
2. Is a pre-treatment of lignin, such as acetylation, essential to improve the properties of PLA?
3. Which type of lignin is the most suitable for mixing with PLA, to produce lignin/PLA biocomposites with improved properties?

In order get an overview of lignin's functionality as a filler mixed into the PLA matrix, different types of technical lignin were combined with PLA. Both softwood and hardwood-sourced lignin were employed, as well as lignin isolated via different techniques, showing various structural properties. The lignin-PLA materials were synthesized via a grafting reaction and simple blending. Furthermore, lignin was subjected to acetylation pre-treatment. The biocomposite samples obtained via different methods, containing various types of lignin were characterized and compared for their mechanical and optical properties.

3 Experimental

3.1 Materials

For this research, four types of lignin have been used: Indulin lignin (Ingevity), Fabiola lignin (TNO, The Netherlands), Lignoboost (Valmet) and pyrolytic lignin (BTG, The Netherlands). The L-lactide >98% (Total Corbion, The Netherlands), TBD catalyst: triazabicyclodocene (Sigma-Aldrich) and the PLA pellets (GoodFellow) were all stored in a moisture-free environment. In addition, different solvents were used, such as deuterated chloroform, diethyl ether, methanol, 2-propanol, p-dioxane, acetic acid, acetic anhydride, dimethyl carbonate (all

from Sigma Aldrich), acetone, dichloromethane (Avantor), chloroform (Biosolve) and tetrahydrofuran (Boom BV), all used without purification.

3.2 Laboratory Procedures

Acetylation of lignin

Lignin was pre-treated according to the acetylation procedure described by Chung et al. [31]. Lignin (2.0 g) was mixed with acetic anhydride (5.6 g) and diluted with p-dioxane (3.6 mL) in a round-bottom flask, conditioned under stirring at 50 ℃ for 2 hours. Next, the lignin was recovered by precipitation with deionized water, followed by centrifugation at 4000 rpm for 15 minutes for two rounds. The final product was dried overnight in an oven at 50 ℃.
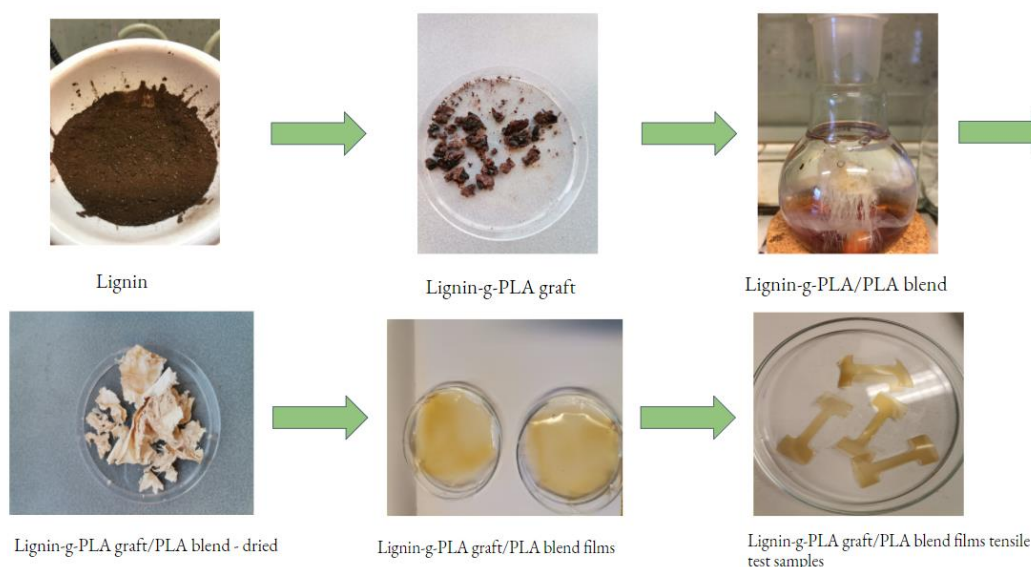
Synthesis of lignin-g-PLA copolymer

The lignin-g-PLA copolymer was synthesized via a ring-opening polymerization reaction, using an organosolv catalyst, according to Chung et al. [31]. The reaction took place in a sealed three-necked flask equipped with a stirring bar, which was first flushed with N_2, to ensure a moisture-free environment. Lignin (1 g, 10wt%) was mixed with L-lactide (9 g, 90 wt%) and TBD catalyst (0.1 g, 1 wt%). The flask was placed in an oil bath at 130 ℃ for 3.5 hours under stirring. After, the reaction was cooled to room temperature and quenched with a solution of dichloromethane (5 mL) and acetic acid (0.1 g). After dissolution, The remaining crude mixture was then washed with methanol (0.5 l). The methanol was subsequently discarded, and the viscous polymer was collected via dissolution in dichloromethane. Finally, the copolymer was dried in a vaccum oven at 50 ℃ and analyzed via ^{1}H-NMR. The same procedure was repeated for both non-acetylated and acetylated lignin samples. One adjustment, however, was made for the pyrolytic lignin, as its washing was done with ethanol instead of methanol.

Synthesis of lignin-PLA bio-composite

The PLA-lignin bio-composites were obtained via solvent blending. Commercial PLA pellets (1.89 g) were mixed with lignin-g-PLA graft (0.21 g) and chloroform (15 mL). The mixture was stirred at room temperature for 15 hours. Afterwards, the viscous blend was precipitated with isopropanol (100 mL), which was then evaporated in vaccum at 40 ℃ and 78 mbar in the rotavap. Finally, the bio-composite was dried in a vacuum oven at 70 ℃ for three days, then stored in a moisture-free environment. The same method was used for all the (acetylated) lignin-g-PLA samples. As a reference, the non-grafted and unmodified Indulin lignin (1 wt%) was blended with PLA, following the same procedure.

Preparation of lignin-g-PLA/PLA bio-composite films

The lignin-containing PLA-biocomposite films were prepared via a solvent casting method, adopted from Yang et al. and Wardhono et al. [41], [44] 5 w/v % of the lignin-PLA bio-composite was mixed with chloroform and stirred for 3 hours at room temperature. Next, the blend was poured in Petri dishes covered with a Teflon sheet, and left for 3 days to allow the solvent to slowly evaporate at room temperature conditions. The same procedure was applied for all the different lignin-PLA bio-composite samples. Due to the high toxicity of chloroform, different other solvents were experimented for solvent casting to eventually replace chloroform. PLA pellets (5 wt%) were also dissolved in solvents such as: acetone, dichloromethane (DCM), dimethyl carbonate (DMC) and p-dioxane, to evaluate whether or not the bio-composite films can be obtained, without the use of chloroform. In the case of DMC, a temperature of 50 ℃ was necessary to facilitate the dissolution of PLA.

Lignin

Lignin-g-PLA graft

Lignin-g-PLA/PLA blend

Lignin-g-PLA graft/PLA blend - dried

Lignin-g-PLA graft/PLA blend films

Lignin-g-PLA graft/PLA blend films tensile test samples

Figure 11 - Visual representation of experimental lab work

3.3 Material Characterization

^{1}H-NMR analysis of lignin-g-PLA graft copolymers

The lignin-g-PLA copolymers were characterized by H-nuclear magnetic resonance analysis (^{1}H-NMR). Spectra were recorded on a 600 MHz spectrometer, with peaks disclosed in ppm (parts per million), referenced to the residual solvent peak (deuterated chloroform). The samples were prepared by dissolution (10-15 %) in deuterated chloroform (CDl_3). Furthermore, in order to estimate the conversion ratio of l-lactide to the PLA chains, the following equation (1) was used:

$$Conversion\ ratio\ (\%) = \frac{HA}{HA+HB} * 100 \hspace{2cm} \text{(Eq. 1)}$$

With H_A representing the integrated area of the signal of PLA methide ($\delta = 5.1$ ppm) and H_B is the integrated area of the peak corresponding to l-lactide methide signal ($\delta = 4.3\text{-}4.5$ ppm).

Solvent tests

To determine whether the grafting reaction indeed occurred, several control experiments were carried out. Solvent tests were performed on non-acetylated and acetylated lignin with tetrahydrofuran (THF) and diethyl ether, respectively. The non-acetylated lignin-g-PLA copolymer (1 g) was dissolved into a vial with THF (15 mL) and exposed to sonication. After the complete dissolution, the solvent was evaporated at room temperature overnight. The same procedure was applied for acetylated copolymers, but with diethyl ether solvent in place of THF. After the evaporation of the solvent, ^{1}H-NMR samples in CDCl$_3$ were taken for both non-acetylated and acetylated copolymers, and the ^{1}H-NMR spectra were compared to the ones before solvent dissolution.

Tensile and UV-Vis Tests

The lignin-g-PLA/PLA blended films were cut into tensile specimens, using a standardized tensile cutting machine. The samples have a gauge length of 20 mm and a width of 5 mm. The thickness of the samples varied between 0.1 and 0.4 mm and it was measured with a caliper. The tensile tests were carried out using a universal tensile tester: Instron 5565, using a deformation speed of 20 mm/min. The specimens were kept at room temperature prior to testing and the tests were replicated three times to determine different mechanical properties like tensile strength (MPa), elongation at break (%) and Young's modulus (MPa).
The UV-vis analysis was carried out using a UV-Vis spectrophotometer, which measures the intensity of light transmitted through the sample. The lignin-g-PLA/PLA biocomposite films were simply placed in the spectrophotometer and the analysis was initiated.

4 Results and Discussion

4.1 Lignin characterization

Three types of technical lignin are employed: Indulin (obtained from the Kraft process), Fabiola (obtained via organosolv process) and Lignoboost (via Kraft process), and one pyrolytic lignin (pyrolysis of oil). All types of lignin are obtained as industrial by-products and are highly abundant and cheap. By analyzing the amounts of each functional unit in the

structure of lignin: S (sinapyl units), G (guaiacyl units) and H (p-hydroxyphenyl units), its biomass source can be identified. For instance, a higher percentage of G-units indicates that it originates from softwood biomass [25]. Table 4 on the following page shows an overview of the different lignin types, their biomass source, extraction process and their main properties. The data enclosed in the table was obtained from earlier research at the University of Groningen, via elemental analysis, gas chromatography (GC) and HSQC spectroscopy.

The lignins also differ in molecular weight (g/mol). Indulin and pyrolytic lignin have the lowest molecular weights, according to the data obtained from gas chromatography (GC). This is owing to the harshness of the industrial extraction process, in which various linkages are cleaved. Moreover, it can be noticed that the lignins resulting from the Kraft process show no presence of β-5 linear linkage (per 100 C9 units), mainly having β-O-4 ether linkages (e.g. 12.7 linkages per 100 C9 units). In contrast, organosolv Fabiola lignin shows various bonds: β-5, β-O-4 ether and β- β linkages.

Determination of the hydroxyl groups content and type in the different lignins was not done in this investigation. This is usually estimated via ^{31}P-NMR analysis [31]. In any case, a brief literature research indicates that softwood Kraft lignins generally show a higher content of phenolic hydroxyl groups, compared to an organosolv lignin. For example, total phenol amount in Kraft lignin is approximately 3.92 mmol g^{-1}, with an aliphatic group content of 2.18 mmol g^{-1}. In comparison, organosolv lignin shows 2.50 mmol g^{-1} phenolic hydroxyl and 3.00 mmol g^{-1} aliphatic [56]. Pyrolytic lignin is found to have lower contents of both phenolic and aliphatic functional groups, compared to the other types of lignin.

Lastly, some impurities contaminate lignin's structure, such as ashes, sulfur and some types of sugars. Elemental analysis discloses that the highest amount of sulfur is present in Lignoboost lignin (1.57 %), while the rest show insignificant amount. Furthermore, literature indicates that the amount of polysaccharides in Kraft lignins is relatively low (~3.4 %) [24].

*Table 4 – Relevant properties of different types of lignin used in this project and their properties (N/A = data not available) * Literature-estimated data*

Type of lignin	Biomass source/ Extraction process	Phenolic/ Aliphatic groups (mmol g$^{1)*}$)	SGH Ratio (%)			Molecular weight (g/mol)	Linkages per 100 C9 Units			Elemental composition (%)				
			S	G	H		B-O-4	B-5	B-B	N	C	H	S	O
Indulin lignin (IL)	Pine, soft wood/ Kraft	3.92/ 2.18	0	100	0	9.85E+02	12.7	-	6.4	0.7	61.9	5.9	0.1	29.1
Fabiola lignin (FL)	Beech wood, hardwood/ Organosolv	2.50/ 3.00	75	25	0	1.68E+03	19.5	3.8	10.5	0.06	63.8	5.8	0.04	30.2
Ligno-boost lignin (LGB)	Pine, softwood/ Kraft	3.92/ 2.18 (±)	11	89	0	1.61E+03	2.8	-	1.9	0.05	64.3	5.6	1.57	28
Pyrolytic lignin [45], [58]	Pine, softwood/P yrolysis	0.7/1.7	-	99	1	6.5E+02	N/A	N/A	N/A	0.01	65.9	6.4	0.11	27.5

4.2 Lignin-g-PLA graft copolymer characterization

Different types of (non)acetylated lignin were grafted with PLA via organocatalytic reactions with TBD catalyst, to obtain the (non)acetylated lignin-g-PLA graft. In order to determine if the grafting reaction was successful and that lignin was covalently bonded to the PLA residues, the ^{1}H-NMR spectrums of the obtained lignin-g-PLA copolymers were compared to the spectrum of the same copolymers after dissolution in specific solvents.

If grafting occurred, the peaks indicating the presence of both lignin (δ = 6-7 ppm) and PLA (δ = 5.1 ppm; δ = 1.46 ppm), appear in the ^{1}H-NMR spectrum of the copolymers.

The non-acetylated copolymers were dissolved in THF, while the acetylated copolymers in diethyl ether. The reason for this is that non-acetylated lignin itself is not soluble in THF and acetylated lignin, respectively, is not soluble in diethyl ether. However, if the grafting took place, the PLA residues in the lignin-containing copolymer, will make the copolymer soluble in these specific solvents [46].

Figure 12 shows the ^{1}H-NMR spectra of non-acetylated Indulin-g-PLA graft after undergoing dissolution in THF. The ^{1}H-NMR results prior to dissolving in THF can be found in Appendix A (Figure 26).

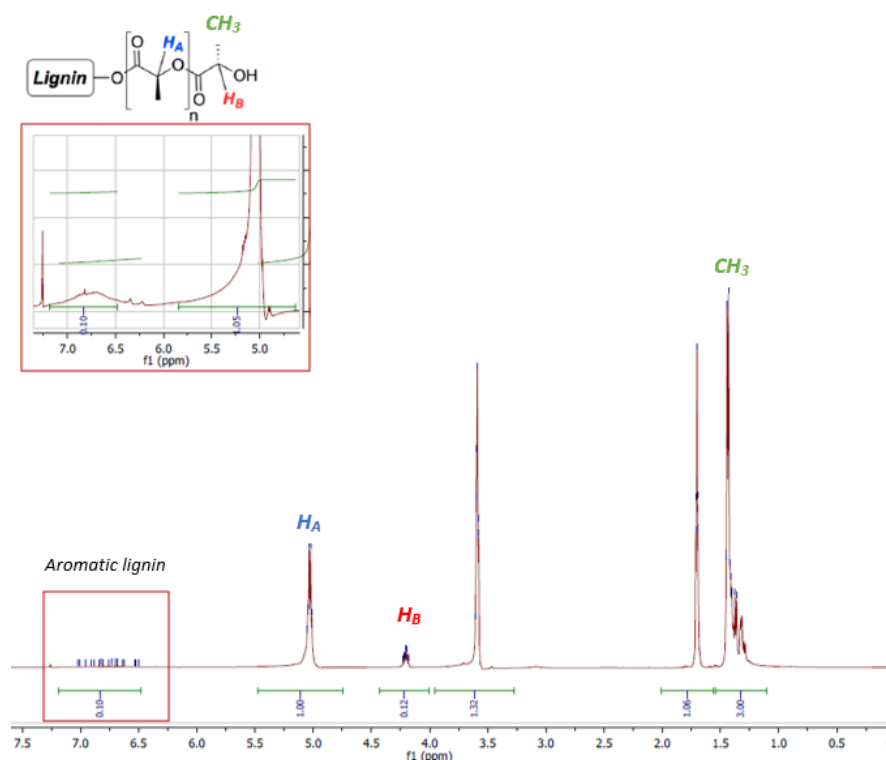*Figure 12 - ^{1}H-NMR spectra of non-acetylated Indulin-g-PLA after THF dissolution*

The signals indicating the PLA's methyl and methide protons can be seen at δ =1.46 and 5.1 ppm [32], accordingly. The lignin signals are not visible due to the small amount of lignin incorporated in the sample; however, the zoomed-in display of the spectra shows the integration of the peaks associated with lignin (the broad aromatic peak at δ = 6.5 - 7 ppm) versus the methide signal of PLA (δ = 5.1. ppm). The integration is proportional to the number of protons to which the peaks correspond [47]. The molar ratios between lignin and PLA were calculated according to Equation 2. The results of the molar ratios between the two components are in a good range and they can be found in Table 4 on the next page. The calculations are displayed in Appendix A.

$$\frac{molA}{molB} = \frac{\dfrac{area(A)}{N(A)}}{\dfrac{area(B)}{N(B)}} \qquad (Eq.2)$$

In equation 2, A represents the lignin signal, B is the PLA signal, N(A) represents the number of protons of lignin contributing to the peak and N(B) is the number of protons contributing to the PLA peak.

The integration ratio values between the lignin and PLA demonstrates that grafting was successful, and all lignin is covalently bonded to PLA. This is the case for all the non-acetylated lignin-PLA grafts: Fabiola, Lignoboost and pyrolytic lignin (Figure 13).
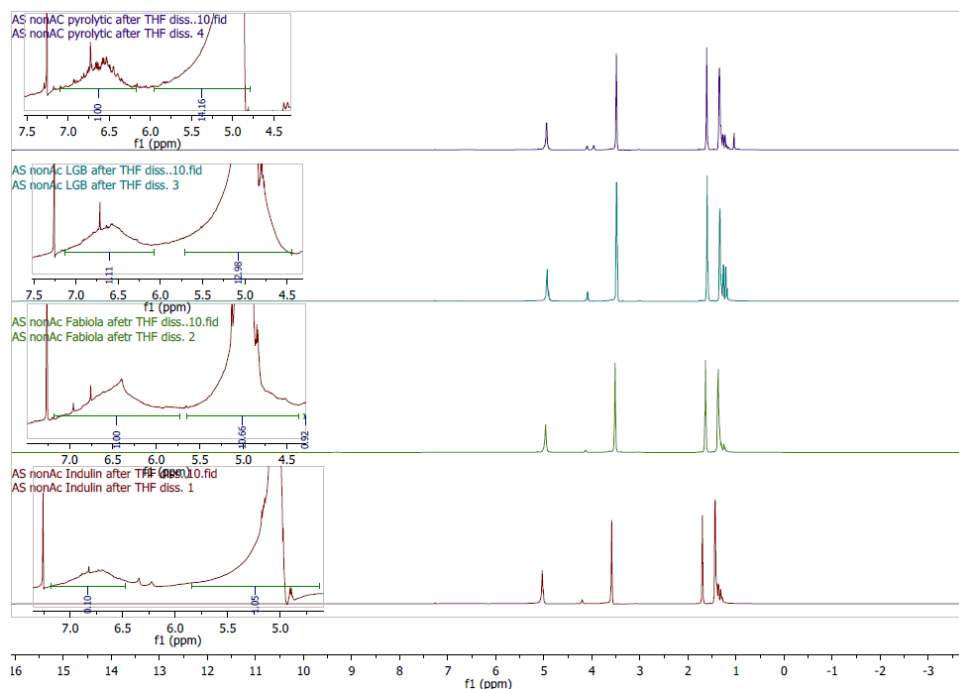

Figure 13 - Overview of ¹H-NMR spectra of non-acetylated lignin-g-PLA grafts after THF dissolution. Note that the zoomed-in figures represent the aromatic lignin signals.

The same approach was used to analyze the acetylated lignin-PLA grafts. In comparison, Figure 14 indicates the ^{1}H-NMR analysis of the acetylated Indulin-g-PLA graft. The existence of an aromatic lignin signal, besides those of PLA, indicated that grafting also took place for the acetylated samples. Similar to the non-acetylated grafted samples, the lignin : PLA molar ratios obtained from the integration of the ^{1}H-NMR peaks show that all lignin was bonded to PLA and grafting was successful (Table 5). Figure 15 shows an ^{1}H-NMR overview of all the acetylated specimens. The spectra of the acetylated lignin samples prior to the solvent test are shown in Appendix A (Figure 27). Table 6 on the next page encloses an overview of all the assigned ^{1}H-NMR proton peaks.
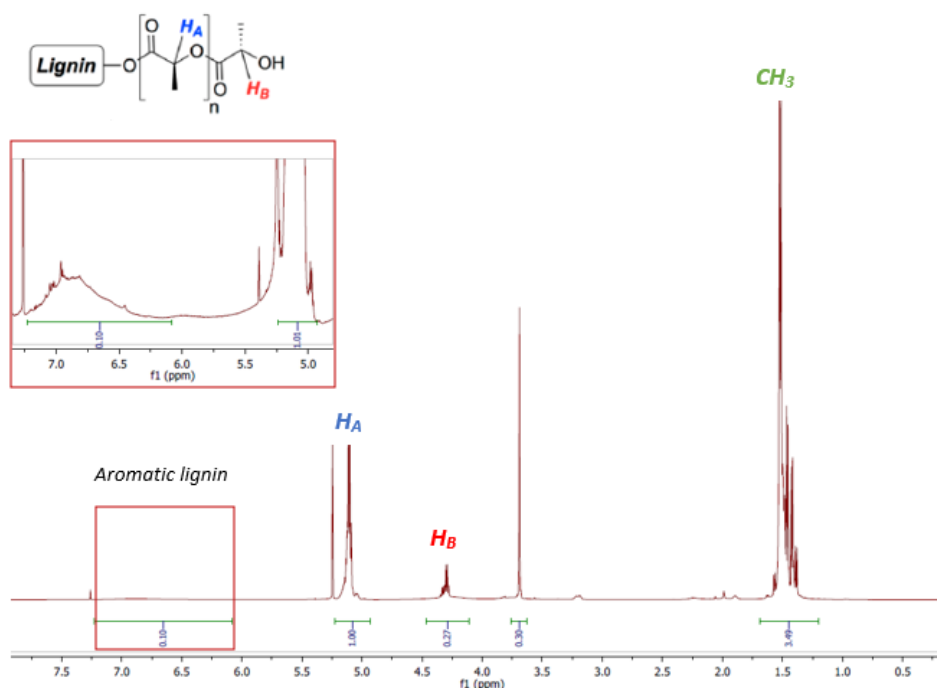

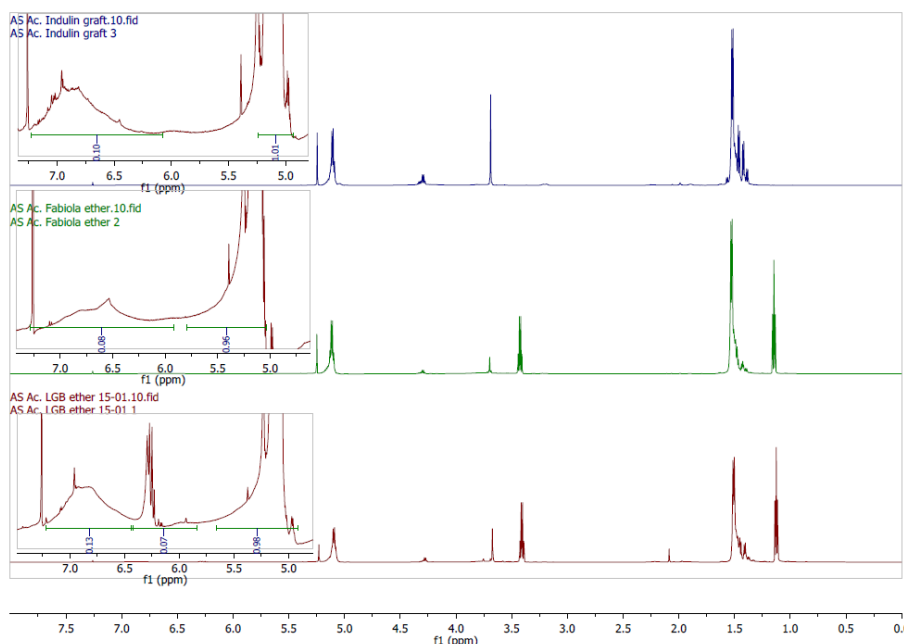*Figure 14 – ^{1}H-NMR spectra of acetylated Indulin-g-PLA after ether dissolution*

Figure 15 - Overview of the ¹H-NMR results of acetylated lignin samples after ether dissolution

Table 5 - Results of molar ratios of lignin to PLA, based on the integration values obtained from ¹H-NMR

Treatment of lignin	Lignin type	Integration lignin peak	Integration PLA peak	Ratio (lignin:PLA)
Non-acetylated	Indulin	0.1	1.05	0.09
	Fabiola	1.0	10.66	0.093
	Lignoboost	1.11	12.98	0.085
	Pyrolytic lignin	1.0	14.66	0.068
Acetylated	Indulin	0.1	1.01	0.099
	Fabiola	0.08	0.96	0.083
	Lignoboost	0.13	0.98	0.132

Table 6 - ¹H-NMR peaks assignment overview

Peak position (ppm)	Peak assignment
6 - 7	Aromatic lignin
5 - 5.2	PLA methide
4.3 - 4.5	Unreacted l-lactide methide
3 - 4	Additionally formed l-lactide dimers/trimers
1.3 - 1.5	PLA methyl
7.26*	Chloroform (CDCl₃)

*All peaks were referenced to the solvent peak: deuterated chloroform 7.26 ppm.

To further substantiate the fact that a grafting reaction has occurred successfully, a simple physical mix between lignin (10 wt%) and PLA was made. The mix was analyzed via ¹H-NMR for its composition and compared to the grafted samples. Figure 17 shows the ¹H-NMR results of the lignin-PLA physical mix and it can be seen that only the PLA peaks are present (δ = 1.46 and δ = 5.2 ppm) and there is no broad peak in the aromatic area to indicate lignin's presence (δ = 6-7 ppm). This being the case, it can be said that without the aid of any pre-treatments, only a surface mixing between the lignin and PLA took place. Lignin seems to have been washed away during the washing procedure with methanol before the analysis of the sample. Thus, grafting is indeed necessary to actually covalently-attach the lignin to the PLA matrix.
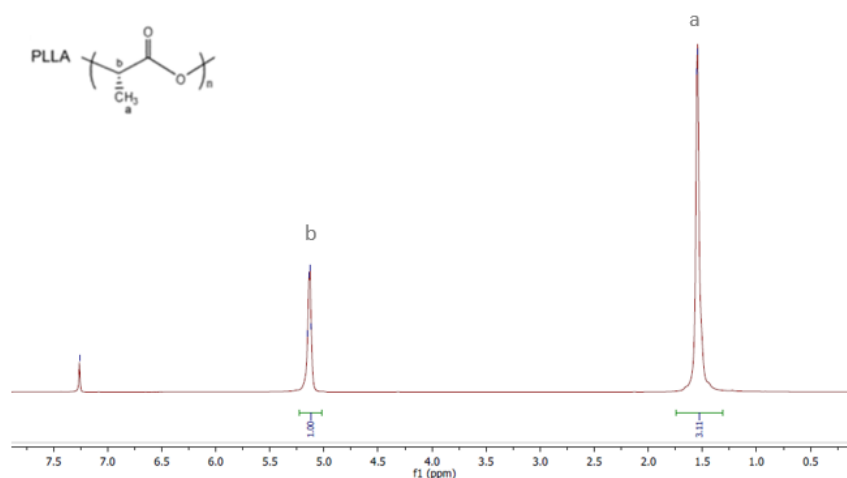

Figure 17 - h-NMR spectra of a physical mix: PLA + 10% Indulin lignin

Conversion of l-lactide

The conversion of l-lactide to PLA was determined using Equation 1, taking the integrated area of the PLA methide signal (H$_A$) versus the l-lactide methide signal (H$_B$) (Figure 18). The calculated conversion values for each of the graft specimens are displayed in Table 7.
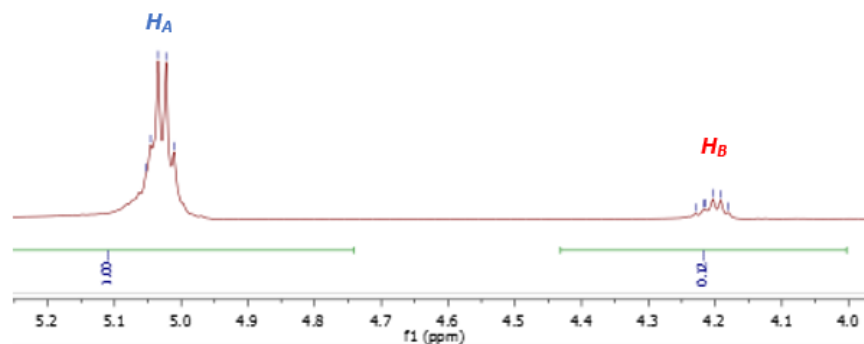
Figure 18 - ¹H-NMR signals for PLA methide vs. l-lactide methide for nonAc. Indulin-g-PLA

Table 7 – Conversion of l-lactide in grafting reaction with different lignins (%)

Treatment of lignin	Lignin type	Conversion of l-lactide (%)
Non-acetylated	Indulin	89,23
	Fabiola	91,23
	Lignoboost	84,06
	Pyrolytic lignin	91,23
Acetylated	Indulin	78,74
	Fabiola	95,60
	Lignoboost	91,9

The conversion values vary, according to the type of lignin grafted with PLA. Amongst the non-acetylated samples, the lowest conversion is the Lignoboost-containing sample, followed by the Indulin graft. Similar pattern is also observed for the acetylated grafts. One reason for this might be the amount of impurities present in the Kraft lignins, which can limit the conversion (Table 4). The highest amount of sulfur is contained by Lignoboost lignin (1.57 %) and Indulin (0.1 %), while Fabiola lignin, which gives the highest conversion, contains the lowest amount of sulfur (0.04 %). Thus, a higher amount of sulfur impurities in the lignin's structure seems to have a detrimental effect on the conversion for the reaction of lignin with PLA[3]. Furthermore, other impurities present in lignin's structure, such as ashes and sugars might also have an influence on the conversion. However, further research should be carried out regarding the effects of sulfur and other impurities in the structure of lignin, as this was out of the scope of this project.

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[3] It is important to note that the conversion values were only determined from a single batch of samples, just to obtain a brief overview. For a better accuracy and determination of the standard deviations, multiple batches should be analyzed for the conversion.

4.3 Lignin-PLA biocomposite characterization

The lignin-g-PLA/PLA blends were produced via solvent mixing and shaped into biocomposite films through solvent casting. Normally, the two mixing phases i.e., matrix phase and filler phase, would be combined in only one step (casting) to form the films. However, due to the necessity of grafting pre-treatment of the samples, two steps were employed[4].

Acetylation

In order to evaluate the importance of acetylation, two samples were prepared for comparison. Non-acetylated, non-grafted Indulin lignin was solvent-mixed with plain PLA and compared to acetylated, non-grafted PLA-mixed Indulin. The comparison of the two mixtures is displayed in Figure 19. From the figure, it is clear that the acetylated sample was uniformly blended with PLA, forming a consistent solution, with a bright brown color. In comparison, the non-acetylated lignin mixed with PLA had very low dispersibility and exhibits a visible phase separation, where lignin had formed agglomerations at the surface.

Since the need for acetylation pre-treatments is not attractive from a practical and economic viewpoint, this project investigated whether or not covalent bonding via grafting is sufficient for obtaining materials with improved properties. The outcome is disclosed later in this report.
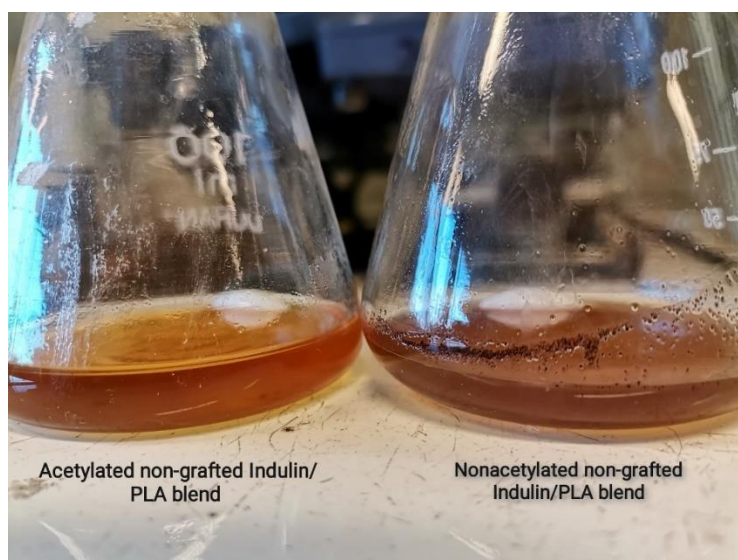
Figure 19 - Solvent blending non-acetylated Indulin/PLA vs. acetylated Indulin/PLA

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[4] Of course, in industrial context, it is recommended to avoid the two-step processing (solvent blending and solvent casting) and combine the two in an efficient and less wasteful manner.

Shaping of biocomposites

Initially, for shaping the obtained biocomposites, a hot press procedure was adjusted from literature and attempted [31]. Appropriate samples, however, could not be obtained despite many trials with adjusting temperatures and pressure stages[5]. Figure 29 in Appendix B shows the unsuccessful attempt.

Furthermore, a solvent casting of the samples, adopted from the literature [44], also displayed some challenges. The method implied drying the film in the vacuum at a temperature of 50 ℃. However, it was noticed that too high evaporation rates led to the formation of irregular films with many solvent bubbles (Figure 20).

Seeing this, the films were exposed to multiple drying stages, increasing the temperature slowly to prevent the formation

Figure 20 - Films obtained after solvent evaporation in the vacuum oven

of solvent bubbles. This was, nevertheless, not efficient; thus room temperature conditions and drying for a longer time, was found to be the most efficient to obtain uniform and smooth films (Figure 21).
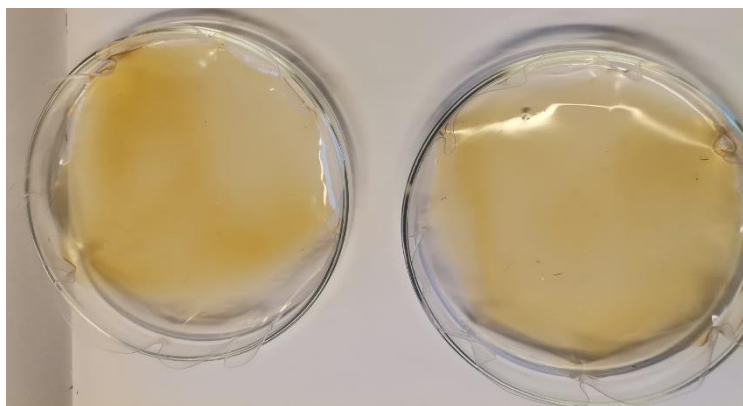
Figure 21 - Uniform biocomposite films obtained at room temperature conditions

Most of the literature [23], [27], [39] disclose that the solvent casting of PLA material is done using chloroform as solvent. Chloroform was also used as the solvent in this project to obtain suitable samples for tensile testing. However, being a highly toxic and carcinogenic chemical, its consistent use is strongly discouraged. Thus, it was investigated instead whether solvent

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[5] More research on finding suitable parameters for hot-pressing the PLA blends is necessary as hot press is a more efficient technique than solvent casting.

casting can be successfully done using other (less toxic) solvents, such as acetone, dichloromethane (DCM), dimethyl carbonate (DMC) and p-dioxane. Interestingly enough, proper biocomposite films were only obtained using DCM, concluding that a halogen-containing solvent is suitable. The rest of the solvents yielded peculiar films, non-uniform and not suitable for testing (see Figures 31, 32, 33 in Appendix B).

Several explanations for this are related to the intramolecular interactions which take place between the material and solvent. For instance, chloroform causes higher chain mobility of the polymer. Thus, the crystallinity of the film is highly affected by solvent-induced conformational changes. Both chloroform and dimethyl chloride yield random conformation of the molecules and result in homocrystallization, owing to the strong interactions between the polymer matrix and the solvent. In contrast, different solvents might cause stereocomplex crystallization, which results in surface aggregation and other conformational changes [48]. The difference in crystallinity was visible on the samples, some showing segments with hazy, opaque aspects and spherulite presence. Furthermore, the higher crystallinity also affected the mechanical properties, leading to very brittle films, which is not in accordance with the aim of this project. Further research is necessary in discovering a less toxic solvent suitable for solvent casting of PLA biocomposites. It would be interesting to look into the employment of mixtures between two solvents, to minimize the toxicity, as well as optimizing the concentration of the sample in the solvent mixture.

Mechanical properties

The mechanical properties of the different lignin-PLA films were analyzed with respect to two reference points. First, in order to perform a more detailed analysis, one reference was set as the blend obtained via mixing a (in-house) polymerized l-lactide with commercial PLA pellets (REF1). This mimicked the grafting procedure, without incorporating lignin.

A second reference was the film obtained from a physical mix of the in-house polymerized l-lactide with unmodified Indulin lignin (1%) and commercial PLA pellets (REF2). Figure 22 shows an overview of the ultimate tensile strength results.
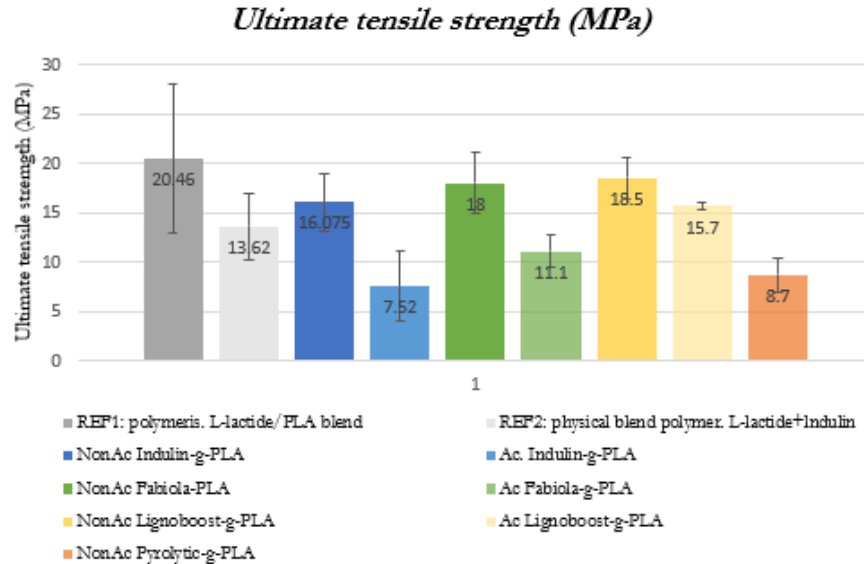
Figure 22 - Tensile strength (MPa) results of the samples

Analyzing the two reference samples (the grey shades), it can be seen that, compared with plain PLA, the PLA sample which incorporates unmodified lignin (physical mix) has a significantly lower tensile strength. The reason for this is that the interfacial bonding between the two phases (PLA matrix and unmodified lignin) is very poor, the existence of unmodified lignin particles hindering the continuous formation of long PLA chains [49], [55]. It is, however, noticeable that the standard deviation of plain PLA is very high, while the results have lower reproducibility. This might be because of moisture contamination in the sample and possible degradation.

Next to that, all the lignin-g-PLA/PLA blends showed a decreased tensile strength, compared to the plain unmodified PLA. In accordance with the literature, the incorporation of lignin via grafting with or without acetylation pre-treatment, decrease the tensile strength. Interestingly, while it was initially hypothesized that the grafted samples exposed to acetylation would show higher strength, this hypothesis was not validated, as it can be seen from the lighter shades in Figure 22. In fact, the tensile strength was even lower than that of the non-acetylated specimens. Thus, one can suggest that both treatments: acetylation of the lignin and grafting to PLA are not necessary, but even detrimental. Perhaps too much modification in the structure results in lower compatibility and ultimately reduces the strength.

It should be noticed, however, that the non-acetylated samples (Indulin, Fabiola, Lignoboost) show only slightly lower tensile strength, compared to pristine PLA. This decrease can be negligible and overlooked, given that the elongation is improved. Nevertheless, an exception was pyrolytic lignin-g-PLA/PLA sample, which has the lowest tensile strength. This is because of its inherent structure, modified by the harsh extraction treatment.

While the tensile strength of the biocomposites containing PLA/lignin grafts is relatively decreased, compared to plain PLA, the elongation at break showed a different behavior.
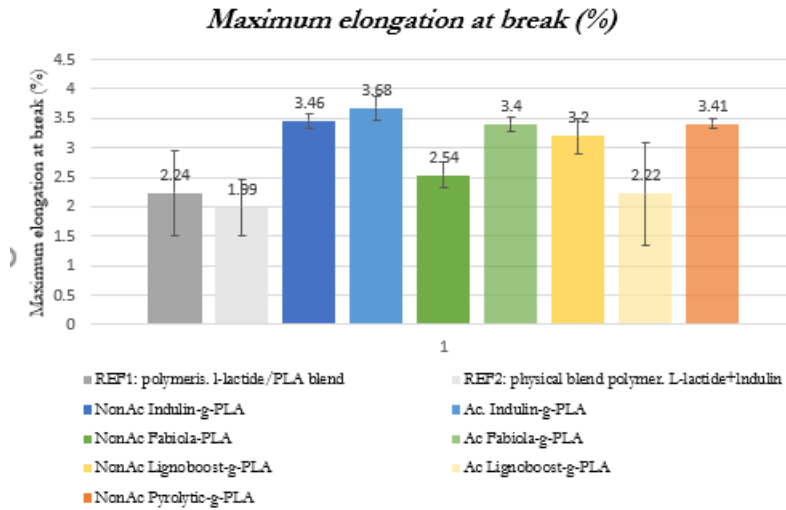

Figure 23 - Elongation at break (%) results

Figure 23 shows the results of the maximum elongation at break. It is easily noticeable that, compared to the references, the elongation at break is significantly increased with the addition of lignin, regardless an acetylation pre-treatment. The highest and most reproducible values are obtained for acetylated and non-acetylated grafted specimens with Indulin (4.68% and 3.46%, respectively), pyrolytic lignin (3.41%) and Lignoboost (3.2%), respectively, and the acetylated Fabiola graft also approaching the top (3.4%). It is interesting to see that both Kraft lignins: Indulin and Lignoboost-containing grafts also show increased elongation without pre-treatment. Even though it is noticeable that the acetylated grafted samples showed higher elongation at break, compared to non-acetylated, however, the difference was not exponential. Additionally, considering the extreme decrease in tensile strength, it can be stated that acetylation is not a necessary pre-treatment. It may be that with the incorporation of higher quantities of lignin, a pre-acetylation would have a greater effect. Table 8 comprises an overview of the results of mechanical properties of the obtained blends, with regards to the references.

Table 8 - Overview results mechanical properties

Treatment	Sample	Tensile strength (Mpa)	Elongation at break (%)
Simple blending	REF1: polymerized L-lactide/PLA blend*	20.46	2.24
Simple blending	REF2: physical blend 1% lignin	13.62	1.99
Grafting, no acetylation	Indulin-g-PLA/PLA	16.07	3.46
	Fabiola-g-PLA/PLA	18	2.54
	Lignoboost-g-PLA/PLA	18.5	3.2
	Pyrolytic lignin-g-PLA/PLA	8.7	3.41
Grafting + acetylation	Indulin-g-PLA/PLA	7.52	3.68
	Fabiola-g-PLA/PLA	11.1	3.4
	Lignoboost-g-PLA/PLA*	15.7	2.2

Note that for some of the samples the standard deviation was quite high, so the data is not precise but approximated.

Relevance of lignin's properties in fine-tuning the biocomposites

With the overview of the mechanical properties available, it can now be seen how lignin influences these properties and which characteristics are crucial for optimizing the lignin-PLA grafts. The unmodified lignin has high amounts of polar groups which self-aggregate through hydrogen bonding. Grafting PLA chains changes lignin's polarity from hydrophilic to hydrophobic, thus the resulting grafts have a favorable interaction with the hydrophobic PLA matrix. Furthermore, varying the lignin species can fine-tune the grafts to achieve good dispersion and improved mechanical properties.

It appears that the grafted Kraft lignins behave best in terms of mechanical properties, showing significant increase in the elongation at break, excluding the need of lignin pretreatment and without a high sacrifice in the tensile strength. Therefore, it can be noticed that the biomass source plays a significant role as, softwoods are behaving better than hardwoods (e.g., Fabiola). A similar explanation can be provided for the lignin extraction processes. Although the Kraft process is harsher than the organosolv process, it can yield lignins with more suitable properties for biocomposite applications. However, it is important to recognize that when developing an actual application, the amount of impurities present in the Kraft

lignins (e.g. sulfur, sugars) might cause some complications and it would require lignin purification, which is an additional costly and time-consuming step.

Analyzing the structure of Kraft lignins, as to other lignins (Table 4), it can be seen that Indulin and Lignoboost have lower average molecular weights, compared to Fabiola. While an explanation can be that lignin with a lower molecular weight acts more like a plasticizer (because of the smaller size), and its presence increases the elongation at break, this cannot be stated at full confidence. On the grounds of this reasoning, pyrolytic lignin, which has the lowest molecular weight, should be leading to considerable increase in the elongation. While this is not the case in reality, it also causes a great decrease in tensile strength. Nevertheless, a lower molecular weight could reduce the probability of chain aggregation, creating a more favorable environment for covalent bonding with PLA.

Another trend, related to the extraction process and the biomass source, is given by the content of coniferyl alcohol (G-units) in lignin's structure. Table 3 shows that Indulin (100 %) and Lignoboost (89 %) contain the highest amounts of such units, while hardwood Fabiola, only 25 %. The presence of these units plays a crucial role. These unit structures display no methoxy group attached to C5. Owing to this, they can form several bonds such as 5-5', 4-O-5', etc., which lead to crosslinking. In contrast, hardwoods contain more structures (S-units) that own a methoxy group on C5 and have the ability to form hydrogen bonds with the other functional groups on the surface of lignin. The formation of such bonds creates linear structures, which further aggregate in the composite and disrupt the matrix by forming clusters. This phenomenon leads to a decrease in the miscibility between the two composite phases, and results in materials with inferior mechanical properties. This is the case for organosolv hardwood lignin (Fabiola). In the future it might be worth analyzing an organosolv softwood lignin in order to find out whether it yields comparable outcomes.

Regarding the necessity for pre-treatment, it is expected that while replacing lignin's hydroxyl groups with non-polar acetyl groups during acetylation, the molecular weight of lignin increases. In addition, literature shows that acetylation leads to a less polydisperse lignin. While such treatment targets both aliphatic and phenolic hydroxyl groups of lignin to create a more hydrophobic character [22], it is necessary to take into account that the functionality differs with respect to aliphatic and phenolic character. It is known that a high content of phenolic hydroxyl groups can be detrimental for the synthesis of polymeric materials, while the amount of aliphatic groups should be preserved for reaction with the polymeric matrix. This is in the case that grafting mainly targets the aliphatic hydroxyls in lignin. One approach is to carry out a partial acetylation prior to grafting in which the amount of phenolic hydroxyl groups is reduced, offering less initiation points for the graft polymerization. In this way, there are less

locations where chain growth can begin, resulting in longer polymeric chains. Furthermore, another controlled pre-treatment proved to be efficient is methylation, which is selective and targets mostly the phenolic hydroxyls.

UV-vis Properties

As discussed, the UV-vis barrier of the biocomposites is of utmost importance when considering food packaging to protect foods from spoilage due to light exposure while storage. Thus, the UV-vis transmittance was integrated and examined in this study.

Due to time constraints, however, it was not possible to analyze and compare all the samples that contained different types of lignins. Though, an overview was obtained, which comprised the reference (in-house) polymerized l-lactide-PLA blend, a commercial PLA blend, a non-acetylated lignin-g-PLA/PLA blend and an acetylated lignin-g-PLA/PLA blend. In this way, the influence of grafting, as well as acetylation on the UV-vis barrier was possible to observed. The results are shown in Figure 24 on the following page.

The pristine PLA indicates light transmittance, starting with the lower range: UV-C light spectrum (100-230 nm). Furthermore, it can be seen and reported that the samples containing 1 wt% of lignin (non-acetylated and acetylated lignin-g-PLA/PLA) block all of the UV-C light (100-280 nm) and most of the UV-B (280-315 nm). Therefore, the addition of a well-dispersed small amount of lignin, via grafting, acts as a light-blocker agent and significantly improves the UV-vis barrier of the PLA biocomposite. Additionally, it can be seen that both acetylated and non-acetylated samples containing lignin behave fairly similarly. This can, thus, constitute another argument that acetylation prior to grafting is not essential as it does not improve any properties significantly.

Moreover, literature suggests that the incorporation of lignin fractions with higher average molecular weight would have even an even higher positive impact on the UV-light barrier of the biocomoposites [49]. This is because of a larger number of chromophores in lignin's structure, enabling for more UV-light to be blocked. This should be validated further by testing the samples which comprise higher molecular weight lignin[6]. In the analysis presented above, the non-acetylated pyrolytic lignin-g-PLA/PLA and acetylated Indulin-g-PLA/PLA samples were included; Both samples showed improved UV-barrier properties despite having low molecular weights.

In this manner, the chemical structures of the lignin-g-PLA grafts copolymers were identifiable via ^{1}H-NMR, along with the UV-spectra analysis, gave enough evidence for the presence of lignin in the copolymer. The results of the tensile tests further confirm the successful synthesis of the grafts and biocomposites with improved properties.

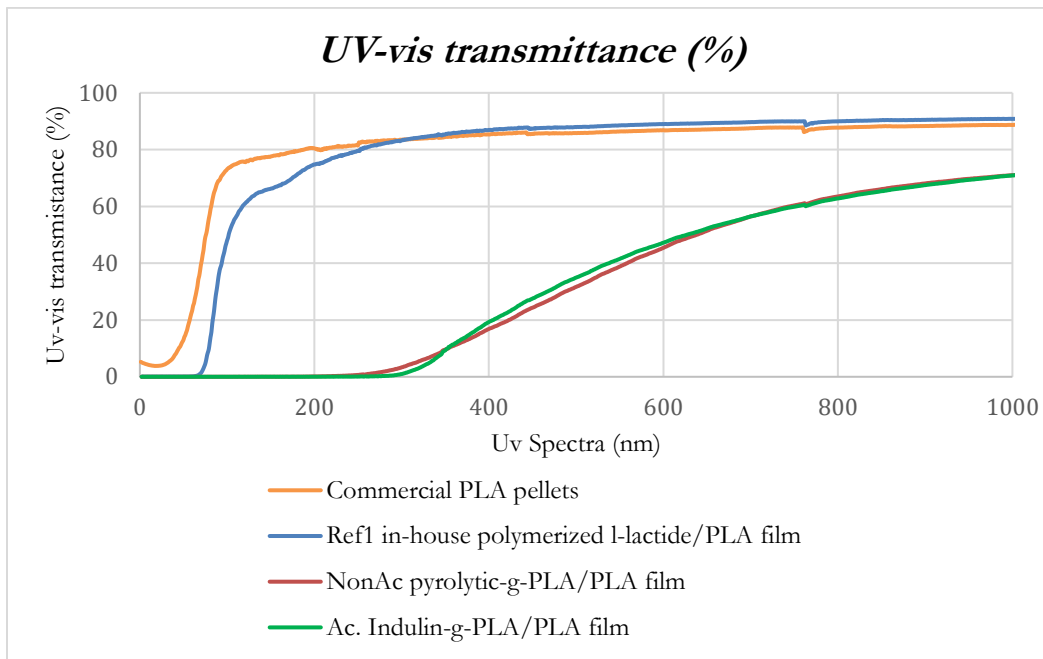[6] Unfortunately, this was not possible for this project due to time restrictions.

Figure 24 - UV-Vis Transmittance results (%)

Other properties

There are other aspects that should be taken into account regarding such lignin-based materials for food packaging applications. As mentioned in the introduction, one of these aspects is the importance of a high oxygen barrier to extend shelf-life of foods and decrease food waste. The impact of lignin on this issue however, was out of the scope of this project and was not practically examined in this project.

Another property to be considered is the water barrier of the biocomposite. Previous research finds that a significant impact of lignin is only observed at higher concentrations. These findings, however, apply for physical mixtures and not for blends containing grafted copolymers [18].

Concerning the thermal behavior, from past research on the thermal properties of lignin-PLA blends it is strongly suggested that the addition of lignin increases the glass transition temperature of PLA [31], [6]. This is expected, as lignin inherently has a considerably higher glass transition temperature, compared to PLA.

Lastly, the biodegradability could be affected. Integrating lignin would decrease the biodegradability rate of the material, due to its pre-modification. The synthesis of these biocomposites entails the use of synthetic chemicals, which negatively affect the biodegradability. Studies show that even though the disintegration occurs slower, ultimately, they achieve 100 % biodegradability, under specific compost conditions [50].

6 Conclusion

This research project addressed the issues of plastic pollution by investigating alternative biodegradable materials. The aim was to synthesize novel biocomposites from lignin and PLA to improve PLA's properties with regards to food packaging applications and simultaneously decrease the PLA's cost by adding a cheap filler like lignin. Firstly, the copolymers were produced via graft polymerization of lignin with PLA using a non-toxic organocatalyst (TBD). Furthermore, the copolymers were blended with commercial PLA to produce the biocomposites (1 wt% lignin). Finally, the shaping was done via solvent casting and the resulted materials were tested for their mechanical and optical properties. In addition to previous research, where the focus stands on only one type of lignin, in this project different types of lignins were employed: Kraft lignins (Indulin and Lignoboost), an Organosolv lignin (Fabiola) and a pyrolytic lignin. All of them were added to PLA and their effects on the mechanical and optical properties were compared. In addition, acetylation pre-treatments were carried out for all the samples. The grafting occurrence was proved by ^{1}H-NMR analysis of the copolymers, clearly showing the presence of both lignin and PLA in the samples. In addition, a comparison of the grafted copolymers with a simple physical mix indicated that lignin was covalently bonded only via grafting reaction. The mechanical testing of the biocomoposite films indicated that the addition of lignin reduces the tensile strength, however significantly increasing the elongation at break for some samples. The best mechanical behavior was shown by the Kraft lignins, with a slight reduction in tensile strength (16-18 MPa) and considerable increase in elongation at break (3.4-3.6 %). This can be owed to their biomass source, softwoods, with a higher amount of coniferyl units, which form beneficial bonds and increase the miscibility between the matrix phase and the filler phase. Furthermore, it was found that acetylation of lignin before the grafting reaction with PLA is not necessary as it does not generate notably better properties. It can be considered, however, effective in improving the compatibility between lignin and PLA, in the case that grafting is not employed. Finally, confirming previous research, the UV-Vis analysis indicated that the addition of a small amount of well-dispersed lignin improves the UV-light barrier of PLA as it manages to block most of the detrimental light (UV-C and UV-B spectra) that causes food spoilage and waste.

In conclusion, it was found that a grafting reaction of lignin with PLA is more efficient to produce lignin-PLA biocomposites with improved properties, compared to the simple blending of the components, while a lignin pre-treatment is not necessary. With this, novel PLA biocomposites can be developed in an efficient way, by incorporating a suitable type of lignin. With improved brittleness and UV-Vis barrier, these biocomposite materials can provide improved food packaging materials, decrease the cost of PLA and accelerate the transition from conventional plastics to green materials.

7 Future recommendations

A couple of future recommendations and adjustments to be suggested, whose implementation in the future can bring about benefits and optimizations.

Firstly, the processing of the biocomposites can be done in a more time-efficient manner by using different techniques. One such technique can be processing via twin-screw extrusion. While this method might imply some complications due to the complex thermal behavior of PLA, it is necessary to consider it and to analyze the resulting samples for their properties. Another technique that can replace solvent blending is electrospinning. This technique is solution-based and works with an electric charge. Though it still implies the use of solvents, it is a more time-efficient method to produce the biocomposites, given that equipment is available. Optimization parameters for hot-pressing should also be investigated and obtained as this method generates shapes with equal dimensions, facilitating the testing afterwards.

In the case that the solvent casting technique is approached, it is recommended that solvent mixtures are researched, for example a mixture of methyl chloride: acetonitrile (50:50) [51].

Secondly, while the mechanical tests of the biocomposites generate reasonable data, some of the samples presented low reproducibility and high error bars. More accurate data might be obtained if the materials are moisture-free and less contaminated. It could be that the l-lactide and the PLA pellets that were used in this project have been stored for a long period of time and they have been somewhat degraded. With regards to lignins, identification of impurities such as ashes and sugars should be carried out and further analyze the effect of such and whether or not purification is necessary.

Further investigations need to be done on the degree of acetylation and how it influences the properties of the final graft. It could be that a different degree of acetylation targets a different amount of functional groups in lignin, which can lead to increased mechanical properties. Furthermore, methylation is shown to be an efficient pre-treatment to control the functionality of lignin. Methylation is a controlled mechanism which targets the phenolic groups in lignin, without affecting the aliphatic hydroxyl groups [53]. Employing such pre-treatment is an attractive method to obtain lignins with a fine-tuned content of phenolic functional groups. This can lead to better miscibility with the matrix phase and ultimately to obtain biocomposites with better mechanical properties.

Lastly, the research would be more compelling provided that other properties are investigated. In food packaging applications, equally relevant are the thermal properties, as well as the oxygen-barrier, water-barrier and the influence on biodegradability of the biocomposites. Literature suggests that lignin has no significant effect on the oxygen barrier of PLA [25], though it would be interesting to research if that is the case. Moreover, research into the water barrier properties of materials containing grafted lignin/PLA copolymers would be pioneering

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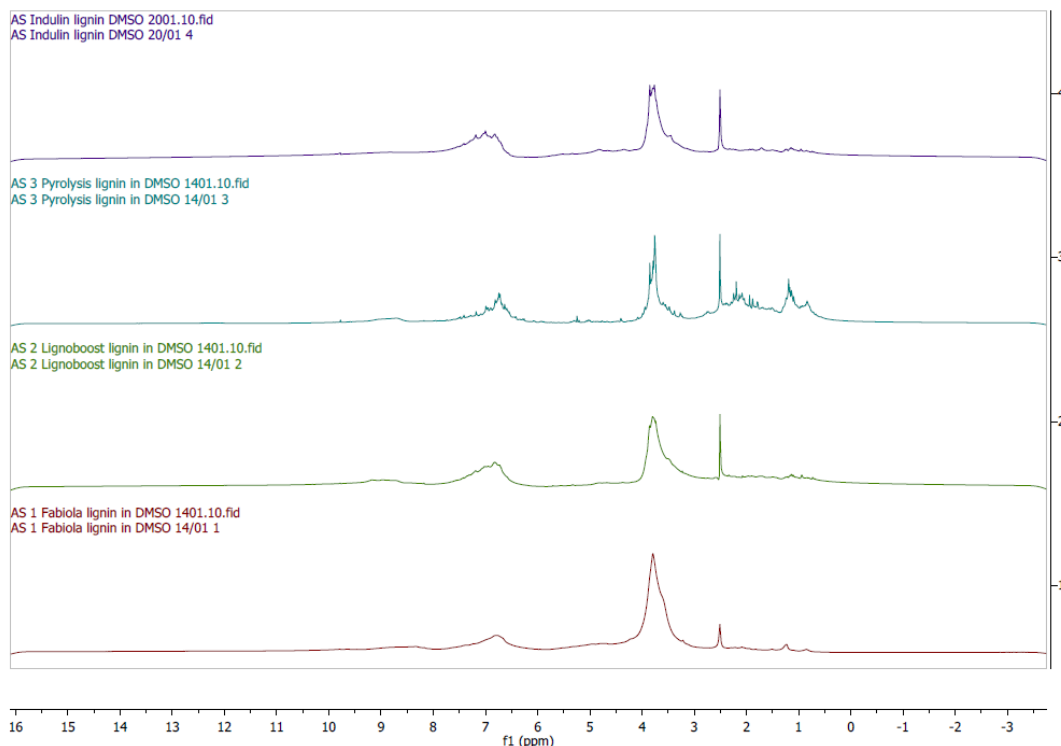
9 Appendix

Appendix A – ¹H-NMR Characterization

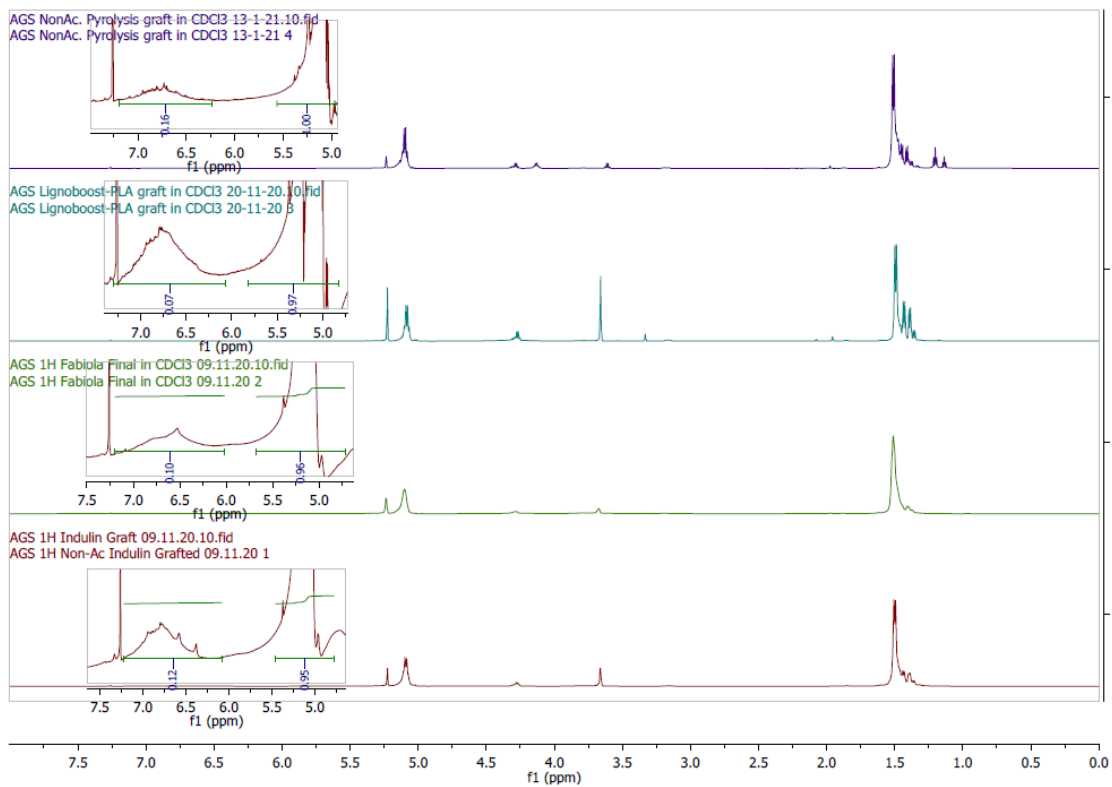*Figure 25 - Overview of ¹H-NMR spectra of the different types of lignin*

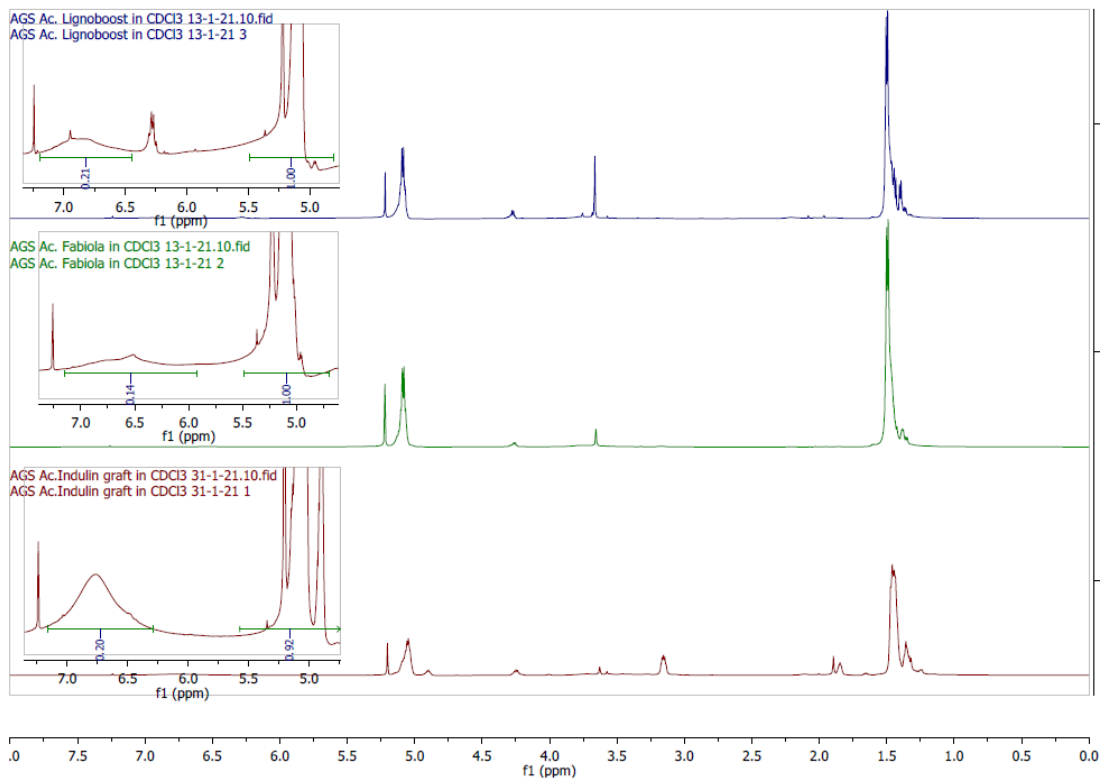*Figure 26 - ¹H-NMR overview of Non-acetylated grafts before THF dissolution*

Figure 27 - ¹H-NMR overview of Acetylated grafts before diethyl ether dissolution
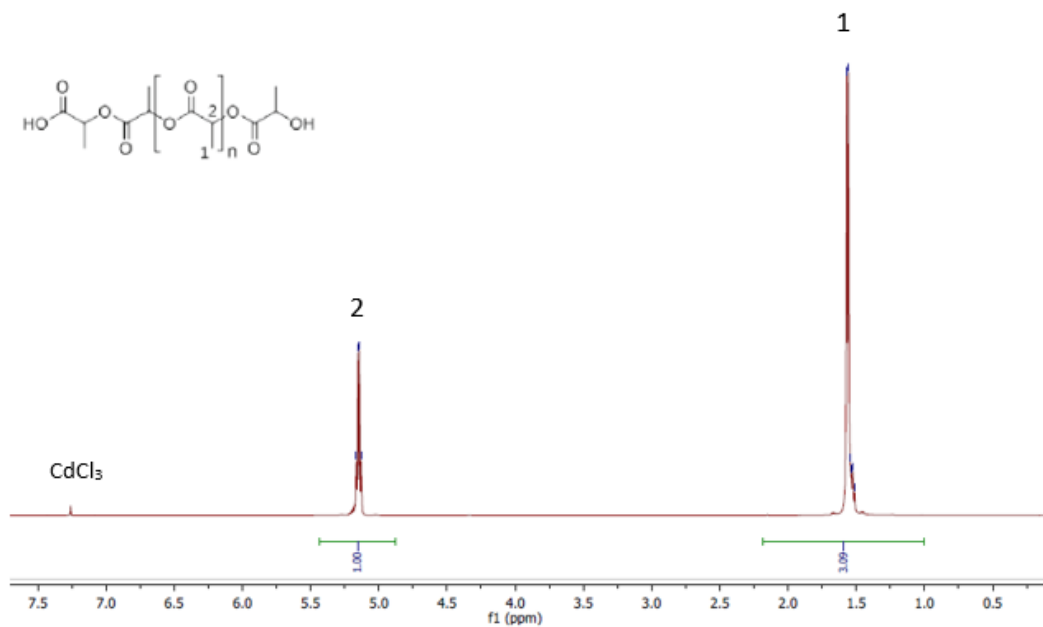
Figure 28 - ¹H-NMR spectra of plain commercial PLA

Calculations of molar ratios lignin:PLA

$$nonAc.Indulin - PLA: \frac{0.1}{3} * \frac{3}{1.05} = 0.09$$

$$nonAc.Fabiola - PLA: \frac{1.0}{3} * \frac{3}{10.66} = 0.093$$

$$nonAc.Lignoboost - PLA: \frac{1.11}{3} * \frac{3}{12.98} = 0.085$$

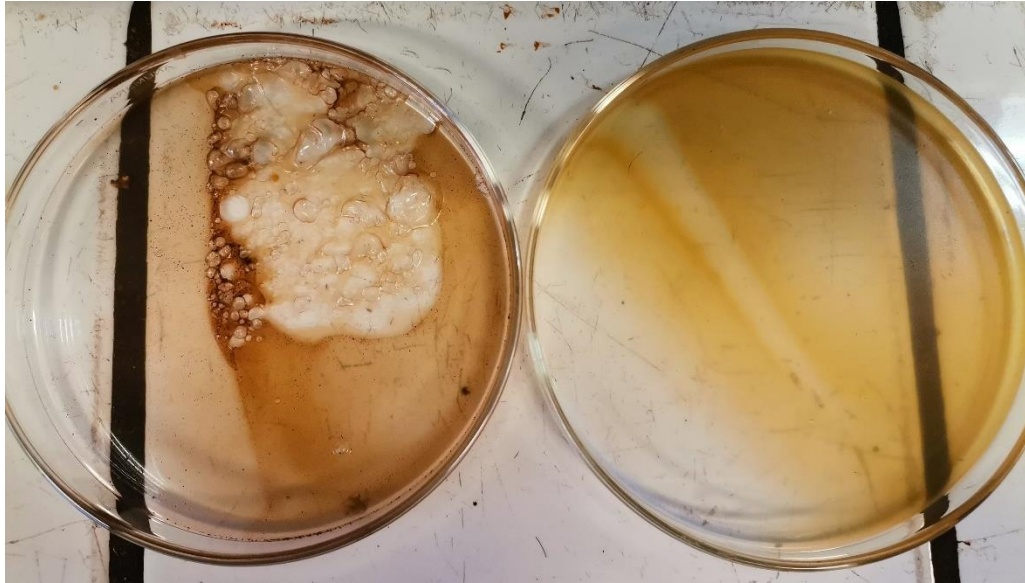$$Ac.Indulin - PLA: \frac{0.1}{3} * \frac{3}{1.01} = 0.099$$

$$Ac.Fabiola - PLA: \frac{0.08}{3} * \frac{3}{0.96} = 0.083$$

$$Ac.LGB - PLA: \frac{0.13}{3} * \frac{3}{0.98} = 0.132$$

Appendix B – Processing and shaping

Figure 29 – Unsuccessful sample obtained via hot-pressing

Figure 30 - Comparison of solvent casted films: Non-grafted, nonAc. lignin/PLA (left) vs. Non-grafted Ac. lignin/PLA (right)

Figure 31 - Film obtained via solvent casting of PLA with acetone as solvent
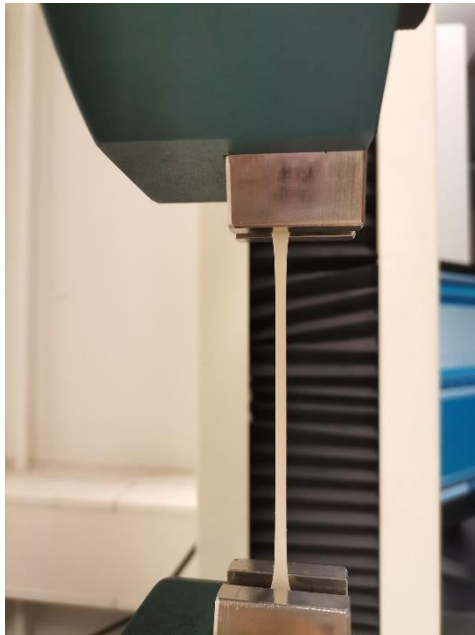
Figure 32 - Film obtained via solvent casting of PLA with p-dioxane as solvent

Figure 33 - Film obtained via solvent casting of PLA with dimethyl carbonate (DMC) as solvent
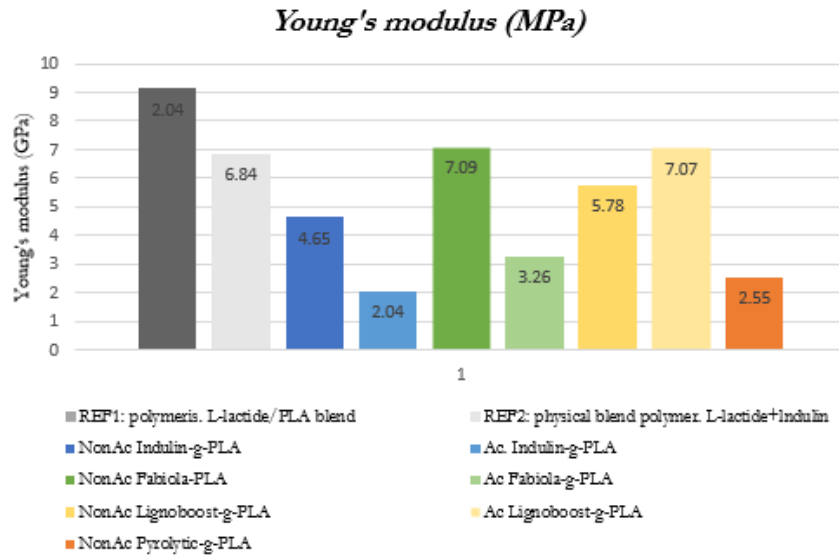
Appendix C – Mechanical testing

Figure 34 - Elongated sample during tensile testing

Figure 35 - Cut samples: non-acetylated. non-grafted lignin-PLA blend (left) vs. non-acetylated grafted lignin-PLA blend (right)

Figure 36 - Young's modulus (MPa) results