

# An overview of the influences on the properties of lignin-PLA composites for the purpose of food packaging



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This BSc thesis has been carried out during the COVID-19 global pandemic (spring-summer 2020). In order to comply with all the learning goals specified for the BSc final project in Chemical Engineering at the University of Groningen, (some of) the results presented in this thesis were not experimentally obtained but provided by the main supervisor based on previous unpublished data and personal experience, or obtained from published literature. The source of data has also been specified explicitly or referenced wherever they appear in this text.

## Abstract

PLA is regarded as a promising sustainable alternative for conventional food packaging plastics, yet compared to current food packaging plastics it has a relatively high brittleness, poor UV and water barrier and high price. These shortcomings limit its possibility for wider applications. In order to reduce brittleness, the elongation at break needs to be improved. This would preferably be done while maintaining the high tensile modulus and strength. Research is being done into employing lignin to improve these properties. Lignin originates from biomass and is a by-product of the pulp and paper industry, which means that it is renewable and relatively cheap. The biomass source and separation method both affect the irregular structure and properties of lignin. In order to determine which type of lignin results in the lignin-PLA composite with the most desirable properties various researches have been compared in terms of tensile and barrier properties. Additionally, there are different ways to mix lignin and PLA and there are certain pretreatments that can be done to lignin. It was found that hardwood lignin from the kraft process resulted in higher tensile strength and modulus, whereas the same lignin from organosolv processes increased the elongation at strength more. For softwoods there was not enough literature on organosolv lignin to draw proper conclusions. There were some differences in the absolute properties of PLA between solvent mixing and extrusion due to the plasticizing effect of chloroform from solvent mixing. In spite of that, the relative improvements after adding lignin were not significantly different between the two methods. Several lignin pretreatments were found to be beneficial for the final composite; acetylation and PLA grafting reduced aggregation and rubber/PLA grafting drastically increased elongation at break. Finally, the addition of lignin to PLA was found to increase the UV-barrier and hydrophobicity.

# Introduction

## Research problem

Environmental pollution is becoming an ever increasing problem and plastic waste plays a major role in that. Much of this waste comes from food packaging and biodegradable polymers could help decrease this waste. A prospective biodegradable polymer is poly lactic acid (PLA), which already has some uses in food packaging. However, its high price, low flexibility and relatively poor barrier properties restrict it from broader use. Combining PLA with lignin might help improve these properties but there are many aspects that could influence this material. Therefore, the main question to be answered with this thesis is:

How can lignin-PLA composites be formed and what influences the characteristics that make them suitable for the use as food packaging?

## Polymers

Polymers are materials that are quintessential to modern day life. They are used in a great capacity every day and come in many different forms and varieties. Examples include but are not limited to plastic bags, car tires and latex gloves. Although they all have vastly different properties, they all have some similarity of how they are formed at a chemical level.

Polymers are macromolecules built up of many smaller molecules called monomers. There are various ways in which monomers can react to form polymers. The most common ways include addition, condensation and radical polymerisation. The type of polymerisation depends on the monomer, the catalyst and the reaction conditions. Some polymers have multiple reactive groups from which chains can grow resulting in branching or cross-linking. Multiple different chemicals can also form a polymer together, these are called copolymers and can be formed in various ways; there are random and alternating copolymers, where the different repeating units form the backbone in a random or alternating order, respectively. Additionally, there are graft copolymers where the homopolymeric backbone has side chains of a different polymer attached to it and there are block polymers which have interchanging series of the same monomer.

The physical properties of polymers are highly varying and depend on many factors including chemical structure, chain length, polymerisation pathways, purity, crystallinity, degree of branching or cross-linking, type of copolymerisation and how it was processed. Most commercially used polymers are not pure and have fillers and/or coatings applied to them to improve certain characteristics like for example ductility, UV-blocking ability or a change of colour.

Many polymers used nowadays are petroleum based and have a low recyclability and accumulation of plastic waste is a growing problem [1]. Finding and utilizing proper alternatives could help increase global sustainability, which is an objective of ever increasing importance. The most promising alternative is polymers made from chemicals found in or derived from plant biomass, since plants are easily and renewably harvestable in large quantities [2]. Furthermore, since these chemicals are naturally occurring, they often cause

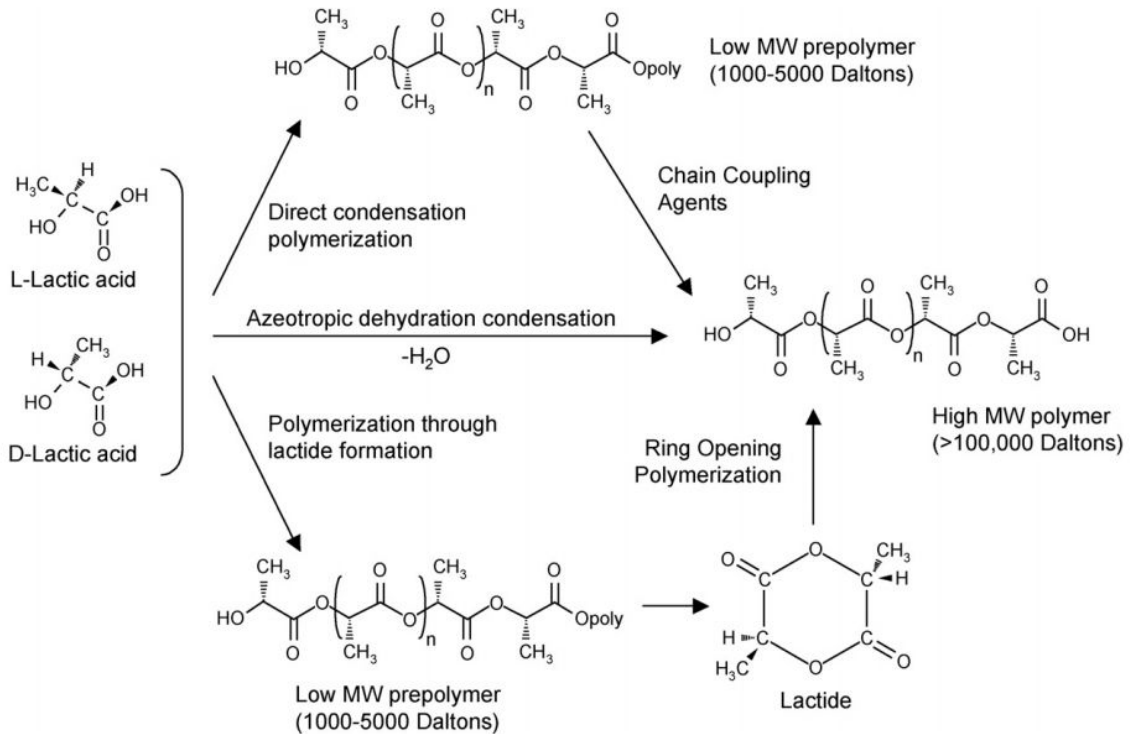
little harm to the environment and can be biodegradable. One of the most researched and generally considered a very promising bioplastic is PLA.

## PLA

PLA is one of the most promising sustainable polyesters since it can be made from biomass sources. It is built up of lactic acid monomers which can be obtained in various ways but is done industrially through fermentation of various mono- and disaccharides obtained from starch. Most lactic acid producing bacteria cannot utilise starch and require starch to be hydrolysed prior to converting it to lactic acid. In addition to this, the lactic acid formed by the bacteria is not readily usable for polymerisation and requires various complicated purification steps [3].

There are multiple pathways to forming PLA, the three most common ones are depicted in figure 1. The most popular method is the ring opening polymerization mechanism in which lactic acid first reacts to cyclic lactides before polymerizing to high molecular weight PLA. These lactides have three stereoisomeric forms, *l*-lactide, *d*-lactide and meso-lactide. Depending on the process, different amounts of each stereoisomer is formed when generating lactides. This is of importance because PLA derived from at least 93% *l*-lactide can be semicrystalline, whereas a PLA with more *d*-lactide will always be amorphous [4]. Semicrystalline polymers have different properties than amorphous ones. Their mechanical properties are usually higher and the material tends to be more transparent.

The glass transition temperature of PLA ranges from 50 to 80 °C and the melting temperature is within the range 130-180 °C both depending on several factors including optical purity and thermal history. The tensile strength and Young's modulus of PLA are its more redeemable properties at around 60 MPa and 3-4 GPa, respectively [5]. Currently, PLA has found limited use in food packaging, due to its relatively high cost and somewhat undesired properties compared to petroleum based plastics.



**Figure 1:** Various reaction pathways for forming PLA from lactic acid [6].

## Composites

In order to enhance the properties of polymers, composites can be made. Composites are made up of multiple different solid materials which are combined to obtain a product with enhanced properties. Some common examples are fibres with high tensile properties in a light polymer matrix resulting in a strong yet light material. Not all combinations of materials result in enhanced properties as some materials might have negative interactions and weaken the resulting structure. Furthermore, the materials usually need to mix well to form a desirable composite, which means that the two components usually need to have intermolecular interactions with each other that are stronger than the intermolecular interactions the molecules have with themselves. Forming such a composite of PLA and lignin could prove beneficial and provide a cheaper sustainable plastic.

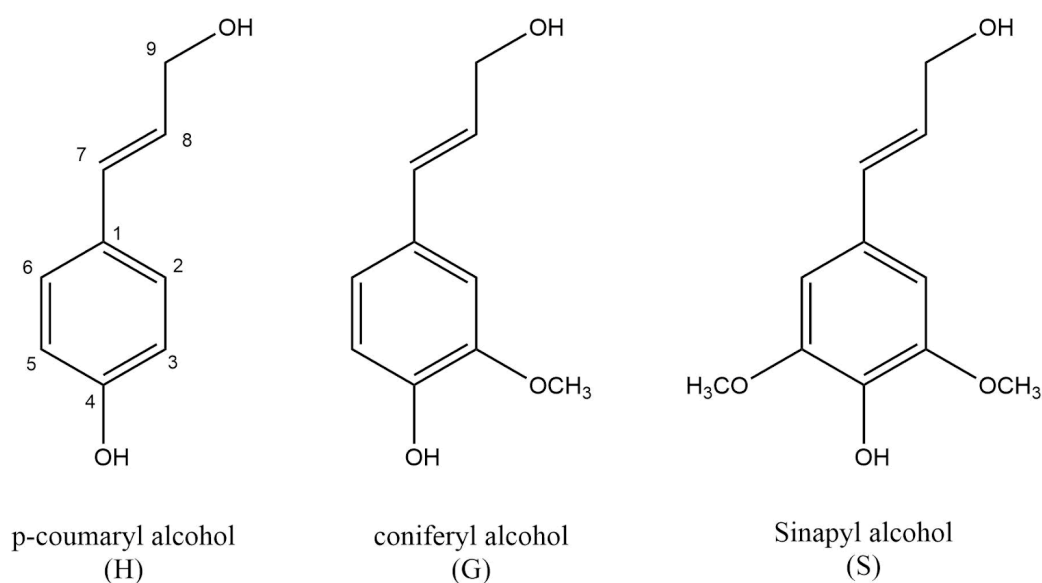
## Native lignin

Lignin is one of the most abundant materials in nature, making up approximately 10-30% of plant biomass. It is a macromolecule found in all vascular plants providing structure and stiffness to the plant and its cells. The amount of lignin found in a plant varies between species. Woody plants have a higher lignin content (15-40 %) than plants such as grass and herbs (<15 %) [7]. Another difference is found in the structure of the molecules themselves.

Lignin consists of monomers called monolignols, of which there are a few different types. The three most abundant monolignols are *p*-Coumaryl alcohol, Coniferyl alcohol and Sinapyl alcohol or H-, G-, and S-units for short. These monolignols are depicted in figure 2. The amount of each monolignol present varies between plant sources and a general overview of

monolignol contents for different plant groups is given in table 1. The different amounts of each monolignol have influence on the polymerization and the lignin's structure as a whole. The plant classifications used are as follows, hardwoods are mostly angiosperms or flowering plants (eg. birch, oak) while softwoods are generally gymnosperms or conifers (eg. pine).

Monolignols undergo radical polymerization and can form various different linkages, some of which cause branching or crosslinking [7]. The various linkages and their names are shown in figure 3. Due to the nature of radical polymerization some linkages are more prevalent in lignin with more or fewer H-, G-, and S-units.



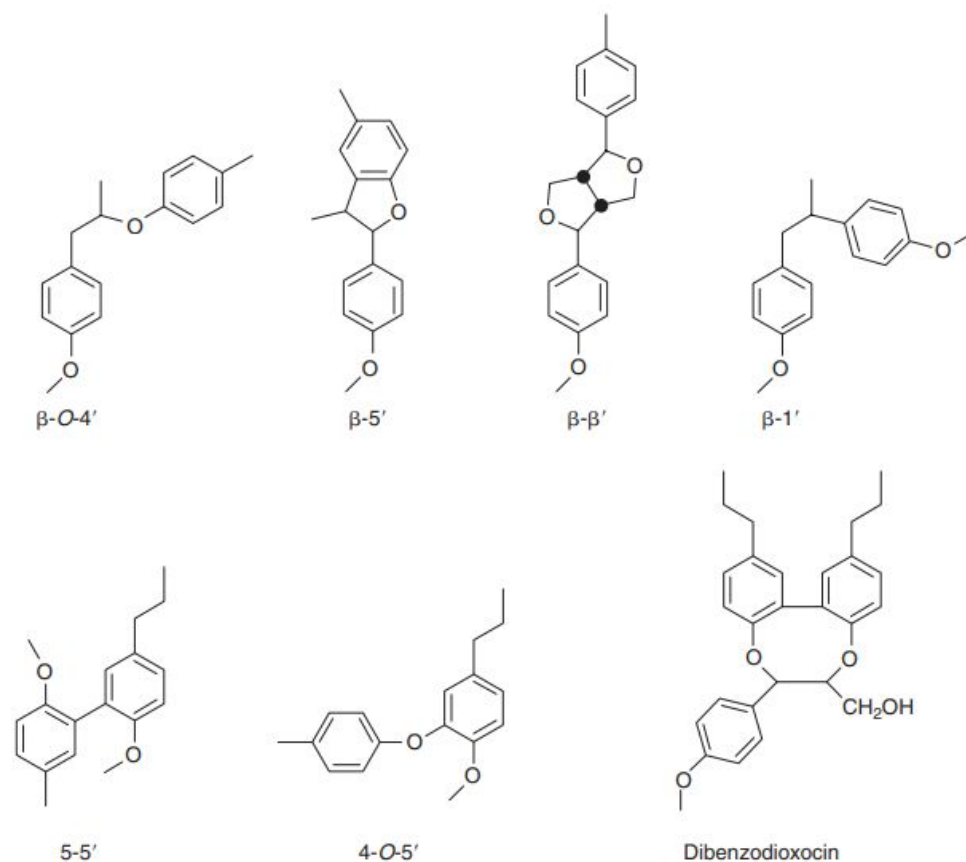
**Figure 2:** The three main monolignols, including carbon numbering on *p*-coumaryl alcohol. Carbons 7, 8 and 9 are more commonly referred to as  $\alpha$ ,  $\beta$  and  $\gamma$ , respectively

Plant type	<i>P</i> -coumaryl alcohol (%)	Coniferyl alcohol (%)	Sinapyl alcohol (%)
Softwoods	<5 <sup>a</sup>	>95	0 <sup>b</sup>
Hardwoods	0-8	25-50	45-75
Grasses	5-35	35-80	20-55

<sup>a</sup> Higher amount in compression wood

<sup>b</sup> Some exceptions exist [8]

**Table 1:** The participation of different monolignols for various plant groups [7]



**Figure 3:** inter-unit linkages between monolignols and their names [7]

### Technical lignin

Industrially, lignin is most abundant in the paper and pulp industry where it is separated from cellulose and hemicellulose. This is done because lignin is not desired in paper products, it is regarded as a waste product and utilized as a low energy fuel that is burned on site to power the paper mill. This means that lignin is relatively cheap and has the possibility of being abundant, if it wouldn't be burned. In addition, the fact that it originates from biomass and is biodegradable makes it a good candidate for the use in sustainable materials.

There are various industrial processes employed to separate lignin, cellulose and hemicellulose, where each process results in lignin with different properties. The most common processes are the kraft, soda and organosolv processes. Each of these processes uses an aqueous solution to cleave the bonds between lignin and cellulose and further solubilise lignin in order to separate it. In the past, sulfite pulping was also widely used, however, this is becoming increasingly more unpopular mainly due to environmental issues and will therefore not be considered here.

The kraft process is the most common chemical pulping process and employs a solution of sodium hydroxide and sodium sulfide at 170 °C in order to achieve separation. Due to the use of sodium sulfide, kraft lignin contains around 1.5-3.0% sulphur atoms some of which are chemically bonded to the lignin itself [9]. After the lignin is solubilized and the cellulose is



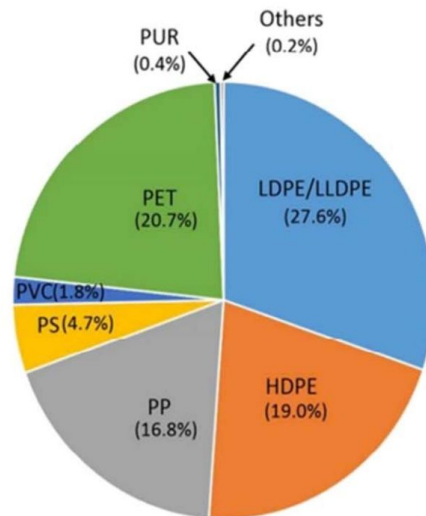
filtered off, lignin can be precipitated by lowering the pH. This acid insoluble lignin is called klason lignin. The price for kraft lignin is between 260-500 USD/MT [10].

Soda pulping is done with an aqueous solution of sodium hydroxide at 160 °C. Similar reactions to the kraft process take place, however there is no sulphur present in this process. Due to this, there is also no sulphur in the final lignin product and it can be regarded as more similar to native lignin. Soda lignin has average molecular weights comparable to kraft lignin. Soda lignin costs around 200-300 USD/MT [10].

Recently organosolv processes have been gaining attention lately due to the need for a more environmentally friendly process for pulp and paper. Organosolv processes use organic solvent often mixed with water. Ethanol and methanol are a rather common solvent to use for this process. These organic solvents are easily recoverable and result in less waste. This process is still relatively new and many variations with different catalysts are still under development [11]. For example, Zijlstra et al. recently showed a lab-scale semi-continuous lignin extraction with an ethanol/water mixture and H<sub>2</sub>SO<sub>4</sub> as an acid catalyst resulting in lignin with high β-O-4 contents, while other organosolv process result in lignin with almost no β-O-4 linkages [12][13]. Zijlstra et al. also stated there are still many variations of organosolv processes left to explore and each process should be specialised based on the biomass source. Though this process seems to be the most eco-friendly it is more expensive than the conventional methods and only pilot scale plants exist [14]. Prices for this lignin are around 280-520 USD/MT [10].

### Current food packaging properties

The most common plastic food packaging materials include poly (ethylene terephthalate) (PET) which is most commonly known for the plastic bottles, polyethylene (PE) which comes in various different grades of density of which low and high density polyethylene are most common (LDPE and HDPE), polypropylene (PP) and polystyrene (PS), which are more commonly known for takeaway food packaging [15]. Figure 4 shows the relative amounts of each of these plastics used in the packaging industry. These plastics can be used as a frame of reference for desired properties for food packaging materials and PLA can be placed in this frame of reference. This should give an overview of what could be altered about PLA in order to make it a more desirable food packaging material. In table 2 various properties of PLA and these food packaging plastics are given.



**Figure 4:** Plastic use in the packaging industry in the world in 2015 [15]

The first parameter that is important for food packaging are the mechanical properties. The tensile modulus of PLA is relatively high compared to other food packaging materials at around 3.5 GPa it is only matched by PET and PS. Similarly, its tensile strength is higher than most other food packaging plastics with only PET and PS having higher values. Finally, the elongation at break of PLA is only comparable to that of PS at around 6 % and 2 %, respectively. The other plastics have elongations at break far exceeding these two values. From this data it can be seen that although PLA has a relatively high strength, it is also extremely stiff and brittle compared to most other food packaging materials. This can also be seen when comparing the impact strength of PLA to that of other polymers. PS and PP have values twice as high as that of PLA and PET has numbers more than four times as high [16].

The second parameter important for food packaging materials is the barrier properties. The main barrier properties are those of UV-light, oxygen and water.

The UV barrier of materials can be compared by investigating the transmittance of certain wavelengths of light. A graphical representation of this is shown in figure 5. In figure 5 it can be seen that PLA blocks most light of wavelengths lower than 230 nm, but lets through most light of higher wavelengths. The only material shown in figure 5 that has worse UV barrier properties is LDPE. PS and PET, on the other hand, absorb much more UV light.

The oxygen barrier properties can be compared through the oxygen permeability (OP) given in  $10^{-7}$  mL.m/(m<sup>2</sup>.day.Pa). At atmospheric pressure, these values are 2.7 and 0.1-0.5 for PLA and PET respectively. The other plastics all have higher values.

The final barrier of interest is the water barrier. This is most commonly measured by water vapour permeability (WVP) which is given in  $10^{-14}$  g.m/(m<sup>2</sup>.s.Pa), the equation of which is shown below.

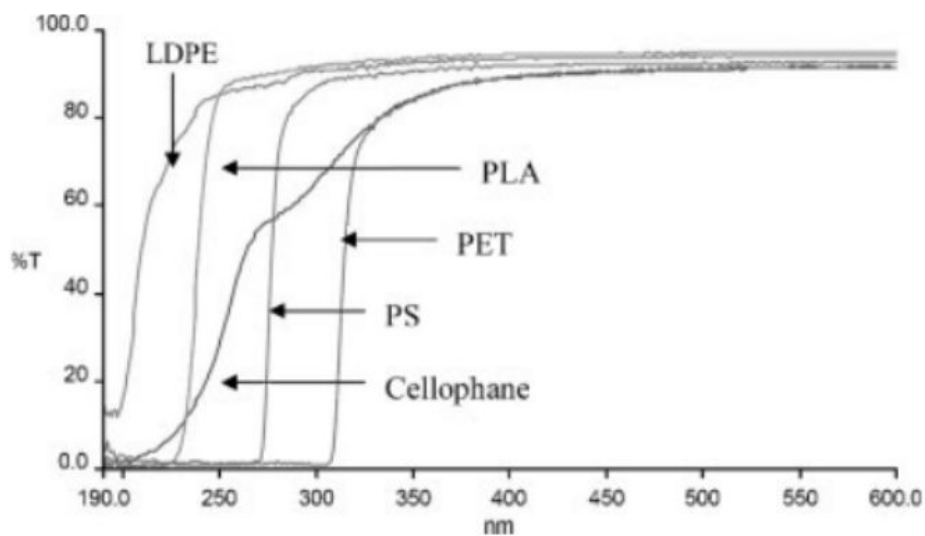
$$WVP = WVTR * d / \Delta p$$

Where WVTR is water vapour transmission rate in g/(m<sup>2</sup>.s), d is the film thickness in m and  $\Delta p$  is the partial water vapor pressure difference across the two sides of the film in Pa. Here

PLA has somewhat poor performance as it is only better than PS, which has by far the highest values amongst the common food packaging materials.

Another measurement that can be made is the water contact angle (WCA), which indicates the hydrophobicity of a material. PLA has a WCA of around 71 °. This is around the same as PET which has a contact angle of around 72 °. The other plastics have considerably higher values than this. However, caution should be taken when interpreting this parameter since a high water contact angle does not always correlate to low WVTR.

Finally, the price of PLA is also shown in table 2. It is important to note that the price for PLA is from 2016, while the other prices are from June 2020, not too long after the collapse of oil prices. Regardless of the recent oil price drop PLA is far more expensive than the conventional plastics which hinders commercial interest in PLA.



**Figure 5:** The percentage transmittance of light at different wavelengths of several food packaging plastics [4].

Plastic	E (Gpa)	$\epsilon$ (MPa)	$\epsilon$ (%)	OP	WVP	WCA (°)	Price (€/kg)
PLA	3.5	60	6.0	2.7	9.63	71	2
PET	3.5	157-177	70	0.1-0.5	5.803	72.5	0.72
LDPE	0.15-0.34	7-25	300-900	44.76	6.7-8.7	96	0.84-0.93
HDPE	0.98	19-31	20-50	7.13	1.7-3.5	96	0.87-0.89
PP	1.18	27-98	200-1000	4.9-9.9	2.3-4.6	102.1	0.93-1.05
PS	2.7-3.4	31-49	2-3	9.9-14.8	11.3-45.5	87.4	1.10-1.20

**Table 2:** The properties of PLA and common food packaging plastics. OP is given in  $10^{-7}$  mL.m/(m<sup>2</sup>.day.Pa). WVPC is given in  $10^{-14}$  g.m/(m<sup>2</sup>.s.Pa) [4] [5] [17]-[21]

In light of this gathered information it is clear that PLA is very brittle and has relatively poor oxygen and water barrier. Attempts have been made to reduce brittleness with plasticizers like lactide monomers and poly ethylene glycol however, these usually cause the tensile modulus and strength to drop drastically [22]. Furthermore, PLA is relatively expensive and the cost needs to be reduced in order for it to become economically competitive.

There are many different factors in making a lignin-PLA composite. Firstly, as mentioned previously the botanical source of the lignin has an influence on the structure and characteristic groups of lignin, this can influence miscibility and structure of the lignin. Secondly, the separation method used to obtain the lignin from the original biomass source has an influence on the characteristic groups, the linkages present and the average size of the lignin molecules. Furthermore, there are multiple ways of mixing lignin and PLA into a composite. Finally, several lignin pretreatments exist that are actively being researched in order to improve the composite's properties.

All of these factors can potentially have an influence on the final properties of the composite and not all papers explain their choices, especially when it comes to the lignin's origin and separation method. The goal of this thesis is to take a closer look at these factors and analyse what influence they have on the final properties. Initially the mechanical properties and how the different factors influence them will be discussed. After this, other important properties of food packaging will be discussed. Using the gathered information, suggestions will be made about what lignins are suitable for food packaging and how these can be processed into food packaging.

## Methodology

In order to clarify some of the unknowns surrounding lignin-PLA composites, various literature has been studied. Of this literature, tables were made summarising what type of lignin was used, how this was processed with PLA and what pretreatments were applied. In addition to this, the results found by each source were gathered in the same table and ordered by lignin content. The properties found for PLA by each source was also noted and were not consistent with each source. In order to correct for this the properties of the composites were divided by the properties of PLA found by that same source. This resulted in normalised data for the lignin-PLA composites where a value higher than 1 indicates increased properties with respect to pristine PLA and a value lower than 1 indicates decreased properties with respect to pristine PLA.

The biomass source of some lignins used were not explicitly stated in the text. If available, the structural analysis of these lignins was reviewed. From the FTIR and/or HSQC data provided the biomass source could be determined through comparison of data from "*Methods in Lignin Chemistry*" [23].

## Results & Discussion

#	Lignin type	Biomass source	Pretreatment	Mixing method	Shaping method	Source
1	Kraft	Softwood	Acetylation, PLA grafting	Solvent mixing	Hot press	[24]
2	Kraft	Softwood <sup>a</sup>	Acetylation	Solvent mixing	Solvent casting	[25]
3	Kraft	Softwood <sup>a</sup>	Acetylation	Extrusion		[26]
4	Kraft	Softwood	Plasticizers and transesterification catalyst	Extrusion	Hot press	[27]
5	Kraft	Softwood	None	Extrusion	Hot press	[28]
6	Kraft	Hardwood	Additional plasticizers	Extrusion	Hot press	[29]
7	Kraft	Hardwood <sup>a</sup>	Acetylation	Extrusion		[30]
8	Organosolv	Softwood	Fatty acid esterification	Solvent mixing	Solvent casting	[31]
9	Organosolv	Hardwood	Fatty acid esterification	Solvent mixing	Solvent casting	[31]
10	Organosolv	Hardwood	Acetylation	Extrusion		[26]
11	Organosolv	Hardwood	None	Extrusion	Hot press	[28]
12	Organosolv	Not stated	Rubber and lactide grafting	Solvent mixing	Solvent casting	[32]
13	Soda	Grasses	None	Extrusion	Hot press	[33]
14	Soda	Grasses	Acetylation, PLA grafting	Solvent mixing	Injection moulding	[34]
15	Steam explosion	Grasses	Lignin nanoparticles	Extrusion		[35]
16	Steam explosion	Grasses	Lignin nanoparticles	Solvent mixing	Solvent casting	[35]

**Table 3:** Overview of materials and methods used by various literature describing lignin-PLA composites. Blank cells indicate the information was not given or derivable from the given information. <sup>a</sup> This information is not directly stated in the source, but was deduced from the available structural analysis.

### Data collection

An overview of the sources from which data was used is given in table 3. Table 3 includes the materials and methods used by these sources; the normalised data is displayed graphically in the appendix in figures A1-A3 and in figure 7.

## Lignin biomass source

The amount of lignin present in plants varies greatly between species. Softwoods contain around 30% lignin, hardwoods contain around 10-25% and grasses generally contain less than 15%, all with some exceptions [7]. While the amount of lignin found in a plant doesn't add any relevant information for the formation of biocomposites, it is still noteworthy when attempting to accomplish an economically feasible product.

A more technically relevant difference between hardwoods, softwoods and grasses is that they have different amounts of each monomer, as mentioned earlier. The main difference between each monomer is the linkages it can form and the amount of methoxy groups present.

Softwoods have almost no methoxy group on C5 and can therefore form 5-5', 4-O-5' and dibenzodioxocin bonds, resulting in crosslinking and branching. Hardwoods have more methoxy groups on C5 and can therefore form fewer of these linkages, resulting in a more linear structure. The amount of methoxy groups present could influence miscibility of lignin with PLA. These methoxy groups are esters and therefore hydrogen bond receivers, which means they could form such bonds with any hydroxyl groups that are in the lignin, this would lead to aggregation in the composite. Generally, high miscibility of two components in a composite results in a desired increase in mechanical properties.

Literature shows that lignin-PLA composites often have decreased tensile properties compared to pristine PLA. The tensile modulus has been shown to more often decrease than increase. It doesn't seem to be dependent on biomass source, but rather the separation method used to isolate lignin, especially for hardwoods, this will be discussed in the next section. Both hardwoods and softwoods usually don't improve the tensile strength. However softwoods seem to be slightly better than hardwoods. Finally the elongation at break also seems to be more dependent on other factors than the wood species (Table 3, #2, #3, #6 and #10). An overall trend that is clear is that higher lignin contents, especially above 15 wt%, most often have a negative effect on tensile properties. This is believed to be caused by larger aggregations of lignin disrupting the continuous phase of PLA [36].

Seemingly the biomass source is of not much importance to the mechanical properties of the lignin-PLA composite. Although there are some differences between the native lignins, these differences don't seem to be as impactful as the type of technical lignin it is.

Despite there not being a large mechanical difference between hardwoods and softwoods, it might be more economically interesting to use softwoods, due to it being more commonly processed in the EU in total, as well as the EU pulp and paper industry [37]. This means that this type of lignin should be more abundant. Furthermore, some studies utilise lignin from grasses, however, using grasses to make paper and pulp is very uncommon. For this reason, lignin from grasses were not considered for this research.

## Technical lignins

Lignin is found in plant biomass alongside cellulose and hemicellulose and is separated from them during the paper making process. There are several methods industrially used to

achieve this, all of which cleave the linkages between lignin and carbohydrates. They also cleave linkages between monolignols, to varying degrees, leading to a decrease in the resulting lignins average molecular weight. Currently, the most researched lignin are from the kraft, soda and organosolv processes. A short description of these processes was given earlier and now a description of the lignins from each process follows.

Kraft lignin contains 1.5-3 wt.% sulphur, some of which is elemental sulphur and some is chemically bound to the lignin [38]. Ash contents are lower than 3 wt.% and sugar content below 2.3 wt.%. A comparative study found Indulin AT (softwood kraft) to have 7.4 ether linkages per 100 aromatic units, which were mainly  $\beta$ -O-4. It was also found that this lignin has around 1.8 mmol/g aliphatic OH groups and 2.8 mmol/g phenolic OH groups. Its average molecular weight and polydispersity were also higher than that of soda and organosolv lignin [13].

Soda lignin comes from the soda process, which is almost exclusively used for grasses. This type of lignin is not studied to the same extent as lignin from wood sources. As mentioned earlier, grasses and therefore soda lignin will not be compared with other lignin types in this study.

Since the term organosolv is more of an overarching term, the structure of organosolv lignin can vary greatly between processes and is largely dependent on the processing conditions. For this reason, when researching organosolv lignin, it is important to document and report what the conditions were for lignin extraction and to perform characterization of the lignin structure and its functional groups. Some statements can be made that are generally true for organosolv lignins. Generally, sugar contents are below 1 wt.% and ash contents below 0.5 wt.% [39][13]. Organosolv lignins typically have fewer aliphatic hydroxyl groups than kraft lignin, but similar amounts of phenolic OH groups, though this seemingly varies between processes and biomass sources. Organosolv lignin also seems to have a lower average molecular weight and polydispersity than kraft lignin. The amount and type of ether linkages also varies greatly between processes and biomass sources, while some reports show only 3 ether linkages per 100 aromatic units and almost no  $\beta$ -O-4 linkages, other reports isolated lignin with up to 67  $\beta$ -O-4 linkages per 100 aromatic units [13][12]. The former had mostly  $\beta$ -5 or  $\beta$ - $\beta$  bonds.

To determine which process results in more suitable lignin, the source of the lignin also has to be taken into account. When comparing mechanical properties from various researches it seems that, for softwoods, kraft is the more common method (Table 3, #1 - #5). However, organosolv softwoods don't seem to be studied as extensively (Table 3, #8). Increases in the tensile modulus in composites with up to 15% lignin have been reported for softwood kraft. The tensile strength is generally decreased with the addition of this lignin, though the extent to which it decreased varied greatly between reports. Elongation at break is normally decreased with the addition of softwood kraft lignin, though various lignin pretreatments have resulted in substantial increases instead. These pretreatments will be discussed in more detail later.

For hardwoods more diverse research is available (Table 3, #6, #7, #9, #10, #11). Overall, a higher tensile modulus is achieved when PLA is blended with kraft hardwood than when blending with organosolv hardwood. Similarly to softwoods, the tensile strength is decreased

with the addition of lignin, although this seems to be more severe with hardwood than with softwood. There is no discernable difference between kraft and organosolv hardwood lignin when comparing tensile strength changes. The elongation at break is usually increased for composites with organosolv hardwood lignin, whereas composites with kraft hardwood lignin generally have a decreased elongation at break.

Granted that softwood kraft lignins don't always result in worse mechanical properties, it is unfortunate that softwood organosolv is not explored more, since this might also reveal beneficial composites.

When considering hardwoods, a larger variety of results seems to be available. This has revealed that the kraft lignin typically yields a higher tensile modulus, whereas the organosolv lignin generally resulted in greater elongation at break. These differences can be explained both by the functional groups present and by the average molecular weight of the lignin, respectively. The apparent trend for kraft lignins compared to organosolv lignin was that kraft lignin typically has more total and aliphatic hydroxyl groups. These groups can form hydrogen bonds with the ester bonds in PLA and, by doing so, will increase the overall bonding strength between lignin and PLA. This could be a reason why hardwood kraft lignin composites generally have a higher tensile modulus than their organosolv counterparts. Alternatively, these hydroxyl groups are often subject to alteration in pretreatments and with a higher hydroxyl group content, pretreatments can have a greater effect. This will be discussed later. The higher elongation at break for the organosolv composites could be explained by the observed trend of lower average molecular weight of the organosolv lignin compared to kraft lignin. Plasticizers often have a similar effect; the presence of plasticizers in a matrix usually results in an increase of elongation at break. In this case, lignin particles could be considered plasticizers, especially for lower lignin loading [40]. The organosolv lignin could act better as a better plasticizer than kraft lignin due to its smaller size.

## Processing methods

Before discussing various pretreatments, it should be noted that there are two different ways in which lignin is introduced into PLA. These methods are solvent mixing and double extrusion. In solvent mixing, both the PLA and the lignin are solubilized in an appropriate solvent. After they are both dissolved, the chloroform is evaporated off leaving behind a mixed composite (one source precipitated the composite using isopropanol, this seems to be an exception [24]). The dissolving is usually done around room temperature, while the evaporating is usually done in a vacuum oven at 40-80 °C.

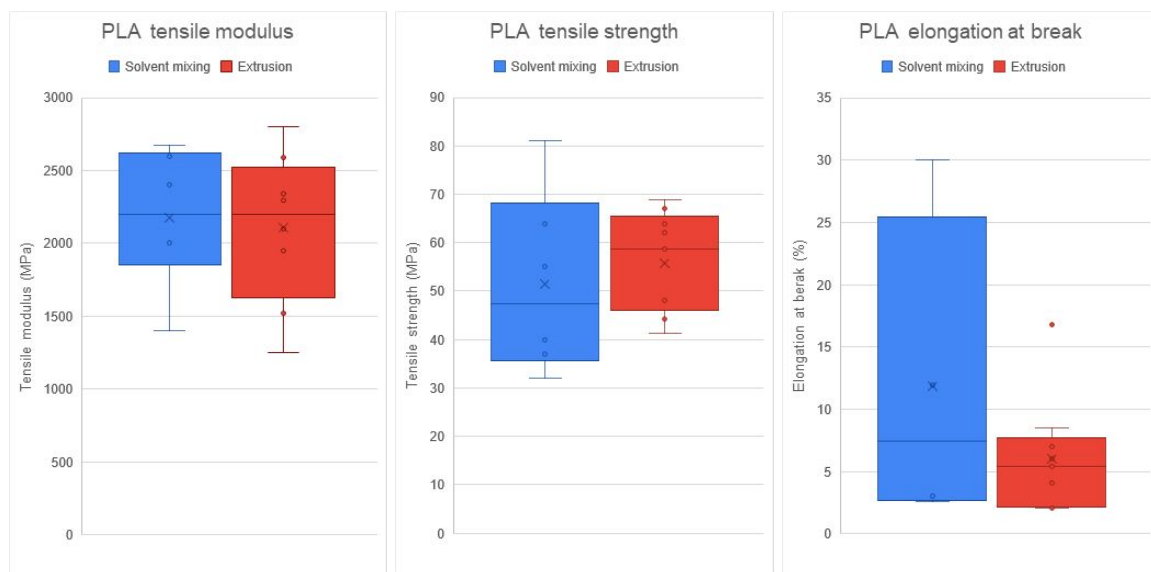
Double or twin-screw extrusion is a form of extrusion involving two screws, instead of the conventional single screw. The two co-rotating screws are supposed to yield a more consistent and mixed product [41]. In the reviewed sources, this was done at temperatures of around 150-200 °C. These temperatures are chosen in order to melt the polymers, which should also increase miscibility. Rahman et al. compared two different processing temperatures, 160 °C and 200 °C, and concluded that processing at 160 °C resulted in higher mechanical properties [27].



After either mixing techniques, the composites are often shaped using injection moulding or hot press moulding. Composites that are made through solvent mixing are often mixed in the desired mould, eliminating the requirement for an additional moulding step. This is called solvent casting.

When comparing the mechanical properties of PLA from various literature, there seems to be a considerable difference. This difference could be the result of the processing methods or the fact that not all PLA were of the same commercial grade or from the same company. A comparison of the tensile properties of PLA from various literature based on processing methods is shown in figure 6. When comparing the processing methods, it seems that, on average, the literature that used solvent mixing had PLA with slightly higher mechanical properties. The elongation at break is where the largest difference can be found, where reports varied from 2.1 - 30% (table 3, #7, #12). Tensile moduli and strengths were rather similar for both processing methods, though the literature with solvent mixing had a larger deviation in tensile strengths.

A possible explanation for this could be that not all the solvent evaporates during the drying step and some is left in the final product. This solvent could then act as a plasticizer within the PLA matrix, often increasing the elongation at break.

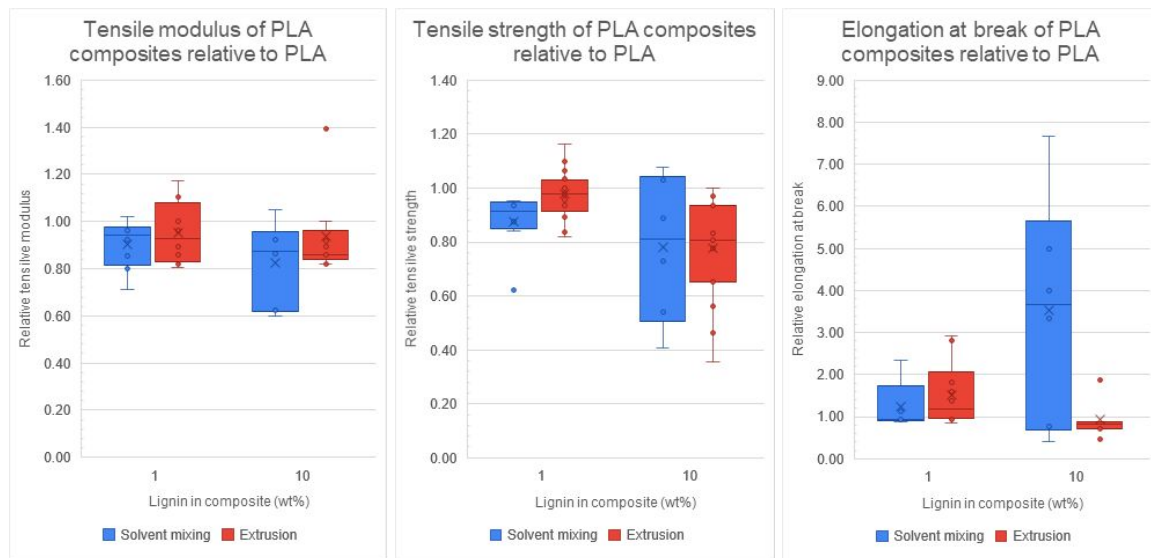


**Figure 6:** Box plots of mechanical properties of PLA as reported by various sources sorted by the sources' processing method.

Moreover, solvent mixing is a less common practice. This might be due to the several problems involved with this method. Firstly, it uses a relatively large amount of the very toxic solvent chloroform [42]. On a lab scale, the quantities used might still be manageable however, on an industrial scale this would be unsafe and irresponsible. Secondly, this method is very time intensive, since samples often have to dry in vacuum ovens for a week before all the chloroform is evaporated. Such an extensive drying process would not be suitable for an industrial scale.

Figure 7 shows the mechanical properties of various lignin-PLA composites, normalized to pristine PLA. It is important to realise when looking at these graphs that, although they are sorted by mixing method, there are many other factors contributing to the mechanical properties which are not apparent from the graph. Additionally, it should be noted that of the six solvent mixing sources, two different sources had a pretreatment that most likely caused a large alteration in mechanical properties, especially elongation at break.

Taking these nuances into account, it seems that at 1 wt.% lignin the mechanical properties are more favoured for the extrusion method, while at 10 wt.% solvent mixing seems to result in slightly higher mechanical properties. At 10 wt.% the deviation of results is also much larger than at 1 wt.%. Yang et al. showed a side by side comparison of the difference between solvent mixing and extrusion for steam explosion lignin from grasses and actually found extrusion to yield in higher mechanical properties overall [35]. This suggests that the observation made here is likely due to external factors and the difference in mechanical properties between the two mixing methods is negligible.



**Figure 7:** Box plots of various mechanical properties of lignin-PLA composites relative to PLA at 1 and 10 wt.% lignin content. Note that there are other variables, which are not shown, affecting the mechanical properties aside from mixing method

Keeping in mind the final goal of making appropriate lignin-PLA composites for food packaging at an industrial scale, it would be more logical to work with twin-screw extrusion rather than solvent mixing. Extrusion is much more environmentally friendly due to several reasons. The lack of need for solvents reduces waste and the need for solvent recovery equipment. Furthermore, it is much more suitable for upscaling for the same reason as well as the need for much shorter processing times. Finally, industrially produced PLA is made using extrusion and injection moulding, this means that relatively few alterations in the process would be required to introduce lignin into PLA [6].

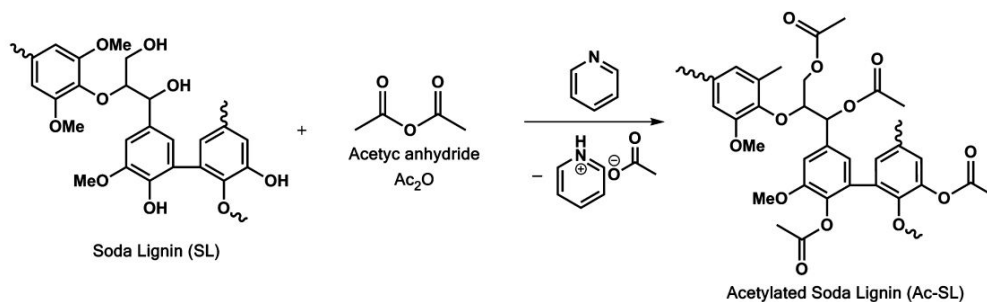
There seems to be no strong evidence suggesting solvent mixing yields better mechanical properties. Furthermore, there are various problems regarding the upscaling and practicality

of the solvent mixing process. For these reasons, extrusion should be the mixing technique employed in future studies, if possible.

### Lignin pretreatment

When it comes to introducing lignin into PLA, there is a limited amount of combinations possible and the general trend displayed seems rather clear. Lignin often aggregates, resulting in a negative effect on the composite's mechanical properties, with the exception of very low lignin loading. Luckily, lignin has many functional groups that can be altered through chemical reactions. This is done in order to (further) improve certain mechanical properties and/or prevent aggregation of lignin. Below, some common pretreatments found in literature are described.

The most researched lignin pretreatment is acetylation. In this pretreatment the lignin hydroxyl groups react with acetic anhydride and pyridine as a catalyst, to replace their hydrogen with an acetyl group. A general reaction scheme for acetylation of soda lignin is shown in figure 8. This reaction has been proven to be quite effective and able to convert most hydroxyl groups. A 2.5 equivalent (to the number of hydroxyl groups) portion of acetic anhydride is sufficient to convert all hydroxyl groups in lignin. Furthermore, the degree of acetylation can be controlled by limiting the amount of acetic anhydride present during the reaction [43].



**Figure 8:** The reaction scheme of acetylation of soda lignin [43].

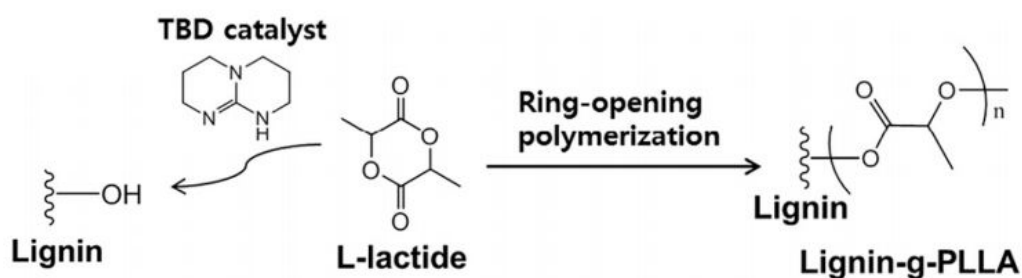
This pretreatment is meant to decrease lignin aggregation in the PLA matrix. Most literature showed that this was indeed the case. At lignin loadings of 5 wt% and upwards composites with acetylated lignin had higher tensile properties than composites of non-acetylated lignin at the same loading. At lower loadings, the difference was less pronounced and some reports even showed a slight decrease compared to the composite with non-acetylated lignin. It has been shown that the size of lignin aggregates is smaller for acetylated lignin than for unmodified lignin. Where acetylated lignin aggregates stay mostly the same size, unmodified lignin aggregates become larger with increased lignin loading [25]

This difference in miscibility can be explained by how lignin interacts with PLA and itself. Before acetylation, the lignin contains more hydroxyl groups, which can undergo hydrogen bonding with each other or with ester groups present in the lignin, these interactions cause

aggregation. After acetylation, there is a reduced amount of these hydroxyl groups and the lignin has less intramolecular association with other lignin molecules [44]. Instead, the acetyl groups will interact with the ester bonds in PLA, due to their similarities in structure.

Another pretreatment that is being explored by various researchers is grafting PLA onto lignin (table 3 #1, #14). This pretreatment is also done by performing a chemical reaction on the hydroxyl groups in lignin. In this case, lactides undergo a ring opening polymerization in the presence of a triazabicyclodecene (TBD) catalyst where the hydroxyl groups of lignin act as initiators. The reaction scheme is shown in figure 9.

PLA chain length can be controlled by varying the ratios of lignin to lactide during the grafting process. The drawback of controlling the chain length in this manner is that the lignin contents in the copolymer become very low. In order to overcome this problem the lignin can be partially acetylated before grafting [24]. As a result of partially acetylating, the amount of hydroxyl groups in lignin decreases and there are fewer initiator points where PLA grafting can occur. Though there are fewer places where chain growth can start, the same amount of PLA will react, resulting in longer PLA chains.



**Figure 9:** Reaction scheme of the graft polymerization of PLA onto lignin through a ring opening polymerization reaction [34].

The goal of grafting PLA onto lignin is again to increase miscibility of lignin in PLA. In this case the miscibility should increase due to the PLA that is now chemically bound to the lignin. This was indeed found to be effective and a better dispersion of lignin in the PLA matrix was achieved resulting in improved tensile and UV barrier properties.

Lignin-PLA graft copolymers have yet to be mixed with PLA at higher quantities than 5 wt%. Though the results of lower loading has been promising, it would be interesting to see how the properties are affected at higher lignin loadings.

Aside from lactides other monomers have been grafted onto lignin to improve certain properties. For example, Zong et al. grafted polyacrylates onto lignin which improved dispersion and had limited effect on the mechanical properties at lignin loadings of up to 10 wt% [45]. One exception was PBMA grafted lignin which led to a sharp increase in elongation at break. This was attributed to the long side groups in the PBMA causing a toughening effect on the composite.

Sun et al. grafted rubber composed of caprolactone and lactide monomers onto lignin and subsequently grafted *d*- or *l*-lactide monomers onto the ends of the rubber chains [46]. This

was compared to lignin grafted with only lactide monomers and found that the addition of rubber had little effect on the tensile modulus and tensile strength, but resulted in a remarkable increase of elongation at break. Interestingly, the lignin grafted with caprolactone and *d*-lactide performed better than the lignin grafted with caprolactone and *l*-lactide. It was suggested that this was because the rubber aggregated with the *l*-lactide and didn't form a stereocomplex, whereas with *d*-lactide the opposite was the case.

Gorbodil et al. esterified the hydroxyl groups of lignin with fatty acids (table 3, #8, #9). The theory behind improving the miscibility here being similar to that of acetylation with the addition of a longer carbon chain. The results were similar to that of unmodified lignin, where the tensile modulus and strength decrease with increasing lignin content. The only difference was that elongation at break increased with increasing lignin content, up to 25 wt.% lignin, after which the elongation at break decreased.

Park et al. plasticized lignin by adding 20%  $\epsilon$ -caprolactone to the lignin (table 3, #6). Polymeric diphenylmethane diisocyanate was also added in small amounts for the same purpose. It was found that these modifications improved lignin dispersibility in PLA. However, both of these additions did not yield improved tensile properties with respect to unmodified lignin in PLA or neat PLA.

## UV resistance

Food quality can be degraded due to the exposure to visible and ultraviolet (UV) light. This is true for products containing vitamins, oils and dairy products, among others [47]. In order to prevent this from happening, certain food packaging materials can block the harmful light from reaching the product.

Of all the wavelengths of light that commonly affect food products, UV (100-400 nm) seems to be the most harmful. UV light can be subdivided into UV-A (400-315 nm), UV-B (315-280) and UV-C (280-100), of which only UV-A and UV-B reach the earth surface from the sun. PLA has rather poor light barrier properties. Though it does block most UV-C, it blocks barely any UV-B and almost no UV-A [4]. The addition of lignin is thought to be a solution for this and has been shown to yield positive results.

For lignin-PLA composites, where successful mixing with little aggregation was achieved, the light barrier properties greatly improved compared to pristine PLA. Blocking of all UV-B and up to 80% of all UV-A for lignin contents of 5 wt.% and up have been reported [24][45]. Composites made through solvent casting as well as extrusion both reported this result. These reports were also true for lignin that had undergone acetylation and PLA grafting. Although no comparative research has been done on the effect that the different lignin types have on UV absorption, there is no reason to believe a different lignin type would result in a different result, since the aromatic regions are similar for most lignins.

It is noteworthy that the addition of lignin to PLA often causes a change of colour. Where PLA is a white/colourless plastic, lignin is light to dark brown, depending on the type of lignin. This results in most lignin-PLA composites to have a brown colour, with increasing darkness

with increasing lignin contents. This might have a negative impact on a consumer's perception of the material, since the colour makes the material look somewhat degraded.

Acetylation of the lignin prior to mixing can reduce this discolouration [25]. A method to decolourise lignin also exists and is based on changing the methoxy groups to hydroxyl groups and subsequently oxidising those to ketones [48]. By doing this, the aromaticity is lost and thereby its ability to absorb and emit certain photons. This would also mean that lignin loses its UV-blocking ability. Furthermore, this would disrupt the structure of lignin which would most likely not be beneficial for the mechanical properties of the material, although this appears to not yet have been tested.

### Oxygen barrier

Most food is negatively affected by oxygen during prolonged storage. The oxygen can cause oxidation of proteins and otherwise affect flavour and colour negatively [49]. To limit the extent to which this happens and increase the shelf-life of these food items, the packaging material must limit the amount of oxygen it permeates. Though the oxygen barrier properties of PLA are already relatively good, it is important to investigate if the addition of lignin has any affect on it.

Only one report of the effect of lignin in PLA on the oxygen barrier was found and concluded that there was no significant change at 10 wt.% lignin. This was true for both acetylated and non-acetylated lignin.

### Water barrier and hydrophobicity

Another important property for food packaging materials is the ability to prevent water from permeating through the material. It is often desired to maintain a certain level of moisture inside the packaging and in order to achieve this the packaging material should permeate as little water as possible. Though the most common way of measuring water barriers is through the WVTR, water contact angle and hydrophobicity seems to be reported more often for lignin-PLA composites.

Partially due to lack of reports, no clear trend can be seen in the effect of lignin to the WVTR, though Kim et al. did report that acetylated lignin had a positive effect on this [25] [31].

The water contact angle describes the angle between a single water droplet and the surface on which it is placed. A smaller angle occurs when the surface material undergoes positive interactions with the water, the material is then described as being hydrophilic. A larger angle would be the opposite and indicate hydrophobicity [50]. Kim et al. reported no significant impact of 10% lignin, regardless of acetylation, while Gorbodil et al. reported increases for both acetylated and non-acetylated samples up to 5 wt.% lignin after which the contact angle decreased with increasing lignin, though maintaining an increase compared to neat PLA [25] [30]. This difference between these two sources could be explained when considering Gorbodil et al. achieved better tensile properties, indicating a more homogenous mixture and therefore a more consistent surface. In addition, the acetylated samples also showed higher water contact angle than the non-acetylated samples. This was also reflected

in lignin-PLA composites, where the composites with acetylated lignin were more hydrophobic than the samples with unmodified lignin.

### Biodegradability

One of the redeemable properties of PLA is its biodegradability. If the addition of lignin would negatively affect this trait then the goal of creating a suitable biodegradable food packaging alternative would not be reached. Though lignin is naturally found in plants and should be biodegradable, one should consider the fact that lignin from the pulp and paper industry has been chemically modified.

Yang et al. investigated how lignin affected the biodegradability of PLA and found that the addition of 1 and 3 wt.% both hindered the disintegrability. At an incubation temperature of 58 °C the composites started disintegrating later and at a lower rate than neat PLA. This was attributed to an increase in hydrophobicity of the material which would limit the water diffusion and delay the hydrolysis. Eventually all samples reached the same degree of degradation ( $\approx 100\%$ ).

### Recommendations

Though numerous researches have introduced lignin into PLA with varying degrees of success, not all the elements have been fully investigated. For example, organosolv softwood lignins have not been researched to the same extent as other lignins and there is a lack of information regarding lignins effect on the OP and WVP. Additionally, some more aimed research could be done into, for example, the direct effect of linkage content in lignin. This could be investigated by isolating lignin from the same biomass source but with different organosolv isolation techniques, since this has been proven to greatly affect linkages.

Aside from these fundamentals, there are several pretreatments that deserve some additional exploration. Reacting hydroxyl groups through acetylation has been proven to increase miscibility, yet there is another simple way to reduce hydroxyl group content. Methylation of hydroxyl groups in lignin using dimethyl carbonate has been shown to be effective for both phenolic and aliphatic hydroxyl groups [51]. The application of methylated lignin in PLA might yield some interesting results.

As mentioned earlier, Sun et al. grafted rubber and lactide onto lignin and found that *d*-lactide performed better than *l*-lactide [46]. Perhaps an experiment could be done with direct grafting where *l*- and *d*-lactide are compared to see if *d*-lactide also achieves better results here.

It is known that lignin can be decolourised by oxidising hydroxyl groups, however, there seems to be no attempt in researching how this decolourised lignin affects a PLA matrix. Though this is not a priority per se, it might be worth investigating nonetheless.

## Conclusion

Lignin has shown the ability to mix with PLA and enhance some of its properties. A general trend that was observed and holds true for most lignin-PLA composites is that the tensile properties decrease with increasing lignin content, though some exceptions exist. Brittleness of PLA can be reduced by adding lignin which increases the elongation at break. Hardwood organosolv lignin has shown to be more effective in doing so than hardwood kraft lignin has, yet the latter showed a higher tendency to maintain tensile strength and modulus. Softwood lignin from organosolv processes was rarely researched and could not be properly compared to softwood kraft lignin. The two main methods of mixing lignin and PLA are solvent mixing and extrusion. There are some differences in the absolute properties of PLA between these two methods. This was attributed to the plasticizing effect of remaining chloroform from solvent casting. In spite of that, the relative improvements after adding lignin are not significantly different between the two methods. Various pretreatments that aimed to increase miscibility of lignin have been evaluated. Acetylation of lignin seems to be a common technique that has a positive effect on the miscibility in PLA and the final tensile properties. Furthermore, certain monomers can be grafted onto lignin to increase miscibility. This is commonly done with lactic acid, though a combination of  $\epsilon$ -caprolactone and lactic acid was also quite promising. Aside from tensile properties, the addition of lignin to PLA has also proven to positively affect the materials hydrophobicity and its UV-barrier properties.

The goal of this study was to show what factors affect PLA-lignin composites and if they could be applied for a wider commercial use in food packaging. The important influences found in this study have been highlighted above and certain composites appeared to be suitable for wider food packaging applications.



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## Appendix

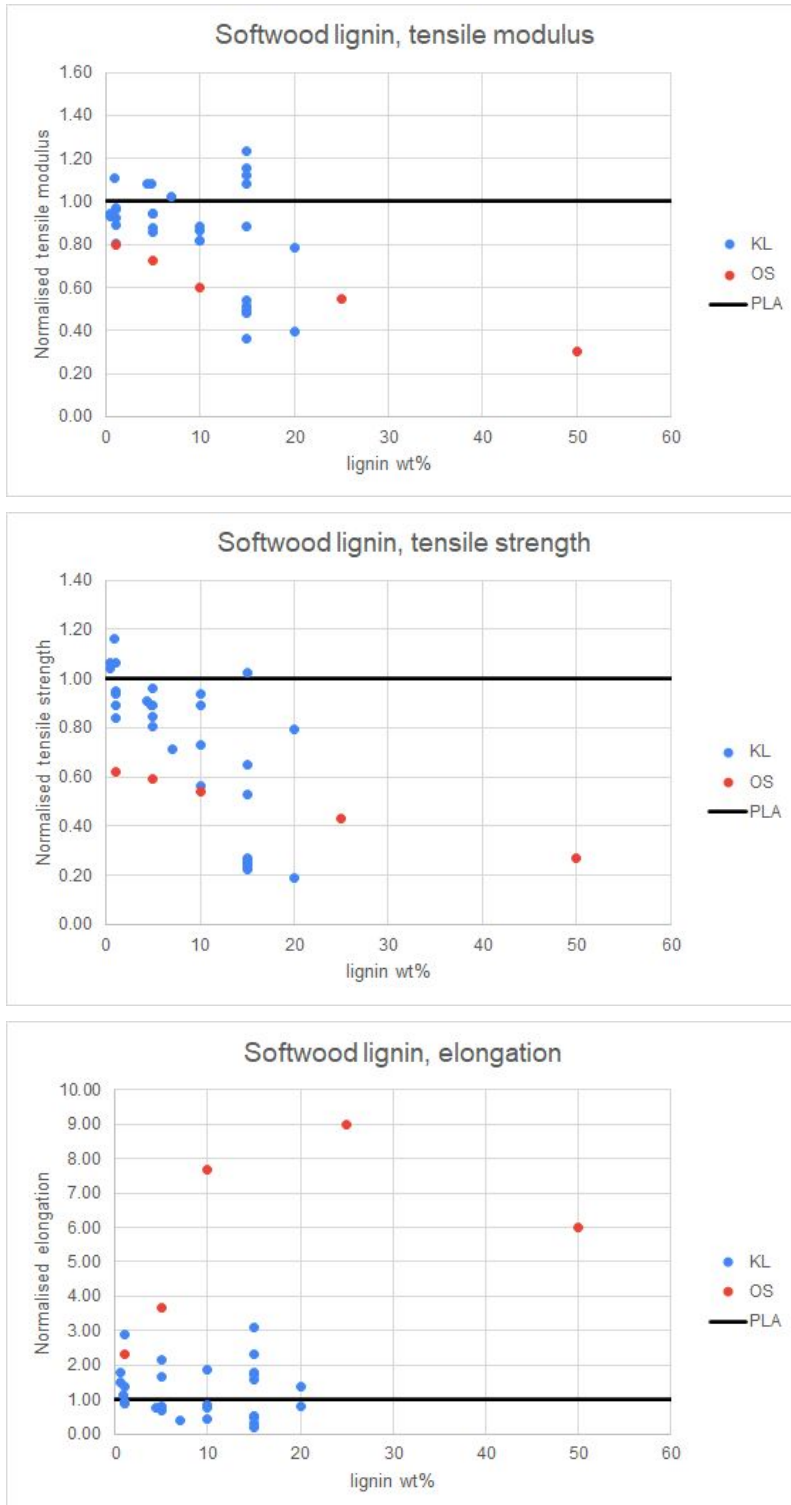


Figure A1: Normalised tensile properties of softwood lignin-PLA composites relative to PLA. (The organosolv lignin in these graph has undergone a pretreatment that most likely had a dominating effect on the final properties)

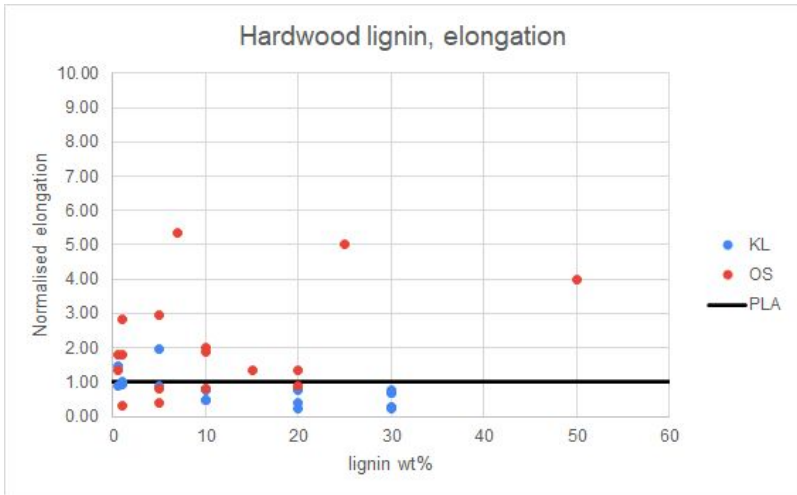


Figure A2: Normalised tensile properties of hardwood lignin-PLA composites relative to PLA.

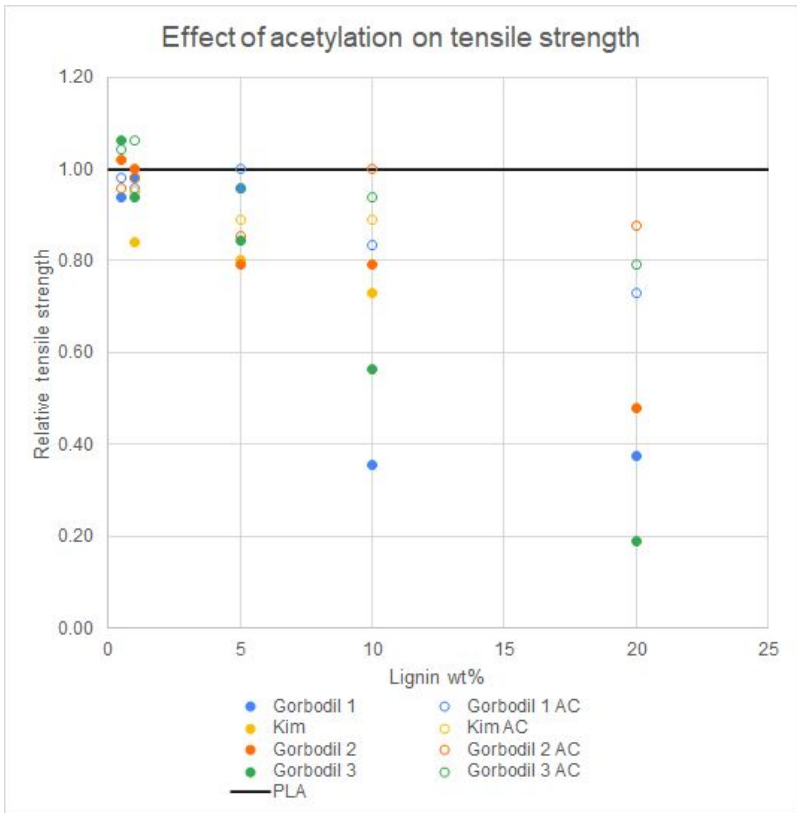
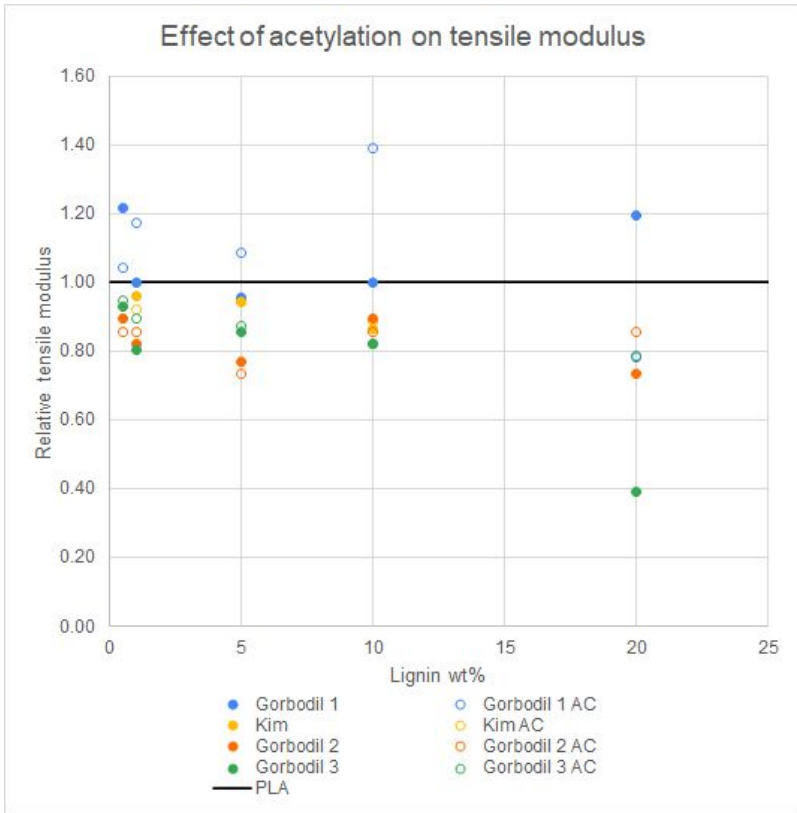


Figure A3: Normalised tensile properties of lignin-PLA composites with and without acetylation.



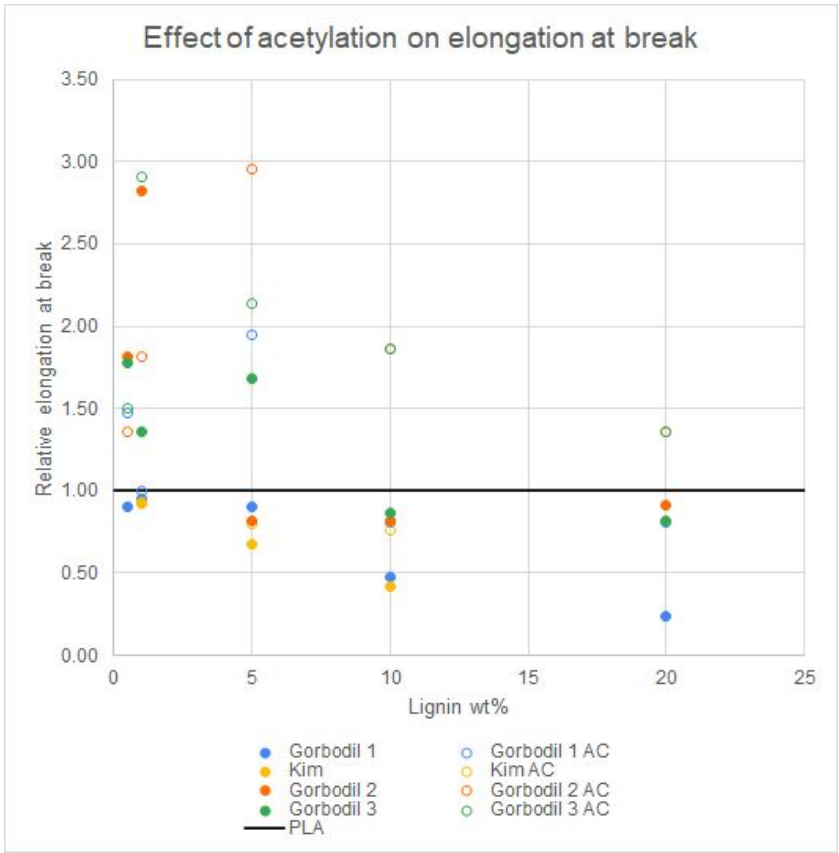


Figure A3 (Continued)