

Synthesis and Physiochemical Characterization of Biobased, Compostable  
Polymers Containing Lignin

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Stephanie Beret Harris

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## Dedication

This thesis is dedicated to Sabine Benda and Quinn Benda, who supply the sparks for my inner fire.

## Abstract

Biobased and compostable materials have gained in popularity as sustainable solutions for reducing waste and minimizing environmental impacts. Polylactide (PLA) continues to be a popular biobased polymer, but has limited use due to its brittleness, high vapor and ultraviolet (UV) light permeability. This study addresses these shortfalls through copolymerization of lactide (LA) with organosolv lignin from switchgrass (OSL) and delta-valerolactone (DVL) to produce 100 % biobased polymers with improved properties. Incorporation of hydrophobic OSL into poly(L-lactide) (PLLA), even in small quantities (up to 0.26%) resulted in a considerable decrease in water vapor transition rate (WVTR) of up to 64 %, nearly a 20 % decrease in UV light transmission, and slowing of hydrolytic degradation. Unfortunately, lignin appears to stop the chain propagation and effectively reduces overall  $\bar{M}_w$  of the copolymer. Young's modulus for these copolymers is affected little as stress and strain decreased proportionally with the addition of OSL, resulting in a copolymer that is nearly equal to PLLA in stiffness. To improve elasticity, terpolymers of PLLA-DVL-OSL were explored. The addition of DVL to the polymerization was found to increase UV transmission rate, an effect that could be counteracted through OSL addition. PLLA-DVL co and terpolymers showed low Young's modulus, characteristic for polymers with elastomeric properties. WVTR was seen to decrease with the addition of DVL and was even further reduced through addition of OSL, resulting in an overall WVTR reduction of up to 79 %.

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## **Introduction**

Polymers have become invaluable materials in modern society with seemingly endless uses. They can be made to function as inexpensive durable containers, soft fabrics, spongy materials, recyclable packaging, and protective films which collectively offer convenience and utility not previously attainable. Many industrial polymers are fluid at elevated temperatures, allowing for ease of processing. Polymers can be made moldable, ductile, flexible, chemically resistant, sealable, printable, lightweight, inexpensive, and with a wide range of physical and optical properties (Shogren, 1997; Marsh, 2007).

For decades, polymers have offered solutions to countless market-driven problems without considering the implications of these materials on health and the environment. Due to increasing understanding and publicity of the negative effects of chemical degradation products from plastics, the market for sustainable solutions is expected to continue to grow (Barnes, 2011).

Relatively recent advancements in the field of life cycle analysis have made it possible for scientists to objectively study the impacts of all the inputs and outputs related to a product from the time that materials used in production are originally extracted or synthesized, to the time that a product reaches its end of life. This capability has offered scientists the tools needed to understand the true impacts of products by examining the cumulative inputs and outputs including all of the resources and energy that go into making the product. Inputs can include fertilizer use, land use, carbon dioxide sequestration, raw materials,

and electricity. Outputs can include a variety of impacts on land, air and water coming from a product including carbon dioxide equivalents and other air emissions, aquatic toxicity, acidification, and eutrophication. Because of the exhaustive and careful analyses of everyday products, we are faced with making choices based not only on monetary values, but also on sustainability for the environment. For this reason, biopolymers – especially those that are compostable or biodegradable – have gained in popularity in recent years.

Poly lactide (PLA), despite drawbacks of being brittle and having high water permeability, continues to be a useful biobased and compostable biopolymer with numerous applications in industry, packaging, and medicine. As PLA is derived from plant starch, it has the ability to sequester large amounts of carbon dioxide. PLA also has FDA approval in both food and biomedical applications. One of the most important properties of PLA is its compostability. In a commercial landfill PLA breaks down to inert carbon dioxide and water, offering the potential to reduce landfill volumes. PLA is already commercially available and is produced on a commercial scale by NatureWorks in the United States, as well as by many other companies around the globe.

In order to address some of the drawbacks of polylactide, we have chosen to incorporate lignin into a copolymer with L(-)lactide (LA). Lignin is a plentiful natural biopolymer which is currently produced in vast quantities by the paper and biofuels industries. Carbon-rich lignin is usually a waste byproduct of cellulose industries, but is of particular interest to the growing bioeconomy



where the valorization of lignin could be an important step in making biorefinery processes economically feasible (Karlsson, 2014; Kautto, 2014). Though difficult to extract, and easy to condense, lignin also has the attributes of being inexpensive as well as hydrophobic (Campbell, 1996). Since both PLA and lignin are brittle polymers, we also explored the option of overcoming this characteristic property through the incorporation of delta-valerolactone (DVL), another biobased monomer derived from sugars that improves elasticity (Xiong, 2014).

With these things in mind, it will be possible to produce a 100% biobased material with improved properties. Our unique copolymerization approach was to incorporate organosolv switchgrass lignin (hereinafter referred to as OSL), a low molecular weight lignin that results from an organic extraction process, into polylactide and a PLA-DVL biopolymers. Our goals were to improve the water barrier properties and UV permeability of poly L(-)lactide (PLLA), while maintaining or improving mechanical properties. We also expected to slow, but not prevent, hydrolytic degradation.

Because our goal from the start has been to decrease the negative impacts of polymers on the environment compared to polymers derived from fossil fuel resources, we also worked to keep toxicity in processing to a minimum by using the least amount of solvents necessary to conduct good and verifiable research. We have worked to replace toxic catalysts with environmentally friendly catalysts and continue to work to develop methods that allow us to process our polymers without the use of toxic substances.

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## **Chapter 1 – Polylactide**

### **1.1 PLA as a renewable polymer**

Polylactide (PLA) continues to be an important renewable and compostable biopolymer with numerous applications in industry, packaging, and medical science and biotechnology. PLA, which is derived from renewable materials such as starch, has the ability to sequester large amounts of carbon dioxide and has FDA approval in both food and biomedical applications. Some of PLA's benefits include its ease of processing, stain resistance, and transparency. One of the most important properties of PLA is its compostability. In a commercial landfill, PLA breaks down to inert carbon dioxide and water, offering the potential to reduce landfill volumes. Other important advantages of PLA in medical science is its ease of removal by the body system and its ability to retain its shape over time (Ahmed, 2011).

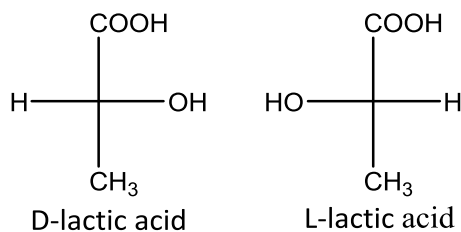
PLA is commercially available and is produced by companies around the globe. Though the polymer is still expensive compared to fossil fuel-derived plastics, it's expected that the price will drop over time as demand increases and companies such as BASF AG, NatureWorks, DuPont and Eastman Chemical Co. invest in increasing their production volumes (Guglielmo, 2008).

Despite its early peak as a polymer of value with multiple applications, science and industry have been challenged with shortcomings of PLA, including its brittle nature, poor ductility, high permeability, low thermal resistance, and

poor UV light barrier properties, all of which limit its uses (Nampoothiri, 2010, Okamoto, 2008).

## 1.2 Synthesis of PLA

The polymerization of PLA from the lactic acid monomer is well understood. Lactic acid is a three-carbon chain with a hydroxyl moiety end group as well as a carboxylic acid end group. Lactic acid exists as two isomers, L-lactic acid and D-lactic acid, as seen in Figure 1.1. L-lactic acid is the dominant form found in natural plant materials. Both the optically pure L- and D-lactic acid forms are only produced through fermentation of carbohydrates (Groot, 2010; Mirdamadi, 2002).

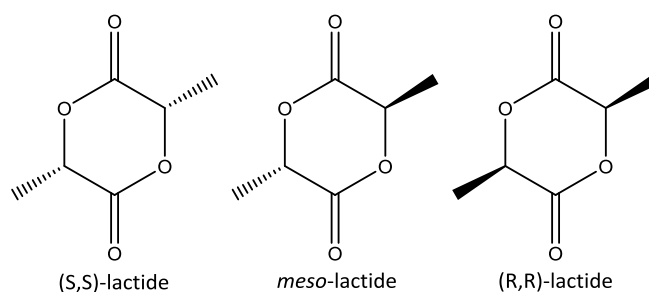


**Figure 1.1.** Stereoisomers of lactic acid, shown here as Fischer projections to emphasize the chirality of the isomers.

The lactic acid monomer can be heated and polymerized through a condensation reaction, but because this reaction is reversible. The water formed in the system actually limits the molecular weight achievable, as it also acts as an agent of depolymerization. For this reason, and because it is possible to control

the stereochemistry more accurately, it is preferred to dimerize lactic acid to form the lactide molecule, which is then polymerized using a catalyst through a ring-opening polymerization (ROP). This is most typically done in a bulk-polymerization, as described by Neiuwenhuis in 1992, in which the polymerization is heated to a temperature below the  $T_m$  of the resulting polymer.

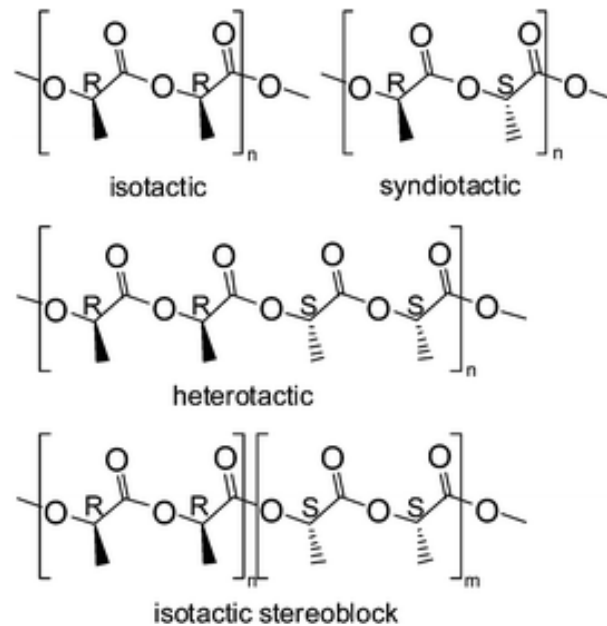
The lactide dimer has three isomers which are shown in Figure 1.2: (S,S)-lactide or L-lactide; (R,S)-lactide or *meso*-lactide; and (R,R)-lactide or D-lactide.



**Figure 1.2.** Stereoisomers of lactide: L-lactide, *meso*-lactide, and D-lactide (Ahmed, 2011).

By combining the stereoisomers of the lactide dimer, the structure of the PLA polymer can be varied. A 1:1 mixture of D-lactide, and L-lactide forms a racemic mixture, resulting in a heterotactic polymer that is amorphous and appears clear (Ahmed, 2011), whereas using only L-lactide, or D-lactide dimers results in a isotactic polymer which is typically over 72 % crystallized and appears cloudy (Nijenhuis, 1991, Ahmed, 2011). A syndiotactic polymer can be achieved by polymerizing *meso*-lactide. These configurations are shown in Figure 1.3. Varying the stereochemistry of the lactide monomers can have a

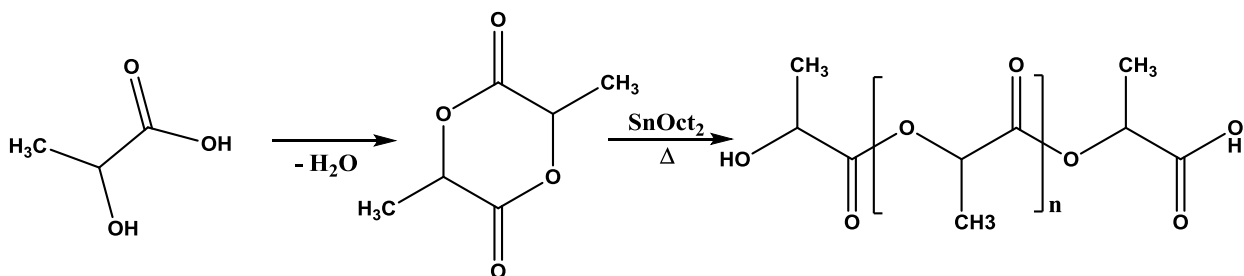
significant effect on molecular weight of the resulting polymers, and thus on the thermal and mechanical properties. Racemic mixtures of stereochemically pure PLLA/PDLA have been found to display a melting temperature ( $T_m$ ) 50 °C higher compared to PLLA and PDLA homopolymers (Duan, 2006). Glass transition temperature ( $T_g$ ) increases as a function of molecular weight. Degree of crystallinity also increases as a function of molecular weight, with no crystallization being detected in PLA with molecular weight lower than 550-1400 Da (Ahmed, 2011). In 1996 Kolstad found that for every 1% increase of *meso*-lactide, there is a 3 °C reduction in  $T_m$  of PLA and that with 3% *meso*-lactide being added to L-lactide, crystallization was more than two times slower compared to PLLA. With 6% *meso*-lactide being added to L-lactide, crystallization was up to ten times slower compared to PLLA. In 1997, Thakur, et al. reported stereosequence distributions and stereospecific preferences of lactide in ring-opening polymerization with tin (II) octoate ( $\text{Sn}(\text{Oct})_2$ ) as a catalyst. Their findings showed that there is a preference for stereo syndiotactic addition during the polymerization process when a mixture of D-lactide, L-lactide, and *meso*-lactide were fed into the polymerization (Thakur, 1997).



**Figure 1.3.** Structures of PLA polymers based on stereoisomer configuration of the lactide dimer in ROP (Dijkstra, 2011).

The polymerization of the lactide dimers through ROP commonly utilizes a catalyst such as  $\text{Sn}(\text{Oct})_2$  and takes place in an atmosphere absent of water, such as in a nitrogen atmosphere. This reaction is shown in Figure 1.4 below. Though cationic catalysts and organocatalysts have also been used to polymerize lactide, metallic catalysts, and  $\text{Sn}(\text{Oct})_2$  specifically, is used most commonly in industry because it yields high molecular weight PLA, it is stable for storage, highly soluble in organic solvents and has been approved by the US Food and Drug Administration (FDA) for biological uses in both food and medical applications (FDA, April 1, 2015, Mastutani 2015). Though FDA approved, it is important to note that  $\text{Sn}(\text{Oct})_2$  and other metal catalysts do have potentially toxic

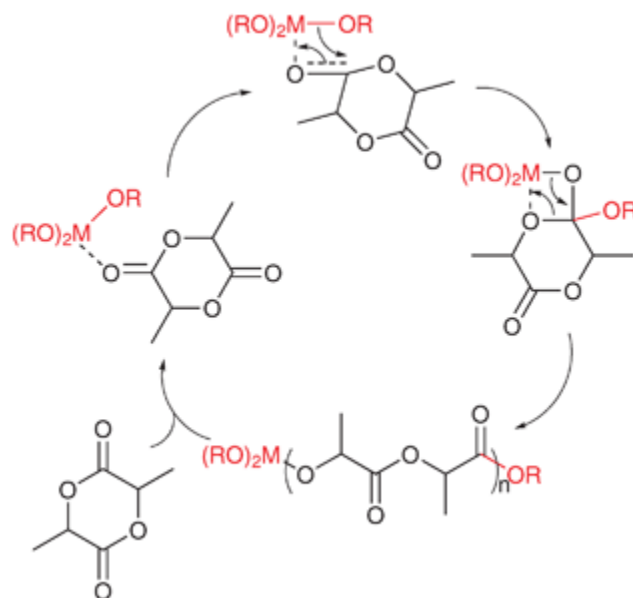
effects that should not be ignored in biomedical applications particularly (Xiao, 2012). In this reaction type, ring strain, which is directly related to the number of atoms in the ring, is the driving force for polymerization (Hiemenz, 2007).



**Figure 1.4.** Polymerization mechanism of lactic acid via lactide intermediate (Modified from Xiao, 2011).

Poly(lactide) propagates through a ring opening polymerization, adding to the growing chain in a coordination–insertion mechanism catalyzed by a metal-alkoxide catalyst. The proposed mechanism is shown in Figure 1.5 below.





**Figure 1.5.** The attraction of the metallic nucleophile of the catalyst is shown to open the lactide ring, allowing a coordinate-insertion to the end of the growing polymer chain. Reproduced from Thomas, 2009 with permission from The Royal Society of Chemistry.

Synthesized PLA is dissolved and reprecipitated after polymerization to remove any excess monomer which acts as a plasticizer, and has the effect of lowering the strength and stability of the polymer (Hartmann, 1998).

PLA is a thermoplastic polymer with mechanical and thermal properties depending on stereochemistry, as suggested previously. Typical physical properties of PLA reported by Masutani and Kamura are shown in Table 1.1 below (Masutani, 2015).

**Table 1.1.** Typical properties of PLA. Modified from Fiori S. Industrial Uses of PLA. In: Poly(lactic acid) Science and Technology: Processing, Properties, Additives and Applications. The Royal Society of Chemistry, Cambridge. 2015. 317-333, with permission from the Royal Society of Chemistry.

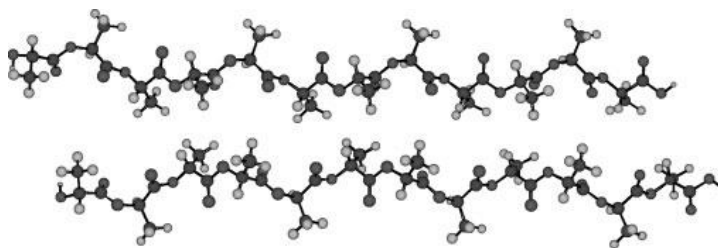
$\bar{M}_w$ of PLA (kDa)	$T_g$ (°C)	$T_m$ (°C)	$X_c$ (%)
100-300	55-65	130-180	10-40

$T_g$  = glass transition temperature

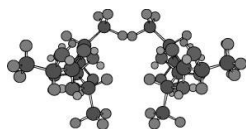
$T_m$  = melting temperature

$X_c$  = percent crystallinity

It is interesting to note that the stereocomplex form of PLA (sc-PLA), which is a blend of the PLLA and PDLA homopolymers, has more use in industrial applications as  $T_m$  is 230 °C, or 50 °C higher than that of either homopolymer due to the crystal form of sc-PLA, which is trigonal as opposed to the orthorhombic structures of PLLA and PDLA, as seen in Figure 1.6 (Fukushima and Kimura, 2006). In 1987, Ikada, et al. reported that an exact 1:1 ratio of the two enantiomers is most favorable for the stereocomplex blend, noting that the optical purities of the monomer units were also important. It is preferred to utilize monomers of more than 90% purity.



a. Conformations of PLLA and PDLA, respectively.



b. Conformation of sc-PLA.

**Figure 1.6. a. and b.** Conformations of PLA. Reprinted with permission from Ikada Y, Jamshidi K, Tsuji H, Hyon S-H. Stereocomplex Formation between Enantiomeric Poly(lactides). *Macromolecules*. 20, 904-906. Copyright (1987) American Chemical Society.

### 1.3 Properties of PLA

Many properties are of interest when describing polymers. These include average molecular weight of the polymer, glass transition, melting and crystallization temperatures, percent crystallinity and tensile properties.

Weighted average molecular weight ( $\bar{M}_w$ ) is a common representation of molecular weight based on the average weight of polymer chains in the distribution of all polymer chains, determined according to Equation 1.1.

$$\bar{M}_w = \frac{\sum(N_i M_i)^2}{\sum N_i M_i} \quad (1.1)$$

Where  $M_i$  is the molecular weight of a chain, and  $N_i$  is the number of chains of

that molecular weight.

Number average molecular weight ( $\bar{M}_n$ ) is determined according to Equation 1.2.

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i} \quad (1.2)$$

The polydispersity index (PDI) of the polymer chains is determined by the ratio of  $\bar{M}_w$  to  $\bar{M}_n$ , as seen in Equation 1.3 and describes how close together the molecular weights of all polymer chains are to each other. A PDI = 1 where  $M_w = M_n$  represents a monodisperse polymer where all chain lengths are equal. As polydispersity increases, PDI increases, indicating a broader range of molecular weights.

$$PDI = \frac{M_w}{M_n} \quad (1.3)$$

Temperatures that are of interest to the study of polymers include the glass transition temperature ( $T_g$ ) which is of particular interest because it describes the temperature at which a polymer becomes rubbery, or pliable. This transition point also represents a change in tensile properties of the polymer, and when low, can represent a flexible polymer. Below the  $T_g$  the polymer becomes glassy, or rigid. Between the  $T_g$  and the  $T_m$ , polymers range from nearly 100% crystalline to 100% amorphous. This parameter is inherently connected to the application of the polymer. The melting temperature ( $T_m$ ), is of interest because it represents the temperature above which all polymer strands become mobile and

the material is a liquid.  $T_m$  is very important in processing polymers. The temperature of crystallization ( $T_c$ ) is also of interest to polymers that exhibit some crystallization, such as PLA.  $T_c$  is affected by the rate at which a polymer is cooled.

The percent crystallinity ( $X_c$ ) is of interest as it influences mechanical strength, degradation resistance, and barrier properties. The parameter  $X_c$  is calculated using heat of fusion ( $H_f$ ) of an experimental polymer in relation to the  $H_f$  of the theoretical 100% crystalline polymer which must be extrapolated, according to Equation 1.4.

$$X_c = \frac{\Delta H_m - \Delta H_c}{\Delta H_{m100\%}} \times 100\% \quad (1.4)$$

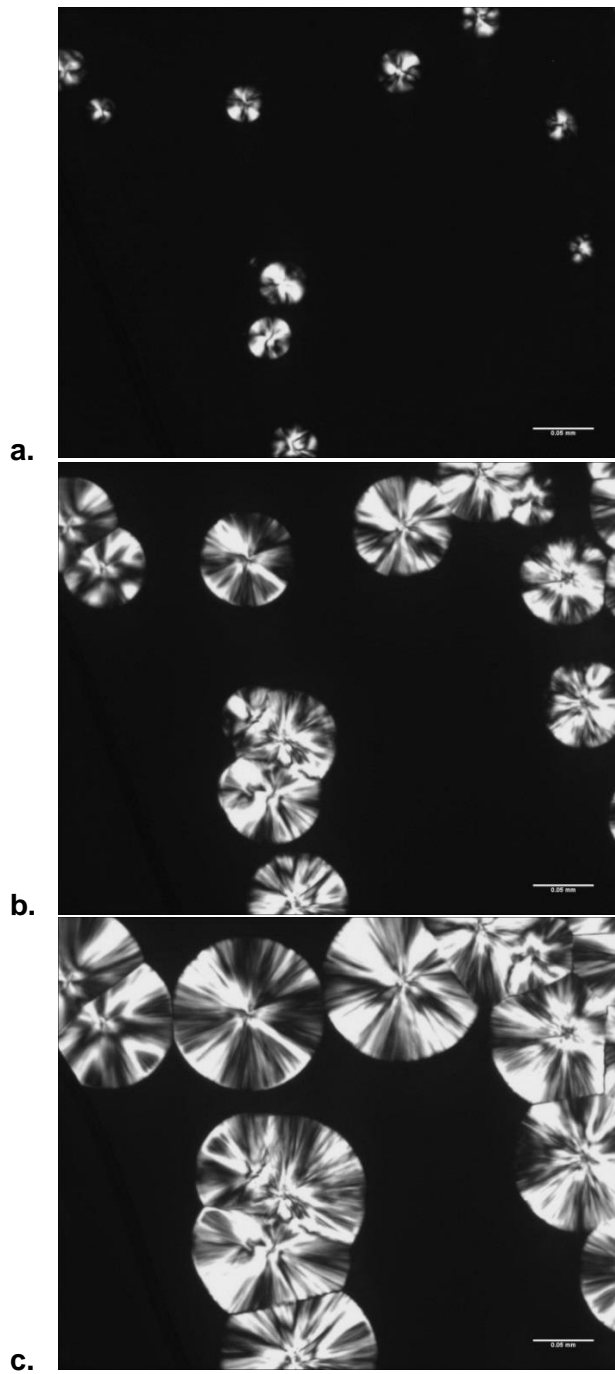
Where  $\Delta H_m$  is the enthalpy of melting in J/g,  $\Delta H_c$  is the enthalpy of crystallization in J/g, and  $\Delta H_{m100\%}$  is the enthalpy of melting 100% crystalline polymer. The  $\Delta H_{m100\%}$  of PLLA, 93.1 J/g according to Henton, 2005, was used here to estimate  $X_c$ .

Molecular weights and parameters such as  $T_g$ ,  $T_m$ , and  $X_c$  are dependent on a variety of factors including polymerization methods, thermal history, stereochemical purity, molecular weight, and stereochemical structure of the polymer – amorphous versus crystalline, including the thickness of the rigid amorphous fraction of the polymer (Jiang, 2010). Typical property values for PLA are shown in Table 1.1.

PLLA and PDLA are semicrystalline polymers, with both crystalline and amorphous phases, while PDLLA is amorphous due to the random distribution of

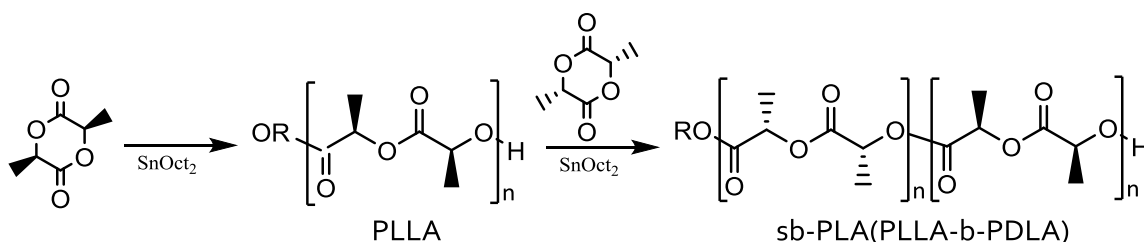
the optically active isomers. Crystallinity of PLLA and PDLA can vary greatly depending on thermal history and molecular weight. Crystallinity has even been shown to have dropped to 0% upon rapid cooling, such as that is most likely to occur during injection molding (Ke, 2003). Methods of inducing crystallization by adding compounds that act as nucleating agents have been developed to counteract this effect (Liao, 2007; Li, 2007).

Park, et al. determined that the growth of PLA spherulite crystals is faster around 100 °C, a proper annealing temperature, than at lower temperature (Park, 2006). Long chain polymers of polylactide form structures composed of both amorphous and crystalline areas. The spherulites can be witnessed forming in vitro with a polarizing light microscope, as shown in Figure 1.7, revealing both the crystalline structure and speed of crystallite growth over time. The Maltese cross pattern seen here is characteristic of poly(L-)lactide (PLLA) crystallization.



**Figure 1.7.** Polarized light microscopy image time series shows spherulite growth at ambient temperature of pure L-lactide at **a.** 5 seconds; **b.** at 5.5 minutes; and at **c.** 11 minutes. Photo credit: Harris S, 2012.

Stepwise ROP of the L-lactide and D-lactide enantiomers via bulk polymerization utilizing a tin-octoate ( $\text{SnOct}_2$ ) catalyst has become the most common method for PLA polymerization. This method was first successfully introduced by Komazawa and Tang while forming a diblock stereoblock PLA (sb-PLA) with  $\bar{M}_w$  200 kDa by first polymerizing one isomer to a low  $\bar{M}_w$ , and then adding the second monomer to the reaction. It was found that the  $\bar{M}_w$  of the first monomer must be kept low to allow mixing with the second monomer in bulk. This process is represented in Figure 1.8.  $T_m$  was seen to increase to 214 °C by using a ratio of 20:80 PDLA:PLLA and to 216 °C using a ratio of 50:50 PDLA:PLLA. There is the added significance of this result due to D-lactide being much more expensive to produce than the L-lactide isomer (Komazawa, 2010).



**Figure 1.8.** Synthesis of sb-PLA by stepwise ROP (modified from Thomas, 2009).

Mechanical properties are also important to the understanding and selection of polymers for specific applications. Stress ( $\sigma$ ) is the maximum engineering stress, or applied directional force, without fracture. The stress at the point of fracture or breaking of a material is known as the tensile strength. Strain



( $\varepsilon$ ) is the material deformation response in the direction of an applied force in relation to the length of the material. The ratio of stress to strain yields the Young's modulus ( $E$ ), a common parameter of interest which reveals the flexibility, or stiffness of a polymer. A value of  $E$  below 1 represents a highly compressible and flexible polymer, while higher values represent more brittle polymers. Typical tensile values for PLA are shown in Table 1.2. These values are compiled from tensile testing of the materials according to ASTM standards (ASTM D882, ASTM 638).

**Table 1.2.** Mechanical properties of PLA. Modified from Ruellan A, et al. Plasticization of Poly(lactide). In: Poly(lactic acid) Science and Technology: Processing, Properties, Additives and Applications. Jimenez A, et al. (Eds.). The Royal Society of Chemistry, Cambridge. 2015. 124-170. Reproduced by permission of the Royal Society of Chemistry.

$\bar{M}_w$ of PLA (kDa)	$\sigma$ (MPa)	$\varepsilon$ (%)	$E$ (GPa)
74-137	38-57	7 $\pm$ 2	2.05 $\pm$ 0.04

#### 1.4 Modifications of PLA: Plasticizers

There has been much success in improving many of the properties of PLA including mechanical and thermal properties for a variety of applications utilizing plasticizers. Because one of the most attractive properties of PLA is its

compostability, plasticizers used with PLA tend to be both biobased and either compostable or biodegradable, which adds an extra layer to the challenge of improving PLA's mechanical and processing properties.

Plasticizers are typically molecules that interact with a polymer to produce swelling without chemically reacting with the polymer. Intramolecular forces between the plasticizer and polymer are important, however, so that the plasticizer will not leach out of the system due to a lack of attraction which can initiate the tendency to migrate from the polymer over time, in which case the brittle nature of the plastic material returns. Therefore, the choice of a plasticizer should also rely on the structure of the polymer (Shtarkman, 1983). Good plasticizers have the effect of lowering the  $T_g$  of PLA, thus offering more flexibility and decreasing the brittleness of the polymer (Yuan, 2016).

PLA plasticizer blends can be tailored to meet specific needs, depending on how the polymer is to be used, to reach the appropriate processing characteristics, toughness, flexibility, and compostability or biodegradability (Mekonnen, 2013).

A variety of small molecular weight polymers and macromolecules have been successfully added as plasticizers to modify PLA. Some common PLA plasticizers include poly(ethylene glycol) (PEG), poly(ethylene oxide) (PEO), poly(propylene glycol) (PPG), poly( $\epsilon$ -caprolactone), oligomeric polyesters, and citrate esters which have all been shown to have significant effects on  $T_g$  and

tensile properties compared to the PLA homopolymer (Tsuji, 1996, Labrecque, 1997, Jacobsen, 1999, Ke, 2003, Maglio, 2004).

In 2013, Mekonnen, et al. published a review of the properties of PLA blends including many common plasticizer blends. These properties can be seen in Table 1.3 below.

**Table 1.3.** Mechanical and thermal performance of PLA plasticized with different modifiers. Mekonnen T, Mussone P, Khalil H, Bressler D. 2013. Progress in bio-based plastics and plasticizing modifications. Journal of Materials Chemistry A. 1, 13379-13398. Published by the Royal Society of Chemistry.

Modifier	$\bar{M}_w$ (Da)	Conc. (wt %)	$T_g$ (°C)	$\sigma$ (MPa)	$\varepsilon$ (%)	$E$ (MPa)
PLA (no modifier)	137000	100	59	51.7	7	1720
Triethyl citrate	276	20	32.6	12.6	382	
Triethyl citrate	360	20	17.6	7.1	350	
Acetyl triethyl citrate	318	20	30	9.6	320	
Acetyl tributyl citrate	402	20	17	9.2	420	
PEO*	10000	21	31	49	7	320
Poly( $\varepsilon$ -caprolactone)	10000	20	35	19	25	961
Glycerol	92	20	53	-	-	
PEG <sup>†</sup> monolaurate	400	20	21	-	142	1750
Plasticized TPS	1500	25	-	30.2	2.9	1460
PEG <sup>†</sup>	1500	10	34.3	15.1	150	
PEG <sup>†</sup>		20	23.2	14.6	150	

\* PEO = polyethylene oxide

† PEG = polyethylene glycol

As seen in Table 1.3, many biobased plasticizers have the desired effect of decreasing  $T_g$  compared to the PLA homopolymer. This, in turn, has the desired

effect of increasing flexibility, as can be seen by the increase in elongation at break in most cases. However, there is also the unfortunate effect of a loss in toughness, as displayed by the decrease in tensile strengths.

Inexpensive and effective nanoparticle fillers have been successfully added to improve the crystallinity, thermal stability and Young's modulus of PLA (Thakur, 1996; Sinha Ray, 2003). In 2016, Xue, et al. found that a blend of PLA with up to 20% ultrafine fly ash, considered a waste material, yielded a material with increased tensile strength, though the thermal stability compared with the homopolymer was decreased.

### **1.5 Modifications of PLA: Composites**

Composites are made from two or more materials with different physical properties that remain distinctly different and are used to make new materials with properties other than those of any of the component materials. The properties of specific composites can be designed for a variety of applications and depend on the materials chosen in a composite. Important properties for biocomposites include water absorption, degradation, strength, strain, thermal properties, and biodegradability or compostability. Uses for composites containing PLA include building materials, sporting equipment, automobile components, biomedical applications and short life-span products that are ultimately considered disposable.

Because PLA is biobased, compostable, functions as a thermoset material

whose properties can be finely tuned (as discussed previously), and is relatively inexpensive to obtain compared to other biobased polymers, it is of special interest in the field of natural composites.

There are several advantages, as well as some disadvantages, of using biobased and compostable PLA in composites with natural fibers, which are commonly referred to as “green composites.” Depending on the function of a specific material, one of the greatest strengths, but also one of the greatest drawbacks of degradable composites containing PLA is their limited durability due to their degradation. When they do degrade, however, they have the added bonus of not leaving toxic residues. When used to form a composite with natural fibers, fungal and bacterial growth are also a concern. (Dicker, 2013). The limitations of PLA in green composites can be overcome by using adhesion promoters, additives and fillers, or by chemically modifying either the PLA or the natural fibers (La Mantia, 2011).

Successes have been found incorporating PLA with a variety of green materials. One example is a composite of PLLA and kenaf fibers which was shown to have good mechanical properties, contributed to the strong interaction between the kenaf and PLLA fibers (Nishino, 2003). In 2006, a PLA/bamboo fiber composite with improved mechanical properties, increased thermal stability, and decreased degradation behavior was produced by using a lysine-based coupling agent was produced (Lee, 2006). Table 1.4 below represents a compilation of the mechanical properties of selected PLA composites that represent improved

properties over the PLA homopolymer for comparison (Lu, 2014; Baheti, 2013; Shu, 2005; Finkenstadt, 2007).

**Table 1.4.** Mechanical properties of PLLA and PLA composites.

Modifier	$\sigma$ (MPa)	$\varepsilon$ (%)	$E$ (GPa)
PLLA	61 $\pm$ 3.2	3.1	1.7-2.5
PLLA-KBCF2*	67 $\pm$ 2.2	13 $\pm$ 2.3	2.4 $\pm$ 0.2
PLLA-1% JNF**	189 $\pm$ 34	57.6 $\pm$ 4.0	1.45 $\pm$ 0.03
PLLA-30%C†	37.9	7.9	1.5
PLLA-10%SBP‡	37.5	6.7	1.04

\* PLLA-KBCF2: Composite of PLLA/silane coupling agent KH560-treated bamboo cellulosic fiber composite

\*\* PLLA-10% JNF: composite of PLLA/1 wt% pulverized, 0.1 wt% sodium sulfate-treated kenaf fiber

† PLLA-30%C: Composite of PLLA/biomass coproduct of cuphea oilseed extraction

‡ PLLA-10%SBP: Compression heated composite of PLLA/finely ground sugar beet pulp (~300  $\mu$ m)

There have been other successes in improving the mechanical properties of composites by incorporating PLA, but these efforts appear stalled due to the challenges of PLA, as stated previously. It should also be noted that the surface characteristics of composite materials and mixing techniques are also important to avoid agglomerates and allowing good dispersion and consistent properties (Zhou, 2015). Common chemical modification methods for natural fibers include alkali treatment, esterification, cyanoethylation, and silane treatment (Ghosh, 2010).

## 1.6 Modifications of PLA: Copolymers

Research on PLA copolymers has continued to generate novel products with a range of uses for several decades. Because the covalent bond of the ether linkage in the PLA dimer can be easily broken using a cationic catalyst acting as a Lewis acid, a variety of monomers can be inserted into the growing polymer through ROP. As more has become known about the properties of the homopolymer and its stereospecific interactions, more finely tuned copolymers have been synthesized for specific uses for biomedical applications, food packaging, and 3D printing more recently, as well as for many other purposes.

Monomer addition to a polymer can occur in different ways. Chain-growth, which describes a series of initiated events in which an active growth center initiates the addition of many monomers. Free radical polymerization and chain transfer polymerization are examples of chain-growth. These may be initiated by chemical reactions, heat, or light. Step-growth, or condensation molecules grow through a series of steps and includes the class of polymers known as polyesters, such as polylactide.

Polyester synthesis methods include esterification, ester interchanges with alcohols or esters, or lactone (such as lactide) polymerization through ring-opening. These reactions are usually catalyzed.


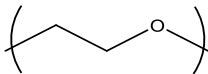

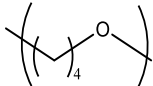
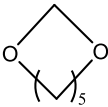
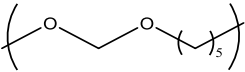

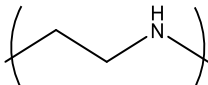
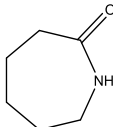
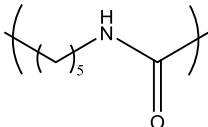
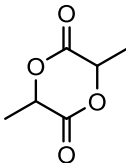
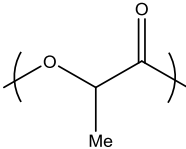
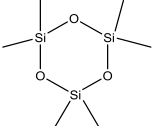
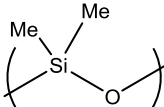
Early co-monomers of PLA included glycolic acid, ( $\epsilon$ -caprolactone), ethylene glycol, ethylene oxide, ethylene vinyl-acetate, phenylene oxide,

polypropylene glycol, other lactones,  $\alpha$ -hydroxy acid, lysine, and oxyethylene, among others. Ethylene glycol, propylene glycol, phenylene oxide, and various lactones remain popular co-monomers found in literature. These co-monomers are representative of a group of monomers that are amenable to ROP, as seen in Table 1.5.



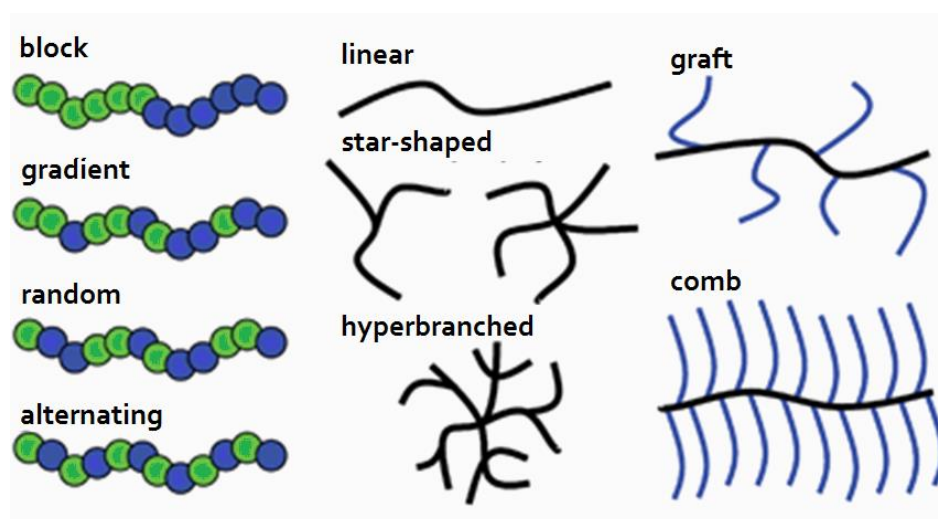
**Table 1.5.** Examples of monomers amenable to ring-opening polymerization.

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Monomer class	Example	Repeat unit
Epoxides		
Cyclic ethers		
Cyclic acetals		
Imines (cyclic amines)		
Lactams (cyclic amides)		
Lactones		
Siloxanes		

There are several advantages to copolymerizing lactide that cannot be reached through combining PLA with plasticizers or forming PLA composites. With copolymerization, the properties of the base material are changed, and there is no leaching of plasticizer, or disconformity, as with composites. Because copolymers have so many tunable parameters, they also offer a variety of advantages not attainable with PLA homopolymers that range in properties and have varied applications.

Because copolymers grow in a variety of ways, there are a variety of architectures that can be obtained with copolymerization. Some of which can be seen in Figure 1.9 (Fournier, 2007).



**Figure 1.9.** Selected copolymer architectures (published by the Royal Society of Chemistry).

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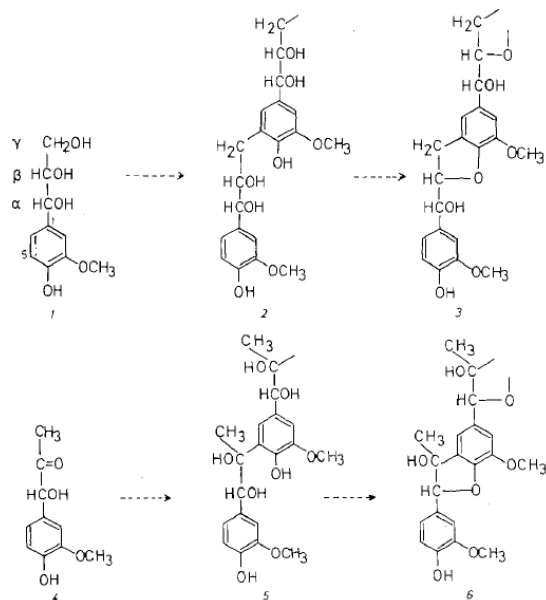
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## Chapter 2 – Lignin

Lignin is a natural biopolymer extracted from lignocellulosic material. Currently, the majority of extracted lignin is burned to recuperate some of the energy that is used in processing cellulosic material in biocellulosics industries such as the paper and pulping, and cellulosic ethanol industries because lignin has a comparatively high energy content. Lignin has also found limited uses as an additive for animal feeds, for use in structural fillers, surfactants and additives for bio-composite materials in order to improve material properties such as hydrophobicity, stiffness, and crystallinity (Olsson, 2014). However, due to its structure and high carbon/oxygen ratio, it is a great source of phenolic carbon compounds with a large potential for higher value applications (White, 1987).

What is known about the composition and structure of lignins, has been discovered through cooperative efforts. This body of knowledge has continued to build for over a century.

Circa 1930, Freudenberg published structures, shown in Figure 2.1, found in lignin. These were based on the elemental composition and chemical reactions of lignin including acetylation, oxidation, acidolysis, sulfide, thioacidolysis, hydrolysis, and alkaline treatments, among others. Freudenberg's structures were based on guaiacyl groups linked in a continuous fashion by condensation – like “building blocks.” Freudenberg further deduced methoxy and hydroxyl groups on a side chain and ether linkages between the basic building blocks (Adler, 1959).

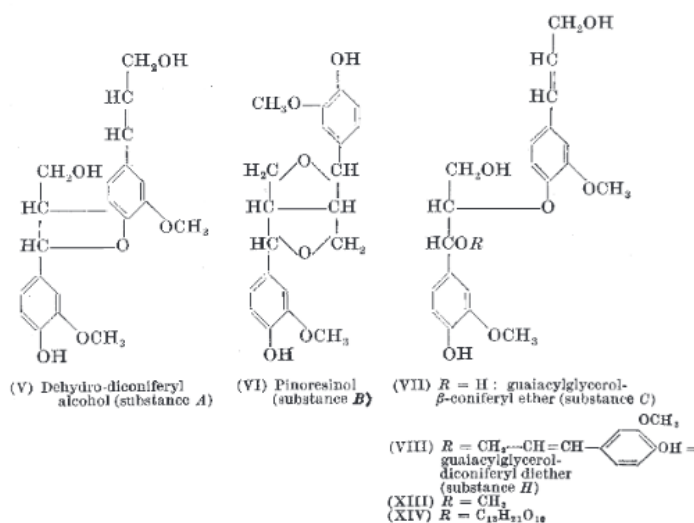


**Figure 2.1.** Proposed model of lignin components proposed by Freudenberg, c. 1930 (reprinted with permission from Acta Chemica Scandinavica).

The Freudenberg model borrowed from Klason's 1907 hypothesis that lignin is an oxidation product of coniferyl alcohol. Others at the time believed that lignin precursors were the same as those for cellulose. Approaches to understanding the structure of lignin focused on degradation reactions that would yield identifiable components, synthesis of model compounds formed from believed precursors to lignin, while analytic spectroscopic methods were still being developed.

By measuring UV absorption of wood sections, Lange showed that lignin was aromatic in nature in a work published in 1954. In an article published by Freudenberg in Nature in 1959, it was reported that lignin is made of similar, but

not identical, subgroups. Lignin was described as being built up from coniferyl and sinapinic alcohols. This was related to the chemical reactions studied previously, as well as reactions that Freudenberg conducted himself. Freudenberg found that the dehydrogenated polymer exhibited a mixture of lignin fragments, as seen below in Figure 2.2. It was unclear whether the lignin subunits formed a regular polymer, like cellulose or other natural polymers (Freudenberg, 1959).



**Figure 2.2.** Proposed structure of spruce lignin fragments by Freudenberg.

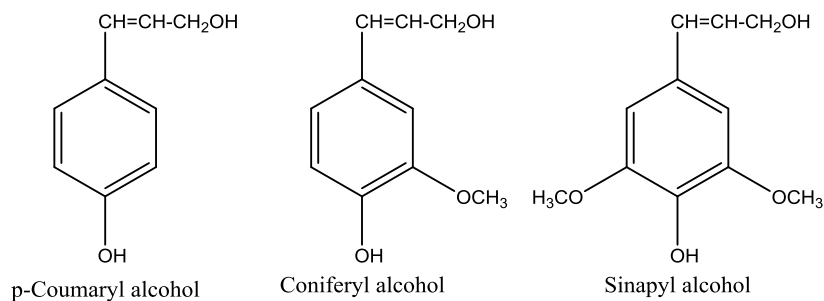
Reprinted by permission of Macmillan Publishers Ltd: Nature, 1959.

Advances were made in infrared spectrometry by a large number of scientists, and in 1960, assignments of infrared (IR) bands were made in coniferyl lignin. In 1954 Aulin-Erdtman and Goldschmid used an ultraviolet spectroscopy (UV) differential method to estimate the phenolic hydroxyl content of lignin in solution (Aulin-Erdtman, 1954, Goldschmid, 1954).



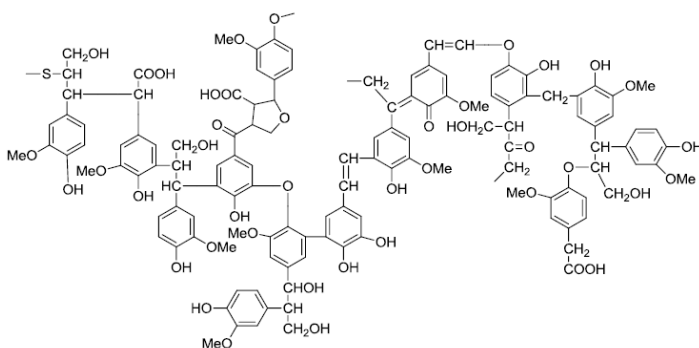
1964 appears to be the first time that nuclear magnetic resonance (NMR) spectroscopy was applied to elucidate the structure of lignin. NMR has the advantage of not altering the substance being tested, but uses the magnetic properties of a substance's atomic nuclei to delineate its makeup. Ludwig, Nist, and McCarthy applied  $^1\text{H}$  NMR to estimate the relative amounts of various functional groups. From this early NMR research, it was found that 50-60% of softwood lignin was condensed, and that the structure contained hydrogen bonding (Ludwig, 1964).

$\beta$ -O-4,  $\beta$ -5 and  $\beta$ - $\beta$  linkages were determined from dimeric and trimeric products obtained, and Freudenberg and Neish published a review of monomeric intermediates in 1968 based on IR spectroscopy, which had also been used to determine carbonyl groups in lignins (Freudenberg, 1968). The monolignol structures determined by Freudenberg and Neish, which are still in wide acceptance today, are shown in Figure 2.3.



**Figure 2.3.** Monolignol structures, modified from Freudenberg and Neish, 1968.

In 1971 Marton proposed a structure for kraft lignin, based on a statistical schematic of the ether phenolic groups. This schematic, shown below in Figure 2.4, exhibits ether and stilbene linkages within lignin based on kraft delignification reactions (Marton, 1971). In that same year, Goring published a paper in which he stated that lignin is a “random, three-dimensional network polymer” (Goring, 1971). This finding included the knowledge that various plant types have varying amount of monolignols, and that these varied not only between hardwoods and softwoods, but also between species, and even between compression wood and noncompression parts of a singular tree.

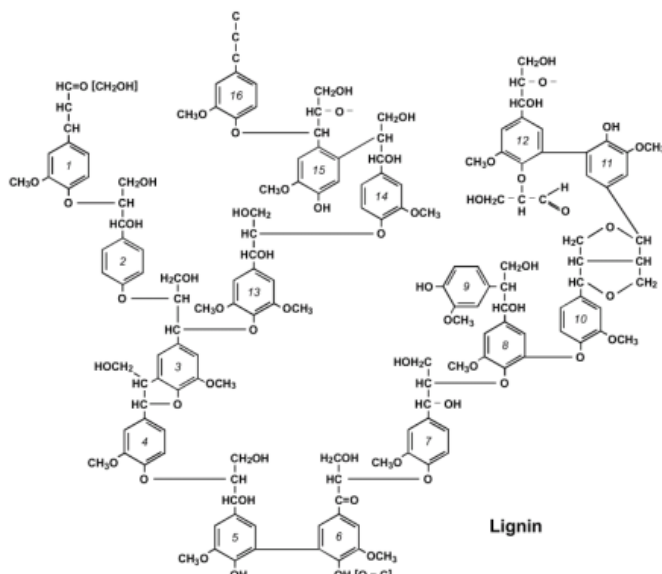


**Figure 2.4.** Proposed structure of alkaline-treated kraft lignin. Republished with permission of John Wiley and Sons, Inc. Marton J. Reactions in Alkaline Pulping. In: Lignin: Occurrence, Formation, Structure, and Reactions. Sarkanen KV, Ludwig, CH. (Eds.). 1971; permission conveyed through Copyright Clearance Center, Inc.

Using  $^{13}\text{C}$  NMR, Nimz was able to show, along with the contributions of several others over a number of years, that lignin is a branched-chain polymer most likely chemically combined with carbohydrates in 1973 (Nimz, 1974). In 1981, Nimz was able to further elucidate the structural differences between hardwoods, softwoods, grasses, and compression wood lignins based on  $^{13}\text{C}$  NMR used to study acetylated lignin products (Nimz, 1981).

Gas chromatography (GC) methods were also developed around this time, as it had recently been discovered as a powerful separation technique. Larsson and Miksche used GC to identify the products of permanganate oxidation of lignin which contributed to the quantification of linkage frequency in several tree types (Larsson, 1971). In 1974, Glasser used  $^1\text{H}$  NMR to elucidate the structure of acetylated liginosulfonates, based on synthesized lignin-like sulfonates and computer modeling to propose a structure for softwood lignin. Adler and Gierer were able to determine the number of benzyl hydroxyl and ethers in milled wood lignin, as well as the number of non-cyclic benzyl ether groups using a method of alkylation with hydrochloric acid (Adler, 1955). Adler proposed a structure of spruce lignin in 1977, shown below in Figure 2.5. The structure shows lignin as a branched polymer with a variety of functional groups including aliphatic and phenolic hydroxyls, carboxy, carbonyl, and methoxy groups. This structure comprised knowledge Adler had gained from others, as well as from his own experiments with acidic dioxane-water showing that one fourth to one third of the guaiacyl propane units were joined by  $\beta$ -aryl ether

linkages, and from experiments quantifying phenylcoumaran moieties through acid dehydrogenation studies resulting in stilbenes (Adler, 1977).

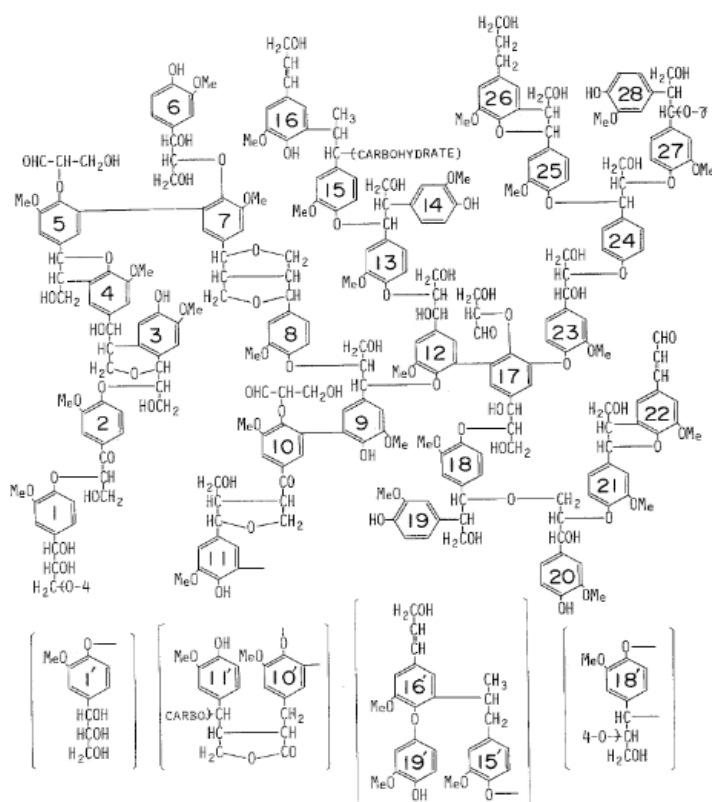


**Figure 2.5.** Proposed model structure of spruce lignin by Adler. *Lignin Chemistry – Past, Present and Future. Wood Science and Technology*. 11, 1977. 169-218. Adler, E. Fig. 30. Prominent Structures in Softwood Lignin. With permission of Springer.

In 1989, Goring refined his previous view of lignin, stating that rather than a random, three-dimensional network polymer, a more encompassing description needs to include all that has been learned about lignin and its soluble derivatives. He revised his earlier statement regarding the lignin structure to say that lignin in the true middle lamella of wood is a random three-dimensional network polymer comprised of phenylpropane monomers linked together in different ways, and that lignin in the secondary wall is a nonrandom two-dimensional network polymer. He notes that lignins differ based on their location in the plant and

among plant varieties (Goring, 1989). This updated definition was inclusive of knowledge gained from various sources over the years.

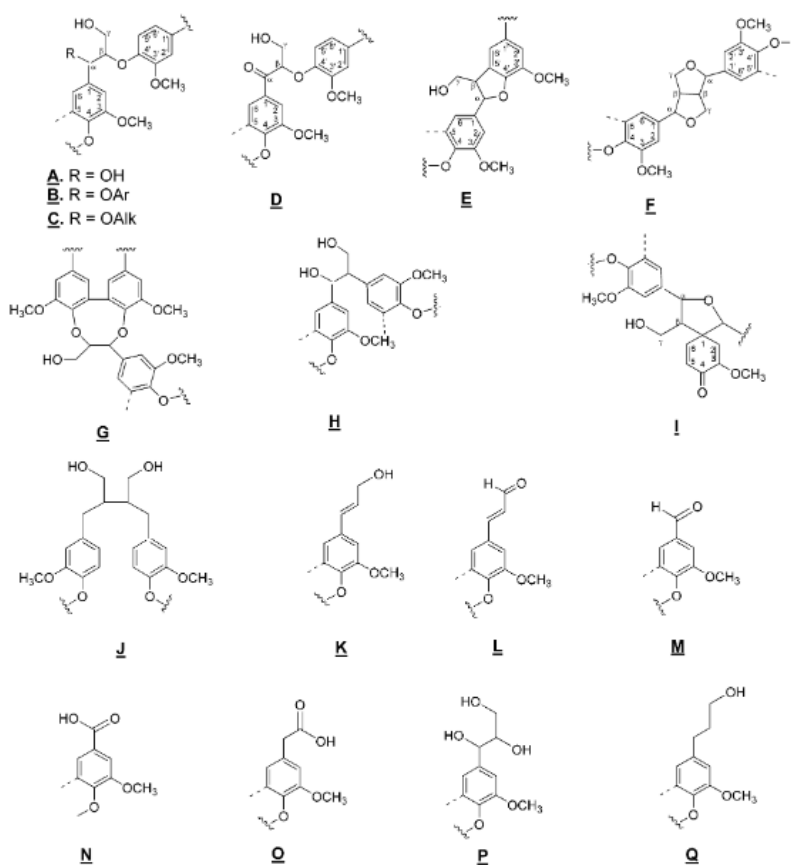
A further structure of softwood lignin shown in Figure 2.6 was proposed by Sakakibara in 1980. This structure includes 28 separate units in the lignin structure and is based mainly on the degradation products of hydrolysis by dioxane-water and catalytic hydrogenolysis.



**Figure 2.6.** Proposed structure of softwood lignin by Sakakibara, 1980.

Sakakibara A. 1980. A Structural Model of Softwood Lignin. *Wood Science and Technology*. 14, 89-100. With permission from Springer.

NMR techniques have continued to be the most popular way to characterize lignin. In 2004, Capanema et al. published a comprehensive characterization using NMR techniques, outlining the presence and relative amounts of a variety of structures found in lignins based on the NMR research of many people over a number of years, as seen below in Figure 2.7 (Capanema, 2014).

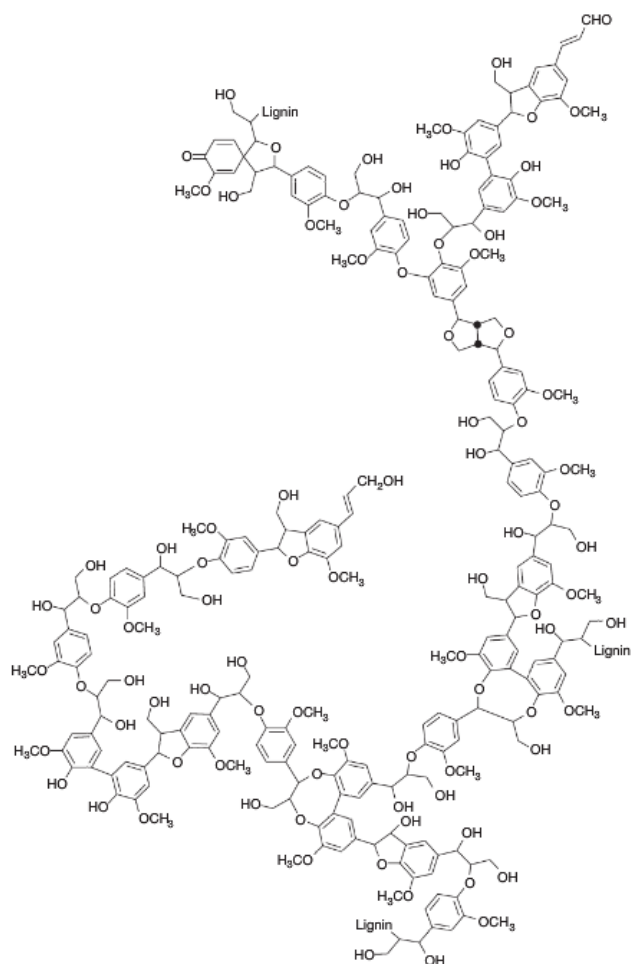


**Figure 2.7.** Structures present in lignin, determined by 2-D and 3D NMR

techniques. Reprinted with permission from Capanema EA. 2014. A

Comprehensive Approach for Quantitative Lignin. *Journal of Agricultural and Food Chemistry*. 52, 1850-1860. Copyright 2004 American Chemical Society.

In 2008, Gellerstedt and Henriksson published a structure based on more complete NMR spectroscopy as well as wet chemistry methods data that incorporated the work of many others, combining this knowledge to form a more complete lignin structure (Gellerstedt, 2008). They note that NMR does not degrade lignin samples and allows structural features to be visualized. Also noted is the benefit of using 2-D studies which separate the proton signals from carbon the signals and 3-D analysis from which quantitative data can be derived. The authors acknowledge that it has become apparent that the lignin structure is not uniform, but that it adapts to its formative environment, based on structure, chemical surroundings, and other possible unknown factors. This makes finding statistical representations of a generic lignin structure difficult. They do, however, propose a structure of lignin from spruce, based on statistical findings of a collection of research, in Figure 2.8 below.

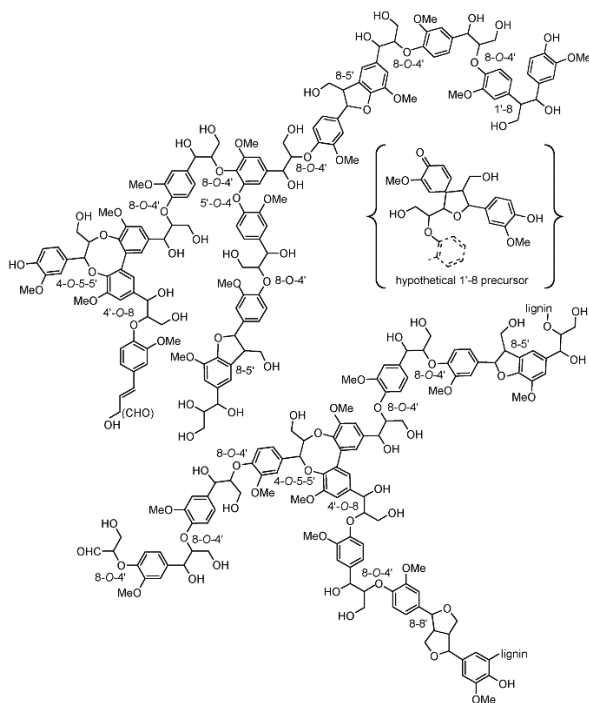


**Figure 2.8.** Proposed structure of lignin from spruce by Gellerstedt and Henriksson. Reprinted from Gellerstedt G, and Henriksson G. Lignins: Major Sources, Structure and Properties. Pages No. 201-224, (2008), with permission from Elsevier.

As NMR methods improved, Brunow et al. presented a lignin structure in 1998 that is currently in use by the United States Department of Energy to characterize lignin (DOE, 2015). The structure is based on multidimensional NMR techniques including 2-D TOCSY (total proton-proton correlation) as well as



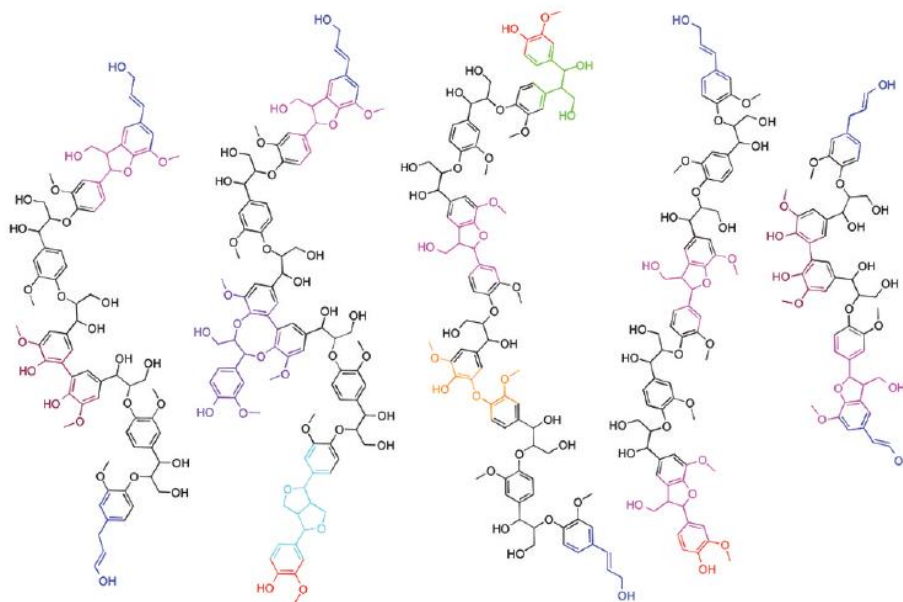
2-D and 3-D NMR (carbon-proton correlation) allowing differentiation between phenylpropane units – reliably giving a much closer idea of what the structure of the macromolecule is (Brunow, 1998). This structure is given in Figure 2.9.



**Figure 2.9.** Proposed structure of spruce lignin by Brunow, 1998 (Reprinted with permission from Brunow G, Kilpelainen I, Sipila J, Karhunen P, Rummakko P. Oxidative coupling of phenols and the biosynthesis of lignin. In: Lewis NG & Sarkanen S (Eds.) Lignin and Lignan Biosynthesis, ACS Symposium Series 697. American Chemical Society, Washington, DC. Copyright 1998 American Chemical Society).

A 2011 study by Crestini, et al. shows evidence for lignin existing as a linear oligomer, rather than as a networked polymer, as previously believed (Crestini, 2011). It was found that the degree of cross-linking must be very low

since the number of intermonomer linkages is only slightly larger than the number of monomers themselves. This finding was confirmed by a 2006 study by Gidh, et al. that used end-group titration methods and vapor osmometry molecular weight determination to show milled wood lignin is made up of oligomeric systems rather than polymers (Gidh, 2006). The research utilized more advanced NMR methods including 2D QQ-HSQC NMR,  $^{31}\text{P}$  NMR, and Derivatization Followed by Reductive Cleavage (DFRC) coupled with  $^{31}\text{P}$  NMR in analyzing lignin samples. DFRC was a method developed by Lu and Ralph in 1997 that efficiently cleaves  $\alpha$ - and  $\beta$ - aryl ethers to degrade lignin to monomers that are more easily quantifiable by first treating lignin with acetyl bromide, followed by a reductive cleavage step, acetylation, and then GC analysis. Using this procedure, they were able to define acetoxycinnamyl acetate monomers, the acetylated versions of the monolignols from p-hydroxyphenyl, guaiacyl, and syringyl units (Lu, 1997). Crestini, et al. showed that softwood milled wood lignin consists of p-hydroxyphenyl and guaiacyl monomers held together by  $\beta$ -O-4,  $\beta$ -5, 5-5',  $\beta$ - $\beta'$ , 4-O-5' bonds with terminal aliphatic and phenolic groups, and it is discussed that hardwoods contain all three monolignols, as seen in Figure 2.10.



**Figure 2.10.** Structure of softwood milled wood lignin proposed by Crestini, et al. 2011 (Reprinted with permission from Crestini C, Melone F, Sette M, Saladino R. Milled wood lignin: A linear oligomer. *Biomacromolecules*. 12, 3928-3935. Copyright 2011 American Chemical Society).

One structural element that is generally accepted today is that lignins differ between plant type, and even differ based on location within a plant. Lignin varies between compression vs. noncompression wood, and its structure also depends on its physical and chemical surroundings, such as whether or not it is connected to cellulosic material.

The major differences between generally accepted lignin structures today, versus some of the older models, are mainly based on information gained from methods used to determine the components and linkages in lignin. The methods used today, such as 2-D and 3-D NMR cause fewer side-reactions within the

lignin substance that would alter its makeup. Characterization methods such as mass spectrometry, GC, HPLC, atomic force microscopy (AFM), and  $^{31}\text{P}$  NMR have also been important developments in lignin structure and quantification of groups within the lignin structure (Ralph, 2004; Gidh, 2006; Watkins, 2016).

A comparatively large amount of support has gone into the study of lignin recently due to its importance as a resource in the biorefinery model of attaining industrial fuels, chemicals, and polymer materials. In 2007, the United States Department of Energy established three bioenergy resource centers giving a large boost to the field as these centers focus to work as “integrative, multidisciplinary partnerships with expertise spanning the physical, chemical, biological, and computational sciences, including genomics, microbial and plant biology, analytical chemistry, computational biology and bioinformatics, and engineering (DOE, 2014).” More complex computer modeling tools are also available for chemists to construct more accurate structures.

A topic of much current discussion is whether lignin is a complex crosslinked random polymer or a set of noncrosslinked repeating linear oligomers. In the older “lignin model compounds” lignins are modeled as simple structures compared to what is known about lignin as a three-dimensional amorphous structure characterized by its monolignols with eight or more linkage types, predominated by  $\beta$ -O-4 bonds, identified depending on the lignin source. Research on oligomeric lignin model compounds is currently underway (Katahira, 2006, Chu, 2013). It has become more accepted that lignins are linear oligomers.

Based on more recent studies, such as one by Crestini, et al. in 2011, more types of oligomer linkages have also been determined.

Switchgrass (*Panicum virgatum*), seen in Figure 2.11, the source of the lignin incorporated into the polymers herein, has many desirable characteristics including its high productivity in marginal lands (Yulsman, 2007). Switchgrass can be grown as a way to restore natural prairie in areas that do not compete with agricultural crops, which has led to growing interest in high-yield biomass switchgrass (Kautto, 2014). The delignification rate of biomass has been demonstrated by Chang and Sarkanen (1973) to be related to the syringyl to guaiacyl ratio (S/G ratio). Switchgrass lignin was reported by Hu, et al., 2010 to have an overall S/G ratio between 0.52-0.54, though it was found that the ratio varied more between portions of switchgrass with internodal areas having a S/G ratio as high as 0.68 and leaves having a S/G ratio as low as 0.46.



**Figure 2.11.** Switchgrass grown at the University of Minnesota’s Southern Research and Outreach Center, and as received after harvest in Kaufert Lab, respectively. Photo credits: Karl Foord, 2012; Stephanie B. Harris, 2016.

The organosolv process of lignin removal from lignocellulosic material was used because it yields a clean lignin with a fairly low molecular weight that does not contain any contaminations, such as sulfur (Kautto, 2014). Organosolv switchgrass lignin (OSL) offers potential for a large number of reaction sites in copolymerization, such as free phenolic hydroxyl groups, and as all lignin is also expected to contribute to water impermeability due to the polymer's hydrophobic nature (Campbell, 1996).

Lignin is a good candidate for copolymerization with polylactide because of its plentiful hydroxyl groups which are capable of going through the same chain propagating condensation reaction as lactide along with carboxylic acid end groups of polylactide to form a copolymer (Hu, 2011). It is proposed that OSL will polymerize in a system with lactide due to the plentiful oxygen-rich phenolic groups.

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## Chapter 3 – Delta-Valerolactone

### 3.1 Delta-valerolactone as a biobased and biocompatible raw material

Delta-valerolactone (DVL) is a biobased monomer derived from sugars that has rubbery properties when polymerized (Xion, 2014, Fernandez, 2014). When decyclized, DVL is an amphiphilic molecule, or a molecule with both hydrophobic and hydrophilic moieties.

Lactones as a class are cyclic esters of hydroxycarboxylic acids with one or more carbon atoms in the ring being replaced by a heteroatom, or atom other than a carbon atom in the ring structure. Lactones are derived from hydroxyl carboxylic acid by the intramolecular loss of water. The cyclization takes place spontaneously in a 5-member rings such as DVL. The moniker  $\delta$  signifies the number of carbon atoms in the ring between the C=O and the ring O (Moss 2009).

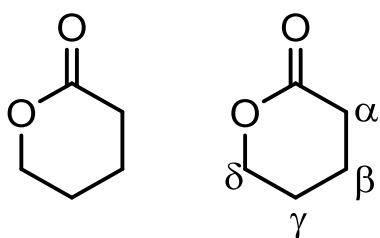


Figure 3.1. Structure of  $\delta$ -valerolactone, and schematic representing the numbering in the ring.



Interestingly,  $\alpha$ -alkylidene- $\delta$ -lactones, of which there are 50 known natural compounds and over 400 known synthetic compounds, make up an important class of flavor and scent chemicals. Many of these compounds are found in foods including butter, cream, milk, vanilla, chocolate, coconut, nuts and fruits (Burdock G. , 1997). Others are used extensively in the perfume industry and comprise natural scents of musk, flowers and fruits (Burdock, 2004).

Using the thermochemistry processes of direct calorimetric heat of combustion and hydrolysis, then studying reduction enthalpies and subsequently applying quantum mechanics using the multidimensional conformational analysis strategy, Houk, et al. found that the polymerization of DVL takes place due to ring strain which in turn is due to the geometric distortion of the ester group (Houk, 2008). DVL has been found to polymerize spontaneously on storage at room temperature and also at high pressure, which is attributed to initiation by hydroxylic impurities (Korte, 1966).

Many synthetic processes have been developed to derive DVL. Yang, et al. found that silver triflate worked as an excellent catalyst for the intramolecular hydroalkoxylation and subsequent hydroacyloxylation of inert olefins to construct lactones with yields up to 95% (Yang C-G, 2005). In 2007 Tellitu, et al. published findings that utilized a hypervalent iodine reagent to promote the intramolecular cyclization producing lactones (Tellitu, 2007). A method was also developed using N-heterocyclic carbenes as imidazolium-derived organocatalysts in ring-expansion reactions to yield five-, six-, and seven-membered lactones (Wang,

2009). In 2013 Murphy and Dong published their findings showing that DVL can be prepared directly via ketone hydroacylation of a 1,5-hydroxy keto alcohol. The alcohol is first oxidized in situ to an aldehyde utilizing the enantioselective Noyori's asymmetric transfer hydrogenation catalyst. They also showed good results using the same method applied to substrates with aryl substituents and reported yields up to 98%. In a 2011 U.S. Patent, Pinkos, et al. describe the formation of DVL with >98% purity from diols.

Since DVL is most commonly derived from sugar diols, the cellulose in biomass material is a plentiful source for starting material (Xiong, 2014; Kricheldorf, 1997). This method is potentially useful to the biorefinery model where high-value products are derived from biomass, and is also important to the medical industry where biobased materials are preferred for biocompatible uses (Cao, 2012; Kulkarni, 1971).

### 3.2 Synthesis of poly(DVL)

Polymerization of DVL is not a new endeavour. The polymerization of several cyclic esters, including DVL, were patented in 1962. Syntheses are recorded in literature going back to the 1930s. The six-membered ring, which is common in nature, was found to have been of particular interest to research looking to understand the formation of naturally occurring macromolecular materials (Carothers, 1932; Cox, 1962).

More uses for the elastomeric polymer are being found as it takes its place as an important biobased and hydrolytically degradable substance (Kasyapi, 2015). DVL is now most commonly found in biobased and biodegradable block copolymers that have a multitude of uses. It has most often been copolymerized with lactide, ethylene glycol, and  $\delta$ -caprolactone (Yang J., 2005, Cao 2012; Schneiderman, 2016). These copolymers are discussed in more detail in Chapter 5 herein.

As a monomer considered for copolymerization with lactide, DVL is also capable via ROP, making it a good candidate for a block copolymer providing more flexibility to otherwise rigid PLA, as seen in Figure 3-2. (Fukuzaki, 1989, Kasyapi, 2014).

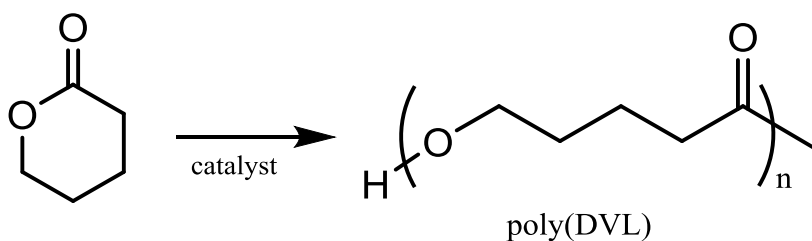


Figure 3.2. Schematic representation of catalyzed ring-opening polymerization of delta-valerolactone.

Polymerization of DVL is most commonly catalysed with a metal catalyst such as the  $\text{Sn}(\text{Oct})_2$  catalyst used herein, but there have also been successful polymerizations using organocatalysts as well. It is often preferable to use an organocatalyst because trace metallic residues can be toxic in biomedical

applications, though they typically do not leach out of polymer until it has degraded (Cao 2012, Zhu 2016, Naumann 2016). In an interesting study from 2015, Chang and Waymouth found that a cyclic polymer of DVL could be produced through a zwitterionic ring opening utilizing N-heterocyclic carbene catalysts, literally building on the previous work discussed in which Wang, et al. formed the original lactone cyclic monomers.

Interestingly, it has been found that the anionic polymerization of DVL reaches an equilibrium as a living ring-chain system in which initially DVL undergoes ROP, followed by back-biting ring-forming. The spontaneous back-biting degradation of the initially formed linear polymer leads to the formation of cyclic oligomers and monomeric lactone when the polymer is heated above 200 °C (Carothers, 1932; Ito, 1979). In 1965 Saotome, et al. found that the polymer can be stabilized by acetylating the end groups.

More complex macromolecular architectures have been attained and have become of interest due to the variation in physical properties of a polymer due to these varying structures. Some of these are illustrated in Figure 3.3.

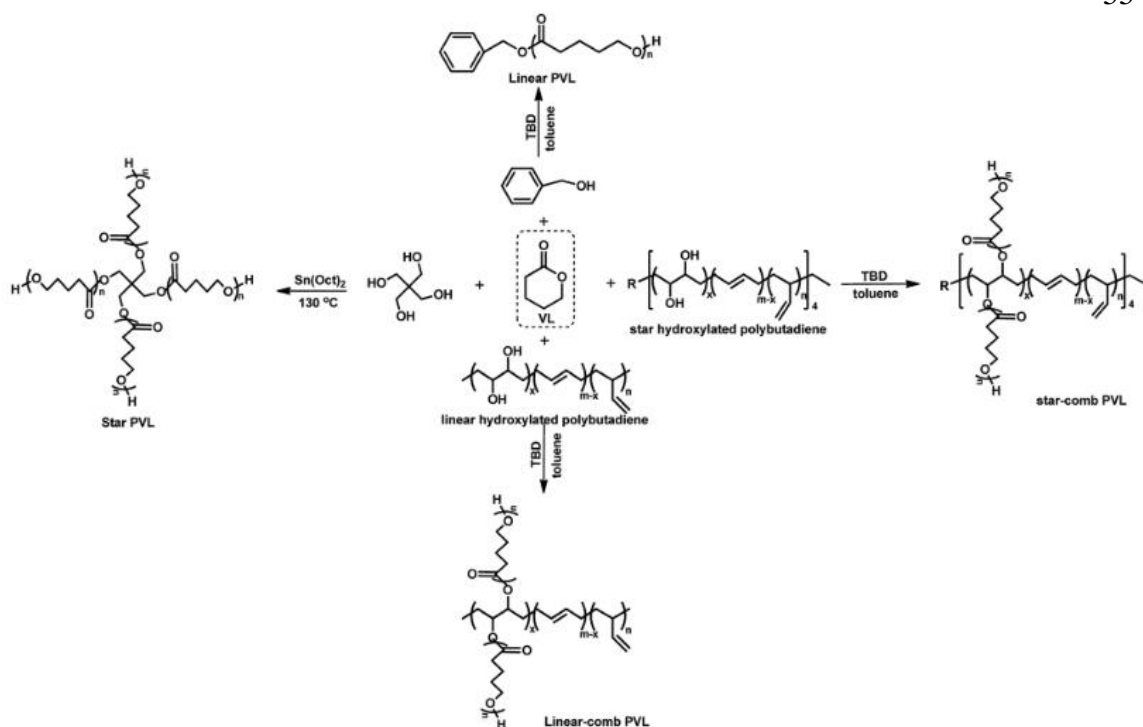


Figure 3.3. Analogues of poly( $\delta$ -valerolactone). Reproduced from Ren Y, Wei Z, Wu T, Bian Y, Leng X, Zhou C, Li Y. 2016. Synthesis of highly branched poly( $\delta$ -valerolactone)s: a comparative study between comb and linear analogues. RSC Advances. 6, 45791-45801 with permission of The Royal Society of Chemistry.

“Click cyclization,” referring to a versatile cyclic reaction that produces a high yield without difficult to remove byproducts and in solvents that are easy to remove or are considered benign, has been used more recently to synthesize useful macrocyclic polymers. In 2009 Misaka, et al. found that a precisely designed macrocyclic DVL polymer could be synthesized with this method utilizing 1-[3,5-Bis(trifluoromethyl)phenyl]-3-cyclohexylthiourea (BCT) as an

organic catalyst, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as an initiator in toluene to yield a polymer with low PDI and predictable molecular weights.

### 3.3 Properties of poly(DVL)

Poly(DVL) is typically an aliphatic polymer with a relatively low  $T_m$  and  $T_g$ . It is semicrystalline and data shows that the polymer acts as an elastomer (Aubin, 1981; Nakayama, 1997; Cao, 2012).

Properties of various conformations of poly(DVL) are shown in Table 3.1. Variations in individual results are due to synthesis conditions. In linear-comb and star comb configurations,  $\bar{M}_w$  and number of arms were tailored based on the number of hydroxyl groups on the backbone chain controlling the number of side chains and the proportion of monomer to hydroxyl groups, together determining the molecular weight of a single side chain (Ren Y, 2016).

**Table 3.1.** Properties of various conformations of poly(DVL). Reproduced in part from Ren, et al. with permission of The Royal Society of Chemistry.

Conformation	$\bar{M}_w$ (kDa)	PDI	$T_m$ (°C)	$X_c$ (%)
Linear	26-68	1.54-1.67	57.1-57.5	52.3-53.9
Star	24-91	1.31-1.74	55.1-56.1	57.2-58.7
Star-comb	118-172	1.15-1.19	56.7-57.0	78.6-82.7
Linear-comb	124-264	1.09-1.13	55.9-56.0	76.6-81.8

Increasing  $\bar{M}_w$  of side chains was found to correlate with increased  $T_m$  (Ren, 2016). Comparing the linear polymer to the branched star-comb and linear-comb structures shows a decrease in  $T_m$  which could be of interest for application in industry where a lower  $T_m$  can indicate that the polymer can be processed with less energy input.

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## **Chapter 4 – Copolymers with Lactide and Lignin**

### **4.1 History of copolymers with lactide and lignin**

Over the years, there have been several attempts to copolymerize lignin with other polymers. In the early 1970's, Phillips, et al. produced a novel polymer by grafting styrene to lignin. Meister and Chen built on this work by copolymerizing lignin with styrene in a free-radical solution reaction (Phillips, 1971, Meister, 1991). In 1993 Hofmann and Glasser published a study of the copolymerization of lignin with poly (propylene oxide) (Hofmann, 1993). These early copolymers were focused on reducing the carbon dioxide footprint of petroleum based polymers, but mainly remained tied to the styrene monomer.

In order to find higher value uses for lignin, other attempts have been made to incorporate lignin in a variety of polymerization types (Kim, 2010, De Oliveira, 1994, Eyser, 2011, Liu, 2013, Liu, 2014, Nemoto, 2012). In 2008, Sena-Martins, et al. published a review which included lignin graft copolymers including copolymers of lignin with creosol, vanillic acid, diisocyanate and acrylamide (Sena-Martins, 2008).

### **4.2 Synthesis of lactide and lignin copolymers**

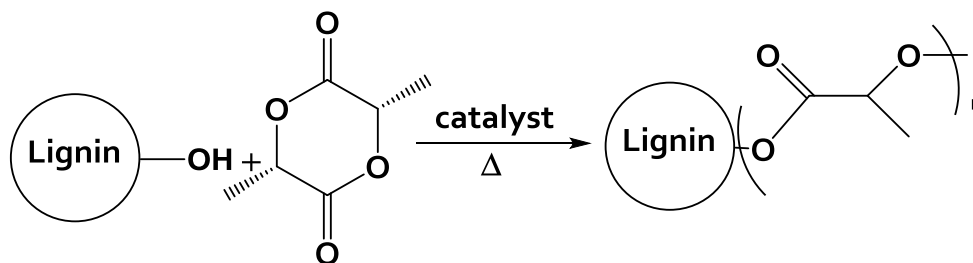
In 2013 Chung, et al. produced PLLA grafted lignin with the goal of improving the compatibility of lignin in biobased composites (Chung, 2013). They were able to successfully control PLLA graft chain length by modifying the free

hydroxyl group content in Indulin lignin, lignin derived from the kraft delignification process, through acetylation.

In 2014, Olsson, et al. patented graft copolymers of Indulin lignin and lactide synthesized with patented organocatalysts with the goal of finding an alternative to toxic metal catalysts (Olsson, 2014). The group modified the stereochemistry of the lactide monomer utilizing mixtures of both the L(-) and D(+) stereomonomers. They modified lignin through preacetylation, and by utilizing varied lactide/lignin ratios in syntheses, were able to tune the properties of the resultant copolymers to range from thermoset to thermoplastic.

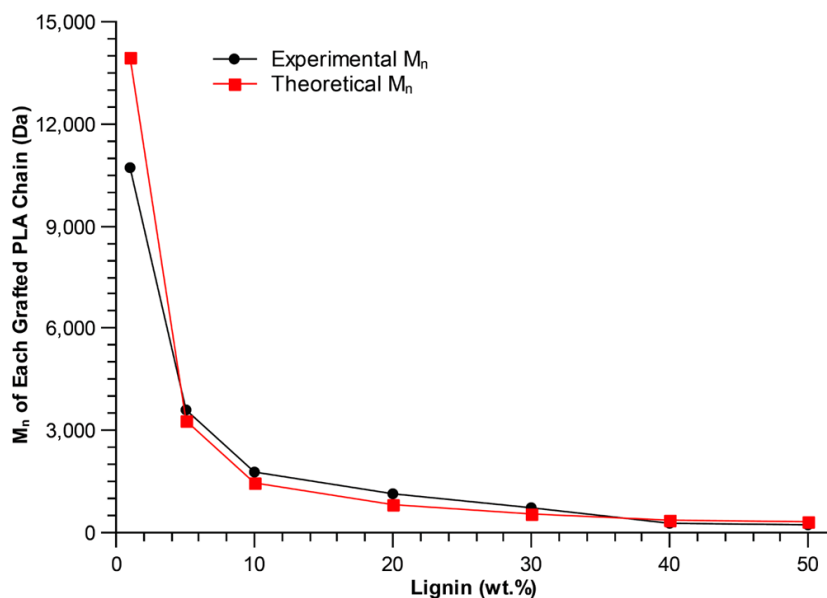
A schematic diagram derived from Chung, et al., 2013 for the copolymerization of lactide and lignin is shown in Figure 4.1. It has been suggested that the lignin may interfere with the polymerization of the polylactide, in essence stopping the polymerization, and shortening polymer chains. Size exclusion chromatography (SEC) data supports this theory.

Using polystyrene standards for  $\bar{M}_w$  calculations, the data in Figure 4.2 below can be seen to support this chain-ending theory. The polymer chain  $\bar{M}_n$  can be seen to decrease as the amount of lignin increases. This may be due to the lignin effectively ending the polymerization of polylactide, or inhibiting it sterically. Using the same standard procedures, the calculations of  $\bar{M}_w$  of OSL are also included in Table 4.1 for comparison.



**Figure 4.1.** Schematic depicting the graft polymerization of lactide to lignin.

Adapted with permission from Chung, et al. A Renewable Lignin–Lactide Copolymer and Application in Biobased Composites. Sustainable Chemistry & Engineering. 2013 American Chemical Society.



**Figure 4.2.** Number-average molecular weight ( $\bar{M}_n$ ) of lignin-g-PLA copolymers where experimental PLA chain length was determined by  $^1\text{H-NMR}$  end-group integration and the theoretical value was determined by calculation (mmole lactide per mmole lignin-OH functionality determined by  $^{31}\text{P-NMR}$ ). Reprinted with

permission from Chung, et al. A Renewable Lignin–Lactide Copolymer and Application in Biobased Composites. Sustainable Chemistry & Engineering. 2013 American Chemical Society.

A decrease in chain length of the polymer is apparent with the increase of lignin in the polymerization.

### 4.3 Properties of lactide and lignin copolymers

The reported physical properties of copolymers of lactide and lignin can be seen in Table 4.1.

**Table 4.1.** Mechanical properties of PLA/Lignin copolymers reported by Olsson, et al., 2014.

Lignin-g-PLA (wt. %)	$\bar{M}_w$ (Da)	$T_g$ (°C)	$E$ (GPa)
1	10,728	54	4500
10	1,800	45	2.764 ±0.111
20	1,008	48	2.586 ±0.161
30	792	53	2.886 ±63
40	281	74	2.968 ±0.116
5 (75% Acetylated)	6,435	55	2.902 ±0.035

Lignin copolymers tend to be brittle, and adding lignin to a copolymer with polylactide tends to make the substance even more brittle. Tensile testing shows

that the average tensile strain at maximum tensile stress decreased with increasing amounts of lignin in the copolymer (Chung, 2013).

An additional challenge is raised due to the chromophores that exist in lignin for developing biobased polymers containing lignin. The lignin chromophores inevitably add a brownish tint to the polymer. Though there are many uses for polymers in which the color is not an issue, such as polymers used to impregnate wood for durability, or to give products a natural appearance, the color may also cause the product to appear less desirable to some consumers. There are also many accepted types of environmentally friendly packaging retaining colors that are reminiscent of the plant materials from which they are derived that are already in existence. These types of packaging include inner wrappings such as those used for some dry foods such as crackers and cereal liners, and can be found coating the internal layer of aluminum and tin cans, where the polymer comes in contact with the stored contents. Color psychology has fascinated scholars and marketers alike for millennia, but there is little conclusive evidence that color preference is innate, and our desire to have sustainable products may outweigh our desire for them to have eye-catching appeal (Elliot, 2015).

#### **4.4 Improving the properties of poly(lactide-co-lignin)**

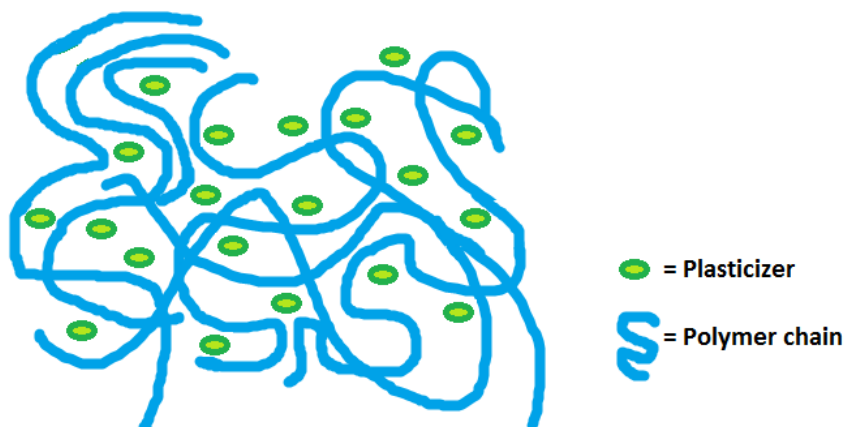
Because both lactide and lignin form brittle polymers on their own, copolymers of lactide and lignin retain this property and are even less tough and

less flexible than polylactide. As with other polymers, one way to improve on the ductility and other properties of polylactide is to add a plasticizer – a common method used in industry. As previously discussed, desirable plasticizers for polylactide are biobased, degradable materials. Depending on the intended application of products made, plasticizers may also need to be food-grade.

From a processing perspective, a suitable plasticizer for use with a copolymer of polylactide and lignin must be miscible in the melt for processing in extrusion or injection molding. Esterification, acetylation or epoxidation of biobased materials are common methods that have been proven beneficial for mixing because moieties that are compatible with polylactide can be formed. Throughout processing, these groups interact well with the aliphatic polyester aspect of polylactide. The polar moieties that are formed through these treatments allow the plasticizer to line up in favorable orientations between the polymer chains creating attraction, while also allowing mobility between the polymer chains.

In a work published in 1965, Innergut and Mark describe the intermolecular forces between the plasticizer and polymer to include the forces of dispersion, induction, dipole–dipole interaction, and hydrogen bonding. All of these forces arise due to varying electronegativities which inaugurate dipole forces between atoms or functional groups in the molecules. The schematic, Figure 4.3, is intended to show the plasticizer molecules in close association with, but not chemically bonded to the polymer chains. As shown, the plasticizer

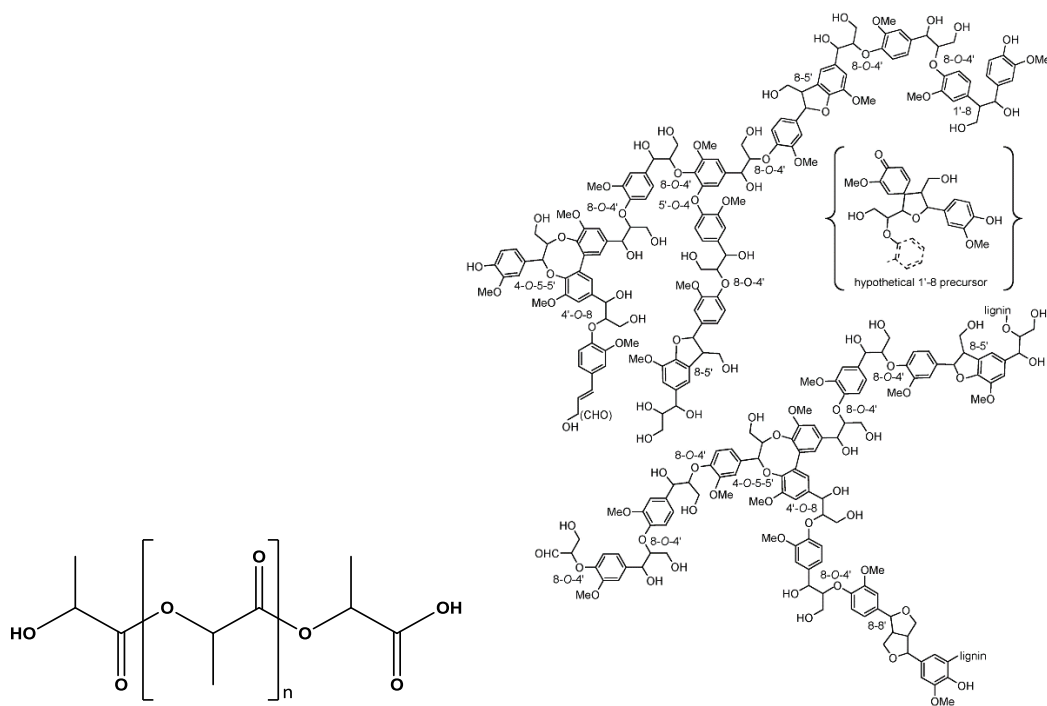
molecules can inhibit the crystallization of the polymer, thereby lowering the glass transition temperature of the compound and reducing the elastic modulus (Young's modulus).



**Figure 4.3.** Schematic of polymer combined with plasticizer.

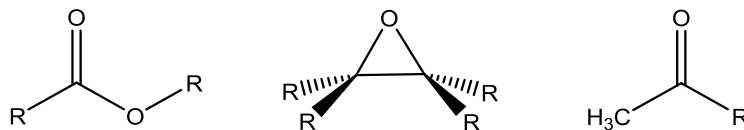
Considering copolymers of lactide and OSL, it can be inferred that ester, acetyl, or epoxide-based plasticizers would be useful due to the intermolecular interactions between the plasticizer and both the lignin and polylactide. Figure 4.4 shows structures of polylactide and of lignin in order to visualize the functional groups within those structures. As can be seen, there are a multitude of ready sites for these interactions noted above to occur due to electronegativity differences between the oxygen atoms and neighboring carbon atoms.





**Figure 4.4.** On the left is the structure generally accepted structure of poly(lactide). On the right is a proposed structure of lignin accepted by the U.S. Department of Energy. (Reprinted with permission from Brunow G, Kilpelainen I, Sipila J, Karhunen P, Rummakko P. Oxidative coupling of phenols and the biosynthesis of lignin. In: Lewis NG & Sarkanen S (Eds.) Lignin and Lignan Biosynthesis, ACS Symposium Series 697. American Chemical Society, Washington, DC. Copyright 1998 American Chemical Society).

Because the structure of the plasticizer also affects the structure and interaction between all parts of the system, it is helpful to look at the individual functionalities of the various plasticizers mentioned above, shown here in Figure 4.5.



**Figure 4.5.** Functional groups found on popular polylactide plasticizers, from left: ester, epoxide, and acetyl.

A study of the electrical molecular quadrupole, the distribution of charges described using a multipole expansion, may be useful in determining the effectiveness of the substituent groups in a plasticizer molecule, and thus their ability to attract opposite quadrupoles in a polymer, and is a field of continuous research. These values are difficult to determine in more complex systems due to the numerous interactions and the effects of steric hindrances. However, dipoles of the functional groups found in these molecules may give some clue as to the molecular attractions. Esters, epoxides and acetyls are electrophilic and tend to seek nucleophiles. Nucleophiles in lignin and polylactide include carbon atoms near electrophilic oxygen atoms and the electron rich pi-bonding systems of the phenolic groups. Due to the high number of hydrogen bonds present in lignin that tend to interfere with intermolecular attractions, a plasticizer molecule with high potential for intermolecular attraction is necessary.

Epoxidized and acetylated oils are commonly used as plasticizers with polylactide. Due to the molecular interactions discussed previously, the exposed oxygen of the epoxide group and the oxygen atoms in the acetyl group, these

molecules also have the ability to interact with both these copolymer substances. A large variety of esters are also frequently used as plasticizers for polylactide including esters of citrates, sugars, fatty and other acids and even wood flour. The oxygen moieties in these molecules also exhibit the intermolecular forces discussed above. Another group of molecules used as plasticizers for PLA are shorter chain polymers such as the glycols, polyethylene glycol (PEG) and polypropylene glycol (PPG). The common attributes include mechanical property enhancement such as improved ductility, increased elongation and elasticity, improvement of impact strength, increased elastic properties, improved tear resistance, decreased glass transition temperature (which can also have the effect of increasing chain mobility at lower temperatures), decreased rate of crystallization (to increase the toughness), reduced melt viscosity, reduced die pressure, retained or increased in biodegradation rate, and improved coating qualities (Wypych, 2012).

The intermolecular interactions between the functional groups of the plasticizer and polylactide have generally been shown to improve tensile strain, but the tensile strength may be decreased by the addition of a plasticizer. This may be due to the interactions of the plasticizer with the polymer interfering with the interactions that would otherwise exist between the polymer chains. The plasticizer molecules can have the effect of shielding the dipole interactions between polymer chains (Reddy, 2010). For this reason, it's important to use a plasticizer in the correct concentration and with the most desirable effects on the

physical properties of the substance, which may depend on the purposes for which the substance is to be used. Plasticizer concentrations vary widely and tend to be specific to applications and the individual plasticizer used, but can be present in amounts up to 30 wt% (weight of plasticizer per weight of polymer percentage). In, "The Handbook of Plasticizers," Wypych reported wt% of plasticizers to polylactide polymer anywhere from 1 wt% for citrate esters to 40 wt% for a glycol polymer. More common percentages range from 5-20 wt% plasticizer in combination with polylactide (Wypych, 2012). In 2013 Mekonnen, et al. reported concentrations of plasticizer from 10-25 wt% plasticizer with polylactide. In this case, a smaller wt% was used for a glycol, while higher percentages were reported for citrate esters. There are thousands of patents related to specific recipes for polymer blends. Hundreds of those are related to polylactide, a polymer that is a relatively recent entrant in the arena of industrial polymers. This study also showed significant increases in the stress (the force per unit area along the axis of deformation), and toughness (the amount of energy absorbed during fracture) in PLA plasticized with a variety of modifiers. Good results were attained with several citrates, triethyl and tributyl in particular, as well as with PEG.

Another study published in 2013 by Rahman et al. compares tensile properties of various molecular weights of PEG mixed with PLA at various temperatures, as well as mixtures of PLA/PEG/lignin. Improved results in tensile strength and elongation and break were attained with PEG of  $\bar{M}_n$  6000 and 8000

when added at 30 wt%. In the systems tested with lignin, it was found that the tensile properties were less improved than in the PLLA/PEG mixtures, but that flexibility was improved over PLLA. Interestingly, when the blends were processed at high temperatures (180 °C), a copolymerization of the PLLA and PEG was achieved that could reduce PEG loss over time which is a common problem with plasticizers. Plasticizers tend to leach out of the polymer matrix over time.

There is some research available on the plasticization of lignin polymers. One study finds that dry lignin takes well to plasticizers involved in hydrogen bonding. Another, discussed above, shows improvement of mechanical properties over polylactide when lignin and PEG are blended with the polymer, but those properties are much improved without lignin in the system. One plasticizer that is found repeatedly in studies with polylactide and lignin is PEG, which is also reported to work well as a plasticizer for polylactide.

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## Chapter 5 – Copolymers of Lactide and Delta-Valerolactone

### 5.1 History of copolymers of lactide and delta-valerolactone

The earliest copolymer syntheses of lactide and DVL go back to c. 1990. As solutions requiring biocompatible and environmentally friendly polymers became better understood, research turned to fine tuning polymers for more specific applications. It has been found that DVL adds a rubbery block to the otherwise brittle PLA, enhancing its mechanical properties while retaining the sustainability aspects of PLA. DVL has been found to lower the  $X_c$  and  $T_m$  of PLA, thus improving its flexibility (Nakayama, 1997).

In 1991, Dubois, et al. published their findings after the synthesis of several copolymers of lactones and lactides via ROP. In this published work, biocompatibility (at least the absence of toxicity) is discussed as being the primary requirement of the target copolymers. It is noted that biodegradation is an advantageous property for implants in living organisms, making polymers such as polylactide, of interest since they are hydrolytically unstable and degrade both in vitro and in vivo (Dubois, 1991). In 1992 Kurcok, et al. published findings that used an anionic polymerization to synthesize a copolymer lactide and DVL for use as a bioresorbable material for pharmaceutical and biomedical applications in the human body. Lactide was noted to have been of special interest as a polymer material because its products degrade to products that are excreted in human metabolic processes. In order to improve on properties that

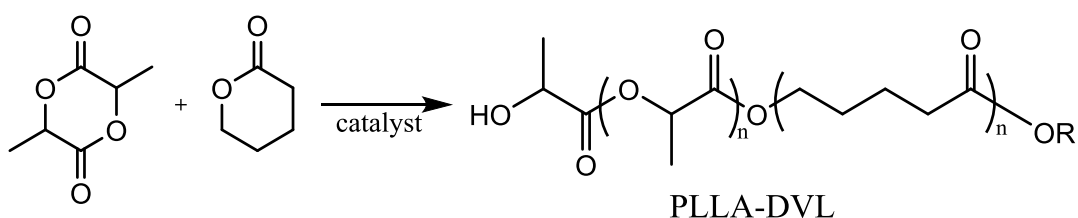
increase drug permeability and soft tissue compatibility, DVL was chosen as a biocompatible co-monomer.

By varying the structure of block polymers of lactide, DVL, and other aliphatic polyesters uses that mimic those of styrene block polymers have even be achieved. These polymers have more brittle polylactide blocks and rubbery poly(DVL) blocks, resulting in useful configurations of biomass-derived materials. In 2016 Schneiderman and Hillmyer reported that alkyl-substituted DVL monomers offer the opportunity to match polymer materials with specific properties unique to the application of the final product (Schneiderman, 2016). The applications of these block polymers may include functions as diverse as soft polymers used in athletic shoe soles and pressure sensitive adhesives to tough, durable plastics and elastomers used for packaging.

## **5.2 Synthesis of lactide and delta-valerolactone copolymers**

Both lactide (LA) and DVL can be polymerized via ROP, as described previously in Chapter 1. A number of catalysts have been found to be useful, and high molecular weights are achievable with many metal catalysts, including  $\text{Sn}(\text{Oct})_2$  – the same catalyst discussed previously that is most commonly used in the synthesis of polylactide. A schematic of synthesis of the copolymer, PLA-DVL), is shown in Figure 5.1.





**Figure 5.1.** Proposed structure of the copolymer.

The ring-opening polymerization method of synthesis allows for good control of molecular weights, polymer architecture, and composition that allow tailoring for specific renewable material applications (Hillmyer, 2014).

Other synthesis methods have been employed. Going back to 1989, Fukuzaki, et al. published findings on the synthesis of a copolymer of L-lactic acid with DVL via polycondensation in the absence of a catalyst for a low molecular weight polymer intended as a biodegradable carrier for drug delivery. A variety of catalysts have been shown to yield good results through ring-opening polymerization of DVL as well (Fernandez, 2014). In the interest of biocompatibility, organocatalysts have also been studied (Thomas, 2012).

### 5.3 Properties of lactide and delta-valerolactone copolymers

Properties of PLLA-DVL formed using varying catalysts via ring-opening polymerization have been reported by Fernandez, et al. as seen in Table 5.1. The copolymer does appear to be a good compromise between the homopolymers of the two monomers from which it is derived, previously reported

herein. The copolymer can be seen to have a lower  $T_g$  than PLA, though higher than poly(DVL). The elongation at break is much greater than for PLLA, showing a significant improvement there. Tensile strength is decreased, however, so though more flexible, the copolymer is not as tough as the PLLA homopolymer.

**Table 5.1.** Properties of PLLA-DVL polymeric materials. Reprinted from Fernandez J, Larranaga A, Etxeberria A, Sarasua JR. Tensile behavior and dynamic mechanical analysis of novel poly(lactide/  $\delta$ -valerolactone) statistical copolymers. 39-50. (2014) with permission from Elsevier.

Catalyst	% VL ( $^1\text{H-NMR}$ )	$\bar{M}_w$ (kDa)	PDI	$T_g$ $^{\circ}\text{C}$	$\sigma$ (MPa)	$\varepsilon$ (%)
BiSS	26.4	90.0	1.81	32.7	3.84 $\pm$ 0.34	830.5 $\pm$ 42.4
PH <sub>3</sub> Bi	31.4	87.7	1.81	27.0	8.25 $\pm$ 0.49	521.8 $\pm$ 60.5
PH <sub>3</sub> Bi	29.2	120.7	1.89	30.3	13.79 $\pm$ 1.22	573.1 $\pm$ 44.5
Sn(Oct) <sub>2</sub>	29.9	129.1	1.88	31.0	27.51 $\pm$ 2.30	620.4 $\pm$ 67.9

BiSS = bismuth (III) subsalicylate

PH<sub>3</sub>Bi = triphenyl bismuth

Sn(Oct)<sub>2</sub> = stannous octoate

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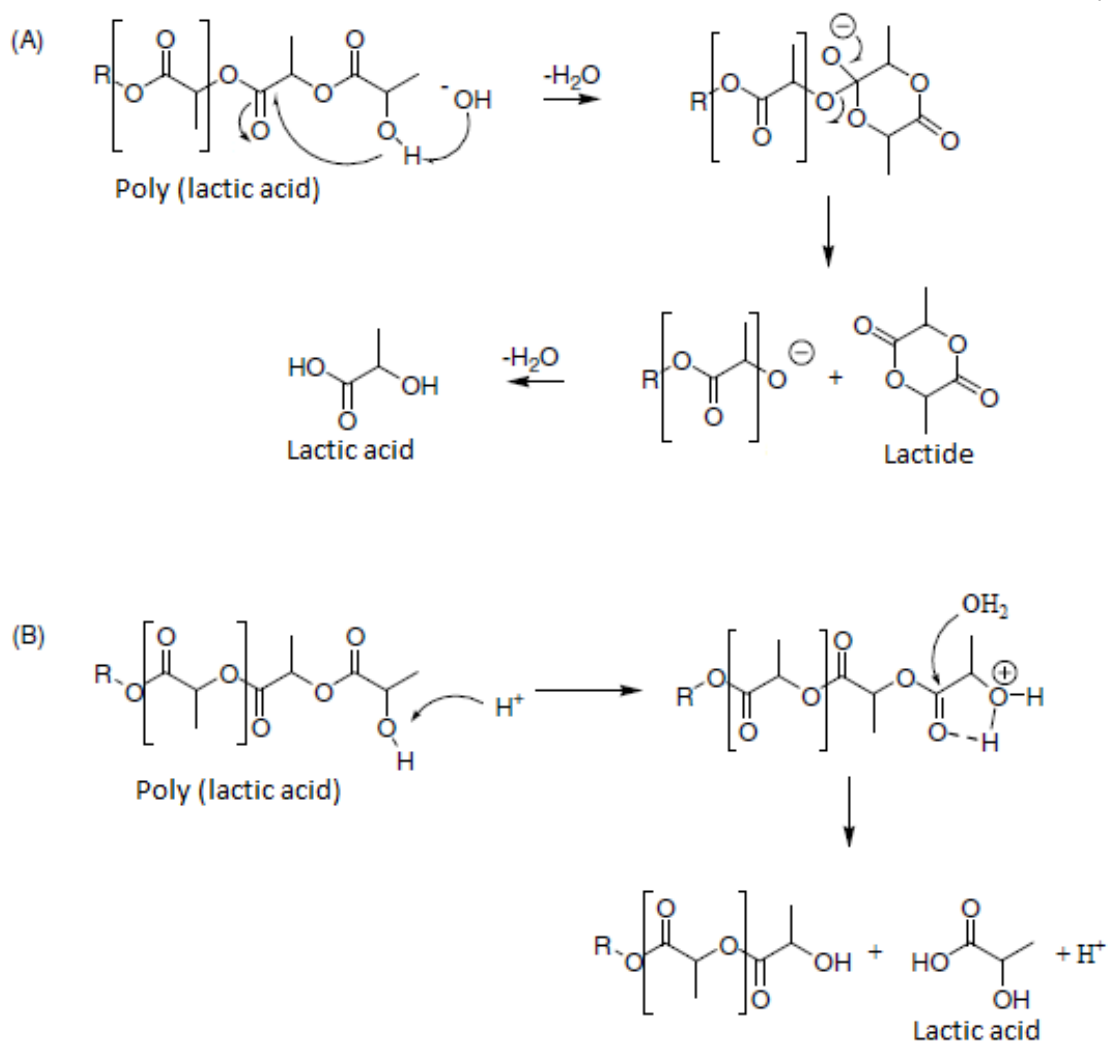
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## Chapter 6 – Hydrolytic Degradation

### 6.1 Hydrolytic degradation of PLA

Hydrolytic degradation of polymers has been well studied, but researchers continue to improve our understanding of the mechanisms and conditions involved in the hydrolytic degradation of polyesters.

There are two types of scission that polyesters are understood to go through via hydrolytic degradation: chain-end scission; and random scission. Chain-end scission refers to reactions that cleave an end group from the polymeric molecule, forming water and causing a backbiting reaction to release an ending lactic acid monomer from the PLA chain. Chain end scission occurs under both acidic and alkaline conditions, as shown in the mechanisms proposed by Kulkarni, et al. in Figure 6.1. Random scission reactions can cleave a molecule at a random point in the polymer chain, and occurs when an ether linkage in the polymer is hydrolyzed, forming a shorter chain with a free hydroxyl end group which is then susceptible to an end scission reaction removing a lactide intermediate due to the backbiting intermediate which is then hydrolyzed into monomers (van Nostrum, 2004).



**Figure 6.1.** Proposed mechanism for end scission hydrolysis of PLA in: (A) alkaline conditions, and (B) in acidic conditions. Modified from Polymer, 42, de Jong SJ, Arias ER, Rukers DTS, Van Nostrum CF, Kettenes-van den Bosch JJ, Hennink WE, New insights into the hydrolytic degradation of poly(lactic acid): participation of the alcohol terminus. 2795-2802, (2001) with permission from Elsevier.

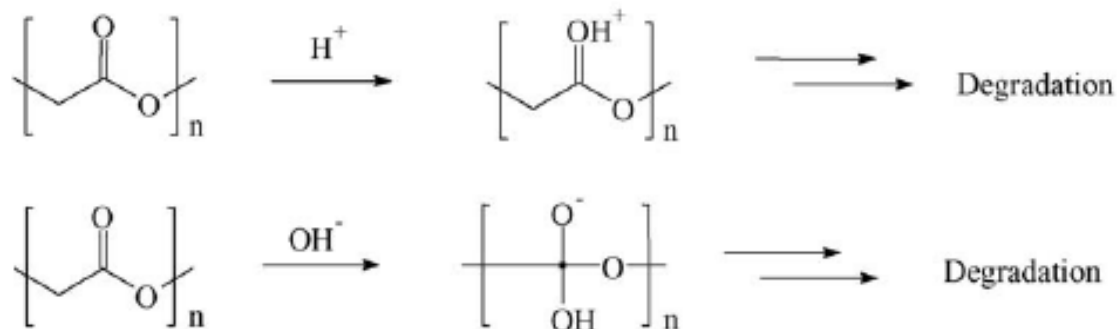
According to de Jong, et al., (2001), in alkali conditions a hydroxide ion attacks on a terminal hydroxyl end group. This leads to a backbiting reaction. A hydrogen is removed from the alcohol combining with  $\text{OH}^-$  to form water, leaving a highly reactive electrophilic oxygen atom which is available for further reaction, as shown Figure 6-1. This oxygen atom instigates a nucleophilic attack of the hydroxyl end group on the second carbonyl, forming a cyclic intermediate known as lactoyl lactate, finally ending with lactic acid and water.

In acidic conditions, a hydrogen ion, or rather a hydronium ion, will attack at the oxygen of an end group, releasing hydrogen to form a bond with a nearby ketone oxygen, which allows another water molecule to break the polymeric bond, releasing a lactic acid monomer in another type of chain-end scission.

It seems that because water acts as a buffer, both of these conditions can be present in neutral water, but will be driven by surrounding conditions. As PLA degrades and releases lactic acid monomers, internal water within the polymer matrix will become more acidic, driving the acidic mechanism as a result (de Jong, 2001). This idea is confirmed by the findings of Lu, et al. (2000), showing that degradation products can lead to the formation of a strongly acidic interior to the polymer, causing auto-catalyzed degradation.

Mechanisms for the random scission hydrolytic degradation of the ester bond in polyesters have also been proposed. In the 2006 study by de Jong, et al., it was proposed that alkaline hydrolysis took precedence over acidic hydrolysis, as seen in Figure 6.2. This was attributed to the carbonyl carbon

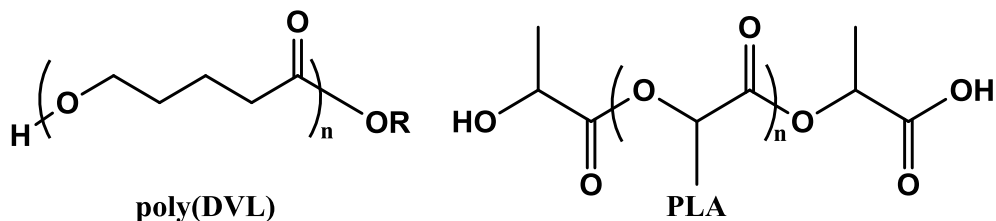
atoms being more susceptible to attack by hydroxide ions, particularly at pH > 13, due to the electronegativity differences found between the carbon and the oxygen atoms.



**Figure 6.2.** Proposed mechanism of random scission hydrolysis of polylactide. Modified from *Catalysis Today*, 115, Jung HJ, Ree M, Kim H, Acid- and base-catalyzed hydrolyses of aliphatic polycarbonates and polyesters, 283-287 (2006) with permission from Elsevier.

Alcohol end groups are believed to be most susceptible to hydrolytic reactions in polyesters. It is useful to consider the structure of the polyester polymer chain when discussing the possibilities. The generally accepted structures of poly(DVL) and polylactide are shown side by side in Figure 6.3 below. Several vulnerable moieties can be seen here, exposed and susceptible to reactions with water. The carboxylic acid with its hydroxyl and ketone constituents, the alcohol end groups, and the internal ester components stand

out as potential reaction sites due to the electronegativities of these groups. Both the alcohol and acid end groups will react with water.



**Figure 6.3.** Structures of poly(DVL) and PLA for consideration.

Interesting findings by Tsuji and Ikarashi in 2004 proposed that the ester groups neighboring end groups are cleaved step-by-step, releasing lactic acid in the process.

It seems logical to expect the reaction rate constant of random scission, as occurs in alkali conditions, to increase steadily as the reaction breaks the polymer chain, exposing two new end groups with each cleavage until there are few chains to cleave and the reaction slows. It also seems logical to expect the reaction rate constant of end scission, as occurs in acid conditions, to remain constant as each reaction releases one monomer, exposing one new end group to further reaction, without slowing, but there is obviously much more at play here than just the reaction types. The reaction rates are actually driven by a host of factors including temperature, pH, and crystallinity.

In the de Jong, et al. 2001 study of hydrolytic degradation discussed above, reaction rate constants were tracked at pH 8 and at pH 2, corresponding



to random scission that occurs in alkaline conditions, and chain end scission that occurs in acidic conditions. In the alkaline random scission conditions, it was found that the reaction rate constant was lower in general compared to the reaction rate constant found in acidic end scission conditions, and this was especially true as the degree of polymerization became lower. This effect was also found to be so strong that the counter-intuitive result in which larger particles degrade at a faster rate than smaller particles is found due to the increasing acidity in the polymer interior (Dunne, 2000).

In 2004, van Nostrum, et al. reported that PLA oligomers that had free hydroxyl chain ends degraded with the chain end scission backbiting mechanism described above with a reaction rate constant of  $k = 2.7 \text{ h}^{-1}$  in aqueous solution of pH 7.2 held at  $37.8 \text{ }^\circ\text{C}$ . This group also found that when they protected the exposed hydroxyl groups by acetylating them, the rate limiting step of hydrolytic degradation became random chain scission which they found to be  $k = 0.022 \text{ h}^{-1}$  in the same conditions. Therefore, it was concluded that the rate of end scission was at least one hundred times faster than random scission in PLA. Shih also found that in solid state PDLLA, an ester group adjacent to the polymer chain terminal end is more susceptible to hydrolytic degradation than other ester groups within the chain (Shih, 1995).

A 2008 study by Zhou and Xanthos found that the degradation rate constant increased as the temperature of hydrolytic degradation increases for PLLA, but did not follow the same pattern as for PDLLA. It is noted that the

degradation rate constants for both polymers increase significantly around 60 °C, however, as the system reached a temperature above the glass transition temperature of the polymer at which point water is able to gain access to polymer chains. This phenomena is discussed further below.

Although PLA was discovered in the 1920s at Dupont Chemical, these effects have really been studied with great interest more recently since the invention of a process to produce PLA was invented in 1989 by Dr. Patrick Gruber, which would allow the polymer to be produced on an industrial scale. These factors – pH, temperature, and crystallinity as well as others such as the size and shape of the polymer, surface area, copolymer materials, and the molecular weight of the polymer, have been found to have an influence on the hydrolytic degradation of PLA. In turn, these factors affect the mechanical properties of the polymer.

The effect of pH on hydrolytic degradation of PLA has been determined to increase as pH deviates from neutral. In a 2005 study, Tsuji and Ikarashi determined that both hydronium and hydroxide ions have catalytic effects on the hydrolytic degradation of crystalline PLLA residues, the portions of the polymer typically recalcitrant to hydrolytic cleavage due to hindrance. Kulkarni et al. found that degradation of PDLLA was also catalyzed by both low and high pH in a 2007 study. In a study published in 1999, Li and McCarthy found that degradation at varying pH is also temperature dependent, as raising the temperature above the  $T_g$  of the system, which is about 56 °C for PLLA, drastically increases the rate of

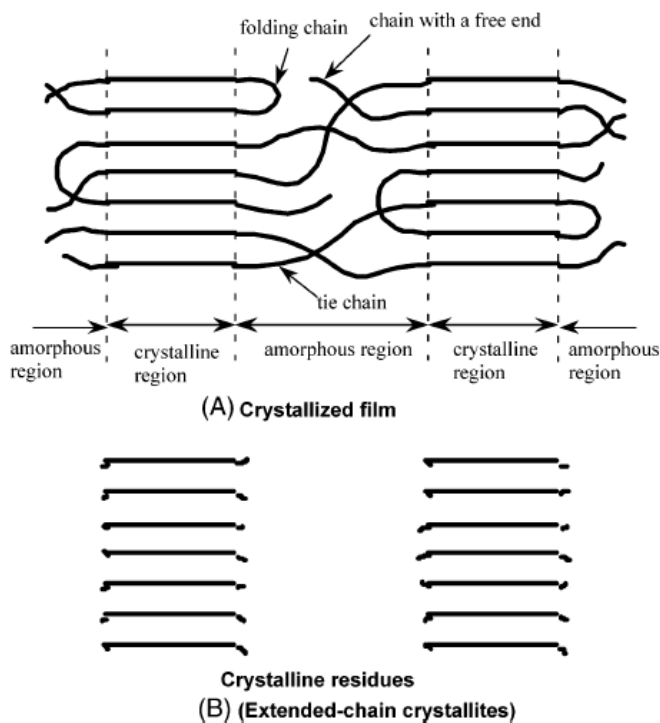
degradation at any pH. These findings were supported by findings by Chu, et al. in 2000.

Temperature has been shown to have the effect of increasing reaction rate constants of hydrolytic degradation of PLA. Even in a buffered solution to ensure constant pH, it was found that as lactic acid monomer is released during the hydrolytic degradation process, temperature increases the rate of degradation (Fukushima KA; 2009; Hyon, 1984). More recently, Tsuji and Ikarashi showed definitively in their 2004 published study a direct correlation between increased temperature and increased rate of reaction. This study follows the  $\bar{M}_n$  of degraded polymers over a period of 256 days at temperatures of 50, 70, and 97 °C. They found  $\bar{M}_n$  to decrease linearly, and that the highest percentage of PLLA chains were broken down to soluble oligomers or lactic acid as temperature increased. These findings are confirmed in later studies, including a study by Tsuji et al. in 2011 in which the hydrolytic degradation at different temperatures of several substituted PLA polymers are compared with PLA.

Long chain PLA polymers of polylactide are described as semicrystalline, forming structures composed of both amorphous and crystalline areas. The crystals grow in the form of spherulites, which can be witnessed in vitro with a polarizing light microscope as was shown previously in Figure 1.6.

Hydrolytic attacks begin from outside the crystalline areas in so that amorphous segments are degraded at a much faster rate than crystalline regions

(Fukushima, 2014). The crystalline areas are described as being hydrolysis resistant compared to the amorphous areas. Tsuji proposed that this is due to water molecules having better access to the amorphous regions, being prohibited from gaining access to the crystalline regions and proposes a schematic showing the degradation of amorphous regions of the polymer, shown in Figure 6.4 below, which leave behind, “crystalline residue,” areas that resist hydrolytic degradation (Tsuji, 2004).



**Figure 6.4.** Schematic proposed by Tsuji showing the formation of crystalline segments. Reprinted with permission from *In Vitro Hydrolysis of Poly(L-lactide) Crystalline Residues as Extended-Chain Crystallites: II. Effects of Hydrolysis Temperature*. Copyright 2004 American Chemical Society.

A study published in 2006 by Cairncross, et al. found that moisture sorption seems to be controlled by the hydrophilic end groups of PLA and it was found that sorption was not correlated to crystallinity. In fact, it seems that crystalline areas actually propagate with hydrolytic degradation, even when amorphous PLLA has been used as the degradation substance. In 1987, Leenslag, et al. conjectured that the measured increase in crystallinity upon degradation was up to 83 % and was contributed to crystallization of “tie-chain” segments, or amorphous segments found between crystalline regions. Once the temperature of the system rises above that of the  $T_g$ , however, water molecules have better access to all parts of the polymer chain and degradation rates increase substantially (Itavaara, 2002).

## **6.2 Hydrolytic degradation of PLA-DVL copolymers**

Fernandez, et al., 2015 found that segments of DVL in a copolymer with lactide had the effect of accelerating the degradation rate due to a more amorphous morphology with lower stereoregularity. This effect was also found by Kasyapi, et al. in 2014 when it was discovered that more crystalline copolymers of DVL and lactide degraded more slowly than those with a more random morphology which tended to be more amorphous.

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## **Chapter 7 – Materials and Methods**

### **7.1 Lignin**

#### **7.1.1 Switchgrass**

Organic switchgrass was obtained from the University of Minnesota Southern Research and Outreach Center in Waseca, Minnesota.

#### **7.1.2 Organosolv lignin extraction**

Lignin was extracted from switchgrass using an organosolv extraction method. 958 air dry g switchgrass was massed and added to a 5 gallon Parr 4843 reactor, shown in Figure 7.1. The material was covered with 10 L of a 60% (v/v) solution of ethanol: water to reach a substrate-liquor ratio of approximately 1:9 (w/w). The reactor was ramped up to 190 °C in 30 minutes and was held at temperature for three hours before cooling overnight. The solids were filtered and discarded. Ethanol was evaporated from the resulting filtrate in a ventilation hood overnight. 2L DI water was added to the liquid to precipitate the lignin. Organosolv lignin was filtered using a glass filter and vacuum. The recovered lignin was washed several times with DI water to remove carbohydrates. The extracted OSL was subsequently dried in an oven at 40 °C for two hours.



**Figure 7.1.** PARR 4843 pressure reactor used for organosolv method lignin extraction.

### **7.1.3 Organosolv lignin characterization**

#### **7.1.3.1 Chemical characterization of OSL**

Klason lignin and ash content were determined following NREL test procedures NREL TP-510-42618 and NREL TP-510-42622, respectively. Acid soluble lignin was determined utilizing TAPPI UM 250.

#### **7.1.3.2 Determination of phenolic hydroxyl groups in OSL**

Phenolic hydroxyl content of the OSL was determined by UV



spectroscopy. A 0.2 M stock solution of sodium hydroxide was prepared by dissolving 8.00 g NaOH in 1.0 L deionized water. Half of this solution was diluted to a 0.1 M solution for preparation of buffers. A pH 12 buffer solution was prepared by adding 3.10 g boric acid to 500.0 mL of the 0.1 M NaOH solution. A pH 6 buffer solution was prepared by dissolving 2.10 g citric acid in just under 1.0 L deionized water. This solution was then buffered to pH 6 by titrating with 0.1 M NaOH solution and was used as a reference solution for UV spectroscopy. A stock solution was prepared by dissolving 10.00 mg lignin in 5.0 mL p-dioxane and 5.0 mL 0.2 M NaOH. This was filtered with a 0.45  $\mu\text{m}$  membrane filter. 2.0 mL of this stock solution was diluted to three separate 25.0 mL lots using the pH 6 buffer for the first lot, the pH 12 buffer for the second lot, and the 0.2 M NaOH for the third lot to make three separate solutions of 0.80 g/L. The spectrum was measured at 300 and 350 nm on a double-beam Cary 50 UV spectrophotometer. The data obtained from the difference spectra were used to determine total, non-conjugated, conjugated, and weakly acidic phenolic hydroxyl contents according to Tamminen & Hortling, 1999. Total phenolic hydroxyl content was determined from the sodium hydroxide solutions according to Equations 7.1 and 7.2.

$$OH = (0.425 A_{300nm} + 0.182 A_{350nm}) * a\left(\frac{mmol}{g}\right) \quad (7.1)$$

Where  $A$  is the UV absorbance at the given wavelength and  $a$  is the correction term:

$$a = \frac{1}{(cl)^{\frac{10}{17}}} \quad (7.2)$$

Where  $c$  = concentration, and  $l$  = path length through sample.

#### **7.1.4 Methods of lignin oxidation**

For some syntheses, lignin was oxidized prior to polymerizing with lactic acid in order to increase its reactivity and brighten its color to produce more attractive polymers. In the oxidation process, it was expected that the lignin will be broken down into smaller molecular groupings with more acidic and hydroxyl end groups.

##### **7.1.4.1 Ozone treatment of OSL**

An OZV-8 ozone generator was rented from Ozone Solutions to oxidize lignin samples. Oxygen gas was entered into the ozone generator at a flow of up to four liters per minute. Lignin was treated in a dry state with ozone flowing through a reaction vessel as well as dissolved in chloroform with ozone bubbled through continuously for varying amounts of time. Ozone was bubbled through the reaction vessel and then through two wash bottles containing 0.5 M sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) to destroy any remaining ozone in the gas stream, as shown in Figure 7.2.



**Figure 7.2.** Ozone oxidation of lignin, in round-bottom flask at left and subsequent reduction of ozone released into the environment by saturation of  $\text{Na}_2\text{S}_2\text{O}_3$  solution. Photo credit Harris, 2011.

#### 7.1.4.2 Peracetic acid treatment of OSL

Approximately 3 g OSL was mixed with 25 mL of 39% peroxyacetic acid (Sigma Aldrich, Austria). The mixture was subsequently placed in a 80 °C water bath for 3 hours. After cooling, 100 mL chloroform was added to the mixture which was stirred overnight. This mixture was then transferred to a separation funnel, shaken, settled, shaken again and settled for five hours. The chloroform layer was removed and the chloroform allowed to evaporate. 100 mL ethanol was added to the remaining water layer to separate overnight. A light solid, most likely a salt, was seen to have settled to the bottom of the separation funnel

overnight. The solid was filtered off and the ethanol evaporated. Both remaining products were transferred to a vacuum desiccator after solvent evaporation.

### **7.1.4.3 Peroxide treatments of OSL**

#### **7.1.4.3.1 Alkaline peroxide treatment 1**

A common alkaline hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) lignocellulosic pulp bleaching pretreatment was applied to OSL. Aqueous stock solutions of 100 g/L sodium hydroxide ( $\text{NaOH}$ ), 20 g/L magnesium sulfate ( $\text{MgSO}_4$ ), 100 g/L sodium silicate, and 100 g/L  $\text{H}_2\text{O}_2$  were prepared. 10 mL of the  $\text{H}_2\text{O}_2$  stock solution was titrated with sodium thiosulfate utilizing 10 mL 4 N sulfuric acid ( $\text{H}_2\text{SO}_4$ ), 10 mL 1 N potassium iodide ( $\text{KI}$ ), and 3 drops of ammonium molybdate as a catalyst to determine accurate  $\text{H}_2\text{O}_2$  concentration. Starch was added to the titration once the brown solution became yellow to better visualize the endpoint of the titration. The  $\text{H}_2\text{O}_2$  concentration was determined according to Equation 1 and volumes of stock solutions were calculated to conclude with a mixture that was 0.1%  $\text{MgSO}_4$ , 3% sodium silicate, 4%  $\text{NaOH}$ , and 5%  $\text{H}_2\text{O}_2$  which were subsequently added to the lignin in that order in a covered beaker and left to react in a 80 °C water bath for one hour. The product was filtered, then dried overnight in a desiccator at 40 °C.

#### **7.1.4.3.2 Alkaline peroxide treatment 2**

80 mL 30%  $\text{H}_2\text{O}_2$  and 40 mL NaOH were added to 1.50 g of OSL, and the solution was stirred. The solution reacted slowly at first, then gained momentum and reacted quickly. The solution was left overnight and became the color of amber. 20 mL 4 N  $\text{H}_2\text{SO}_4$  was added to precipitate the lignin which caused the solution to become a very pale light yellow color. The solids had completely dissolved, and the liquid was evaporated. The precipitated product was dried overnight in a ventilation hood.

#### **7.1.4.3.3 Peroxide treatment 3**

A higher ratio of peroxide to lignin and increased stabilizers were determined to have an optimal effect on the reaction. Reactants were added to a 100 mL beaker in the following order: 1.00 g OSL, 0.04 mL  $\text{MgSO}_4$  stock solution, 0.6 mL sodium silicate stock solution, 0.8 mL NaOH stock solution, 10 mL DI, and 8.36 mL  $\text{H}_2\text{O}_2$  stock solution. This was left to react in a 80 °C water bath for one hour, then at ambient temperature for 24 h. Ethyl acetate was added to the solution to separate the nonpolar layer, which was removed via a separation funnel, as shown in Figure 7.3. The organic solvent was subsequently evaporated, and the bleached OSL product collected in a scintillation vial.



**Figure 7.3.** Organic and aqueous layers after peroxide treatment shown in separatory funnel. Photo credit Harris, 2016.

#### 7.1.5 Method of OSL acetylation

OSL was acetylated according to Gellerstedt, 1992. 2 g lignin was dissolved in 30 mL 1:1 v/v mixture of pyridine-acetic anhydride at ambient temperature, which was left to stir overnight. Excess acetic anhydride was then decomposed by the addition of ice cold methanol. After evaporation of the liquid, the residue was suspended in toluene and again evaporated. This was repeated three times, thereby removing remaining traces of the acetylation mixture by azeotropic distillation. The toluene was removed by the addition of methanol which was subsequently evaporated. Acetylated OSL (acOSL) was then used to determine the  $\bar{M}_w$  of OSL.

### 7.1.6 Method of molecular weight determination of acetylated OSL

The molecular weight value of the acetylated OSL was determined using a dynamic light scattering (DLS) system (Nano-flex, Microtrac Inc., Montgomeryville, PA). The Nano-flex uses a red (780nm) laser and was operated in the hydrodynamic measurement mode, which extends the DLS technique to molecules and molecular clusters down to one nanometer in hydrodynamic diameter. For the measurements, acetylated lignin was dissolved in THF at concentrations of 0.001, 0.0025, 0.005, and 0.05 g/ml. DLS was used to determine the  $\bar{M}_w$  of the OSL since lignin tends to aggregate in solvent systems and gives a higher  $\bar{M}_w$  value than accurately portrays the polymer in SEC, even when acetylated.

## 7.2 Methods of Synthesis and Characterization of Copolymers

### 7.2.1 Materials

L(-)-lactide with optical purity of 99.5 % was obtained from Purac, USA. Tin octanoate ( $\text{SnOct}_2$ ) was obtained from Aldrich. Anhydrous toluene, 99.8 % (Aldrich) was refrigerated with molecular sieve to control water absorption. HPLC grade chloroform (Sigma Aldrich) and methanol (Sigma Aldrich) were used as received. Denatured ethanol (Sigma Aldrich) was used as received. Raw beeswax was attained from the Bee Squad at the University of Minnesota's Department of Entomology, and filtered before use. Rosin was purchased from Schmitt Music and was used as received.

### 7.2.2 Method for synthesis of polymers

The SnOct<sub>2</sub> catalyst was dissolved in anhydrous toluene in a ratio of 1.0 g SnOct<sub>2</sub> per 10.0 mL toluene.

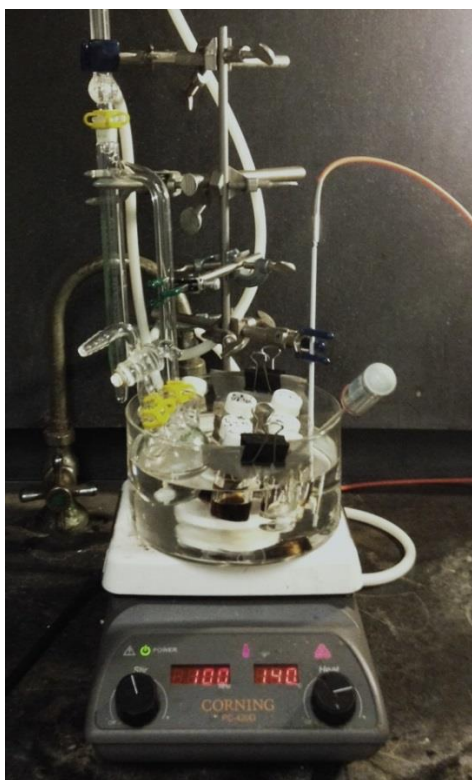
For PLLA, 5 g L(-)lactide was massed into a scintillation vial in a nitrogen tent.

For copolymer, 5 g L(-)lactide and 0.025 g OSL were massed into a scintillation vial in a nitrogen tent. OSL was restricted to 0.025 g since we found this to result in optimum lignin content a previous study by Harris, et al., Submitted 2016 showing that higher lignin contents resulted in comparatively brittle polymers.

For terpolymers, varying ratios of L(-)lactide and DVL were added to scintillation vials to total 5 g to make up the 90:10 and 80:20 LA:DVL ratios in a nitrogen tent.

Stir bars and 1 mL of the SnOct<sub>2</sub>/toluene mixture was added to each scintillation vial before sealing. Scintillation vials were subsequently transferred to a 140 °C silicone oil bath and heated for 3 hours, as shown in Figure 7.4.





**Figure 7.4.** Polymer synthesis in scintillation vials at 140 °C in silicone oil bath. Photo credit Harris, 2015.

The resulting polymeric materials were dissolved in 100 mL chloroform and reprecipitated in methanol to remove unreacted lactide, lactic acid, DVL, oligomers, and small lignin fragments.

For the composites of acetylated OSL and PLLA, acetylated OSL was dissolved in chloroform with synthesized PLLA at varying percentages: 2 %, 5 %, 10 %, and 20 % acetylated OSL. Films were then solvent cast in Teflon<sup>®</sup> dishes, which were left overnight in a ventilation hood in order to evaporate the majority

of the solvent and moved to a 40 °C desiccator for 48 hours before subjecting to further testing.

### **7.2.3 Characterization**

#### **7.2.3.1 Determination of lignin retained in the copolymer**

Ultraviolet light (UV) spectroscopy on a double-beam Cary 50 UV spectrophotometer was utilized to determine the percent of lignin retained in the copolymer. UV spectra were measured at 280 nm on a double-beam Cary 50 UV spectrophotometer and compared to a calibration curve of the original OSL dissolved in a 50:50 v/v chloroform:methanol solution diluted to 0.03 – 0.13 g/L to determine the percent of OSL retained in the copolymer. Poly[(L)-lactide] (PLLA) was used as a reference solution for absorbance correction. Five replicates of the copolymer were tested and averaged to determine the average absorbance.

#### **7.2.3.2. Determination of UV transmission through polymer films**

UV spectrometry was also used to determine UV transmission through the copolymer film compared to PLLA. UV spectra were measured from 190-400 nm on a double-beam Cary 50 UV spectrophotometer. Films were cut into strips to fit the UV test area. Thickness of each film was tested in five separate areas on each film with a Mitutoyo Digimatic Indicator. Film thicknesses were found to range from  $0.03022 \pm 0.0006$  to  $0.03088 \pm 0.0001$  mm. Three replicates of each film type were tested.

### 7.2.3.3 Molecular weight determination of synthesized polymers

All polymers were precipitated in methanol and filtered with methanol wash in order to remove monomers, dimers and small molecules. The molecular weights were examined by size exclusion chromatography (SEC) using a 1200 series Agilent High Performance Liquid Chromatography (HPLC) system equipped with a quaternary pump, autosampler, and thermostat-column compartment held at 40 °C utilizing a refractive index detector to perform analyses. HPLC grade chloroform was used as the mobile phase passing through an Agilent guard column and two Jordi Labs analytical columns connected in series to increase separation efficiency (Jordi Gel DVB mixed bed column - 250 x 10 mm, and Jordi Gel DVB 100 liner column). The chromatography was performed at an elution rate of 1 mL/min. with injection volumes of 50  $\mu$ L. Molecular weights were calculated based on a calibration with Agilent polystyrene standards. Weighted average molecular weights ( $\bar{M}_w$ ) and polydispersity indices (PDI) were calculated based on greater than ten replicates of each polymer.

### 7.2.3.4 Differential scanning calorimetry analysis

Differential scanning calorimetry (DSC) scans were collected using a Texas Instruments Q1000 DSC thermal analyzer with indium as the standard reference under nitrogen atmosphere. Samples of PLLA and PLLA-co-OSL were heated from 25 °C to 250 °C at a rate of 10 °C /min, then kept at an isotherm for

5 minutes before cooling from 250 °C to 0 °C at a rate of 20 °C /min. They were heated again from 0 °C to 250 °C at a rate of 10 °C/min. Samples containing DVL were heated from 25 °C to 200 °C at a rate of 20 °C/min, then cooled from 200 °C to -50 °C at a rate of 200 °C /min. and held at isotherm for 5 min. They were heated again from -50 °C to 200 °C at a heating rate of 10 °C/min. and held at an isotherm for 5 min. before cooling from 200 °C to -50 °C at a rate of 2 °C/min. in order to maximize the profile of the crystallization peak upon heating. The second heating cycle rates of 3-5 replicates of each polymer are reported here. Percent crystallinity ( $X_c$ ) was determined according to Equation 1 per Sichina, 2000 based on 4 replicates of each polymer.

$$X_c = \frac{\Delta H_m - \Delta H_c}{\Delta H_{m100\%}} \times 100\% \quad (7.3)$$

Where  $\Delta H_m$  is the enthalpy of melting in J/g,  $\Delta H_c$  is the enthalpy of cold crystallization in J/g, and  $\Delta H_{m100\%}$  is the enthalpy of melting 100% crystalline polymer. The  $\Delta H_{m100\%}$  of PLLA (93.1 J/g according to Henton, 2005) and the  $\Delta H_{m100\%}$  of poly(DVL) (18.8 J/g according to Pyda, 2014) were used here to estimate  $X_c$ . The weighted averages of the two (85.7 J/g for polymers with a 90:10 ratio of PLLA: DVL and 78.24 J/g for polymers with a ratio of 80:20 PLLA:DVL) were used to estimate the crystallinity of the co and terpolymers.

### 7.2.3.5 Characterization by <sup>1</sup>H-NMR

Hydrogen nucleus magnetic resonance (<sup>1</sup>H-NMR) was used to compare end groups in PLLA and the copolymer. <sup>1</sup>H-NMR spectroscopy spectra were collected

at ambient room temperature with a Varian Inova 400 MHz spectrometer with an autosampler. Samples were prepared by dissolving 7 mg of polymeric material in 1 mL deuterated chloroform with tetramethylsilane (TMS) as the internal standard for reference at  $\delta = 0.00$  ppm.

#### **7.2.4 Mechanical testing**

Thin films of resulting polymers were prepared on a Carver hot press for use in tensile testing, hydrolytic degradation and water vapor transmission rate determination. Approximately 2 g of synthesized polymer was placed between two aluminum plates, lined with silicone sheets.

Homopolymer films of PLLA were pressed at 1000 lb. of pressure for one minute, then at 1500 lb. of pressure for 30 s at 180 °C.

PLA-OSL copolymer films were pressed at 1000 lb. of pressure for one minute, then at 1500 lb. of pressure for 30 s at 170 °C.

PLA-DVL copolymer and PLA-DVL-OSL terpolymer films were pressed at 1000 lb. of pressure for one minute, then at 1500 lb. of pressure for 30 s at 150 °C.

Composite films were pressed at 1000 lb. of pressure for one minute, then at 1500 lb. of pressure for 30 s at 180 °C.

Test pieces were cut from resulting films using a standard die to a test area of length 25.4 mm, width 3.18 mm. Polymer films were conditioned for 48 hours at 50 % relative humidity (RH) before cutting and testing, following ASTM

Standard Test Method D638 for tensile properties of plastics. Thickness of each film was tested in five separate areas on each film with a Mitutoyo Digimatic Indicator within the testing length, and an average thickness found for determining Young's modulus, strain at maximum tensile stress, and maximum stress. Tensile testing was performed using an Instron 5542 testing machine with a  $\pm 500$  N load cell, and Bluehill2 v.2.35 processing software. Five replicates of each film type were tested.

### 7.2.5 Hydrolytic degradation

Degradation of control polymers and copolymers was performed following a modified procedure developed by Petinakis, et al., 2010. Pieces of previously formed thin films were cut to a mass of 0.03 g and placed on a glass microscope slide on top of a 50  $\mu$ L droplet of deionized (DI) water, then covered with another 50  $\mu$ L droplet of DI water and a second glass microscope slide before being heat sealed in a polypropylene bag, minimizing trapped air. The sealed bags were placed in 400 mL beakers filled with 100 mL DI water. This beaker was covered with aluminum foil and placed in a heated oven. This method was chosen in order to have the ability to study the degradation product fragments. Samples were held for a total of 16 days at 40 °C and at 60 °C. Three separate samples of each film type were removed at 1, 2, 5, 9, 12, and 16 days to determine  $\bar{M}_n$ ,  $\bar{M}_w$ , and PDI using SEC, as described above.

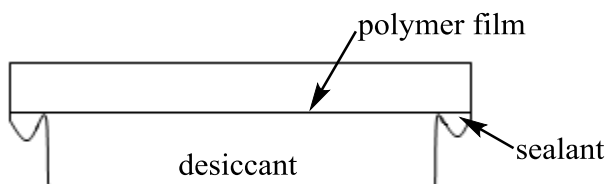
### 7.2.6 Water vapor transmission rate

Water vapor transmission rates (WVTR) were determined in a study taking place over 32 days according to ASTM E96 Standard Test Methods for Water Vapor Transmission of Materials using the desiccant method. Thin polymer films were made using a Carver press as described previously, then cut into rounds to fit specified test cups for the WVTR testing. The thickness of each circular film was tested in five separate places using a Mitutoyo Digimatic Indicator, and an average thickness calculated. Polymer samples ranged in thickness from 0.2378 to 0.3487 mm. Polymer film test specimens were sealed with 50% w/w mixture filtered beeswax/rosin to the open mouth of a test dish containing Drierite® calcium sulfate desiccant within 3 mm of the material being tested as shown in the diagram, Figure 7.5. The desiccant below the film acts to create a pressure differential related to the difference in relative humidity between the air above the film and the air below the film, where the desiccant keeps the relative humidity (RH) at zero. The test assembly, as seen in Figure 7.6, was then placed in a controlled atmosphere with constant temperature and relative humidity (ASTM, 2014). Mass gained by the assembly due to water vapor transmission through the film that was absorbed into the desiccant was measured. Three replicates of each the polymers with varying ratios of DVL were tested at 27, 75, and 95 ±1% RH. The hygrostats were reached using magnesium chloride, sodium chloride, and potassium sulfate salt solutions, respectively. All three hygrostatic humidors

were held at  $22.8 \pm 0.3$  °C, determined by live feed from an Onset HOBO MX Temp/RH logger throughout the duration of the testing period. The test dishes were massed every two days over a period of 32 days to determine the rate of water vapor movement through the film into the desiccant. The water vapor transmission rate was calculated based on the change of weight, according to Equation 7.4, (Labuza, 1984).

$$WVTR = \frac{Gx}{tA} = \left(\frac{G}{t}\right) \left(\frac{x}{A}\right) \quad (7.4)$$

In this equation, G represents weight change in grams of H<sub>2</sub>O, t is the time during which G occurred in hours, x is the film thickness, and A is the test area (cup mouth area), where G/t is the slope of the H<sub>2</sub>O mass gain over time graph.



**Figure 7.5.** Diagram of test cups used for determining WVTR. Polymer films are sealed over a layer of desiccant, creating a pressure gradient. Test cups were held at various fixed RH, according to ASTM E96 desiccant method. Figure credit: Harris, 2014.





**Figure 7.6.** Assembled test cups with films sealed over the desiccant before being placed in varied hygrostatic conditions. Variation in color due to lignin content is apparent. Photo credit Harris, 2014.

Water absorbance by individual films was also measured by leaving three replicates of each film type in each of three controlled humidors regulated to 27, 75, and  $95 \pm 1\%$  RH in order to determine whether the water mass gain by the WVTR systems would be affected by water absorbance by the polymers themselves. Polymer film samples were cut to approximately 1 cm x 4 cm and placed in a 40 °C oven under vacuum for three days. The films were then massed before setting into the various hygrostatic conditions. Films were left to equilibrate in controlled humidity environments for one week before massing

again. The difference in relation to the thickness of the films was calculated and is reported herein.

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## Chapter 8 – Results and Discussions

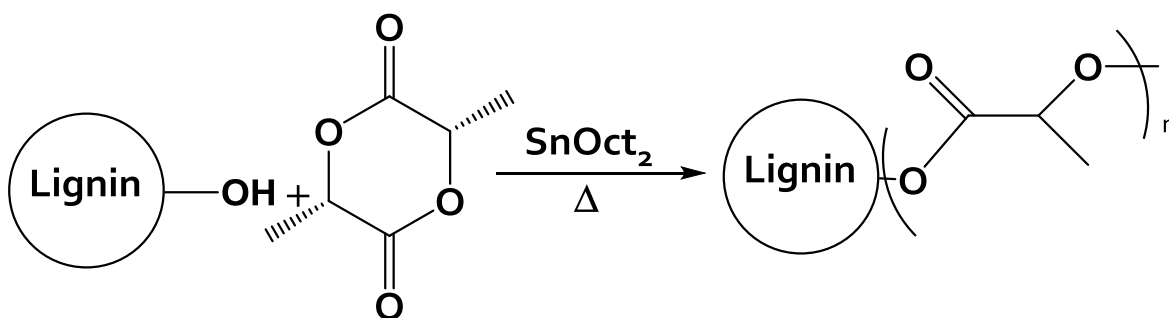
### 8.1 Introduction

There are important mechanisms to understand when designing a polymer for a given functionality. In food and beverage applications, it is important to attain a polymer that will not break down during storage, will provide an effective moisture barrier, and offer UV light protection. It is also imperative to consider the environmental aspects of a polymer since synthetics end up in landfills as well as in our lakes, rivers, and oceans. For this reason, it is key that biodegradable or compostable polymers from renewable resources are engineered to meet diverse needs.

Poly lactide, the first commercially available biopolymer, continues to be popular because it is both renewable and compostable, and has FDA approval for food and biomedical uses. However, it has limited use due to its brittleness, high vapor permeability, low thermal resistance, and poor ultraviolet radiation barrier properties. It is hypothesized that a substance with higher hydrophobicity and UV light absorbency, such as lignin, will improve vapor permeability, provide some UV protection and slow hydrolytic degradation. Lignin has been described as an encrusting agent that limits water's influence on the carbohydrate fraction of lignocellulosic material (Rowell, 2005). Lignin has also been established as a material capable of reducing dimensional change in lignocellulosics with moisture-content fluctuation due to its rigidity and hydrophobicity (Bowyer, 2003). Still, in a copolymer material, there are many factors at play. Lignin is bulky in

comparison to polylactide and it is believed that lignin could interfere with polymer crystallization, thereby allowing water easier access to stretches of polylactide that would otherwise be resistant to degradation. Alternatively, lignin may act to keep water away from the end groups that are most susceptible to degradation as it attaches to the growing chain.

The unique approach used here was to incorporate OSL, a low molecular weight lignin that results from an organic extraction process, into the polylactide biopolymer, as shown in the schematic, Figure 8.1. The end goals are to improve the water barrier properties and UV permeability of polylactide, while maintaining or improving mechanical properties. Furthermore, it is expected to slow, but not prevent, hydrolytic degradation of the copolymer.



**Figure 8.1.** Schematic depicting potential structure of a PLLA-OSL co-polymer.

Unfortunately, both lignin as well as PLA are brittle polymers which significantly limits their usefulness. As proposed by other researchers, we also

explored the option of utilizing delta-valerolactone (DVL) to improve brittleness of PLA and our PLLA-OSL copolymer.

DVL is a biobased monomer derived from sugars that has rubbery properties when polymerized (Xiong, 2014; Fernandez, 2014). This monomer is capable of ring opening polymerization, much like lactide, making it a good candidate for a block PLLA-DVL-OSL terpolymer providing flexibility (Fukuzake, et al., 1989; Kasyapi & Bhowmick, 2014). Figure 8.2 below shows one possible structure for the terpolymer.

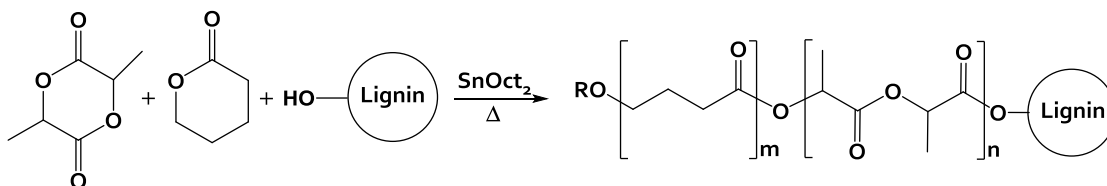


Figure 8.2. Diagram depicting of one possible option for the terpolymer of LA, DVL, and OSL (PLLA-DVL-OSL)

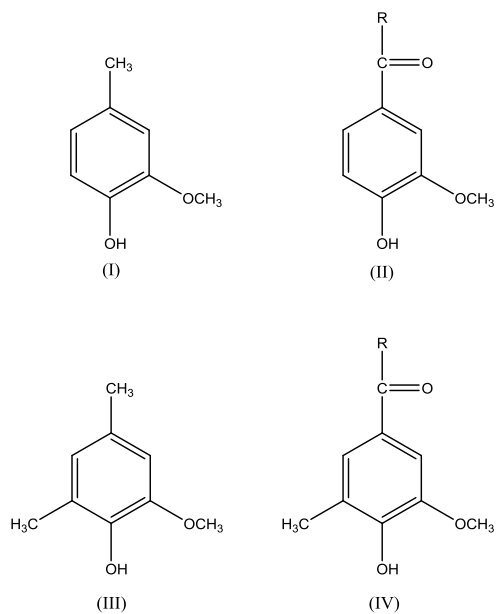
## 8.2 Lignin

All our experiments were performed using commercial lactide and organosolv lignin from switchgrass (OSL). OSL has a low  $\bar{M}_w$  ( $971 \pm 32$  Da) and is very clean. Klason lignin content of this lignin was found to be 96.4%, and acid soluble lignin was determined to be 1.9%, giving a total lignin content of 98.3%. Ash content of the OSL was 0.94%, leaving the carbohydrate portion below 1%.

As described earlier, several attempts were made to oxidize and bleach lignin. While some of these attempts looked promising, we were not able to successfully produce copolymers with oxidized lignin. All oxidation reactions of this lignin did not result in material that could be utilized in our experiments. The H<sub>2</sub>O<sub>2</sub> treated lignin did not mix with the lactide, and instead stayed in clumps which were dispersed throughout the PLLA that polymerized. Peracetic acid treatment had an amber color and a sticky consistency. We were not able to attain a polymer of high enough  $\bar{M}_w$  to continue with characterization of copolymers using peracetic acid treated OSL. Ozone treated lignin also resulted in polymers of significantly low  $\bar{M}_w$  when copolymerized with LA, from which it is not possible to form films for further testing. Therefore, all results described here were obtained using the unmodified OSL.

In order to determine the potential availability of active sites, and to confirm that our untreated OSL is a good lignin choice for polymerization with lactide, we determined the total phenolic hydroxyl content based on the four types of phenolic groups that occur in lignin, as seen in Figure 8.3. UV showed the total phenolic content of OSL to be 2.04 mmol/g. Complete phenolic hydroxyl content results are shown in Table 8.1. This high phenolic hydroxyl content, and especially the fact that close to 10% of that is conjugated, shows that switchgrass lignin has many sites for chemical bonding in ring-opening polymerization with lactide. For comparison, Jaaskelainen, et. al., 2003 reported that total phenolic hydroxyl content of enzymatically extracted lignin was 1.37 mmol/g.





**Figure 8.3.** Non-conjugated phenolics (I, III), Conjugated phenolics (II, IV), phenolics ionized in pH 12 (I, II), weakly acidic phenolics (III, IV) were determined using UV spectroscopy.

**Table 8.1.** Phenolic hydroxyl content of OSL determined for characterization. The phenol types correspond to those shown in Figure 2.

Phenol Type	Concentration (mmol/g)
Non-conjugated (Type I + III)	1.89
Conjugated (Type II + IV)	0.15
Total phenolic content	2.04

### 8.3 PLLA-OSL copolymer

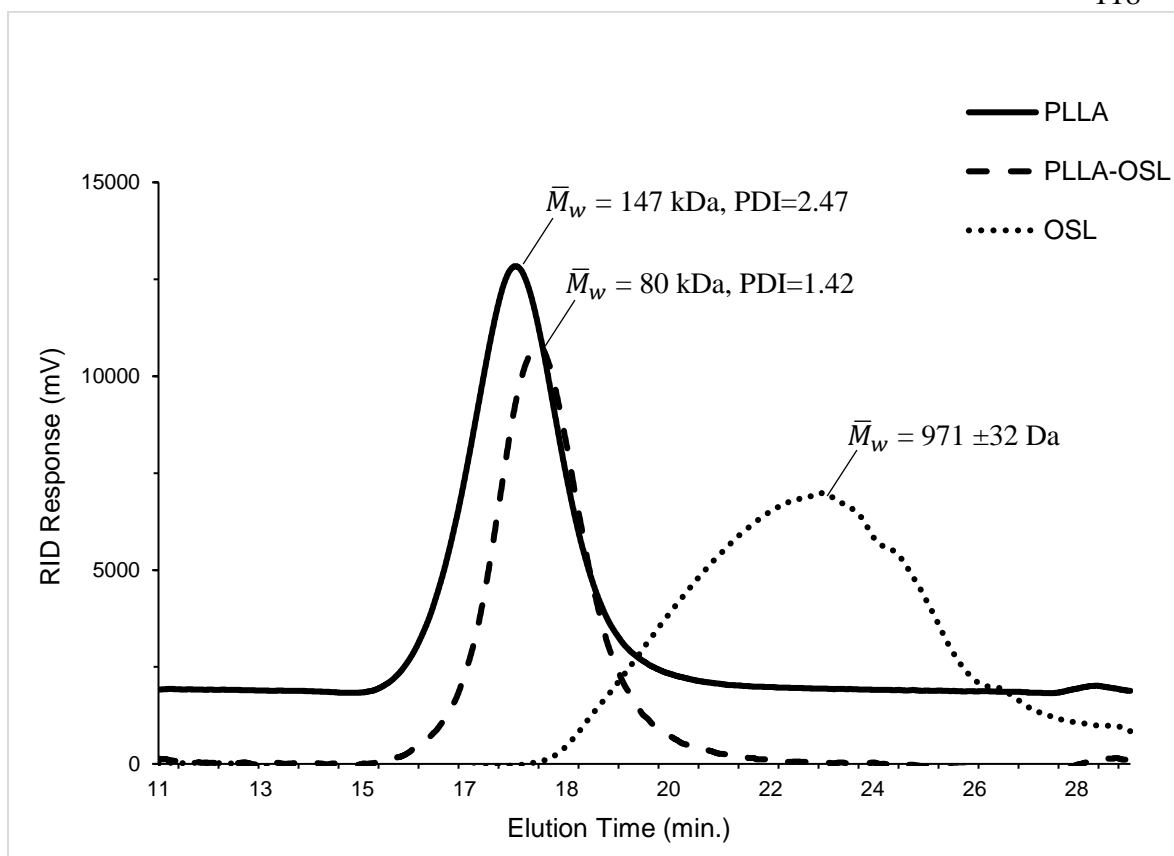
OSL addition rate was restricted to 0.025g lignin with 5.00g of L-Lactide because higher lignin content resulted in very brittle polymers. This was necessary in order to study the effects of even small amounts of lignin in the copolymer. Overall polymer yields after reprecipitation to remove remaining monomers and oligomers, were found to be  $62 \pm 1.6$  % for the PLLA homopolymers and  $56 \pm 2.2$  g for the PLLA-OSL copolymers.

The percentage of OSL retained in the copolymers was determined by UV spectroscopy (Table 8.2). It was found that polymers in which OSL was directly added to L(-)lactide in the polymerization in a ratio of 1:0.005 L(-)lactide:OSL w/w retained  $51.2 \pm 0.17$  % of the lignin, resulting in a copolymer with a 0.26 % w/w OSL content. Up to  $85.8 \pm 0.10$  % of the lignin introduced was retained when OSL was introduced at higher w/w ratios. Clearly, a higher percentage of OSL was incorporated into the copolymer as the mass of lignin introduced into the polymerization increased. Nevertheless, for most of our experiments the actual addition of OSL was restricted to 0.5 % OSL, resulting in an actual lignin content in the polymers of 0.26%, in order to maintain a polymer with enough flexibility to conduct further testing.

**Table 8.2.** The ratio of lignin introduced into the PLLA-OSL copolymer compared with the percent OSL that was retained in the copolymer was determined by UV analysis.

PLLA:OSL Introduced (g)	OSL Retained (%)
1:0.005	51.2 ±0.17 %
1:0.01	76.4 ±0.23 %
1:0.02	85.8 ±0.10 %

To assure that we indeed were able to produce a true copolymer between lactide and OSL, we examined the reprecipitated polymeric material using SEC. SEC data showed that the PLLA-OSL copolymer had an overall lower  $\bar{M}_w$  than the PLLA homopolymer synthesized using the same methods, though it was found to be significantly higher than that of OSL. The molecular weights and molecular weight distributions, based on three replicates each of PLLA, OSL and PLLA-OSL can be seen in Figure 8.5. The figure demonstrates that after reprecipitation, there are no fragments with the molecular weight of the original OSL present in the copolymer, indicating that the lignin is indeed bonded covalently to the polymer chain.



**Figure 8.4.**  $\bar{M}_w$  Comparison of polymers and OSL, determined by SEC and DLS, respectively. The overlay of the chromatograms shows the variation in elution times of the three polymers, related to molecular weight.

To avoid the well known issues with lignin aggregation in SEC, the lignin was acetylated and  $\bar{M}_w$  was determined using a dynamic light scattering (DLS) system. As expected, the polydispersity index (PDI) increased with the addition of OSL from 2.42 for PLLA to 3.38 for the copolymer as seen in Table 8.3<sup>1-2</sup>.

**Table 8.3.**  $\bar{M}_w$  of polymers is given here as the average results of four repetitions.

$\bar{M}_w$  of OSL was found by DLS, while  $\bar{M}_w$  of all other polymers was estimated by SEC.

Polymer Type	$\bar{M}_w$ Da	PDI
OSL	971 ±32	-
PLLA <sup>1</sup>	147 000	2.47
PLLA-OSL <sup>2</sup>	80 000	3.38
90:10 <sup>3</sup>	105 000	2.83
90:10-OSL <sup>4</sup>	70 000	3.66
80:20 <sup>5</sup>	40 000	2.60
80:20-OSL <sup>6</sup>	26 000	2.79

<sup>1</sup>PLLA homopolymer

<sup>2</sup>copolymer of PLLA and OSL

<sup>3</sup>copolymer produced with 90:10 LA:DVL ratio

<sup>4</sup>terpolymer produced with 90:10 LA:DVL with 0.025 g OSL added

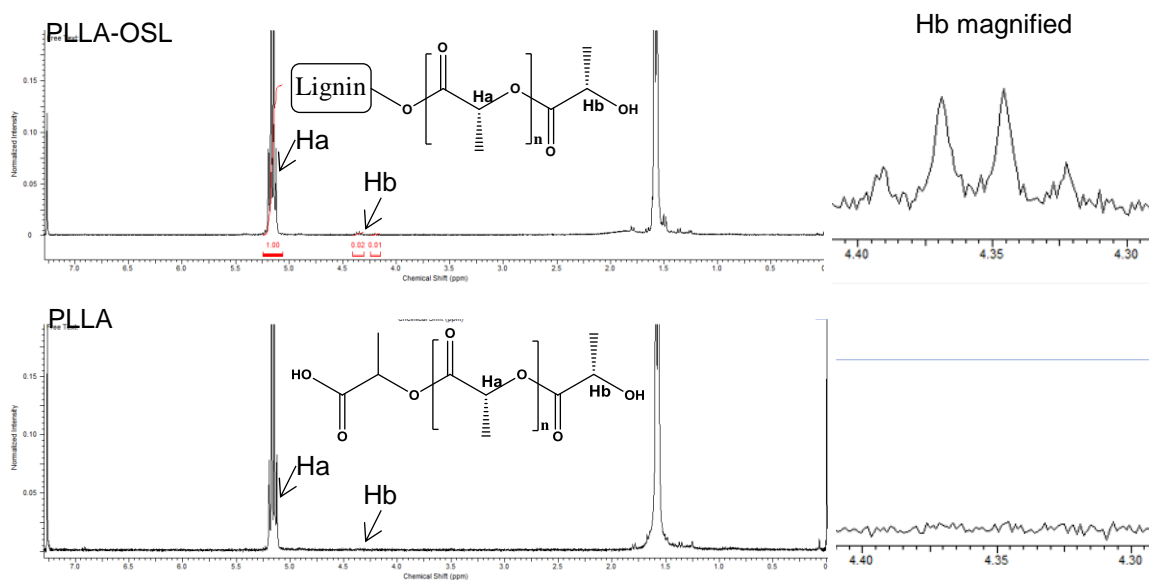
<sup>5</sup>copolymer produced with 80:20 LA:DVL ratio

<sup>6</sup>terpolymer produced with 80:20 LA:DVL with 0.025 g OSL added

It was found that the PLLA did have significantly higher  $\bar{M}_w$  than that of PLLA-OSL. Polymerization with OSL clearly affects the overall  $\bar{M}_w$  of the polymers compared to the polymers that do not include OSL.

The SEC findings suggesting that the polymer chain length decreases with lignin addition are confirmed through <sup>1</sup>H-NMR data which shows that the number of terminal end groups in the polymer increases when OSL is added, thus resulting in shorter polymer chain length, as shown by the peak at 4.35 ppm in Figure 8.5. This corroborates findings by Fernandez, 2015 and Chung, 2013.

This peak, shown as Hb represents the hydrogen on the terminal carbon of the PLLA chain at the hydroxyl end group.

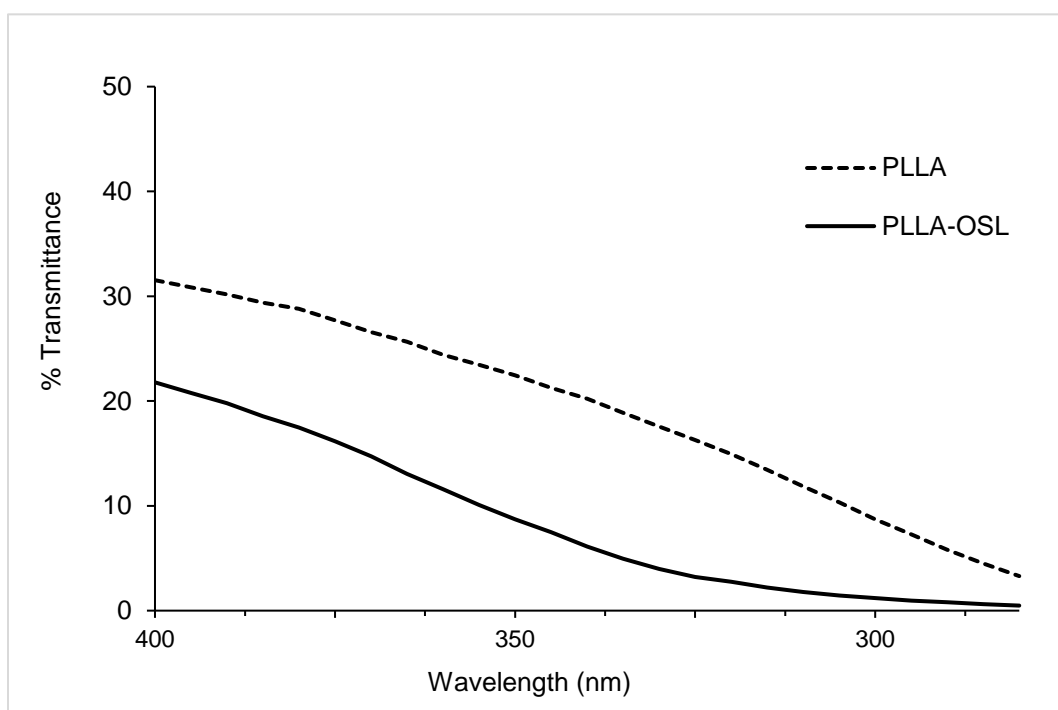


**Figure 8.5.**  $^1\text{H-NMR}$  spectra of PLLA-OSL. A small peak detected around 4.35 ppm indicates an increase in end groups in the copolymer compared to PLLA.

The range of this peak is enlarged to the right of each spectra.

It is hypothesized that in most cases, lignin addition to the growing polymer chain stops any further monomer addition. The stronger Hb signal confirms a significant increase in end groups. It also appears reasonable to assume that the majority of the lignin is added to the polymer end with the carboxylic acid end group.

UV transmission is seen to decrease with the addition of OSL to the copolymer by approximately 20 %, as seen in Figure 8.6. It was expected that lignin addition would have an effect on light transmission. It is known that the aromatic moieties in lignin absorb light, especially around 280 nm. The films have a brown tint, so also absorb light in the visible light range, which may make them less desirable to consumers.



**Figure 8.6.** Average UV transmission through polymer films comparing polymers with and without OSL at various wavelengths. It can be seen that UV transmission is greatly decreased with the addition of OSL to the polymerization.

DSC scans show that the addition of OSL to the polymers decreases the glass transition temperature, and melting point of the polymers, as seen in Table

8.4<sup>1-2</sup>. This effect can also have a negative impact on some potential applications.

**Table 8.4.** The average results of DSC, showing the comparison of  $T_g$  and  $T_m$  and the degree of crystallinity of polymers.

Polymer Type	$T_g$ (°C)	$T_m$ (°C)	$X_c$ (%)
PLLA <sup>1</sup>	53.1 ±2.9	175.0 ±3.0	48.47 ±2.9
PLLA-OSL <sup>2</sup>	50.9 ±2.9	164.2 ±2.0	55.79 ±2.4
90:10 <sup>3</sup>	43.3 ±1.3	158.6 ±2.1	6.17 ±1.7
90:10-OSL <sup>4</sup>	30.1 ±4.2	149.6 ±8.1	10.37±0.69
80:20 <sup>5</sup>	28.8 ±2.0	142.0 ±6.8	3.98 ±1.7
80:20-OSL <sup>6</sup>	23.0 ±6.4	137.1 ±7.5	1.38±0.74
PLLA/2% acOSL <sup>7</sup>	54.36 ±2.1	174.1 ±0.0	-
PLLA/5% acOSL <sup>8</sup>	57.5 ±0.04	175.5 ±0.19	-
PLLA/10% acOSL <sup>9</sup>	57.9 ±0.02	171.8 ±2.4	-

<sup>1</sup>PLLA homopolymer

<sup>2</sup>copolymer of PLLA and OSL

<sup>3</sup>copolymer produced with 90:10 LA:DVL ratio

<sup>4</sup>terpolymer produced with 90:10 LA:DVL with 0.025 g lignin added to polymerization

<sup>5</sup>copolymer produced with 80:20 LA:DVL ratio

<sup>6</sup>terpolymer produced with 80:20 LA:DVL with 0.025 g lignin added to polymerization

<sup>7</sup>PLLA composite containing 2 % acetylated OSL

<sup>8</sup>PLLA composite containing 5 % acetylated OSL

<sup>9</sup>PLLA composite containing 10 % acetylated OSL

Physical properties of PLLA and the PLLA-OSL are listed in Table 8.5<sup>1-2</sup>.

The average percent tensile strain at break ( $\epsilon$ ) is shown to decrease as lignin is added to the copolymer, and tensile stress ( $\sigma$ ) also decreases. The ratio of stress



to strain, or the Young's modulus ( $E$ ), is affected little as stress and strain decreased proportionally with the addition of lignin to the copolymer, resulting in a copolymer that is nearly equal to PLLA in stiffness.

**Table 8.5.** The average results of tensile testing.

Polymer Type	$\varepsilon$ (%)	$\sigma$ (MPa)	$E$ (GPa)
PLLA <sup>1</sup>	3.02 ±0.59	52.78 ±0.01	2.49 ±0.20
PLLA-OSL <sup>2</sup>	1.47 ±0.19	36.92 ±6.06	2.48 ±0.32
90:10 <sup>3</sup>	52.92 ±1.3	26.34 ±0.76	1.80 ±0.09
90:10-OSL <sup>4</sup>	10.93 ±1.4	6.81 ±3.8	0.67 ±0.04
80:20 <sup>5</sup>	97.64 ±4.8	14.27 ±1.3	1.03 ±0.11
80:20-OSL <sup>6</sup>	28.57 ±4.9	6.25 ±0.32	0.23 ±0.05
PLLA/2% acOSL <sup>7</sup>	2.08 0.74	28.14 1.1	2.48 0.17
PLLA/5% acOSL <sup>8</sup>	2.47 0.75	20.1 1.7	1.96 0.59
PLLA/10% acOSL <sup>9</sup>	2.32 0.31	12.90 3.2	1.11 0.33

<sup>1</sup>PLLA homopolymer

<sup>2</sup>copolymer of PLLA and OSL

<sup>3</sup>copolymer produced with 90:10 LA:DVL ratio

<sup>4</sup>terpolymer produced with 90:10 LA:DVL with 0.025 g lignin added to polymerization

<sup>5</sup>copolymer produced with 80:20 LA:DVL ratio

<sup>6</sup>terpolymer produced with 80:20 LA:DVL with 0.025 g lignin added to polymerization

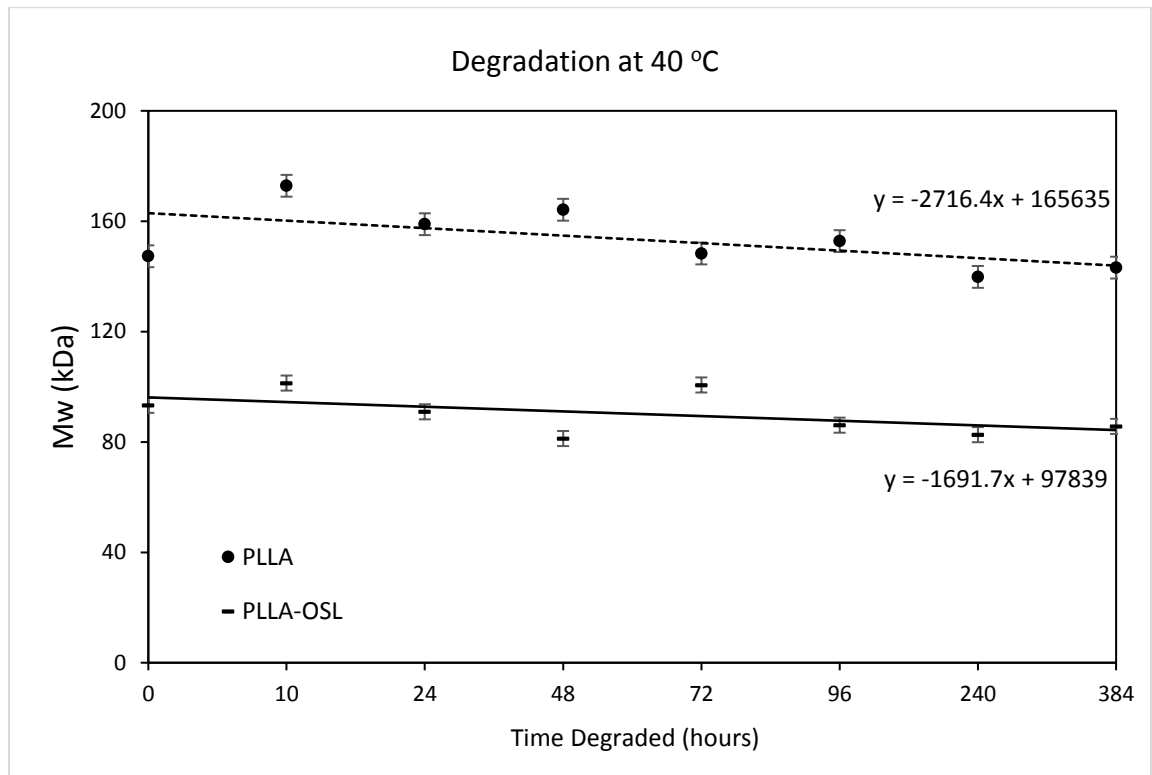
<sup>7</sup>PLLA composite containing 2 % acetylated OSL

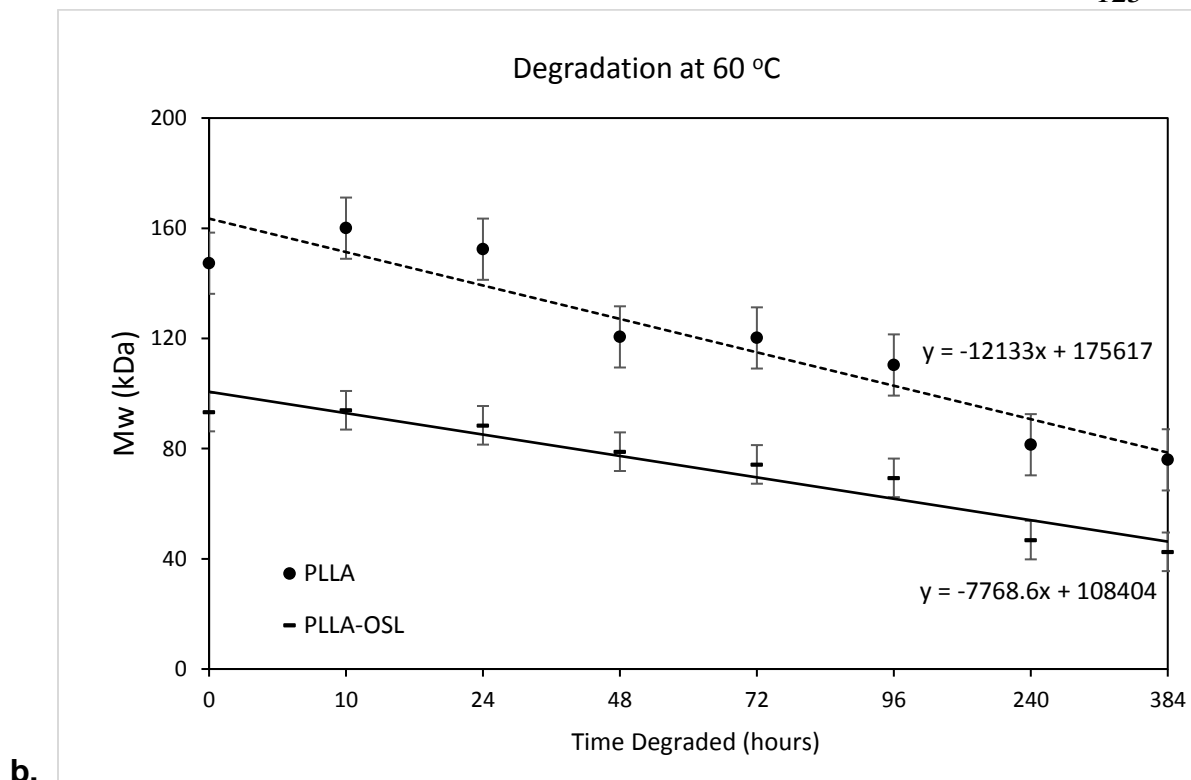
<sup>8</sup>PLLA composite containing 5 % acetylated OSL

<sup>9</sup>PLLA composite containing 10 % acetylated OSL

Hydrolytic degradation studies revealed that copolymers containing as little as 0.05 % lignin degrade at a lower rate than PLLA. This effect can be observed at both 40 °C and 60 °C, but is more pronounced at the higher

temperature, ( Figure 8.7.a-b.) The percent degradation at 40 °C was found to be reduced by 39 % and at 60 °C it was found to be reduced by 44 % over a period of sixteen days.



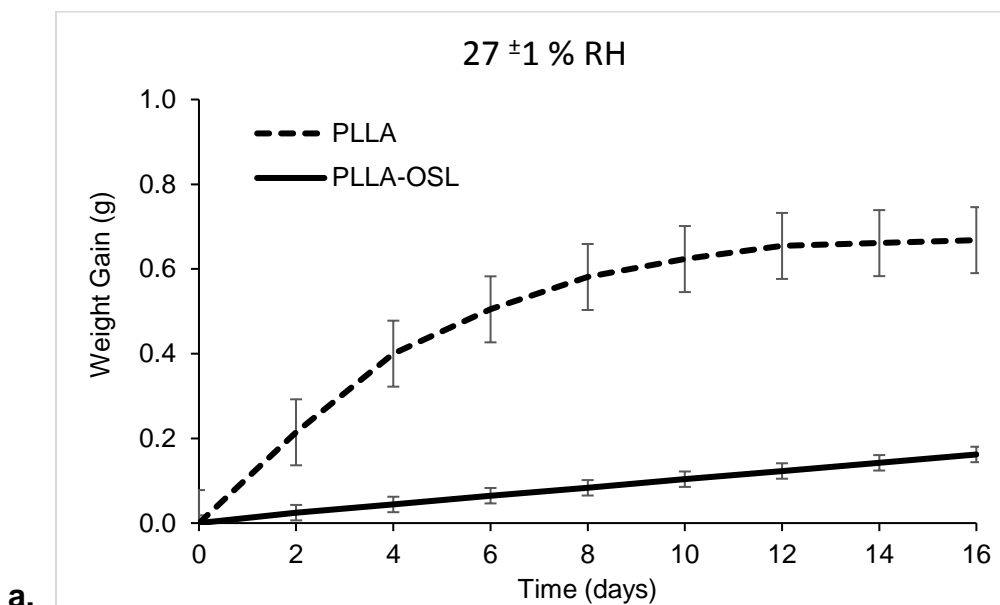


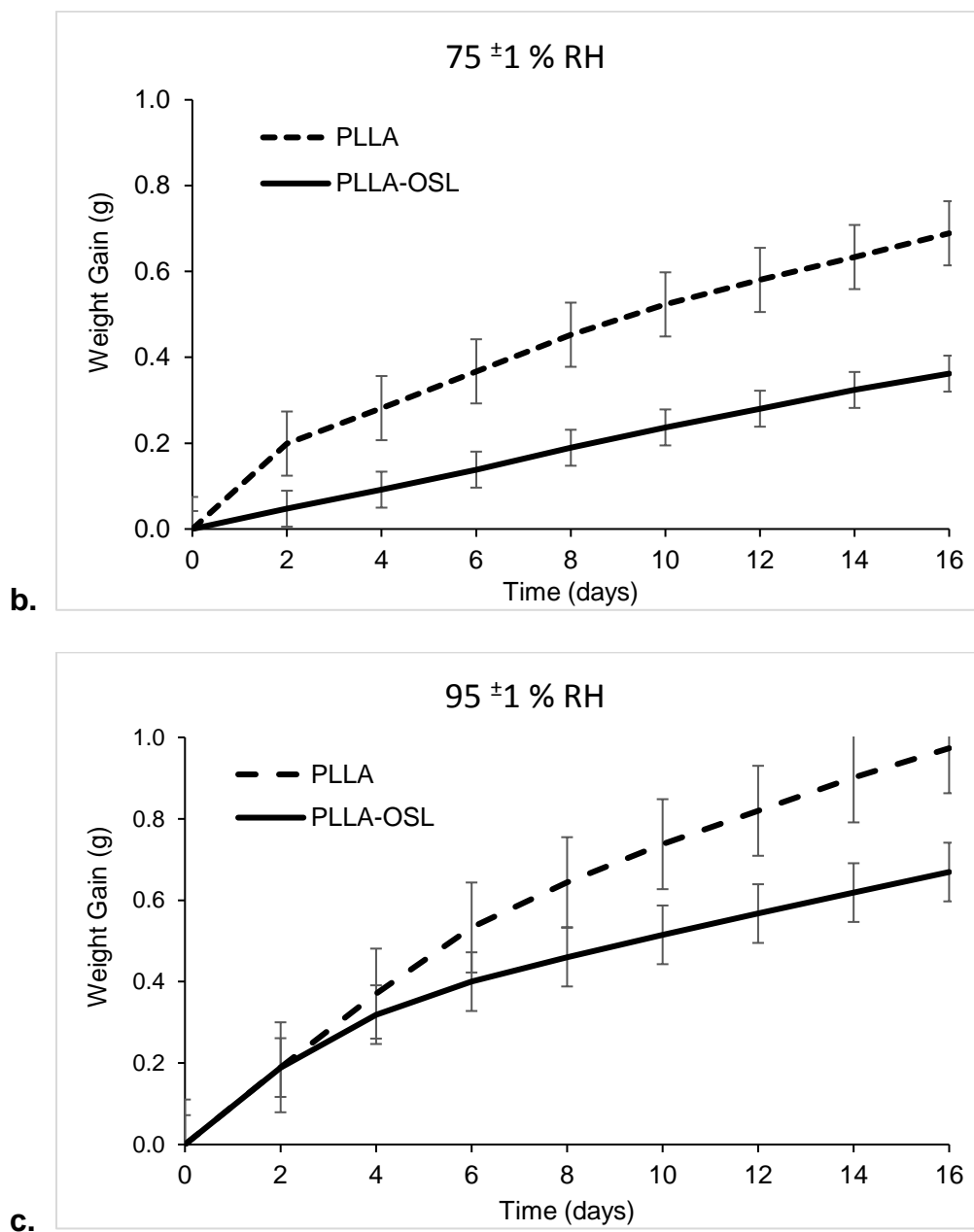
**Figure 8.7.** The change in weighted average molecular weights over time of PLLA and PLLA-OSL due to hydrolytic degradation represent the variation in four replicates taken at each degradation time for each temperature at **a.** 40 °C **b.** and at 60 °C.

It appears that even the presence of small amounts of lignin in the PLLA structure slow, but don't prevent the hydrolysis. The most obvious explanation is the assumption that water diffusion into the polymer is hindered by the presence of the hydrophobic lignin. Another determining factor could be the blocking of hydrophilic end groups by lignin. A study published by Cairncross, et al. in 2006 found that moisture sorption seems to be controlled by the hydrophilic end

groups of PLA, the addition of lignin to the PLLA polymer will reduce these end groups.

To further study water permeability, Water Vapor Transmission Rate (WVTR) studies were used to determine the rate of water vapor transmission through the PLLA and copolymer films. As can be seen in Figure 8.8. a-c., water vapor passed through the PLLA homopolymer at a faster rate than through the copolymer with 0.05 % OSL added at all three relative humidity rates.





**Figure 8.8.** Water transmission through polymer films in varied hygrosstatic conditions showed that the addition of lignin into the polymer reduced the rate of water vapor transmission through films of the copolymer compared to films of the homopolymer. Error bars represent the variation in three films at **a.** 27 ± 1 % RH, **b.** at 75 ± 1 % RH, and **c.** at 95 ± 1 % RH.

WVTR calculations reveal that water vapor passed through the polymers containing lignin at a slower rate than through those without lignin (Table 8.6<sup>1-2</sup>). WVTR was reduced by 32, 36 and 64 % at RH of 27%, RH 75% and 95% respectively in the case where lactide was copolymerized with OSL.

**Table 8.6.** Summary of water transmission rates (g/m<sup>3</sup>/day), not available for 80:20-OSL.

Polymer Type	WVTR (g/m <sup>3</sup> /day)		
	27 ±1 % RH	75 ±1 % RH	95 ±1 % RH
PLLA <sup>1</sup>	1.76 x 10 <sup>-3</sup>	2.21 x 10 <sup>-3</sup>	2.54 x 10 <sup>-3</sup>
PLLA-OSL <sup>2</sup>	5.59 x 10 <sup>-4</sup>	8.06 x 10 <sup>-4</sup>	1.62 x 10 <sup>-3</sup>
90:10 <sup>3</sup>	1.39 x 10 <sup>-3</sup>	1.77 x 10 <sup>-3</sup>	1.84 x 10 <sup>-3</sup>
90:10-OSL <sup>4</sup>	1.09 x 10 <sup>-3</sup>	1.47 x 10 <sup>-3</sup>	1.47 x 10 <sup>-3</sup>
PLLA/2% acOSL <sup>7</sup>	1.02 x 10 <sup>-3</sup>	2.05 x 10 <sup>-3</sup>	2.30 x 10 <sup>-3</sup>
PLLA/5% acOSL <sup>8</sup>	8.62 x 10 <sup>-4</sup>	1.19 x 10 <sup>-3</sup>	2.52 x 10 <sup>-3</sup>
PLLA/10% acOSL <sup>9</sup>	4.20 x 10 <sup>-4</sup>	1.07 x 10 <sup>-3</sup>	2.19 x 10 <sup>-3</sup>

<sup>1</sup>PLLA homopolymer

<sup>2</sup>copolymer of PLLA and OSL

<sup>3</sup>copolymer produced with 90:10 LA:DVL ratio

<sup>4</sup>terpolymer produced with 90:10 LA:DVL with 0.025 g lignin added to polymerization

<sup>7</sup>PLLA composite containing 2 % acetylated OSL

<sup>8</sup>PLLA composite containing 5 % acetylated OSL

<sup>9</sup>PLLA composite containing 10 % acetylated OSL

Overall, the films themselves (no desiccant) were shown to absorb negligible amounts of water as seen in Table 8.7. Films held at RH hygrostats for 16 days absorbed 0.13 – 0.53 % water by mass. As expected, films absorbed

more moisture when held at higher humidity. Table 8.7 show the average percent mass gain of films held in hygrostatic conditions for 16 days. Because the standard error of the weight gain is  $\pm 1$  %, and the overall weight gain is less than 1%, it can be assumed that the weight gain by the polymer itself was negligible when considering WVTR.

**Table 8.7.** Average percent water uptake of neat films held in hygrostatic conditions for 16 days.

Polymer Type	% Water Uptake		
	27 $\pm$ 1 % RH	75 $\pm$ 1 % RH	95 $\pm$ 1 % RH
PLLA <sup>1</sup>	0.13 $\pm$ 0.12	0.18 $\pm$ 0.05	0.43 $\pm$ 0.12
PLLA-OSL <sup>2</sup>	0.04 $\pm$ 0.08	0.08 $\pm$ 0.05	0.34 $\pm$ 0.04
90:10 <sup>3</sup>	0.31 $\pm$ 0.11	0.35 $\pm$ 0.06	0.43 $\pm$ 0.13
90:10-OSL <sup>4</sup>	0.31 $\pm$ 0.09	0.31 $\pm$ 0.10	0.37 $\pm$ 0.09

<sup>1</sup>PLLA homopolymer,  $\bar{M}_w = 147$  KDa

<sup>2</sup>copolymer of PLLA and OSL,  $\bar{M}_w = 80$  KDa

<sup>3</sup>copolymer produced with 90:10 LA:DVL ratio,  $\bar{M}_w = 105$  KDa

<sup>4</sup>terpolymer produced with 90:10 LA:DVL with 0.025 g lignin added to polymerization,  $\bar{M}_w = 70$  KDa

Findings show that water absorption results differ from those of water degradation. The addition of OSL to the polymers influenced a decrease in degradation rates, while the addition of OSL shows an increase in percent water uptake. This increase in water absorption could be due to the OSL disrupting the crystallinity of the polymer, allowing an increase in water activity in the matrix. Although there may be more water in the matrix, the covalently bonded OSL

seems to act to decrease degradation, pointing to OSL bonding to an end group, thereby not allowing end scission reactions that take place in the hydrolytic degradation of the polymers without OSL.

#### **8.4 PLLA-DVL-OSL terpolymer**

As mentioned before, both PLLA and Lignin are two very brittle materials. Therefore, it was not surprising that the PLLA-OSL polymer was brittle and difficult to process, especially at higher lignin addition rates. To overcome this issue we decided to incorporate delta-valerolactone (DVL) into the PLLA-lignin copolymer in order to add flexibility to the lignin copolymers.

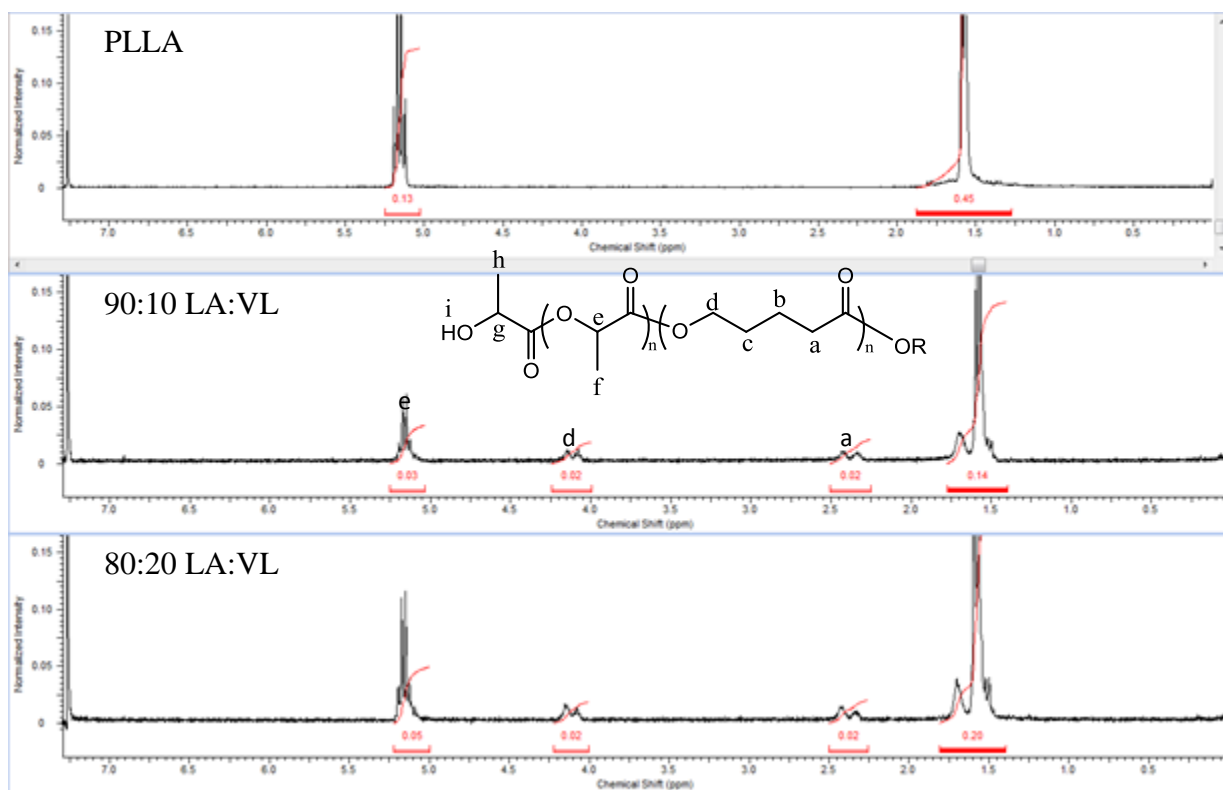
Because DVL has been shown to act as an elastomeric material and improve the flexibility of PLLA, as outlined above, it was hypothesized that when DVL is polymerized with lactide and OSL, the resulting terpolymer will have increased tensile stress and lower Young's modulus, while maintaining the improved moisture vapor transmission rates and reduced UV permeability when compared to PLLA.

L(-)lactide and untreated OSL were polymerized with varying amounts of DVL. Again it was found through SEC analysis that the co and terpolymers did have significantly higher  $\bar{M}_w$  than that of OSL by itself (Table 8.3<sup>1-6</sup>). All polymers have a lower molecular weight than the PLLA synthesized using the same reaction conditions. PLLA-OSL copolymers and PLLA- DVL-OSL terpolymers have an overall lower  $\bar{M}_w$  than the polymers synthesized using the same



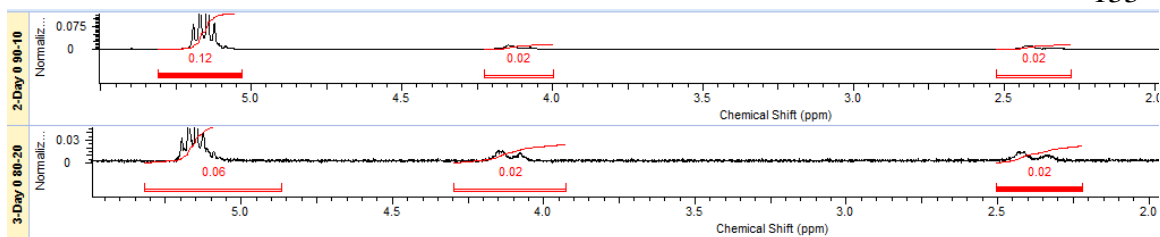
methods without the addition of OSL. Polymerization with OSL clearly affects the overall  $\bar{M}_w$  of the polymers compared to the polymers that do not include OSL. As seen before, lignin reduces the polymer chain length compared to the PLLA homopolymer by stopping further monomer addition. Table 8.3<sup>1, 4-6</sup> also demonstrates that  $\bar{M}_w$  is also decreased through addition of DVL as compared to the original PLLA homopolymer.

Figure 8.9 shows <sup>1</sup>H-NMR spectra of the polymers produced with lactide to DVL ratios of 90:10, and 80:20 compared with PLLA. The methylene H next to ether moieties give a signal that is seen at 5.15 ppm (PLLA signal). The signal centered around 4.1 ppm corresponds to the methylene of DVL (d), and the signal centered around 2.35 ppm corresponds to the a methylene of DVL (a), while other H are included between 1.7-1.3 ppm. It is apparent that the methylenes of DVL give two signals (two triplets). The higher (4.13, 2.37 ppm) of the triplets are assigned to delta Valerolactone-lactide (DVL-LA) dyads, while the lower (4.07, 2.33) are assigned to the DVL-DVL dyad, as is delineated by Fernandez, et al., 2015. Clearly, both types of bonds are present in the terpolymer, with the LA-LA bonds being slightly dominant at higher concentration of DVL.



**Figure 8.9.** <sup>1</sup>H-NMR spectra from top of: PLLA; 90:10 LA:VL w/w copolymer; and 80:20 LA:VL w/w copolymer.

As expected, the ratio of DVL to LA in the copolymer increases with higher DVL addition rates. Integration ratio of the signals at 4.1 and 2.35 ppm (DVL) and 5.15 ppm (PLA) were found to be 6:1 in the 90:10 PLLA:DVL copolymer and 3:1 in the 80:20 PLLA:DVL copolymer (Figure 8.10).

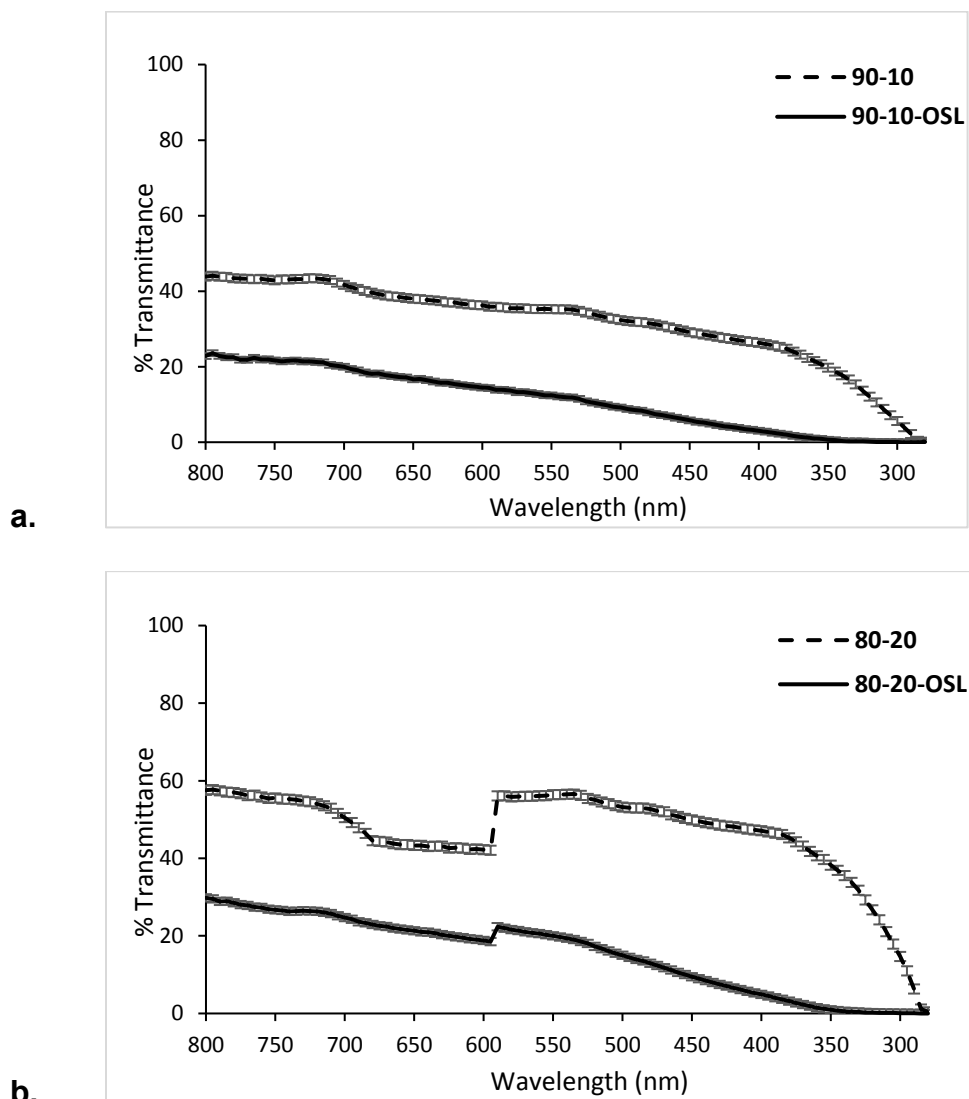


**Figure 8.10.** Integration of  $^1\text{H}$ -NMR peaks in 90:10 and 80:20 LA:DVL copolymers.

DSC scans show that the addition of lignin to the polymer decreases  $T_g$  and  $T_m$  of the polymer in each case (Table 8.4<sup>3-6</sup>). This is most likely due to the reduction in molecular size of the polymers containing OSL. The addition of DVL to the polymer also decreases  $T_g$  and  $T_m$ , which may be due to the polymer becoming less crystalline as the ratio of DVL in the polymer is increased. This low  $T_g$  results in a polymer material that starts to become tacky. This effect has been previously reported by Xiong, et al., 2014.

As seen with the PLLA-OSL copolymer in Figure 8.5, UV light transmission decreases with the addition of OSL to the polymers (Figure 8.11. a-b). The addition of OSL to the polymers can be seen to have a more pronounced effect on the polymer with a higher ratio of LA:VL. Light transmission rate is higher for polymers with higher DVL content. This was expected, since the DVL section contain fewer keto groups capable of absorbing light. OSL in the polymer has a more pronounced effect for the polymers with higher transmission rates.

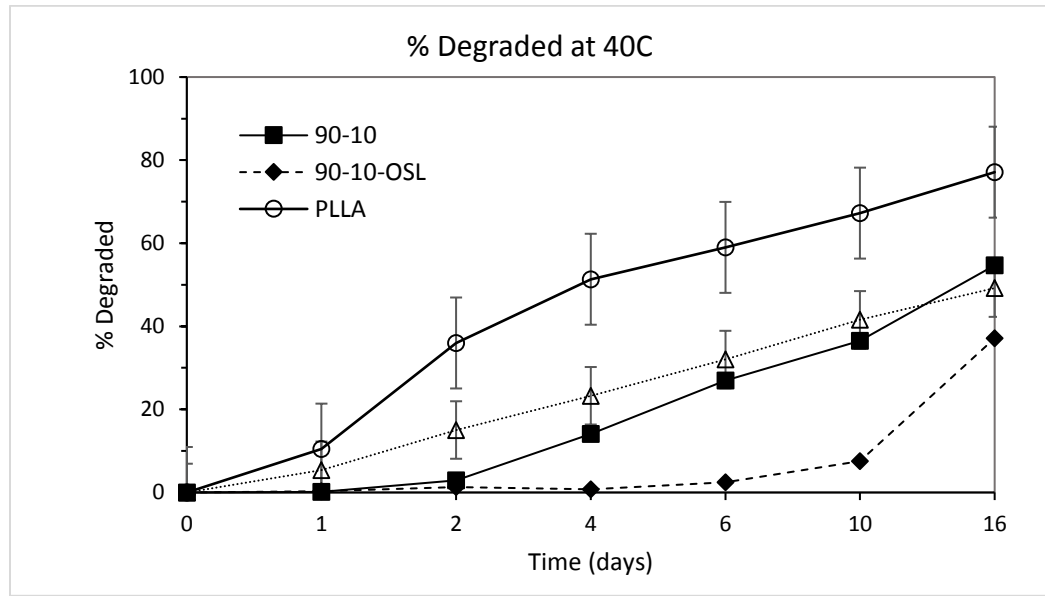
UV light transmission was reduced by up to approximately 22 % for the 90:10 polymer and up to nearly 30 % for the 80:20 polymer.



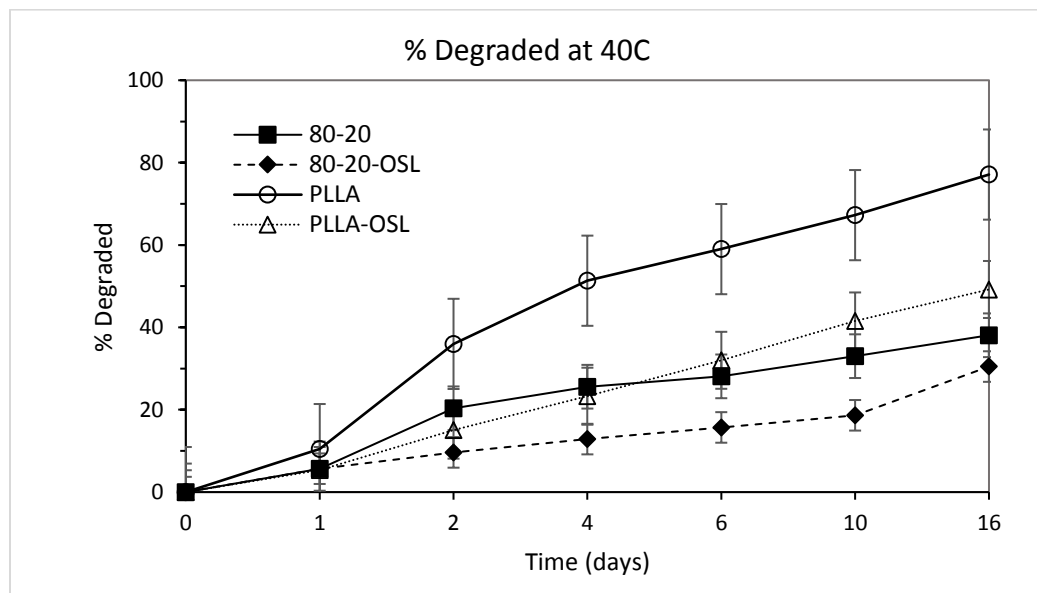
**Figure 8.11.** Average UV transmission through polymer films comparing polymers with and without OSL at various wavelengths: a. 90:10 LA:VL copolymer v. 90:10 LA:VL polymerized with OSL; and c. 80:20 LA:VL copolymer v. 80:20 LA:VL polymerized with OSL.

Strain at break ( $\epsilon$ ) increases significantly with the addition of DVL to the terpolymers, while maximum stress ( $\sigma$ ) is seen to decrease with the addition of DVL as well as with lignin, and Young's modulus ( $E$ ) dropped significantly (Table 8.5<sup>3-6</sup>). The addition of lignin to the polymer has the effect of decreasing the flexibility of the polymer as the polymer becomes more brittle and less tough. The addition of DVL to the polymerization has the effect of increasing the strain at break while decreasing Young's modulus significantly. As expected, the addition of DVL to the polymerization results in a more rubbery, elastomeric polymer. This effect offers an option to "customize" polymers, reducing the brittleness of the polymer while maintaining other desired properties.

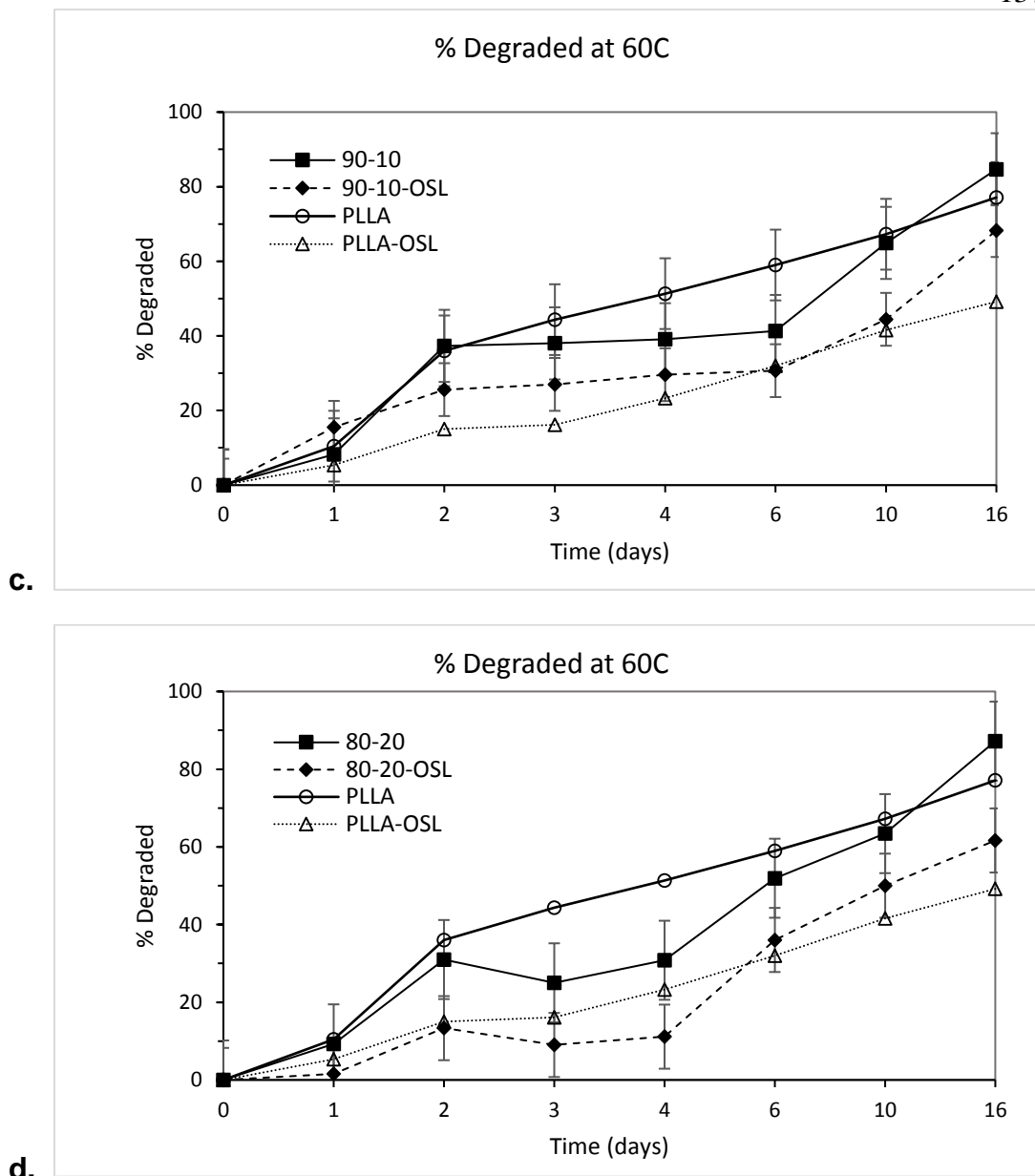
As seen previously, hydrolytic degradation studies revealed that the inclusion of lignin into the copolymers decreased the rate of degradation. This effect is witnessed at both 40 °C and 60 °C, but is more pronounced at higher temperature, as seen in Figure 8.12.



a.



b.



**Figure 8.12.** Percent decrease of  $\bar{M}_w$  over time in days of: a. polymers with a ratio of 90:10 LA:VL polymerized with and without OSL at 40 °C; b. polymers with a ratio of 90:10 LA:VL polymerized with and without OSL at 40 °C; c. polymers with a ratio of 90:10 LA:VL polymerized with and without OSL at 60 °C; b. polymers with a ratio of 90:10 LA:VL polymerized with and without OSL at 60 °C; d. polymers with a ratio of 90:10 LA:VL polymerized with and without OSL at 60 °C.

While it was thought that the addition of DVL would have the effect of decreasing the rate of degradation overall due to the longer carbon chains present in the polymer, this effect was only observed at the lower temperature of 40° C. At 40 °C (Figure 8.12 a,b) PLLA clearly shows the highest degradation rate, followed by the PLLA-DVL co-polymer. In addition, the polymer with the 80:20 LA:DVL ratio degraded more slowly than the polymer with the 90:10 LA:DVL ratio. The PLLA-OSL polymers were similar in degradation behaviour to the PLLA-DVL polymers and considerably slower than the PLLA homopolymer. At 60 °C the influence of the DVL was less pronounced. At both addition rates of DVL, the PLLA and the PLLA-DVL polymers have the highest degradation rate, with the PLLA being only slightly above the PLLA-DVL. In all cases, lignin decreases rate of hydrolytic degradation. This may be due to polymers being above their  $T_g$  at these temperatures, allowing more mobility between polymer strands.

Table 8.6<sup>3-6</sup> summarizes water vapor transmission rate (WVTR) calculations for polymers containing DVL. WVTR is already considerably reduced through the addition of DVL to PLLA. For the 90:10 PLLA:DVL polymer WVTR is reduced by 78, 83 and 79 % at RH of 27%, RH 75% and 95% respectively. As seen with the PLLA-OSL polymers, water vapor passing through the polymers containing OSL is reduced.

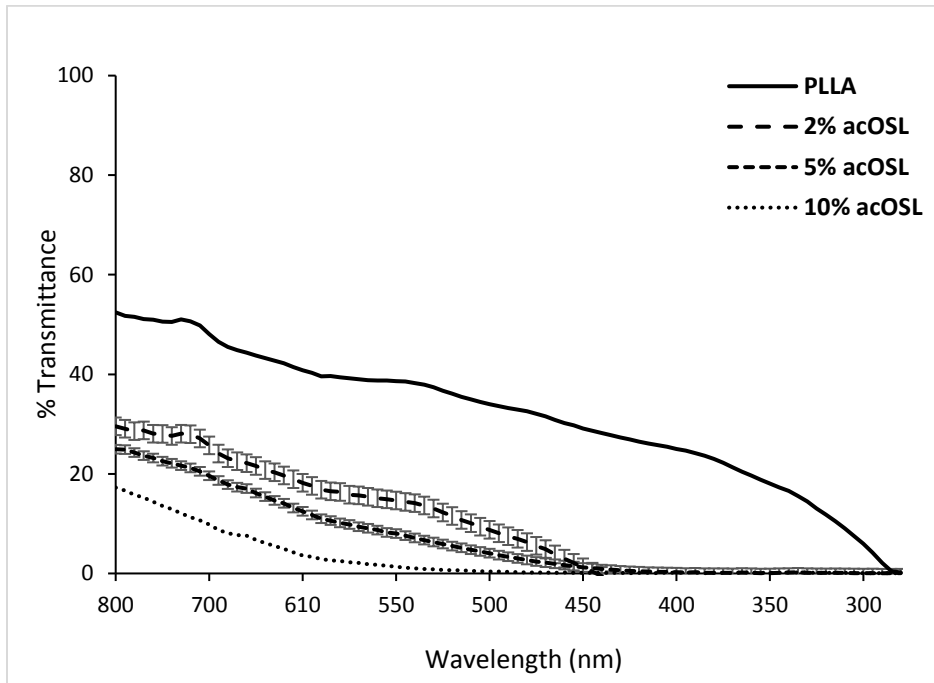


## 8.5 PLLA/acetylated OSL blends

PLLA and acetylated OSL (acOSL) were blended in varying amounts to determine whether the acetylated version of OSL could be incorporated in higher ratios than in the PLLA-OSL copolymer discussed previously. It was possible to mix up to 10% acetylated OSL with synthesized PLLA while maintaining properties that allowed for film formation and physical testing.

DSC scans showed that the addition of acOSL had negligible effects on glass transition and melting points when compared to the PLLA-OSL copolymer in each case, (Table 8.4<sup>7-9</sup>). Since acOSL was only mixed with the PLLA, it had no effect on polymer chain length, allowing the composite material to maintain glass transition and melting points close to the original material.

As seen with previous polymers containing unmodified OSL, UV light transmission was found to decrease in composite blends of PLLA/acOSL when compared with the PLLA homopolymer (Figure 8.13). The addition of acOSL to the polymers can be seen to have a more pronounced effect on the polymer with a higher ratio of acOSL:PLLA. This was expected, since OSL is capable of absorbing light. UV light transmission was reduced by approximately 20, 35, and 40 % for the blends containing 2, 5, and 10 % acOSL respectively.

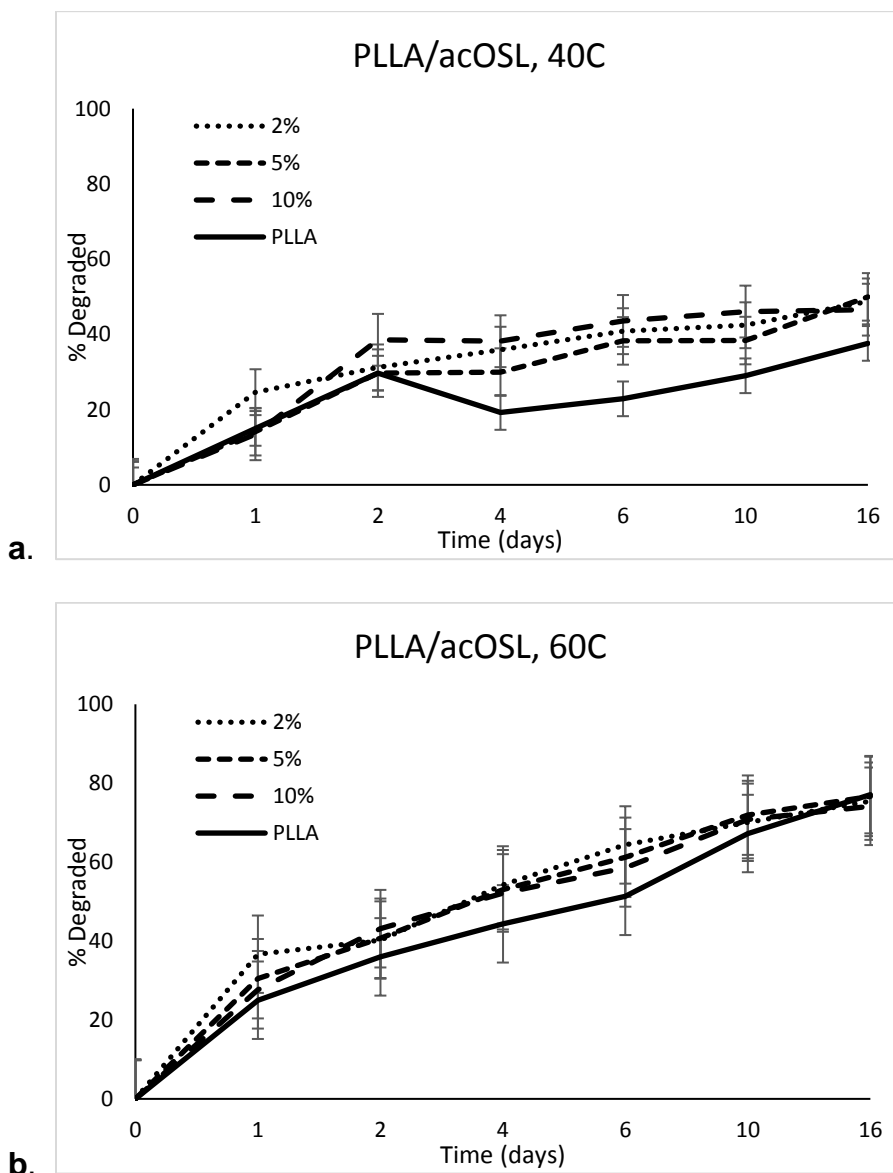


**Figure 8.13.** Average UV transmission through polymer films comparing polymers with and without acOSL at various wavelengths comparing polymer blends of PLLA with 2, 5, and 10 % acOSL.

As seen in Table 8.5<sup>7-9</sup>, the tensile properties strain at break ( $\epsilon$ ), maximum stress ( $\sigma$ ), and Young's modulus ( $E$ ) drop significantly with the addition of acOSL in composites with PLLA. This was not expected as it was thought that the process of acetylation would improve the miscibility of OSL in the blends.

Hydrolytic degradation studies revealed that composites of PLLA and acOSL degraded at a faster rate than PLLA over a period of sixteen days. This effect can be observed at both 40 °C and 60 °C, ( Figure 8.14, a-b.) It is

hypothesized, that lignin and PLLA, even after acetylation of the lignin, show poor compatibility and some degree of phase separation, allowing water to penetrate into the material quickly, actually increasing degradation rate.



**Figure 8.14.** Percent hydrolytic degradation based on reduction in  $\bar{M}_w$  over time comparing composite blends of PLLA and acOSL at a. 40 °C; and b. 60 °C.

Table 8.6<sup>7-9</sup>, shows WVTR calculations for the PLLA/acOSL composites.

As expected, WVTR is reduced through the addition of acOSL to PLLA in a composite. In a blend with 2 % acOSL, WVTR was seen to decrease approximately 10 %. With 5 % acOSL, WVTR decreased up to 66%, and the composite of 10 % acOSL reduced WVTR up to 76%. Nevertheless, these reductions in WVTR are all below the rate reductions observed with PLLA-OSL copolymers, even though the copolymers contained considerably lower amounts of lignin.

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## Chapter 9 – Conclusions

Because of the diverse applications required to meet consumers' needs, polymers must be tunable for engineering purposes. In food and beverage applications, durable polymers are needed that will not break down due to water degradation and can resist gas permeation during storage. Properties such as moisture permeability, UV permeability, stiffness, strength, glass transition temperature and melting points have to be considered. The environmental aspects of polymers must also be addressed since these materials often end up in landfills, lakes, rivers and oceans once they are disposed of. For these reasons, the endeavour to design useful biobased and biodegradable polymers is essential. This study addresses some of the shortfalls of PLA, a popular biobased polymer through copolymerization of L(-)lactide (LA) with organosolv lignin from switchgrass (OSL) and delta-valerolactone (DVL), a monomer obtainable from sugars, producing a 100% biobased polymers with improved properties.

Copolymers of LA and OSL as well as terpolymers of LA, DVL and OSL were successfully polymerized in ring opening polymerization reactions.

SEC shows that the reprecipitated polymers have higher  $\bar{M}_w$  than the original OSL, hereby confirming that PLLA-OSL copolymers and PLLA-DVL-OSL terpolymers are attainable. Unfortunately, OSL seems to stop chain propagation and thereby effectively reduces the overall  $\bar{M}_w$  of all polymers containing even small amounts of OSL. The shorter chain lengths have a negative effect on the

physical properties of the copolymer, decreasing strength and strain. Therefore, OSL addition rate was kept low to allow for reasonable polymer properties.

$^1\text{H-NMR}$  corroborates SEC findings by revealing an increase in polymer end groups as OSL is added. Increased signals for hydroxyl end groups allow for the assumption that the OSL is mainly attached to the carboxylic acid end group of the PLLA, effectively stopping the chain reaction.

The addition of OSL slows hydrolytic degradation and decreases water vapor transmission rates through the polymer films. It is hypothesized that the hydrophobic OSL either directly restricts water permeation, or indirectly slows water absorption through blocking of one of the hydrophilic end groups of PLLA.

OSL addition was also shown to decrease UV transmission through films. Even though this effect was expected as it is well known that chromophoric groups in lignin absorb light at several wavelengths. The effect was surprisingly high considering the low amount of lignin present in the copolymer.

To counteract the low flexibility of PLLA and PLLA copolymers, the inclusion of DVL, known to increase flexibility in copolymers, was explored.

$^1\text{H-NMR}$  spectra of PLLA-DVL show characteristic signals of DVL in the PLLA-DVL copolymer, and these signals increase as the ratio of DVL to LA in the polymerization increases. This demonstrates that as the ratio of DVL to LA was increased, there was also an increase in DVL retained in the polymer. This effect is also observed as an increase in strain and a decrease in Young's modulus in

the polymer which is evidence of a more flexible polymer with tailoring capabilities.

The addition of DVL to the polymerization by itself decreased the  $\bar{M}_w$  of the polymers, but due the incorporation of the longer hydrocarbon chains, significantly improved both stress and the modulus of elasticity when compared to the PLLA homopolymer. This is witnessed as a more flexible and elastic polymer.

DSC analysis demonstrated that  $T_g$  and  $T_m$  decreased significantly with the addition and increase of DVL to the polymers, further indicating that the polymer became more rubbery with the addition of DVL.

As with the PLLA-OSL polymers, WVTR always decreases considerably with the addition of OSL to the polymers, and is seen to increase with the addition of DVL to the polymerization. Though terpolymers of PLLA-DVL-OSL have lower WVTR than PLLA, they do not perform as well as the PLLA-OSL copolymer.

In this study it is shown that it is possible to significantly improve moisture barrier, UV permeability, and stiffness of a biobased PLLA polymer utilizing two additional biobased materials, OSL and DVL. The different properties of OSL and DVL allow the opportunity to customize this important biobased polymer.

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