Development of Lignin-Based Copolymers and Polymer Blends

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Development of Lignin-Based Copolymers and Polymer Blends

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering

by

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Bachelor of Science in Chemical Engineering, 2019

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Abstract

Increasing industrial interest in reducing fossil fuels in virgin polymer production and incorporating bio-based polymeric materials has led researchers to explore the potential of utilizing plant-based polymers such as lignin. Chapter 1 of this thesis presents a comprehensive overview of copolymerization and blending techniques for lignin and synthetic polymers, emphasizing different types of modifications and copolymerization techniques as well as key parameters such as temperature, reaction time, pH level, and solution compositions. These valorization methods are directed towards the development of high-value lignin-based materials with properties well-suited for various commercial applications. Chapter 2 offers a fundamental exploration into the amination of lignin through the Mannich reaction for water remediation applications. The pretreatment of lignin via phenolation—prior to amination—enhances the dye adsorption capacity by increasing the ionizable amino content in aminated lignin. Aminated lignin, with its outstanding properties, emerges as a promising candidate for adsorbing toxic anionic dyes, such as Congo red and methyl orange, from wastewater. Lastly, Chapter 3 focuses on the synthesis and characterization of lignin-grafted-polystyrene (L-g-PS) copolymers using atom transfer radical polymerization (ATRP) along with blends of L-g-PS with polystyrene homopolymer (L-g-PS/PS). The L-g-PS copolymer and L-g-PS/PS blend both exhibit higher thermal stability and improved miscibility compared to the blend of unmodified lignin with polystyrene (L/PS), making them promising bio-based polymeric materials.
Acknowledgements

I would like to thank my advisor, Dr. Keisha B. Walters, for her continuous guidance, support, encouragement, patience, understanding, and advice. She always believes in me even when I do not believe in myself. I have grown a lot as a person and a young researcher under her mentorship and supervision. Her expertise, insightful feedback, and dedication have been invaluable in shaping the direction and quality of this study.

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Lastly, I would like to thank my parents, sisters, family, and friends for their love, encouragement, and support throughout this graduate study.
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Chapter 1: A Review of Lignin Copolymers and Blends/Composites: Techniques, Properties, and Applications

Abstract

Although abundant in nature, bio-based polymers like lignin are generally underutilized commercially compared to synthetic, petroleum-based polymers due to their chemical variability, low miscibility, and poor processability stemming from their inherent branched structure. Efforts to add value and support integration and miscibility of lignin with synthetic polymers would be a way to promote the production of cost-effective and partially bio-based polymeric materials. In this review, we highlight methods employed for lignin valorization, such as copolymerization, and blending methods, along with an overview of the properties of different types of valorized lignin. These chemical and physical modification techniques allow lignin to be utilized in a wide range of applications, from sustainable materials for water remediation to biodegradable fillers in thermoplastic material productions for food and medical packaging, to precursor materials for the carbon fiber industry.

1.1 Introduction

In the last two decades, lignin has become one of the most popular bio-based polymers to study for its valorization because of its abundance in nature, low cost, and biodegradability as compared to petroleum-based polymers. After cellulose, lignin is the second most abundant bio-based polymer found in nature and is produced as a significant byproduct in multiple industries, including paper pulping\textsuperscript{1,2}, ethanol production\textsuperscript{3}, and biofuel industries\textsuperscript{4}. The content of lignin in plant biomass varies depending on the sources, such as softwood (e.g., larch, pine, spruce) or hardwood (e.g., beech, oak, rubberwood) trees. Lignin can comprise up to 15 wt\%, or even 35 wt\% of plant biomass, making it a significant source for the development of bio-based polymer
Various plants can be processed differently to yield four types of technical lignin, such as kraft pulping lignin, lignosulfonate, soda lignin, organosolv lignin. Kraft lignin and lignosulfonate contain sulfur content, whereas soda lignin and organosolv lignin are sulfur-free. Each lignin type has a different pretreatment method, including acid hydrolysis, alkaline pretreatment, enzymatic hydrolysis, physical methods (mechanical grinding, mechanical extrusion, microwave, and pyrolysis), and biological methods. These pretreatments result in lignin with different molecular weights, chemical, and mechanical properties.

Prior to any modification, lignin generally has an amorphous, branched, three-dimensional network structure and is one of the largest sources of aromatic moieties on earth. It is synthesized enzymatically—alongside cellulose and hemicellulose—inside the plant cells, where it is incorporated into the cell wall to support structure, provide increased plant rigidity and strength due to the three-dimensional, rigid network structure and aromatic groups. The aromatic moieties are incorporated into lignin through an enzyme-mediated dehydrogenization of alcohol monomers (monolignols), such as p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. The resulting lignin contains the aromatic units in the polymer chain structure, including p-hydroxyphenyl (H) unit (phenyl group), guaiacyl unit (G) (methoxy phenyl group), and syringyl unit (S) (dimethoxy phenyl group). The structures of monolignol and aromatic units of lignin are shown in Figure 1.1.
The types and relative concentration of these aromatic units in lignin vary based on the plant type and the extraction method. For example, there are 25 – 30% of G units in softwood, 16 – 24% of G and S units in hardwood, and 13 – 18% of G, S and H units in grasses. These aromatic units are the main groups that determine the level of the reactivity of the produced lignin monomers and subsequently polymerized lignin chains. In addition to these lignin monomers, there are also some common interunit linkages in lignin, such as aryl ether (α-O-4’ and β-O-4’), resinol (β-β’), phenylcoumaran (β-5’), biphenyl (5-5’), 1,2-diaryl propane (β-1’). These linkages are generated through in-situ radical polymerization of phenylpropanoid monomer units followed by radical coupling. These linkages and aromatic moieties lead to native lignin with a rigid and complex structure that is difficult to depolymerize and process, limiting its direct use in industrial applications. Further, lignin also has a highly non-linear structure, wide range of molecular weights, high rigidity, low compatibility with synthetic polymers, and poor flow, leading to further processing difficulties.
Lignin has numerous reactive functional groups, providing latent functionality that can directly be used for modifying chemical reactions and, consequently, physical properties. In addition to working directly with native lignin, researchers have explored lignin modification methods to generate more favorable polymer properties, including esterification, amination, azo-coupling, telomerization, hydroxy alkylation. Lignin has also been modified through copolymerization with different synthetic polymers using atom transfer radical polymerization (ATRP), click chemistry, free radical polymerization (FRP), reversible addition-fragmentation chain-transfer (RAFT) polymerization, and emulsion suspension polymerization. The lignin-base copolymers have been evaluated for enhanced properties (vs. native lignin), water remediation, sustainable, biodegradable fillers for packaging thermoplastics, and as a precursor material for the carbon fiber production. Recently, modified lignin has been used in the production of dispersants, adhesives, surfactants, and antioxidants.

Several efforts to blend or form composites from lignin and petroleum-based polymers have been attempted to improve the overall mechanical properties of the blend or composite. However, due to lignin’s polarity and most synthetic polymers being non-polar, their inherent poor miscibility has allowed only a low lignin loading to be utilized as a filler. Even then, lignin is usually chemically modified before being included in blends or composites to increase its dispersion and adhesion with the polymer matrix.

Further investigation into lignin modification and the resulting material properties is needed to broaden its application in polymer and other fields. This review provides an overview of the lignin copolymers and blends/composite examined to-date, along with the polymerization techniques and reaction conditions utilized. In addition, the chemical, mechanical, and thermal
properties of lignin copolymers and blends/composites with degradability, proved compatibility, and potential applications are also highlighted.

1.2 Lignin Copolymerization

Lignin has a complex, branched structure resulting in poor processing properties which makes it difficult to use as a main polymeric material in industrial productions. There are numerous research approaches, which have attempted to improve its properties and overcome these limitations. Lignin copolymerization is one of the effective techniques used to valorize lignin. Among other polymerization techniques, free radical polymerization (FRP), click chemistry, reversible addition fragmentation chain transfer (RAFT) polymerization and atom transfer radical polymerization (ATRP) methods have been implemented in different studies.\textsuperscript{48–50} There are two important methods of lignin grafted copolymerization, including the “graft-from” method and “graft-to” method that show a high success. Moreover, the common polymers used in lignin copolymerization are polystyrene (PS)\textsuperscript{32,51–53}, poly methyl methacrylate (PMMA)\textsuperscript{54,55}, poly acrylic acid (PAA)\textsuperscript{56–58}, polylactic acid (PLA)\textsuperscript{59–61}, polyacrylonitrile (PAN)\textsuperscript{34,35}, and polyacrylamide (PAM)\textsuperscript{31,62,63}. The synthesis and application of several lignin copolymers from prior studies are provided and outlined with various copolymerization methods. Table 1.1 summarizes these lignin copolymers along with reaction conditions, observed properties, and target applications.
Table 1.1 Lignin copolymers examined in the literature including copolymerization method, observed properties, and targeted applications.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Lignin type</th>
<th>Polymerization technique</th>
<th>Catalyst</th>
<th>Initiator</th>
<th>Temp., °C</th>
<th>Time, hr</th>
<th>Yield, %</th>
<th>Properties</th>
<th>Targeted applications</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-g-PS</td>
<td>Kraft lignin</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>90</td>
<td>2</td>
<td>20</td>
<td>• Higher (T_g) than lignin&lt;br&gt;• Lower thermal stability compared to lignin</td>
<td>Water purification (floculant and ion exchange material)</td>
<td>Darestani et al.64</td>
</tr>
<tr>
<td>L-g-PS</td>
<td>Dealkaline lignin</td>
<td>ATRP</td>
<td>FeCl₂</td>
<td>H₂O₂</td>
<td>30</td>
<td>48</td>
<td>-</td>
<td>• Surface structure changed to smoother and homogenous compared to lignin&lt;br&gt;• Become soluble in most organic solvents</td>
<td>-</td>
<td>Li et al.55</td>
</tr>
<tr>
<td>L-g-PS</td>
<td>Softwood lignin</td>
<td>ATRP</td>
<td>Cu(I)Br</td>
<td>BiBB</td>
<td>40</td>
<td>3</td>
<td>23</td>
<td>• Low PDI value</td>
<td>-</td>
<td>Chung et al.33</td>
</tr>
<tr>
<td>L-g-PS</td>
<td>Softwood kraft lignin</td>
<td>FRP</td>
<td>-</td>
<td>AIBN</td>
<td>80</td>
<td>18</td>
<td>-</td>
<td>• More porous structure than lignin and PS&lt;br&gt;• Better compatibility with copper ions</td>
<td>Adsorbent for Cu (II) ions</td>
<td>Ghavidel et al.66</td>
</tr>
<tr>
<td>L-g-PMMA</td>
<td>Lignin</td>
<td>AGET ATRP</td>
<td>FeCl₃·6H₂O</td>
<td>BiBB</td>
<td>110</td>
<td>24</td>
<td>65</td>
<td>• Higher (T_g) compared to lignin&lt;br&gt;• Narrow Mw distribution</td>
<td>-</td>
<td>Li et al.32</td>
</tr>
<tr>
<td>L-g-PMMA</td>
<td>Softwood kraft lignin</td>
<td>-</td>
<td>-</td>
<td>K₂S₂O₈</td>
<td>40-80</td>
<td>2.5-24</td>
<td>40-65</td>
<td>• Higher thermal stability&lt;br&gt;• Higher UV absorption&lt;br&gt;• More hydrophobic</td>
<td>Food packaging&lt;br&gt;Water purification</td>
<td>Alipoormazanda rani and Fatehi.54</td>
</tr>
<tr>
<td>L-g-PMMA-g-PA</td>
<td>Depolymerized lignin</td>
<td>RAFT</td>
<td>-</td>
<td>Photo-initiator</td>
<td>-</td>
<td>16</td>
<td>-</td>
<td>• Narrow Mw distribution&lt;br&gt;• Improved hydrophilicity</td>
<td>Lignin-based copolymer nanoparticles</td>
<td>Liu et al.67</td>
</tr>
<tr>
<td>L-g-PAA</td>
<td>Banana stem lignin</td>
<td>-</td>
<td>(NH₄)₂Fe (SO₄)₂·6H₂O</td>
<td>H₂O₂</td>
<td>60</td>
<td>6</td>
<td>17-60</td>
<td>• Increased water absorbency</td>
<td>Bio-based water absorbent</td>
<td>Azhar et al.37</td>
</tr>
<tr>
<td>L-g-PAA</td>
<td>Acid hydrolysis lignin</td>
<td>-</td>
<td>-</td>
<td>APS</td>
<td>40</td>
<td>2</td>
<td>-</td>
<td>• Higher water absorption and desorption&lt;br&gt;• Higher Pb (II) ions adsorption capacity compared to PAA</td>
<td>Water absorption hydrogel&lt;br&gt;Adsorbent for Pb (II) ions for aqueous solution</td>
<td>Sun et al.68</td>
</tr>
<tr>
<td>L-g-PAA</td>
<td>Kraft lignin</td>
<td>-</td>
<td>K₂S₂O₈ &amp; Na₂S₂O₃</td>
<td>70</td>
<td>3</td>
<td>-</td>
<td>• Soluble under acidic condition</td>
<td>Dispersant for cement admixture&lt;br&gt;Floculant for tailing wastes in mining industry</td>
<td>Kong et al.51</td>
<td></td>
</tr>
</tbody>
</table>
Table 1.1 Cont.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Lignin type</th>
<th>Polymerization technique</th>
<th>Reaction conditions</th>
<th>Yield, %</th>
<th>Properties</th>
<th>Targeted applications</th>
<th>References</th>
</tr>
</thead>
</table>
| L-g-PLA   | Kraft lignin | ROP | TBD | 130 | 3.5 | 69 | • Improved UV absorbance  
• Enhanced mechanical properties such as increased tensile strength by 16% and strain by 9%  
• Dispersion modifier in PLA-based bio-based composites materials | Chung et al. | 59 |
| L-g-PLA   | Alkaline lignin | ROP | DBU | 110 | 6 | - | • Increased elongation at break, ductility, and toughness  
• Excellent UV barrier, water resistance, and controllable gas permeation  
• High-performance and biodegradable Packaging materials | Zhang et al. | 61 |
| L-g-PAN   | Hardwood lignin | FRP | - | CaCl₂ - H₂O₂ | 70 | 6 | 67 | • Improved mechanical properties  
• Carbon fiber precursor | Maradur et al. | 35 |
| L-g-PAN   | Alkaline lignin | FRP | - | CaCl₂ - H₂O₂ | 70 | 6 | - | • More thermally stable than lignin and PAN  
• High carbon content with uniform fiber structure  
• High energy density  
• Carbon fiber precursor  
• High-performance energy storage devices | Kim et al. | 34 |
| L-g-PAM   | Enzymatic hydrolysis lignin | FRP | - | - | 80 | 4 | - | • Self-assembled into octopus-like nanosphere  
• Ability to form micelle when in acidic solution  
• Wastewater treatment | Chen et al. | 63 |
| L-g-PAM   | Akali lignin | ATRP | Cu(I)Br-BiBB | 65 | 24 | 57 | • Narrow Mw distribution  
• Higher Tₕ compared to lignin  
• Lower thermal stability of L-g-PAM than lignin  
• Soft and spongy structure  
• Potentially used as hydrogel or surfactant | Wang et al. | 31 |
| L-g-PAM   | Kraft lignin | RAFT | - | AIBN | 70 | 24 | - | • Precisely tune grafting density  
• Good emulsion stability  
• Novel design for colloidal materials advancement | Silmore et al. | 36 |
<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Lignin type</th>
<th>Polymerization technique</th>
<th>Reaction conditions</th>
<th>Yield, %</th>
<th>Properties</th>
<th>Targeted applications</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-g-PAM</td>
<td>Cornstalk lignin</td>
<td>RAFT</td>
<td>Catalyst: -</td>
<td>AIBN</td>
<td>Temp., °C: 70</td>
<td>Time, hr: 24</td>
<td>Higher Tg compared to lignin</td>
</tr>
<tr>
<td>L-g-PAM-b-(MMA-co-BA)</td>
<td></td>
<td>RAFT</td>
<td>Catalyst: -</td>
<td>-</td>
<td>Temp., °C: 75</td>
<td>Time, hr: 6</td>
<td>Higher Tg compared to pure MMA-co-BA copolymer • Better thermal stability than MMA-co-BA copolymer • Higher Young’s modulus and tensile strength than MMA-co-BA copolymer</td>
</tr>
</tbody>
</table>

"-": not reported
Free Radical Polymerization (FRP)

FRP is one of the most popular methods studied so far for lignin and synthetic polymer copolymerization. As a chain-growth polymerization, FRP involves the addition from free radical sites to form polymer chains and is a relatively simple and relatively inexpensive method to produce lignin copolymers. Different FRP reaction conditions, such as catalysts, initiators, temperatures, and times, have been investigated to obtain various copolymer yields for different target applications. For instance, in a report by Li et al., copolymers comprised of dealkaline lignin and styrene using hydrogen oxide and ferrous chloride as redox co-initiators. Optimum reaction conditions were reported to provide the highest yield, total conversion of and grafting efficiency of polystyrene (PS) onto lignin (0:5:0.1 molar ratio of styrene:H₂O₂:FeCl₂ at 30 °C for 48 hrs). The successful copolymerization of the lignin with PS lead to a reduction in Tₘ, increased thermal stability, and increased surface smoothness compared to the unmodified lignin. PS was also copolymerized with kraft lignin using free radical emulsion polymerization to produce a sustainable superadsorbent for water purification processes by Ghavidel et al. Brunauer-Emmett-Teller (BET) surface area study and SEM image analysis showed the lignin-graft-polystyrene (L-g-PS) copolymer yielded a more porous structure compared to neat lignin and PS. Further, L-g-PS displayed enhanced miscibility with Cu (II) ions compared to the unmodified lignin and polystyrene homopolymers as confirmed by a quartz crystal microbalance with dissipation (QCM-D) experiment. The increased Cu (II) ions adsorption in water for the L-g-PS copolymer was attributed to a combination of copper ion entrapment via ion-dipole interactions with polar lignin groups and cationic-π interactions between the Cu (II) ions and the grafted polystyrene.
FRP has also been employed to copolymerize lignin with other polymers besides PS. Alipoormazandarani and Fatehi studied a lignin-g-PMMA copolymer as a hydrophobic multifunctional material suitable for food packaging and water purification. L-g-PMMA was successfully prepared at a high yield (95 wt.% of L-g-PMMA and 85 wt.% MMA conversion). In this work, a new purification method was also proposed using a water/acetone solution while acidifying the mixture (pH 1.5) to purify L-g-PMMA via stepwise dilution. This purification method led to better quality products, higher yields, and minimized production of side products compared to purification by extraction without water/acetone dilution. As a result, the introduction of PMMA to lignin promoted significantly higher thermal stability, heat resistance, UV absorption, and similar hydrophobicity compared to unmodified lignin and PMMA homopolymer. Overall, this is a simple, cost-effective, and green reaction that could be employed to facilitate the desired lignin-g-PMMA hydrophobic materials.

Several studies have been conducted on the copolymerization of lignin and poly(acrylic acid) (PAA) to create robust hydrogels with high heavy metal ion adsorption capabilities. These investigations have not only yielded insights into the synthesis of such hydrogels but also the parameters influencing the grafting density of PAA onto lignin. For example, Sun et al. prepared an acid hydrolyzed lignin-g-PAA (AHL-g-PAA) hydrogel superabsorbent composite for Pb (II) ion removal. In this study, lignin was first acid hydrolyzed, where an ammonium persulfate (APS) initiator was used to generate free radicals on the hydrolyzed lignin prior to polymerization with AA monomers. After the copolymerization, SEM analysis indicated that AHL-g-PAA had increased surface roughness and a greater porous surface area compared to neat PAA due to the addition of lignin. This led to a maximum water absorbency of AHL-g-PAA hydrogel of 392 g.g\(^{-1}\) in distilled water compared to 180 g.g\(^{-1}\) for PAA. Similarly, the increase in
porosity and surface roughness led to double the Pb (II) ion adsorption capacity for the AHL-\textit{g} PAA hydrogel compared to the capacity measured for the PAA hydrogel. As the addition of lignin in the hydrogel improved the water absorption and Pb (II) adsorption capacity, the AHL-\textit{g}-PAA hydrogel can potentially be used as hydrogel adsorbent for Pb (II) ions in aqueous solution and is favorable for water treatment applications. Kong \textit{et al.} aimed to improve lignin solubility in water by synthesizing water soluble kraft lignin and acrylic acid (AA) copolymer.\textsuperscript{57} Acetylation and methylation reactions were performed on lignin to remove phenolic and aliphatic hydroxyl groups, respectively, before copolymerization of kraft lignin with AA using a 2:1 potassium persulfate:sodium thiosulfate initiator system. \textsuperscript{1}H-NMR analysis indicated that AA was not grafted onto lignin after removal of phenolic hydroxyl groups through acetylation. It was concluded that the main driving mechanism for copolymerization was through lignin radicals derived from phenolic hydroxyl groups due to the higher stability of phenolic hydroxyl radicals and low stability of aliphatic alcohol radicals. Up to 10:1 of AA:lignin, the grafting yield was proportional to the amount of initiator and the AA:lignin ratio used in the synthesis due to the higher collision chance between lignin and AA monomer as the AA:lignin ratio increased. Beyond this ratio, the production of PAA dominated the reaction. As the reaction time and temperature increased, the grafting yield and charge density of the copolymer also increased.

Lignin was also examined in the copolymerization with poly(acrylamide) (PAM) to develop a material suited for wastewater treatment applications. Chen \textit{et al.} reported the preparation of enzymatic hydrolyzed lignin-grafted cationic polyacrylamide in a water flocculant application.\textsuperscript{63} The polymerization was divided into two main stages. In the first stage, linear cationic polyacrylamide (cPAM) was produced through FRP of AM and [2-(methacryloyloxy)ethyl]trimethylammonium chloride using 4-chloromethyl styrene as a chain
transfer agent to introduce chlorine-terminal groups. In the second stage, lignin-grafted cationic polyacrylamide (L-g-cPAM) flocculant was synthesized through the reaction between the chlorine-terminal groups and phenolic hydroxyl group in lignin via the “grafting to” FRP method. This “grafting to” method was used to increase the grafting efficiency, hence, enhancing the flocculation performance of L-g-cPAM for kaolin and poly ammonium chloride (PAC) suspensions under acidic conditions. L-g-cPAM formed micelle with hydrophobic lignin cores and hydrophilic cPAM shells that could effectively flocculate PAC and bound kaolin particles at low dosages due to electrostatic interactions between lignin and the positively charged ammonium groups in PAC.

Copolymers produced from lignin and poly(acrylonitrile) (PAN) can also be used in electrochemical applications, including highly efficient, flexible electrodes. Kim et al., prepared and investigated the use of L-g-PAN copolymer derived carbon nanofibers as novel flexible electrodes for high-performance capacitive-energy storage applications. Similar to the study above, L-g-PAN was prepared in two stages by first polymerizing AN followed by copolymerization of PAN with lignin. It was observed that L-g-PAN was more thermally stable than lignin and PAN homopolymer based on TGA and DSC characterizations. Moreover, the resulting copolymer possessed high carbon content with a uniform fiber structure and high flexibility. As an electrode, the resulting copolymer exhibited high capacitance and excellent cyclic stability (up to 10,000 continuous charge-discharge cycles), which could be useful in various energy storage and electronics applications. In particular, the high flexibility, electrochemical, thermal stability of L-g-PAN makes it a good candidate for carbon fiber precursor and more importantly, a great material for a high-performance electrode for high-energy storage applications.
Overall, FRP technique has been utilized in lignin copolymerization with various commercial polymers. Different reaction conditions have been examined to optimize yields and tailor the physicochemical properties of lignin-based copolymers. As FRP is a versatile and relatively cost-effective polymerization method, it is an effective approach to produce lignin copolymers that provide improved properties and support their development for a wide range of applications. Beside FRP, the demand for precise control over polymer structure and properties in lignin copolymerization has driven the adoption of controlled radical polymerization techniques.

**Controlled Radical Polymerizations (CRP)**

CRP is another polymerization method that has been used for lignin copolymerization because it yields well-controlled grafting density and provides more control over copolymer molecular weight and chain length, leading to a tailored product design. Two of the most common CRP techniques include atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain-transfer (RAFT). In both polymerizations, alkenes or substituted alkene groups on monomers are reacted together through FRP addition and propagation mechanisms, which will be described in the following sections.\(^{73}\)

**Atom Transfer Radical Polymerization (ATRP)**

The ATRP technique developed by Matyjaszewski et al. is one of the most effective controlled polymerization techniques that allows for the production of polymers with well-defined and narrow molecular weight distributions.\(^{74}\) For lignin systems, ATRP requires an alkyl halide initiator to be immobilized on the lignin surface before initiating the polymerization.\(^{73,74}\) Based on a survey of the literature, 2-bromoisobutyryl bromide (BiBB) has been the most widely used initiator for ATRP-based lignin copolymerizations.\(^{31-33,48}\) BiBB is immobilized on the hydroxyl
groups in lignin—creating surface halogen groups (halogen exchange)—which provide radical sites for the polymerization.

ATRP has been employed for lignin copolymerization with different synthetic polymers to achieve a highly controlled polymerized product. For instance, Chung et al. reported the modification of softwood lignin with PS through two different graft copolymerization methods, “grafting from” and “grafting to”. The “graft from” method involves a surface initiated ATRP (SI-ATRP) where lignin was first converted into a macroinitiator by reacting BiBB with the hydroxyl groups present in lignin to form bromoisobutyrate groups, which serve as initiation sites for the subsequent ATRP graft polymerization. Chung et al. found that using CuCl and bipyridine as the catalyst and ligand offered the best control while maintaining a reasonably moderate polymerization rate. No significant chain termination was observed, and the PS growth was well-controlled demonstrating a successful lignin “graft from” copolymerization via a “living” free radical polymerization technique. Wang et al. used ATRP to prepare lignin-g-polyacrylamide (L-g-PAM). In this study, alkali lignin contained the highest hydroxyl group content compared to acid precipitate lignin and cellulolytic lignin. As the hydroxyl groups are used to react with BiBB to form the lignin macroinitiator, it was proposed that alkali lignin would yield a higher chain grafting density compared to acid precipitated or cellulolytic lignin. The L-g-PAM synthesized from alkali lignin had a narrow Mw distribution and a Tg higher than unmodified lignin due to high grafting density of PAM on alkali lignin via ATRP technique.

Other ATRP techniques beyond conventional ATRP have also been utilized to produce lignin copolymers. For instance, Li et al. copolymerized lignin with styrene and methyl methacrylate via activators generated by electron transfer ATRP (AGET ATRP) technique using Fe(III) as a catalyst and triphenyl phosphate (PPh$_3$) as a ligand. As described previously, a lignin
A macroinitiator (L-Br) was synthesized using BiBB followed by AGET ATRP with either PS and PMMA. The Fe(III) catalyst was selected as it is more environmentally friendly and lower in cost than other ATRP catalysts. This “living”/controlled polymerization method also provided a narrow molecular weight distribution copolymer, and the polydispersity index (PDI) value was close to one as expected. It was concluded that compared to conventional ATRP and other FRP methods, the Fe(III)-catalyzed AGET ATRP was a relatively easy and effective method to synthesize lignin with vinyl monomers in a well-controlled manner.

Overall, ATRP has proven to be a highly effective controlled polymerization technique, particularly in the context of lignin copolymerization. The use of BiBB initiator allows for precise control of polymerization, leading to well-defined polymers with narrow molecular weight. ATRP is considered an effective approach to synthesizing lignin copolymers compared to conventional methods. Next, another effective controlled polymerization technique, reversible addition-fragmentation chain-transfer, will be discussed in the context of lignin copolymerization.

**Reversible Addition-Fragmentation Chain-Transfer (RAFT)**

RAFT is another versatile controlled polymerization technique used for copolymerization of lignin. RAFT utilizes a FRP initiator and a chain-transfer agent to initiate the radical polymerization and to “activate” and “deactivate” the radical propagation in a controlled manner, respectively. The suitable RAFT agent normally contains a thiocarbonylthio group that facilitates the chain transfer reaction. The most commonly utilized initiating agent for RAFT mediated copolymerization of lignin is azobisisobutyronitrile (AIBN). During the lignin copolymerization, the RAFT initiating agent begins the polymerization process by generating radicals to react with monomers while the chain transfer agent mediates the “activation” and “deactivation” radical propagation mechanism, leading to further polymer chain growth.
The RAFT technique has recently been employed in lignin and PAM copolymerization as a novel path for developing bio-based copolymers and designing new high value materials. Silmore et al. investigated the ability of polyacrylamide (PAM) grafted lignin (L-g-PAM) nanoparticles to form stable emulsions at neutral pH condition. In this study, the authors employed the RAFT polymerization technique by first preparing lignin macroinitiators through reaction with thionyl chloride, potassium xanthate, and 2-bromopropionic acid to form the immobilized chain transfer agent followed by grafting PAM at the initiated sites using AIBN as an initiator. The impact of L-g-PAM copolymer nanoparticles on the interfacial tension in cyclohexane-water emulsions was examined at PAM grafting density of ~2 and ~17 grafts per particle. The results showed that the surface activities of L-g-PAM were determined by the nanoparticle lignin core due to its hydrophobicity and interaction with salt solution. As the grafting density and salinity changed, the intermolecular force of nanoparticles was also altered, and hence the properties of emulsions. In another study by Xu et al., the characteristics of lignin-based methyl methacrylate copolymerized with butyl acrylate (lignin-based MMA-co-BA) latex were examined. In this work, lignin was first modified with xanthate and graft copolymerized with acrylamide (AM) and AIBN initiator to form L-g-PAM via RAFT miniemulsion polymerization. Then, L-g-PAM was used as a macromolecular chain-transfer agent to synthesize lignin-g-PAM-b-(MMA-co-BA) hybrid latex resins. The authors observed that copolymerization was successful with ~90% grafting conversion at 85 ºC. The hybrid latex resin obtained increased thermal stability and higher $T_g$ compared to neat MMA-co-BA copolymer. Due to the addition of lignin, hybrid latex displayed a better mechanical property such as higher Young’s modulus and improved tensile strength than neat MMA-co-BA copolymer.
Overall, RAFT polymerization stands as an effective and controlled technique for lignin copolymerization, offering a precise means of tailoring lignin copolymers for various applications. RAFT is less studied compared to ATRP technique for lignin copolymerization possibly due to relatively difficult procedure, more expensive and less accessible specialized chain transfer agents. However, this precise and controlled polymerization technique provides promising avenues for the utilization of lignin as a valuable resource in materials advancement. Besides ATRP and RAFT techniques, lignin copolymerization has also been studied via other polymerization techniques.

*Other Polymerization Methods*

In addition to the copolymerization methods described above, lignin and synthetic polymers copolymerization have also been prepared through other techniques to obtain novel hybrid bio-based materials suitable for different targeted applications. These techniques include ring opening polymerization (ROP), a “graft to” click chemistry reaction, and emulsion suspension polymerization.

ROP is a type of chain-growth polymerization where cyclic monomers can be reacted to form longer polymer chains by ring opening synthesis. Chung *et al.* described the development of renewable lignin grafted polylactic acid (L-g-PLA) from lignin and L-lactide for biobased composites via a catalytic and solvent free ROP technique. The transition from hydrophilic lignin to hydrophobic lignin copolymer after grafting with PLA led to a homogeneous dispersion in thermoplastic composite matrix. It was also found that by incorporating L-g-PLA in the PLA-lignin composite, the UV absorbance was improved, and the tensile strength increased without changing the tensile modulus. As a result, the copolymer can be potentially used as a dispersion modifier in PLA-based bio-based composites materials. Zhang *et al.* also reported the successful graft copolymerization of lignin with polylactic acid (L-g-PLA) through ROP method.
the ROP copolymerization, the authors first prepared alkaline lignin through an alkylation process in order to reduce the hydroxyl groups and increase the reaction sites need for graft copolymerization. Composite films formed from blends of PLA and L-g-PLA showed an improvement of mechanical properties such as increased elongation at break, ductility, and toughness compared to neat PLA films. There was also an increase in the gas permeation due to the increased distance between PLA chains resulting from the formed crosslinked network structure of the L-g-PLA copolymer. The copolymer also showed an excellent UV barrier, and water resistance. Due to these improved properties, L-g-PLA was predicted to be a promising candidate as a high-performance and biodegradable packaging material. Overall, ROP has been demonstrated as an efficient method to produce L-g-PLA copolymers with enhanced properties—high UV barrier, favorable mechanical properties, and high water resistance—making it a suitable precursor biomaterial for packaging industry applications.

In addition to ROP, there are several studies that synthesized lignin copolymers by other various polymerization techniques, including emulsion suspension polymerization and “graft onto” click chemistry. For instance, Darestani et al. reported the production and characterization of sulfonated lignin grafted polystyrene with the goal of improving lignin aqueous solubility and increasing the overall molecular weight of copolymer. In this work, the emulsion suspension polymerization method was used to copolymerize PS to aqueous kraft lignin before sulfonation of the styrenic group with sulfuric acid. It was determined that the most significant parameter that impacted the production yield in polymerization was the styrene:lignin molar ratio, with lower styrene:lignin ratios resulting in higher copolymerization yields. In another work, click chemistry (“graft onto”) was employed by Chung et al. for lignin and PS copolymerization (L-g-PS). Through this method, lignin and PS homopolymer were separately modified with an alkyne
functionalization and an azide end-group, respectively. After the functionalization processes, the click chemistry reaction was mediated by a CuBr/N,N,N′,N′,N″-pentamethyl diethylenetriamine (PMDETA) complex at room temperature to perform the “graft to” copolymerization. The weight percent of PS in L-g-PS was relatively low due to the strong steric hindrance of PS extended branches on lignin backbone.

Extensive discussions over various copolymerization techniques and several lignin copolymers aim to provide comprehensive understanding of chemical, mechanical, and thermal properties of the lignin copolymer materials. Notably the role of lignin functional groups, particularly phenolic hydroxyl groups, can impact the lignin copolymerization parameters such as radical stability and grafting density. Among these functional groups, phenolic hydroxyl groups play an essential role in influencing the chemical reactions of lignin. However, phenolation, a process designed to increase phenolic hydroxyl content in lignin, remains relatively underexplored. This approach could potentially help increase reaction sites on lignin, thereby enhancing the copolymerization process. Furthermore, it is also worth noting that properties of lignin copolymers generally surpass the properties of unmodified lignin. Although more extensive research should be performed and investigated, lignin copolymers are plausible candidates for a wide variety of environmentally sustainable applications.

1.3 Lignin Blends/Composites

Lignin has a low compatibility with the majority of synthetic polymers due its relatively polar structure. As such, researchers have focused their efforts on developing ways to improve the compatibility and material properties of lignin with synthetic polymers blends and composites. Commonly, lignin is used in blends or composites with synthetic thermoplastic polymers—such as polyolefins (e.g., PE, PP) and other synthetic polymers (e.g., poly(ε-caprolactone,
poly(lactic acid), poly(ethylene terephthalate)$^{89-94}$, poly(methyl methacrylate)$^{95-97}$, poly(vinyl alcohol)$^{98-101}$, poly(ethylene oxide)$^{102-105}$—to enhance the chemical compatibility and mechanical properties suitable for various applications. In this section, we will highlight several unmodified and modified lignin blends and composites and provide an overview of the mixing techniques and properties. A summary of lignin blends, composites, mixing conditions, and intended applications is depicted in Table 1.2
Table 1.2 Summary of lignin blends/composites examined in the literature including mixing method, observed properties, and intended applications.

<table>
<thead>
<tr>
<th>Blend/Composite</th>
<th>Lignin pretreatment method</th>
<th>Lignin content, wt.%</th>
<th>Mixing method</th>
<th>Mixing conditions</th>
<th>Properties</th>
<th>Intended Applications</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignin/PE</td>
<td>Esterification</td>
<td>50</td>
<td>Torque-rheometer</td>
<td>Temp., °C, 160</td>
<td>Higher tensile and flexural strength (45% and 30%, respectively)</td>
<td>-</td>
<td>Dehne et al.⁸⁷</td>
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<td></td>
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<td>Time, min, 15</td>
<td>Higher miscibility with esterified lignin than lignin</td>
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<td>Screw speed, rpm, 50</td>
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<tr>
<td>Lignin/PE</td>
<td>Methylation</td>
<td>5-25</td>
<td>Twin-screw extruder</td>
<td>Temp., °C, 170</td>
<td>Improved and stabilized the melt viscosity</td>
<td>-</td>
<td>Sadeghifar and Argyropoulos⁸⁴</td>
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<td>Time, min, 10</td>
<td>Increased melt stability</td>
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<tr>
<td>Lignin/PE</td>
<td>-</td>
<td>0-30</td>
<td>Single-screw extruder</td>
<td>Temp., °C, 175</td>
<td>Decreased in T&lt;sub&gt;g&lt;/sub&gt; value</td>
<td>Biodegradable material</td>
<td>Menta et al.⁸³</td>
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<td>Time, min, 5</td>
<td>Increased in tensile modulus</td>
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<td></td>
<td>More thermally stable</td>
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<tr>
<td>Lignin/PP</td>
<td>Alkylation</td>
<td>0-100</td>
<td>Torque-rheometer</td>
<td>Temp., °C, 190</td>
<td>Increased thermal stability</td>
<td>-</td>
<td>Chen et al.⁸⁵</td>
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<td></td>
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<td></td>
<td>Time, min, 10</td>
<td>Decreased in tensile strength and modulus as lignin content increased</td>
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<td>High compatibility between PP and alkylated lignin</td>
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<td>Screw speed, rpm, 60</td>
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<tr>
<td>Lignin/PP</td>
<td>-</td>
<td>10-50</td>
<td>Twin-screw extruder</td>
<td>Temp., °C, 180</td>
<td>Improved tensile modulus and strength</td>
<td>Lignin can be used as a filler in PP composite for high load materials</td>
<td>Dias et al.⁸⁸</td>
</tr>
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<td></td>
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<td>Time, min, 15</td>
<td>Uneven, brittle surface, and phase separation between PP and lignin</td>
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<tr>
<td>Lignin/PLA</td>
<td>Acetylation</td>
<td>0.5-20</td>
<td>Twin-screw extruder</td>
<td>Temp., °C, 165</td>
<td>Increased in strength when used acetylated lignin</td>
<td>-</td>
<td>Gordobil et al.⁹²</td>
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<td>Time, min, 30</td>
<td>Increased elongation at break</td>
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<td>More thermally stable</td>
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<td>Screw speed, rpm, 25</td>
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<td>Lower crystallinity</td>
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<tr>
<td>Lignin/PLA</td>
<td>-</td>
<td>7</td>
<td>Torque-rheometer</td>
<td>Temp., °C, 175</td>
<td>Higher young modulus</td>
<td>New environmentally friendly material</td>
<td>Spiridon et al.⁹³</td>
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<td>Time, min, 10</td>
<td>Higher tensile strength</td>
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<td>Improved thermal stability</td>
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<td></td>
<td>Increased surface energy</td>
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<td></td>
<td>Increased water sorption capacity</td>
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Table 1.2 Cont.

<table>
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<tr>
<th>Blend/Composite</th>
<th>Lignin pretreatment method</th>
<th>Lignin content, wt.%</th>
<th>Mixing method</th>
<th>Mixing conditions</th>
<th>Properties</th>
<th>Intended Applications</th>
<th>References</th>
</tr>
</thead>
</table>
| Lignin/PLA      | -                          | 7                    | Torque-rheometer | 175, 10, 60       | • Higher young modulus  
• Slight decreased in tensile strength  
• Improved thermal stability  
• Increased surface energy  
• Increased water sorption capacity | New environmentally friendly material        | Spiridon et al.⁹³ |
| Lignin/PLA      | Oxypropylation             | 1-40                 | Torque-rheometer | 170, 8, 100       | • Improved thermal stability  
• Decreased $T_g$ value  
• Lower tensile strength with higher amount of lignin added  
• High UV light protection | Food packaging material                      | Esakkimuthu et al.⁹⁴ |
| Lignin/PVA      | Nanolignin                 | 2.5-10               | Solution blending | 90, 30, -         | • Well dispersed blend matrix  
• Increased thermal stability | Packaging material                           | Nair et al.⁹⁹ |
| Lignin/PVA      | Lignin nanosphere          | 1-5                  | Solution blending | 95, 120, -        | • Evenly distributed surface structure  
• Increased mechanical properties  
• High UV absorbing and transparency | Medicine bottle and food packaging          | Xiong et al.⁹⁸ |
| Lignin/PVA      | Lignin-AA copolymerization | 5-50                 | Solution casting | 90, 180, -        | • Good compatibility between PVA and lignin  
• Higher $T_g$ value  
• Improved young modulus and tensile strength | PVA melt processing                         | Hu et al.¹⁰⁰ |
| Lignin/PEO      | -                          | 0-100                | Thermal blending | 160, 30, -        | • Full miscibility between PEO and lignin  
• Strong H-bond between PEO and lignin | -                                           | Kubo and Kadla¹⁰² |
| Lignin/PEO      | Esterification             | 20-80                | Twin-screw extruder | 125-195, 100      | • Enhanced elongation  
• Strong H-bond between PEO and lignin  
• Improved miscibility  
• High young modulus (lignin/PEO : 20/80 ratio)  
• Increased ductility | Carbon fiber precursor                      | Anagnou et al.¹⁰⁶ |
Table 1.2 Cont.

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<tr>
<th>Blend/Composite</th>
<th>Lignin pretreatment method</th>
<th>Lignin content, wt.%</th>
<th>Mixing method</th>
<th>Mixing conditions</th>
<th>Properties</th>
<th>Intended Applications</th>
<th>References</th>
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</table>
| Lignin/PEO      | -                         | 10-30                | Solution blending | 65 | 240 | - | • Good miscibility between lignin and PEO  
• Increased in young modulus and tensile strength  
• Increased elongation at break | • Adhesive for cellulose nanofiber film | Jayaramudu et al.\textsuperscript{103} |

"-" : not reported
Unmodified Lignin in Blends/Composites

Due to the rising concerns of plastic waste, lignin is often directly incorporated with synthetic polymers as a “green” additive to provide biodegradable character and to improve overall chemical, mechanical, and thermal properties of the composites. Recent efforts explore the direct utilization of lignin and polyolefins in blends. For example, Menta et al. reported significant changes in the thermal and mechanical properties of high-density PE (HDPE) composites when mixed with different weight percentages of tobacco-extracted lignin via a single-screw extruder. At 30% of lignin in the blend, the $T_g$ value significantly decreased whereas there was almost no change observed when lower lignin content were in the blends. The onset decomposition temperature of the composites was considerably higher than for neat HDPE. While the tensile strength decreased when 30% lignin was used in the blend, the tensile modulus of all blends was increased compared to neat HDPE. In another polyolefin system, Dias et al. converted lignin into a high-value additive material suitable for the plastic industry by developing composites of kraft lignin with PP and a compatibilizer agent (PP grafted with maleic anhydride (MAPP)) though a reactive extrusion. Blended composites with and without 3 wt% MAPP were prepared by manually mixing lignin (up to 50 wt%) and PP before melt blending in a twin-screw extruder. It was reported that tensile modulus, strength, and heat deflection temperature of the composites containing 3 wt% MAPP were improved compared to composites without MAPP, indicating the improved compatibilization of lignin and PP with MAPP. However, at 50 wt% of lignin, both the tensile strength and heat deflection temperature decreased. The thermal stability of the resulting composite was higher than neat PP, and similarly, the storage modulus was also increased. Overall, it was concluded that lignin/PP composites may be a suitable replacement for engineering plastics in the automotive industry.
In addition to polyolefins, lignin has also been combined with other biodegradable polymers, such as PLA, to form environmentally friendly composites. For instance, Spiridon *et al.* investigated the bioplastic properties of lignin composite with PLA before and after accelerated weathering. In this study, two types of lignin, organosolv (LO) from soft wood and lignoboost lignin (LB) from hardwood, were used to blend with PLA in a torque rheometer. To simulate accelerated weathering, the composites were kept in an artificial environment condition using a mercury lamp, at 30 °C for up to 600 hrs. The purpose of the accelerated weathering simulation was to ensure that the products can withstand the above conditions by investigating the polymer molecular weight reduction and deterioration of the mechanical properties of the composites. LO and LB utilized in composites provided increased Young’s modulus, higher tensile strength, strain at break, and impact strength after the accelerated weathering simulation compared to neat PLA as phenolic hydroxyl groups in lignin exerted antioxidant properties to prevent photo- and thermo-oxidation. The thermal stability and miscibility of both types of lignin/PLA composites also showed a marked improvement. It was concluded that lignin/PLA composite can be used as an environmentally friendly raw material and replacement for neat PLA polymer.

Hydrogen bonding interactions also play an important role when it comes to the compatibility between lignin and synthetic polymers. The hydrogen bonding interaction of polyethylene oxide (PEO) and unmodified lignin in blends have also been extensively investigated. Kubo and Kadla studied the effect of softwood kraft lignin (SKL) on miscibility and interaction of the SKL/PEO blends. It was found that new hydrogen bonds were formed in the SKL/PEO blends between the SKL hydroxyl groups and PEO ether groups. The strong intermolecular interactions formed between the SKL and PEO polymers lead to improved compatibility and full miscibility of their blends as indicated by only a single $T_g$ value was reported from their DSC
analysis. The effect of hydrogen bonding formed between lignin and PEO was also later supported by Taverna et al. who examined crystallization kinetics in PEO solutions blended with lignin nanoparticles where hydrogen bonding played a significant role on the confinement effect in PEO and lignin nanocomposites.\textsuperscript{105} Jayaramudu et al. investigated the adhesive effects of PEO and lignin (PEO-L) blends used in a nanocellulose composite.\textsuperscript{103} It was hypothesized that PEO-L could enhance the adhesion at the interface between cellulose nanofiber and PEO-L matrix in the composite. Hydrogen bond interactions observed between the lignin’s hydroxyl groups and PEO’s ether groups led to good miscibility of the PEO-L blends. The Young’s modulus and yield strength increased up to 2.5 and 1.4 times respectively for PEO-L when using 30\% of lignin compared to the pure PEO. Based on the studies above, strong hydrogen bond interactions between PEO and modified lignin play a significant role in improving the miscibility of lignin in the synthetic polymer matrix.

Overall, the direct incorporation of lignin into synthetic polymers has shown good promise in addressing the growing concerns about plastic waste. Moreover, these findings hold potential for producing lignin-based blends/composites with improved properties and performance as alternatives to traditional polymers, making them promising materials for a wide range of applications. However, synthetic polymer blends with native lignin still face challenges such as low miscibility and poor mechanical properties. Currently, there are emerging studies that attempt to address these challenges by exploring the preparation of modified lignin prior to its incorporation into blends/composites to help enhancing compatibility.

\textit{Modified Lignin in Blends/Composites}

Although unmodified lignin provides some positive properties in blends/composites, there are still limitations arising due to significant polarity differences between lignin and the co-blend
material. Low compatibility has been observed between lignin and some synthetic polymers such as PE, PP, PS. Thus, there have been efforts to modify lignin to increase its compatibility with synthetic polymers through several different reaction methods including esterification, alkylation, acetylation, and oxypropylation.

To increase miscibility of lignin in polyolefins blends, lignin is generally pre-modified. For instance, Dehne et al. prepared esterified lignin to blend with HDPE (50:50 wt%) and investigated the resulting properties in comparison to HDPE blends with unmodified lignin (also 50:50 wt%). Lignin esterification was found to reduce overall polarity of lignin, resulting in higher compatibility with PE when blending. The increase of ester carbon chains in esterified lignin led to better miscibility in the HDPE matrix. Consequently, more favorable mechanical properties were obtained—higher tensile and flexural strength—was observed for the esterified lignin/HDPE blend. In another report by Sadeghifar and Argyropoulos, the melting behavior of different lignin-PE blends was studied. Two types of fractioned lignin—acetone soluble kraft lignin (ASKL) and acetone insoluble kraft lignin (AIKL)—were methylated and utilized in blends. It was observed that methylation of lignin improved and stabilized the melt viscosity due to less cross-linking effects in blends. Chen et al. reported the physical properties of lignin-based PP blends. Alkylation of kraft lignin was prepared to improve the molecular interaction and increase the compatibility between lignin and PP in blends. The thermal stability and flame retardancy property of the blend increased when the amount of alkylated lignin increased. However, when the alkylated lignin content increased beyond 15 wt%, the tensile modulus and strength of the blends decreased. This may be due to the low cross-link density and rigidity of alkylated lignin. Therefore, although different types of lignin may play a role in blending with polyolefins, pre-modification of lignin
has clearly been shown to improve dispersity of lignin in blends and enhance overall thermal and mechanical properties of lignin/polyolefin blends.

In addition to polyolefins, modified lignin has also been shown to increase its compatibility when employed in blends/composites with PLA. In a study by Gordobil et al., lignin was modified through acetylation method before blending with PLA in a twin-screw extruder.\textsuperscript{92} For comparison, both unmodified and acetylated lignin were used in blends with PLA. Compared to lignin/PLA, there was no agglomeration of lignin and less surface roughness observed on the surface of acetylated lignin/PLA blend. This result indicated there was a greater compatibility and interaction of the acetylated lignin than unmodified lignin with PLA. In addition, the acetylated lignin/PLA blend showed an improvement in overall strength and ductility as the amount of acetylated lignin increased in the blends. Esakkimuthu et al. investigated the lignin’s effect on the antioxidant behavior and compatibility of lignin/PLA composite in food packaging application.\textsuperscript{94} Lignin was initially modified via oxypropylation method. For comparison, kraft lignin and oxypropylated lignin were separately used in blends with PLA. Oxypropylated lignin/PLA composites were slightly more thermally stable compared to neat PLA and unmodified lignin/PLA composite. However, unmodified lignin/PLA showed a slightly higher antioxidant activity compared to oxypropylated lignin/PLA composite due to the increase in ether linkages and loss in phenolic hydroxyl groups during the oxypropylation process. Overall, the oxypropylated lignin/PLA composite could be a partially plausible candidate for food packaging application.

Blends of modified lignin and PEO have also been studied as a precursor for carbon fiber applications. Anagnou et al. examined the effect lignin modification on the mechanical and thermal properties modified lignin/PEO blends.\textsuperscript{106} In this work, acid purified lignin was modified with phthalic anhydride to help reduce its polarity and improve its miscibility when blended with
PEO. After blending, hydrogen bond interactions were observed between the ester groups in modified lignin and ether groups in PEO, which led to miscibility improvement between modified lignin and PEO. It was also observed that modified lignin helped enhance the elasticity, ductility, and elongation of the blends compared to blends containing unmodified lignin.

Development of modified lignin has also been utilized with PVA to obtain a compatible polymer blend matrix for biopolymeric raw materials in food packaging. For instance, Nair et al. studied the thermal stability and miscibility of nanolignin and PVA blends where the addition of nanolignin lead to increased surface area and improved compatibility with PVA compared to unmodified lignin. Similarly, Xiong et al. prepared lignin nanosphere (LNS) with PVA nanocomposite films to obtain more evenly dispersed lignin in PVA matrix. While these PVA/LNS composites exhibited a more homogenous distribution of lignin in the PVA matrix, unmodified lignin showed macroscopic phase separation in the composite. The improved lignin distribution was attributed to the strong hydrogen bonding interactions that occurred between LNS and PVA. The mechanical properties of LNS/PVA, such as tensile strength and stress, were also found to be improved between LNS and PVA compared to neat lignin/PVA. Additionally, the UV-absorbing and transparency properties of PVA/LNS were better relative to unmodified lignin/PVA.

Different from the above studies, Hu et al. also prepared a graft copolymer of AA with lignosulfate calcium (GL) before using in blends with PVA. The purpose of the lignin and AA graft copolymer was to increase the hydrogen bond interaction between GL and PVA and produce a more thermally stable blended matrix. The resulting composite exhibited improved mechanical properties, such as Young’s modulus and tensile strength compared to PVA. Further, a single $T_g$ with a value higher than the pure PVA $T_g$ appeared in each composite, which indicated a good
compatibility between GL and PVA composite. Thus, modified lignin/PVA composite is expected to be a potentially good candidate for food and medical packaging material.

Overall, while direct use of lignin into blends and composites may be suitable for some applications, researchers have employed various pre-modification techniques for lignin to further increase intermolecular interactions, and hence the compatibility of lignin when incorporated into blends or composite matrices. It is also important to highlight that lignin copolymers, in addition to these modifications, have demonstrated a capacity to enhance compatibility with synthetic copolymers when utilized into lignin-based blends or composites. Notably, this aspect remains a relatively underexplored area of study. Overall, the resulting products from blends with lignin copolymer can exhibit favorable chemical, mechanical, and thermal properties and are suitable for a wide range of applications.

1.4 Conclusions

Lignin has been studied extensively due to its abundance in nature, low-cost, and biodegradability properties as compared to petroleum-based polymers. However, it is still commercially underutilized due to its highly branched structure which leads to low processibility. To obtain new and improved properties, multiple lignin valorization techniques have been employed including functionality modification, copolymerization, and development of blends and composites. In copolymerization, lignin generally bonds with synthetic polymers covalently to provide better thermal stability, improved mechanical, and surface properties, and more importantly, greater compatibility with other polymers. Lignin is generally used directly or after pretreating through different modification techniques including esterification, acetylation, or alkylation before incorporation into polymer blends and composite to increase intermolecular interactions and compatibility with synthetic polymers. These valorized techniques allow lignin to
be utilized in a wide field of applications ranging from sustainable materials for water remediation, biodegradable fillers in thermoplastic material productions for food and medical packaging to precursor materials for carbon nanofiber industry.

1.5 Motivation and Scope of Work

This review discussed a range of techniques employed in the copolymerization of lignin with various synthetic polymers, as well as mixing strategies for producing lignin blends and composites. Additionally, various lignin modification methods that can be used as pretreatment techniques prior to copolymerization have also been discussed. However, a notable deficiency in this discussion is phenolation, a modification method that will increase the number of phenolic hydroxyl groups, which may potentially lead to improved chemical reactivity of lignin. Since this method has not been examined comprehensively, a primary goal of this work is to investigate lignin phenolation and its impact on the properties and reactivity of lignin (Chapter 2). Once phenolated, lignin will then be used for a subsequent amination reaction which is expected to increase the dye removal efficiency of lignin in water remediation applications. The literature review also highlights that for the development of lignin-based blends and composites improving compatibility between lignin and synthetic polymers is key. However, research using lignin copolymers as a compatibilizer in lignin/synthetic polymer blends and composites remains very limited. Chapter 3 includes the synthesis of lignin-g-polystyrene (L-g-PS) copolymers using activators generated electron transfer by atom transfer radical polymerization (AGET ATRP). Then blends of lignin/polystyrene (L/PS) and L-g-PS/polystyrene (L-g-PS/PS) were prepared and examined to provide a comparative analysis of thermal properties, and surface morphology of films. Finally, overall key findings and future project recommendations will be provided in Chapter 4.
References


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Chapter 2: Aminated Lignin for Efficient Dye Removal Wastewater Remediation

Abstract

Lignin is an abundant, degradable, and renewable biobased polymer derived from plant cell walls. For lignin to be used more widely and to increase its value, it needs to be chemically transformed. Modified lignin has been examined in a broad range of applications such as wastewater treatment\(^1,2\), sustainable packaging\(^3,4\), and precursor for carbon fiber material\(^5,6\). In this work, aminated lignin was synthesized through a Mannich reaction following a phenolation pretreatment. The aminated lignin was then examined as a dye-removing agent for wastewater treatment. Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM) were employed to examine lignin’s chemical, thermal, and morphological changes after each modification. The effect of phenolation pretreatment, pH, contact time on the adsorption capacity and kinetics of aminated phenolation lignin (Am-PL) was also investigated for two anionic dyes. Am-PL effectively removed Congo red (CR) and methyl orange (MO) dyes with maximum removal rates of ca. 96\% and 69\% achieved after 96 hrs, respectively, under alkaline conditions. The adsorption behavior of aminated lignin for both dyes tested follows a pseudo-second order adsorption kinetics model. This study provides a modification method with up to 9.6 wt\% amine groups added to the lignin structure, which allows lignin to effectively function as an adsorbent for anionic dye wastewater treatment applications.

2.1 Introduction

Since the late 18\(^{\text{th}}\) century, synthetic dyes have been extensively utilized in textile\(^7\)–\(^9\), paper\(^10,11\), leather\(^9,11–13\), cosmetics\(^11,14–17\), plastics\(^10,17–19\), agriculture\(^9\), light-harvesting array\(^20,21\), photoelectrochemical cell\(^22\), photosensitizer\(^23,24\), and manufacturing industries\(^11,25\). Approximately
700,000 tonnes of synthetic dyes are produced annually worldwide. Among these dyes, anionic (negatively charged) dyes, such as Congo red, methyl orange, orange G, and alizarin yellow, are some of the most toxic water contaminants that pose serious threats to human health, aquatic ecosystems, and living organisms. In light of the escalating issues related to polluted water and water scarcity, effective wastewater treatment methods are necessary to ensure water security and access and protect the environment. Multiple methods have been examined to mitigate the impact of anionic dyes in wastewater including solvent extraction, photocatalytic oxidation, biological degradation, chemical precipitation, flocculation, ion exchange, dialysis, electrolysis, membrane separation, microbial degradation, and adsorption.

Of these dye removal methods, adsorption is a cost-effective and non-destructive method for contaminant removal that also preserves the dye’s structure (for potential reuse) and generates minimal secondary pollution. Adsorption is a particularly attractive option when renewable and environmentally friendly adsorbent materials are utilized. Renewable adsorbent materials are highly versatile in their capacity to effectively remove pollutants such as heavy metal, toxic dyes, organic compounds from water. Derived from plant-based sources, these materials not only demonstrate environmental sustainability, but also highly accessible, making them suitable for various water treatment needs. Adsorption occurs due to electrostatic interactions and van der Waals interactions between solute and adsorbent. Adsorption processes can generally be categorized as exchange, physical, and chemical adsorption. Wastewater treatment methods involving adsorption utilize solid adsorbents which can range from activated carbon to natural materials (e.g., clay, zeolites, peat) or even industrial/agricultural wastes (e.g., rice husk, bark, saw dust, biochar, petroleum wastes, fertilizer wastes). Adsorbents are often chemically and
physically modified to improve their adsorption performance. The modification enhances their capacity to capture low-concentration pollutants, improving their binding capacity for target molecules. Biosorption is a wastewater treatment approach that involves the utilization of biological materials like microbial biomass (e.g., bacteria, fungi) or plant-based substances (e.g., alga, specific plant tissues) as adsorbents. Lignin is one of the most abundant plant-based biopolymers, and it is well-suited for biosorption due to its unique and irregular three dimensional network structure with a rich phenolic hydroxyl content. These phenolic hydroxyl groups provide numerous adsorption sites—by binding with hydroxyl, carbonyl, methoxyl, amine groups—enabling pollutants to effectively adhere to the surface or penetrate the structure through supramolecular interactions or covalent bonding, leading to effective contaminant removal from water. Ongoing research in this field concentrates on optimizing the combination of adsorption techniques with lignin’s properties, aiming for eco-friendly and sustainable wastewater treatment using biosorption with lignin-based adsorbents.

**Lignin Structure and Chemical Functional Groups**

Lignin is a plant-based biopolymer with an amorphous and highly branched structure. The branched structure of lignin helps provide necessary rigidity and strength to the cell wall allowing plants to transport water and nutrients, and prevent chemical or biological attacks. Lignin contains 10 – 15 wt% of phenolic and aliphatic hydroxyl content; these groups contribute to the polar nature of the biopolymer and facilitates post-extraction modification. In the last two decades, the valorization of lignin has been explored as a potential alternative to petroleum-based polymers due to its natural abundance, low-cost, non-toxicity. Industrially, lignin is generally treated as waste or a low-value commodity such as a fuel for combustion. The major limitations on using lignin are two-fold. The branched structure of lignin makes it a rigid material
and difficult to process in terms of melt flow, production of packaging films or textile fibers. The second issue related to the chemical complexity of lignin combined with varying composition and structure of lignin produced from different plant sources and extraction processes. Therefore, efforts are needed to understand and modify the structure and properties of lignin to support its valorization and broader application.

Various modification methods, including amination, hydroxyalkylation, esterification, phenolation, and azo coupling, have been explored (Figure 2.1) to provide lignin with new reactive sites, alternate functional groups, and increase chemical reactivity. For instance, aminated lignin has been used in water remediation to remove organic dyes, heavy metal ions, and oil. In comparison to native lignin, esterified lignin has better thermal stability, lower glass transition temperature, and exhibits improved miscibility with synthetic polymers. Though the promising potential of modified lignin has been recognized, there has not been thorough research on its applications so far.
Figure 2.1 Schematic showing several lignin chemical modification methods. The aromatic and aliphatic hydroxyl functional groups in lignin can be converted via hydroxypropylation, esterification, amination, phenolation, and azo coupling reactions.

Amination of lignin allows for primary, secondary, and tertiary amine groups to be added as substituents on the benzyl rings via Mannich reaction. These amine groups can gain a positive charge in solution making them useful in water remediation applications, such as removal of harmful, toxic anionic dyes (e.g., Congo red, methyl orange). Although lignin naturally contains phenolic hydroxyl groups, phenolation modification provides additional phenol groups.
such that a subsequent amination reaction will yield a higher amine content for the modified lignin, increasing the adsorption capacity and generating a more effective water treatment.\textsuperscript{2,84,85,87}

Chen \textit{et al.} prepared aminated lignin by reacting kraft lignin with 2-chloroethylamine hydrochloride and studied its adsorption efficiency on Congo red and crystal violet dyes.\textsuperscript{87} Aminated lignin, with its higher specific surface area and porous structure compared to unmodified lignin, demonstrated superior dye adsorption capacity (97.09 and 129.87 mg·g\textsuperscript{-1} for crystal violet and Congo red dye, respectively at 25 °C) compared to other bio-based adsorbents. An \textit{et al.} prepared aminated lignin through modification with (3-aminopropyl) triethoxysilane to explore the adsorption capacity of Congo red and Cu (II) ions in aqueous solution.\textsuperscript{1} The Langmuir isotherm model of the adsorption results for this amino-silanized lignin yielded maximum adsorption capacities of 74.4 mg·g\textsuperscript{-1} for Congo red and 17.8 mg·g\textsuperscript{-1} for Cu (II) ions, with the adsorption process following pseudo-second order kinetics. In a similar study, Heo \textit{et al.} showed a higher Congo red dye adsorption capacity (293.26 mg·g\textsuperscript{-1}) for lignin aminated with different amino-silane molecules.\textsuperscript{82} Primary, secondary, and tertiary amino-silanes were mixed with softwood kraft lignin in methanol and heated under reflux for 24 hrs to react with hydroxyl groups on lignin and form amino-silane lignin (ASL) The Congo red dye adsorption capacity using the primary amine ASL was the highest followed by secondary amine ASL and tertiary amine ASL (~95%, ~86%, and ~85% when using 0.06 g of adsorbent). The dye adsorption involved the electrostatic, hydrogen bonding, NH-π, and π-π interaction between ASL and Congo red dye. An important finding from this work is that it is essential in aminated lignin to have high contents of primary amine group to generate an effective dye removal adsorbent as secondary and tertiary amine groups may offer lower extension of silanization due to steric hindrance effect.
The aim of this study is to modify lignin with ethylene diamine through the Mannich reaction to yield an aminated lignin containing both primary and secondary amine groups. The native lignin will also be modified by phenolation reaction to increase the amount of phenolic hydroxyl groups such that the subsequent Mannich reaction will produce higher amine contents in the resultant aminated lignin. Aminated lignin will be evaluated as an anionic dye-removing agent using two model dyes, Congo red and methyl orange. The lignin chemical composition was examined at each synthesis step by Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS). Thermogravimetric analysis (TGA) was used to examine the thermal stability of lignin and aminated lignin. Scanning electron microscopy (SEM) examined the surface morphology differences between the unmodified alkali lignin and aminated lignin. Dye adsorption was monitored using ultraviolet-visible (UV-Vis) spectroscopy. The effects of phenolation pretreatment, solution pH, and contact treatment time on the adsorption kinetics and adsorption capacity were also investigated. This study shows a facile method to modify lignin and provide an economical and eco-friendly lignin adsorbent that can be used in treating industrial wastewater contaminated with dyes and potentially other contaminants found in surface and agricultural water supplies.

2.2 Materials and Methods

Materials

Alkali lignin (AL) (CAS 9005-53-2) was purchased from TCI America. Phenol solution was purchased from Macron Fins Chemical. Sulfuric acid (H₂SO₄, 98%, CAS 7664-93-9), formaldehyde (H₂C=O, 37% solution, CAS 50-00-0), and sodium hydroxide (NaOH) (CAS 1310-73-2) were purchased from MilliporeSigma. Hydrochloric acid (HCl, CAS 7647-01-0) was purchased from ThermoFisher Scientific. Congo red dye (CR, CAS 573-58-0) was purchased from VWR Chemical. Ethylenediamine (99%, CAS 107-15-3) was purchased from Alfar Aesar.
Experimental Methods

Acid precipitation was used to purify alkali lignin (AL) prior to subsequent chemical modification or characterization to remove residual inorganics, cellulose, and sugars often present at differing contents based on the lignin source and processing methods. The purified lignin was then pretreated through a phenolation reaction to add more phenolic hydroxyl groups onto the lignin. These hydroxyl groups were then used for the subsequent amination reaction. The lignin phenolation and amination reactions (Mannich reaction) are shown in Figure 2.2.

Figure 2.2 Lignin phenolation and amination reactions

Lignin purification by acid precipitation: The lignin purification method was adapted from Pan et al.\textsuperscript{88} AL (2.0 g) was dissolved in deionized (DI) water (30 wt% concentration) and the solution heated to 70 °C and held at this temperature for 15 min to ensure complete lignin dissolution. The resultant dark brown solution was allowed to cool for 10 min at room temperature before 1.44 M of HCl solution was added dropwise to adjust the pH value to 2-3. The acidified lignin solution was kept at room temperature overnight and then was washed 3-5 times using DI water and centrifugation (5000 rpm at 10 °C) to separate the lignin solids from the liquid phase.
Finally, the purified lignin was dried at 80 °C until the solid product mass was stable to ensure complete drying.\(^{88}\)

**Preparation of Phenolated Lignin:** A representative reaction involves 1.0 g of purified AL is dissolved in 2.0 g of phenol solution. Then, 12.96 M of H\(_2\)SO\(_4\) solution (0.033 mL) was added to serve as a catalyst. The mixture was then stirred for 20 min at 110 °C. After completion, the reaction solution was added to HCl solution (pH = 2) under continuous stirring to precipitate the phenolated lignin (PL). The precipitated PL was then filtered and washed with acidified water (pH = 5) followed by DI water until a neutral pH was obtained. Finally, the filtered solid was dried in a fume hood at room temperature overnight, followed by drying in an oven at 50 °C to ensure complete removal of residual water.\(^{79,89}\)

**Preparation of Aminated Lignin:** The Mannich reaction can be performed with AL and PL to produce aminated lignin. To examine any differences in amine content, both AL and PL were aminated using the Mannich reaction outlined as follows. Step one of the lignin amination process involves dissolving 0.5 g of either AL or PL in a NaOH solution (0.04 mol.L\(^{-1}\)) for 10 min under continuous stirring. Ethylene diamine (0.833 mL) and formaldehyde (1.220 mL) were then added to the lignin/NaOH solution. This solution was kept at 100 °C for 3 hrs with continuous stirring, and then the mixed product was dialyzed against DI water (water changed 5-8 times) using dialysis tubing with a 3000 Da molecular cut-off. Finally, the aminated lignin product was dried in a fume hood overnight followed by drying in a vacuum oven at -0.05 MPa and 50 °C overnight to ensure complete drying.\(^{89}\)

**Dye Removal Testing:** Congo red (CR) and methyl orange (MO) were chosen as model dyes for evaluating lignin’s kinetics and capacity for dye adsorption from aqueous solutions. CR and MO chemical structures are shown in Figure 2.3. CR dye solution was first prepared at a
concentration of 0.01 mg.mL\(^{-1}\), producing a solution with a measured pH of 8.86 ± 0.56. Three separate vials were then prepared by adding 10 mL of the dye solution to each vial before adjusting the pH to the desired value—3.84, 8.86 (native), 9.98. pH adjustments were performed through small additions of either 1.0 M HCl or 1.0 M NaOH solutions. For dye removal testing, aminated lignin (0.10 mg) was added to all three vials and the solutions were constantly stirred for 96 hrs. The same procedures were followed for MO dye solution preparation and removal testing. Measured pH values of the MO dye solutions were 3.88, 9.16 (native), and 10.09, respectively.

![Molecular structure of Congo red (CR) and methyl orange (MO) dyes.](image)

Figure 2.3 Molecular structure of (a) Congo red (CR) and (b) methyl orange (MO) dyes.

Adsorption efficiency (\(\eta\)), adsorption capacity, \(q_e\) (mg.g\(^{-1}\)), and adsorption capacity at time \(t\), \(q_t\) (mg.g\(^{-1}\)) was calculated using the initial and final dye concentrations as determined from a 7-point calibration curve using UV-vis analysis over the 1100 – 190 nm wavelength range as described by the following equations:

\[
\eta = \left( \frac{C_i - C_f}{C_i} \right) \times 100\% \tag{2.1}
\]
\[ q_e = \frac{(C_i - C_f) \times V}{m} \quad (2.2) \]

\[ q_t = \frac{(C_i - C_t) \times V}{m} \quad (2.3) \]

where:

- \( C_i \) is the initial concentration (mg.L\(^{-1}\))
- \( C_f \) is the final concentration (mg.L\(^{-1}\))
- \( C_t \) is the concentration of the dye at time, \( t \) (mg.L\(^{-1}\))
- \( V \) is the volume of the dye solution (mL)
- \( m \) is the mass of adsorbent (g).

**Characterization**

**Fourier Transform Infrared Spectroscopy (FTIR):** A PerkinElmer Frontier FTIR spectrophotometer was used to collect spectra for the native, phenolated, and aminated lignin samples. To minimize water peak interference in the spectra, each sample was dried in a vacuum oven at 50 °C for 24 hrs prior to the FTIR scans. Each spectrum is an average of 64 scans collected over the 4000 – 550 cm\(^{-1}\) wavenumber range at a 4 cm\(^{-1}\) resolution. FTIR data collection and spectral analysis was completed using OMNIC (ThermoScientific\(^{TM}\)) software.

**X-ray Photoelectron Spectroscopy (XPS):** XPS elemental analysis was performed to confirm the atomic and functional group compositions for the lignin samples. A Physical Electronics PHI VersaProbe 5000 station XPS instrument (Institute for Nanoscience and Engineering Core Facility, University of Arkansas) with a monochromated 25.0 W Al 1486.6 eV sources was used to collect survey spectra with a pass energy of 117.4 eV and an acquisition angle of 45°. Survey spectra were collected over the binding energy range 1200 - 0 eV at a resolution of
0.5 eV. CasaXPS (Version 2.3.23PR1.0) software was used to collect and analyze the survey and high-resolution spectra.

**Thermogravimetric Analysis (TGA):** Thermal stability was accessed with a Discovery 5500 TGA (TA Instruments). Samples were heated from 25 to 800 °C at a heating rate of 10 °C.min\(^{-1}\) with a 30 mL.min\(^{-1}\) nitrogen flow rate. Trios software (TA Instruments) was utilized to determine thermal degradation onset temperatures and weight loss values.

**Scanning Electron Microscopy (SEM):** SEM (FEI Nova Nanolab 200, Institute for Nanoscience and Engineering Core Facility, University of Arkansas) images were collected with an accelerating voltage of 15.00 kV to examine the surface morphology of lignin and aminated lignin. All samples were placed on double coated carbon conductive tape before analysis.

**Ultraviolet-Visible Spectroscopy (UV-Vis):** A Shimadzu UV-Vis 1601 UV-Vis spectrophotometer was used to determine the concentration of anionic dye in an aqueous water solution before and after adsorption removal treatment. Spectra were collected over the 1100 - 190 nm wavelength range at a spectral resolution of 1 nm. A calibration curve was produced to determine the unknown dye concentration by preparing a series of known concentration dye solutions and measuring absorbance for each solution. (Additional details provided in Appendix A - A1). The equipment was baseline corrected by running with DI Millipore water as a reference at the above wavelength before analyzing the dye solutions.

**2.3 Results and Discussion**

In order to determine which method resulted in more amine content, aminated lignin was synthesized via the Mannich reaction from both AL and PL. As shown in Figure 2.2, amination with PL was achieved by the reaction between ethylenediamine and the phenolic hydroxyl groups.
To confirm successful synthesis reactions, the atomic and functional group composition for purified AL, PL, and aminated lignin were examined using FTIR and XPS analyses.

Figure 2.4 FTIR spectra of purified AL (a), PL (b), Am-AL (c), and Am-PL (d)

Functional groups in purified AL, PL, aminated alkali lignin (Am-AL), and aminated phenolation lignin (Am-PL) were analyzed using FTIR spectroscopy (Figure 2.4). The presence of aliphatic and aromatic hydroxyl groups is noted at 3400 cm\(^{-1}\) for both AL and PL (Figure 2.4 a,b).\(^{90}\) The peaks present at 2943 and 2848 cm\(^{-1}\) are assigned to the asymmetrical and symmetrical C–H stretching vibrations, respectively.\(^{88,89}\) After amination, the synthesized Am-AL and Am-PL display similar spectra, as shown in Figure 2.4 c,d, with small peaks at 1643 and 1260 cm\(^{-1}\) indicating the presence of the N–H and C–N bending vibrations, respectively.\(^{89,91}\) This finding confirms successful for amination reaction and is corroborated by XPS analysis. The XPS survey spectrum (Figure 2.5) which shows the emergence of a nitrogen (N1s) peak at ~390 eV for both the Am-AL and Am-PL samples but not the for the unmodified AL sample. The nitrogen (N1s)
atomic concentration measured for Am-AL was 3.1 wt%, whereas for Am-PL the nitrogen content was 9.6 wt%. More details on the atomic concentrations for other elements present in AL, Am-AL, and Am-PL are given in Appendix A – A3. FTIR and XPS analyses indicate AL and PL were both successfully aminated through the Mannich reaction. Further, these results show more than a three-fold increase in the amine content through a two step-modification involving lignin phenololation prior to amination. Based on this result, only Am-PL will be used for further characterization and dye removal tests.

Figure 2.5 XPS survey spectra of unmodified AL, Am-AL, and Am-PL. The N1s peak appears in both aminated samples, Am-AL and Am-PL, with a significant increase in nitrogen content for Am-PL due to the additional phenolic hydroxyl sites used in the amination reaction.

To compare the thermal stability of AL and Am-PL, TGA analysis was performed with each sample heated from room temperature to 800 °C at a 10 °C.min⁻¹ heating rate. Due to its complex structure, the TGA scans (Figure 2.6) showed AL decomposed in three stages over a wide temperature range, which is consistent with other published studies.⁸⁹,⁹¹ The first stage of weight loss (up to ~ 150 °C) was due to the removal of moisture in each sample. The majority of
the sample weight loss (37.5%) occurred between from 142.4 to 601.7 °C, due to the degradation stage that produces carbon dioxide (CO₂), carbon monoxide (CO), and methane (CH₄). The last decomposition stage showed a 4.8% weight loss between 601.7 and 800 °C. This final stage is attributed to pyrolytic degradation of the lignin backbone structure and loss of the phenol monomers.

Figure 2.6 TGA curves for AL and Am-PL

While the TGA curve of Am-PL has similar features as AL, Am-PL shows a higher weight percent of adsorbed water removed than AL (~5.2 wt% for AL and ~7.4 wt% for Am-PL) prior to 100 °C, which usually occurs for aminated lignin. This initial weight loss difference in the first phase continues at higher temperatures. The overall weight loss was larger for Am-PL compared
to unmodified AL. At 800 °C AL and Am-PL show 51.43 wt% and 46.2 wt% ash contents, respectively.

Figure 2.7 SEM images of purified AL (a), PL (b), and Am-PL (c). Note the size scale bars changes between each image.

Surface morphologies were studied using SEM for AL, PL, and Am-PL (Figure 2.7). In comparison to Am-PL, purified AL and PL are larger and more granular than Am-PL. The increase surface roughness observed for PL vs. AL is attributed to the phenol group addition. Moreover, after the Mannich reaction was performed and the Am-PL was thoroughly dried, Am-PL exhibited a porous structure, giving an increase in surface area. This was attributed to the addition of amino groups the surface of AL. These amino groups allowed Am-PL to adsorb the anionic dyes from water solution due to the electrostatic and van der Waals interaction with positive charged amine groups.

As CR and MO are pH responsive dyes, the effect of pH on the UV-vis response of CR and MO solutions was first investigated before examining the dye removal capabilities of the Am-PL. Figure 2.8 a.d show the initial (0 h) UV-Vis curves for the CR and MO dye solutions, respectively, for different solution pHs. The maximum wavelength ($\lambda_m$) for CR and MO dye solutions were initially located at 498 and 464 nm. However, the UV-Vis curves for CR showed the $\lambda_m$ of CR shifted up to 545 nm when the pH was decreased to 3.84 (Figure 2.8 a-blue) and
the $\lambda_m$ of MO shifted to 475 nm when the pH was decreased to 3.88 (Figure 2.8 d-blue). These peak shifts in $\lambda_m$ match well with the expected UV-vis absorbances for the CR and MO pH indicator dyes due to the color changes that occur at pH between 3-4. To determine the concentration after dye removal, the calibration curves of CR and MO dye solutions were carried out and shown in Appendix A – A2.

![Figure 2.8](image)

Figure 2.8 UV-vis spectra are shown for CR (a) and MO (d) for different pHs at 0 hr. The percent dye removal as a function of pH for CR (b) and MO (e) after 96 hrs was determined using equation 2.1 at the absorbance measurements at 1100-190 wavenumbers. Photograph inserts show the color change of CR (c) and MO (f) for the three different pHs examined for each dye.

Figure 2.8 b,e respectively show the percent removal of the CR and MO dyes after Am-PL adsorption treatment. The percentage of dye removal was calculated using equation 2.1.
Approximately, 96% of CR dye and 69% of MO dye was removed by Am-PL treatment. Notably, the percent removal of both dyes from water solution exhibited an upward trend as the pH level increased. It is noteworthy that the removal percentage for the MO dye from water is lower than the CR. This difference can be attributed to the chemical composition and overall charged state of the dyes. MO contains (CH$_3$)$_2$N$^+$ and −SO$_3^-$ groups, imparting a slightly acidic to the dyes in pure water, whereas CR is negatively charged due to its anionic phenolic and sulfonate groups. Indeed, this difference in charge properties influences their interactions with Am-PL and, consequently, their removal efficiency.

Figure 2.9 a,d show that AL did not contribute to the removal of CR and MO dyes due to the absence of any noticeable changes in the UV-Vis curves even after 48 h. However, significant changes in the initial (0 hr) and final (96 hrs) UV-vis absorbance spectra for the CR and MO dye solutions was observed after Am-PL treatment (Figure 2.9 b,e). The residue resulting from the adsorbed dye and Am-PL remained at the bottom of the solution vial. This settling behavior can be observed in Figure 2.9 c,f, which show the images of the CR and MO dye solutions at the beginning of treatment (0 hr) and after 96 hrs, respectively.
Figure 2.9 UV-Vis curves of CR dye (a) and MO dye (d) using unmodified AL, UV-vis curves CR dye (b) and MO dye (e) using Am-PL, photographs of CR (c) and MO (f) at 0 hr and at 96 hrs.

Am-PL exhibits the ability to remove the CR and MO from the aqueous solutions, which lead to the ability restore the neutral pH of water. Figure 2.10 a,b shows the pH measured as a function of time for CR and MO solutions with Am-PL presence. In each case, the final pH of the aqueous solutions after 96 hrs was within the optimal pH range of 6.5-8 for agricultural water supply. Therefore, Am-PL is an excellent candidate for removing CR and MO dyes from contaminated water and as a result returning the water to a neutral pH.
Adsorption kinetics were examined to determine the relationship between the adsorption capacity and adsorption time. Understanding the adsorption kinetics of the Am-PL is important to determine operational conditions necessary for water treatment using the modified lignin adsorbent. Generally, pseudo-first and second order models are typically used in the investigation of adsorption kinetics, where the pseudo-first order model is generally used to describe the physical adsorption and pseudo-second order model is more suitable for describing chemisorption. The integral expressions of pseudo-first order and pseudo-second order equations are as follows:

\[ \ln(q_e - q_t) = \ln q_e - k_1 t \]  \hspace{1cm} (2.4)

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \]  \hspace{1cm} (2.5)

where

- \( q_e \) is the calculated equilibrium adsorption capacity (mg.g\(^{-1}\))
- \( q_t \) is the adsorption capacity at time t (mg.g\(^{-1}\))
- $k_1$ is the pseudo-first order kinetic rate constant (min$^{-1}$)
- $k_2$ is the pseudo-second order kinetic rate constant (mg.g$^{-1}$.min$^{-1}$)

**Table 2.1** Characteristic adsorption kinetics parameters for CR and MO dye adsorption

<table>
<thead>
<tr>
<th>Dye</th>
<th>Pseudo-first order model</th>
<th>Pseudo-second order model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Equation</td>
<td>$R^2$</td>
</tr>
<tr>
<td>CR</td>
<td>$\ln(q_e - q_t) = -0.510t + 8.487$</td>
<td>0.972</td>
</tr>
<tr>
<td>MO</td>
<td>$\ln(q_e - q_t) = -0.080t + 6.647$</td>
<td>0.982</td>
</tr>
</tbody>
</table>

Adsorption curves are shown along with pseudo-first and second-order model fits in **Figure 2.11**. Kinetic rate order equations, rate constants (k), and correlation coefficients ($R^2$) for CR and MO dye adsorption curve fitting are listed in **Table 2.1**. For both dye solutions, a better linear fit was observed for the pseudo-second order model ($R^2 = 0.996$ for CR and $R^2 = 0.995$ for MO) compare to pseudo-first order model ($R^2 = 0.972$ for CR and $R^2 = 0.982$ for MO), indicating that the pseudo-second order relation provides a more suitable representation for the adsorption behavior as they are most likely follow chemisorption behavior where both dyes are adsorbed to the Am-PL surface through covalent bonds.$^{87}$
2.4 Conclusions

In this study, lignin was modified with ethylene diamine to produce aminated lignin (Am-PL) which was demonstrated as an effective agent for removing anionic dyes, including dyes like Congo red and methyl orange, in water treatment applications. Although it is feasible to achieve this modification using native (or alkali) lignin (AL), the pretreatment of lignin through phenolation has been demonstrated as an effective method to achieve a higher yield of amine content in aminated lignin. The FTIR and XPS analyses confirmed the successful modification of lignin with greater amine content observed in Am-PL. TGA indicated that, at the same temperature, Am-PL lost more weight by the early stage decomposition compared to AL. Additionally, SEM analysis showed that there was porous-like structure with higher specific area on the surface of Am-PL. UV-vis spectroscopy was also performed to examine the anionic dyes.
removal from water solution as a function of pH. In light of the dye removal experiment, it was observed that Am-PL played a significant role in removing Congo red and methyl orange dye under various pH conditions, including both acidic and basic conditions. Specifically, it exhibited maximum removal efficiencies of ~96% for Congo red and ~69% for methyl orange under basic condition (pH = 9.98 for CR and pH = 10.06 for MO). More importantly, it can restore the pH neutrality of water (pH 6.5-8) after the dye removal treatment. The adsorption behavior of both dyes using Am-PL tends to follow the pseudo second-order model of the adsorption kinetic, implying that the adsorption kinetics follows a chemisorption process. Finally, it is essential to highlight that Am-PL holds the potential for multiple applications in dye removal processes, underscoring its suitability as a reusable and environmentally friendly adsorbent in water treatment applications.
References


(61) *Biosorption of heavy metals by lignocellulosic biomass and chemical analysis :: BioResources.* https://bioresources.cnr.ncsu.edu/ (accessed 2023-11-10).


Chapter 3: Synthesis and Characterization of Lignin-Grated Polystyrene and Polymer Blends

Abstract

The growing demand for bio-based and renewable polymer materials has motivated many valorization studies of low-cost and underutilized biomass from agricultural by- and waste-products such as lignin. To promote sustainability through the displacement of petroleum-based polymer content, lignin was graft copolymerized with polystyrene (PS) via activator generated by electron transfer atom transfer radical polymerization (AGET ATRP). Successful polymerization was confirmed by Fourier transform infrared spectroscopy (FTIR), and the structural, thermal, and morphological features were examined for lignin, lignin-graft-PS (L-g-PS) copolymers, and 50/50 wt/wt blends using thermogravimetric analysis (TGA), differential scanning calorimeter (DSC), scanning electron microscopy (SEM), and water contact angle. L-g-PS blended with PS (L-g-PS/PS) had higher thermal stabilities than native lignin and lignin blended with PS (L/PS), as evidenced by the higher onset degradation temperature of 378 °C for L-g-PS/PS versus 340 °C for L/PS. Enhanced miscibility was observed for the L-g-PS/PS blend with only a single $T_g$ value observed, unlike the L/PS blend, which displayed two separate $T_g$ values. Water contact angles of L-g-PS and L-g-PS/PS were increased significantly to 96.6° and 112.6° respectively, as compared to 45° for native lignin. Including lignin in a commercial polyolefin, such as PS, as a copolymer or copolymer blend allows for a reduction in the use of petroleum-derived polymers, contributing to sustainable materials development. Future studies will examine whether the lignin copolymer has the required mechanical properties to allow it for potential commercial applications and analyze the extent to which the lignin content significantly impacts polymer degradation.

3.1 Introduction
Over the past 30 years\textsuperscript{1}, significant efforts have been made to integrate biodegradable components, such as lignin, into petroleum-based polymers to create high-performance thermoplastics\textsuperscript{2,3}, a filler in plastic production to reduce petroleum-based polymer content\textsuperscript{4,5}, and polymer degradation through oxidation by demethylation of aromatic rings.\textsuperscript{6} However, there are several challenges that come along the way. For instance, lignin has an amorphous, branched structure, causing it to be rigid and brittle, and this leads to low processibility and poor compatibility with other polymeric materials, which is needed for effective use in commercial polymer applications.\textsuperscript{7,8} Another consideration is that lignin has a complex chemical composition, with significant aromatic structure and polar functional group content that is dependent strongly on the plant source and extraction methods.\textsuperscript{9–11} The highly branched structure and polar functional group content in lignin result in low compatibilities when added to hydrophobic, linear synthetic polymers. To address these issues, several chemical methods have been examined to modify functionality\textsuperscript{12–16} and reduce branching in lignin.\textsuperscript{17–19} These modifications aim to enhance compatibility with synthetic polymers and improve overall material properties, such as thermal characteristics (e.g., higher glass transition temperature, onset temperature), mechanical properties (e.g., modulus, tensile strength, elongation at break), and wettability.

In addition to blending lignin with synthetic polymers, lignin copolymerization techniques have been developed over the past three decades to incorporate the two components together. The primary synthetic polymers investigated for lignin copolymerization include polystyrene (PS)\textsuperscript{20}, polymethyl methacrylate (PMMA), poly methacrylic acid (PMAA))\textsuperscript{21,22}, and stimuli-responsive polymers (e.g., poly(N-isopropyl acrylamide) (PNIPAM)\textsuperscript{23}, poly(2-dimethylamino) ethyl methacrylate (PDMAEMA)\textsuperscript{24}). The resulting lignin copolymers have been found to be partially biodegradable, superadsorbent\textsuperscript{20}, and thermogelling copolymer materials,\textsuperscript{23} containing improved
properties that are potentially suitable for a wide range of applications from replacing single-use plastics\textsuperscript{25}, to gene delivery\textsuperscript{24}, to thermally responsive materials for shape memory applications.\textsuperscript{26,27}

Atom transfer radical polymerization (ATRP) has been widely implemented for lignin graft copolymerization since this controlled polymerization technique yields well-defined molecular weights and narrow molecular weight distributions.\textsuperscript{28–30} Recently, activator generated by electron transfer atom transfer radical polymerization (AGET ATRP) has been utilized to synthesize lignin copolymers.\textsuperscript{12,31} With AGET ATRP, a non-radical forming reducing agent is introduced to generate the activator from the higher oxidation state transition metal complex, allowing for a lower concentration of transition metal catalyst in the final product.\textsuperscript{32} Furthermore, AGET ATRP has better oxygen insensitivity compared to traditional ATRP, making it a more facile polymerization method, especially for industrial production.\textsuperscript{12,32}

Lignin-\textit{grafted}-polystyrene (L-g-PS) copolymers were developed through lignin functional group modification followed by graft copolymerization using AGET ATRP. Notably, AGET ATRP graft copolymerization between lignin and polystyrene was first reported by Li \textit{et al},\textsuperscript{12} and this synthesis procedure was adapted for this study with lignin converted to an ATRP macroinitiator through immobilization of alkyl halide ATRP initiator via the hydroxyl groups present in the lignin. The immobilized halogen groups on the lignin act as initiation radical sites for the polymerization of styrene. After synthesis, the L-g-PS copolymer, a blend of L-g-PS with PS, and a blend unmodified lignin with PS were characterized with FTIR spectroscopy to confirm lignin modification, and molecular weight and size were determined through DLS and laser diffraction measurements. Thermal analyses examined the thermal stability and glass transition temperatures for lignin, copolymers, and blends via TGA and DSC. Film surface morphology and wettability were examined with SEM and water contact angle measurements, respectively. It was
observed that copolymerization increased the thermal stability with L-g-PS and L-g-PS/PS blend samples exhibiting a higher glass transition and onset decomposition temperatures compared to lignin and L/PS blend samples. As expected, copolymerization with PS improved the compatibility of lignin with PS. In brief, this study demonstrates an approach for developing lignin-based copolymers with thermal properties and miscibilities that support the production of lignin-based polymer films and fibers.

3.2 Materials and Methods

Materials

Alkali lignin (CAS 9005-53-2) and triphenylphosphine (PPh₃) (CAS 603-35-0) were purchased from TCI America. Pyridine (CAS 110-86-1) was purchased from Honeywell. 2-Bromoisobutyryl bromide (BiBB) (CAS 20769-85-1), sodium bicarbonate (NaHCO₃) (CAS 144-55-8), and styrene (CAS 100-42-5) were purchased from ThermoFisher Scientific. N, N-dimethylformamide (DMF) (CAS 68-12-2) and iron (III) chloride hexahydrate (FeCl₃·6H₂O) (CAS 10025-77-1) were purchased from Millipore Sigma. Ascorbic acid (Vc) (CAS 50-81-7) was purchased from Carolina Chemical. Toluene (CAS 108-88-3) and Isopropyl alcohol (IPA) (CAS 67-63-0) were purchased from VWR Chemical. All chemicals were used as received unless otherwise specified.

Synthesis and Processing Methods

Lignin Purification by Acid Precipitation: Alkali lignin was dissolved in deionized (DI) water (30 wt% concentration), heated at 70 °C for 15 min, and then the solution mixture was allowed to cool down for 10 min. Then, 1.44 M of HCl was added to precipitate lignin from the solution and adjusted the pH value to 2-3. The mixture was kept at room temperature for 24 hrs, washed with 300 mL of DI water, and then the lignin was separated by centrifugation (5000 rpm
at 10 °C). This wash-centrifugation process was repeated 3-5 times, until the supernatant liquid became clear, and the solid lignin product was completely separated from the liquid. The purified lignin was vacuum-dried at 80 °C until the mass of the dried solid was stable. This lignin purification technique was adapted from Pan et al.33

**Lignin Macroinitiator Synthesis:** Acid-purified lignin (0.8 g) was dissolved in 20 mL of pyridine in a 100 mL round bottom flask equipped with a rubber septum and magnetic stirrer under nitrogen for 1 hr. After a homogenous phase formed, the mixture was cooled in an ice bath. Within 1 hr, 3.826 g of the 2-bromoisobutyryl bromide (BiBB) initiator was added dropwise at 0 °C into the flask through a glass syringe. The reaction was then allowed to proceed for 24 hrs with constant stirring at room temperature under a nitrogen environment. The product was precipitated using a saturated NaHCO₃ solution, filtered, and washed with DI water repeatedly until a neutral pH was obtained. After washing, the lignin macroinitiator (L-Br) was dried under nitrogen at room temperature until the product mass was constant.

**Lignin-graft-PS Copolymerization through AGET ATRP:** To start the copolymerization, 0.2 g of L-Br was added to a dried 25 mL round-bottom flask equipped with a rubber septum and magnetic stirrer. DMF (4.0 mL) was added to the flask to completely dissolve the L-Br. Then FeCl₃.6H₂O (0.063 g), PPh₃ (0.183 g), Vc (0.021 g), and styrene monomer (4.85 g) were added while stirring. The reaction solution was bubbled with nitrogen gas for 20 min to degas the solution before transferring the reaction flask into a preheated oil bath at 110 °C. The polymerization reaction was then allowed to proceed for 24 hrs. After the reaction was completed, the solution was cooled to room temperature and precipitated into methanol. The L-g-PS precipitate was filtered, washed with methanol, and centrifuged 3 times. Finally, the copolymer was dried for 24 hrs at 50 °C.12 For comparison and to serve as a control, the homopolymerization
of polystyrene was performed using the same synthesis procedure described above, with azobisisobutyronitrile (AIBN) as the initiator—instead of the L-Br macroinitiator used to produce L-g-PS.

**Solution Blending:** To prepare the various polymer blends, 3 mL of 60/40 (v/v) DMF/toluene mixed solvent was transferred to a vial. Lignin, lignin-g-PS, and/or PS were added to the vial and magnetically stirred at 700 rpm for 24 hrs. The solvent was then evaporated, and the blend dried in the vacuum oven at 50 °C for 24 hrs to ensure no residual solvent was present. The following blends were prepared: L/PS (purified lignin and PS homopolymer, 50:50 wt%) and L-g-PS/PS (L-g-PS and PS homopolymer 50:50 wt%).

**Characterization**

All data were collected in triplicate at a minimum to allow for statistical analysis. Averages are presented along with a 95% standard deviation.

**Dynamic Light Scattering (DLS):** Lignin molecular weights were measured by DLS (Anton Paar Litesizer 500) at room temperature in aqueous solution at 3 to 5 concentrations. The aqueous solutions were prepared by dissolving acid-purified lignin in DI water at 70 °C. Concentrations of purified lignin solutions were 0.1, 0.08, 0.06, 0.04, and 0.02 mg.mL⁻¹. Solutions were mixed thoroughly via sonication for 15 min prior to being placed in the quartz cuvette, and then the solutions were allowed to settle for 5 min prior to DLS analysis.

**Laser Diffraction:** Particle sizes of acid-purified lignin were measured at room temperature using a Beckman Coulter LS I3 320 laser diffraction particle size analyzer. Similar to DLS analysis, aqueous lignin solutions were prepared from DI water at 70 °C for 15 min. The solutions were then allowed to cool down and sonicated for 15 min. Three concentrations of lignin
(1.0, 5.0, and 10.0 mg.mL\(^{-1}\)) were prepared and tested. The 5.0 mg.mL\(^{-1}\) solution was selected for conducting the particle size analyses as it provided the highest scattering intensity.

**Fourier-Transform Infrared Spectroscopy (FTIR):** To confirm the success grafting of polystyrene onto lignin, FTIR characterizations were carried out using a PerkinElmer Frontier FTIR instrument, and spectral analyses were performed with Thermo Scientific OMNIC spectra software. Each spectrum was recorded with 64 scans over the wavenumber range of 4000 – 550 cm\(^{-1}\) with a spectral resolution of 4 cm\(^{-1}\). All samples were dried thoroughly before spectra were collected.

**Thermogravimetric Analysis (TGA):** To determine the thermal stability of the polymer samples produced, TGA analyses were performed with a Discovery 5500 TGA instrument (TA Instruments). Each sample was heated from 25 to 800 °C at a heating rate of 10 °C.min\(^{-1}\) in a dynamic nitrogen atmosphere with a flow rate of 30 mL.min\(^{-1}\). The degradation onset temperatures of samples on TGA spectra were analyzed using TRIOS 5.1.1 software (TA Instruments). A higher degradation onset temperature indicates that the sample can endure higher temperatures without losing its structural integrity, signifying greater thermal stability.

**Differential Scanning Calorimetry (DSC):** TA Instruments DSC 25 was used to determine the glass transition temperature (\(T_g\)) of lignin, lignin-grafted copolymers, and homopolymers. All the analyses were performed at a 50 mL.min\(^{-1}\) nitrogen flow rate. Initially, the samples were heated from -50 to 180 °C at the rate of 10 °C.min\(^{-1}\) and then cooled back down to -50 °C at the same rate. Then, during the second heating cycle, the samples were heated again to 180 °C at a rate of 10 °C.min\(^{-1}\). All analyses were performed using the second heating cycle. \(T_g\) values for all samples were determined using TRIOS 5.1.1 software (TA Instruments).
**Scanning Electron Microscopy (SEM):** SEM was used to examine the miscibility and surface morphology of the modified lignin, copolymers, and blends. Film samples were cast from 30 mg.mL\(^{-1}\) solutions of polymer in 60/40 (v/v) DMF/toluene. An FEI Nova Nanolab 200 SEM was used to collect micrographs and SEM-(Energy-Dispersive X-ray Spectroscopy) EDX elemental analyses of purified lignin, macroinitiator, copolymers, and blends. The EDX chemical compositions of lignin, L-Br and L-g-PS are provided in Appendix B - B3.

**Water Contact Angle:** The wettability of the lignin, lignin copolymer, PS homopolymer, and blend films was determined using water contact angle measurements. To prepare films, the samples were dissolved in a mixed solvent (DMF/toluene = 60/40 v/v), drop-cast onto silicon (Si) wafers, and dried in a vacuum oven at 50 °C—with the drop-casting and drying steps repeated 3-5 times until a continuous film was formed completely covering the wafer surface. Prior to drop-casting, Si wafers were cleaned in IPA for 20 min with sonication and then dried using a nitrogen stream. Contact angle analyses involved placing droplets (~3 μL) of DI water on the polymer films at room temperature. Prior to measuring a drop contact angle, 30 sec was allowed to pass to reduce vibrations. A minimum of 3 drops were measured for each film sample to ensure consistency. The water contact angles were analyzed using a sessile drop contact angle goniometer model 100, Rame-Hart Company.

**3.3 Results and Discussion**

Prior to further modification and processing, alkali lignin was purified using an acid precipitation method to ensure that no inorganic, residual cellulose, sugar, etc.\(^{33}\) remained in the sample. The average molecular weight of the purified lignin was measured to be 2.01 ± 0.44 x 10\(^6\) Da. The mean particle size of purified lignin was found to be 1.47 ± 0.23 μm (with additional data presented in Appendix B – B1&B2). After purification, the lignin was converted into an ATRP
macroinitiator (L-Br) by immobilizing acid halide groups to the lignin through reaction of the initiator species with lignin’s native hydroxyl groups. Using the L-Br macroinitiator, styrene monomer was polymerized from the lignin initiator sites using AGET ATRP to form L-g-PS copolymers. The lignin macroinitiator reaction and lignin-grafted copolymerization were adapted from Li et al.\textsuperscript{12}, and these reactions are provided in Figure 3.1. FTIR spectroscopy was then used to confirm that the reactions were successful and theoretical chemical structures were obtained.

Figure 3.1 Synthesis schemes for the lignin macroinitiator and lignin-graft-polystyrene copolymerization. Lignin was modified with a confined initiator moiety, BiBB, in the presence of pyridine, allowing for subsequent copolymerization with PS via AGET ATRP.

Representative FTIR spectra for lignin, L-Br, and L-g-PS copolymer are shown in Figure 3.2. For purified lignin, the O–H stretching from the presence of aliphatic and aromatic hydroxyl groups is confirmed by the broad peak at 3404 cm\textsuperscript{-1}.\textsuperscript{34} Peaks at 2943 cm\textsuperscript{-1} and 2846 cm\textsuperscript{-1} are assigned to asymmetrical and symmetrical C–H stretching vibrations, respectively.\textsuperscript{35} After surface initiation, L-Br has peaks at 1740 cm\textsuperscript{-1} and 1265 cm\textsuperscript{-1}, corresponding to C=O and C–O stretching, respectively, of the ester groups added from reaction with BiBB,\textsuperscript{12,36} confirming immobilization of the 2-bromoisobutyryl ester initiator on the lignin. Synthesis of the L-g-PS copolymer is confirmed by the emergence of two sharp peaks at 750 and 696 cm\textsuperscript{-1}, corresponding to C-H out-of-plane bending vibrations due to the presence of mono substituted aromatic nuclei from the grafted polystyrene.\textsuperscript{12,37–39} Additionally, the sharp peak emerging at 1600 cm\textsuperscript{-1} is due to aromatic
C=C vibrations, and the peaks at 3061 cm\(^{-1}\) and 3025 cm\(^{-1}\) correspond to the C–H stretching vibration absorption observed in benzene rings.\(^{37,39}\) The FTIR data confirm the surface initiation reaction and subsequent AGET ATRP graft polymerization were successful due to the presence of spectral features specific to the initiator ester group in L-Br and the aromatic ring mode from the PS side chain in L-g-PS.

![FTIR spectra](image)

**Figure 3.2** Representative FTIR spectra of purified lignin, L-Br, and L-g-PS.

TGA was used to determine the thermal stability of the purified lignin, L-g-PS, and PS samples, aiming to gain insight on their suitability for industrial polymer processing. Higher thermal stability means higher working temperature where the polymer can maintain mechanical integrity without losing strength or structure. For TGA analysis, the samples were heated from room temperature to 800 °C for lignin and L-g-PS and from room temperature to 600 °C for PS. The resulting TGA curves for all samples are shown in **Figure 3.3**. For purified lignin, three weight loss stages were observed. The first weight loss (~6.3 %) occurred from 25.0 to 142.4 °C due to
the removal of water and any residual solvents from the sample. The second stage showed a 37.5% weight loss over the 142.4 to 601.7 °C temperature range, which is attributed to the initial degradation where volatile phenolic and aliphatic hydroxyl group are cleaved producing carbon dioxide, carbon monoxide, and methane. The last decomposition stage occurred between 601.7 to 800.0 °C and showed a 4.8% weight loss; in this final stage of degradation the backbone structure was degraded. After the graft copolymerization, the TGA curve of L-g-PS shows two stages of decomposition. From 25.0 - 291.1 °C, a 13.4% weight loss was observed due to moisture loss. The second stage of degradation occurred between 291.1 to 475.0 °C with a 77.4% weight loss due to the breakdown of the polystyrene backbone and release of styrene. PS degraded over a similar temperature range as L-g-PS, supporting that this weight loss can be attributed to the loss of styrene. The total weight loss for L-g-PS at the final temperature of 800 °C was 90.9%, which was more than twice the weight loss observed for the purified lignin (48.9%). The additional weight loss observed in the L-g-PS copolymer, in comparison to the native lignin, is attributed to the presence of the polystyrene grafted chains. Since approximately half of the lignin is left intact after heating to 800 °C, this would indicate that L-g-PS comprises about 18% lignin and 82% PS which is reasonable since multiple PS chains are expected to be grafted from each lignin. Notably, as expected, there was almost no residual ash for PS (0.27%). The measured degradation onset temperatures are ca. 325 °C for lignin, 381 °C for L-g-PS, and 397 °C for PS. Ultimately, L-g-PS exhibits higher thermal stability than lignin, approaching the value for the PS homopolymer.
The thermal stability of the L/PS (50/50 w/w) and L-g-PS/PS (50/50 w/w) blends was also examined with TGA (Figure 3.4). Comparing these blends, the amount of ash/char residue for L/PS (~35.5%) was significantly higher than in L-g-PS/PS (~7.5%). This result is not unexpected due to the higher content of the thermally stable lignin in the L/PS blends. The onset degradation temperatures for L/PS and L-g-PS/PS were measured at ca. 340 °C and 378 °C, respectively. The L-g-PS/PS blend has a higher thermal stability than blending native lignin directly with PS. To further examine the thermal properties of the lignin, L-g-PS and blend samples, DSC analysis was also performed.
Figure 3.4 TGA curves of L/PS and L-g-PS/PS blends.

DSC was utilized to provide further insight into the thermal behavior and determine \( T_g \) of purified lignin and L-g-PS (Figure 3.5). For the unmodified lignin, only a single \( T_g \) value was observed at \( \sim13.83 \) °C and two separate \( T_g \) values were observed for L-g-PS at 15.94 °C and 72.74 °C, also observed by Li et al.\textsuperscript{12} The first \( T_g \) corresponds to the lignin backbone while the second \( T_g \) is attributed to the grafted polystyrene.\textsuperscript{12} The first \( T_g \) value of L-g-PS is shifted slightly higher than the \( T_g \) for unmodified lignin due to the rigid bulky side chain of PS over the lignin backbone.

DSC was also used to examine the L/PS and L-g-PS/PS blends. As seen in Figure 3.6, two \( T_g \) values (51.89 and 141.02 °C) were observed for the L/PS blend, whereas only one \( T_g \) value (52.56 °C) appeared for L-g-PS/PS blend. The presence of two separate \( T_g \) values for the L/PS blend indicates a lower degree of miscibility between lignin and PS. This is possibly due to strong self-
interactions in lignin and steric hindrance between lignin’s branched structure and PS’s aromatic rings. This low miscibility is also evidenced by the Hansen solubility parameter differences between lignin (24.51 \, MPa^{1/2}) and polystyrene (18.50 \, MPa^{1/2}). Barzegari et al. also observed limited compatibility and relatively poor interaction between blended lignin and PS resulting poor mechanical properties including modulus, strength and elongation at break as the content of lignin increased in blends. The singular $T_g$ value in L-g-PS/PS blend is likely due to hydrophobic interactions between the PS homopolymer and PS blocks in L-g-PS, leading to compatibilization and miscibility. The DSC findings corroborate that the PS was successfully grafted polymerized from the lignin macroinitiator and the block copolymer was able to provide miscibility between lignin and PS in a blend formulation.

![Figure 3.5 DSC curves of lignin and L-g-PS.](image)
Figure 3.6 DSC curves of L/PS and L-g-PS/PS blends.

SEM was performed to investigate the surface morphologies of purified lignin, L-Br, and L-g-PS copolymer (Figure 3.7). Purified lignin has a smooth, granular morphology with an array of particle sizes (Figure 3.7a), likely due to the precipitation of lignin from solution as part of the washing and drying steps in the purification process. L-Br shows smaller particle size compared to lignin with surface roughness which is attributed to the addition of the BiBB initiator on the lignin (Figure 3.7b). The SEM image for L-g-PS in Figure 3.7c shows a more diffuse microstructure appearance common to polymer-grafted substrates, as observed also for the behavior of grafting polymer brushes to self-assembled monolayer and polymer film substrates. The morphology observed for L-g-PS is due to the polystyrene chains graft copolymerized from the lignin. Thus, the AGET ATRP graft copolymerization has altered the surface morphology of the lignin due to the addition of PS blocks.
To determine the hydrophobicity of the lignin, copolymers, and blends, films were formed and used to collect water contact angle measurements. Generally, a higher water (or other polar solvent) contact angle indicates a more hydrophobic material. However, the contact angle is also dependent on molecule alignment, exposed terminal functional groups, and surface roughness. In the case of the lignin copolymer and corresponding blends, if the hydrophobic polystyrene side chain is present at the surface, then a higher contact angle is expected than if the lignin is at the surface. The contact angle of water on neat PS is expected to be approximately ~100°. Average water contact angles for lignin, L-g-PS, L-g-PS/PS blends, and L/PS blends along with representative drop shape images are shown in Figure 3.8. The contact angle of the purified lignin was 45.0 ± 3.2°; this hydrophilicity is expected due to the high concentration of polar hydroxyl groups. L-g-PS had a contact angle of 112.6 ± 21.5°, indicating its hydrophobic nature. The hydrophobic nature of L-g-PS results not only from the introduction of a large number of hydrophobic styrene chains, but also that these styrene chains expected to be present on the outer surface of the copolymer structure, influencing the water-film interface. The contact angle indicates that lignin is completely surrounded by grafted PS chains, preventing the more hydrophilic lignin from orienting at the surface, similar to a core-shell morphology observed in copolymers formed from branched macroinitiators such as hyperbranched and dendritic.
polymers. These results further confirm a dense grafting of PS polymer blocks from the branched lignin macroinitiator. The blends both showed intermediate water contact angles between the values for lignin and L-g-PS. The L/PS blend had a contact angle of 83.3 ± 0.3°, indicating it was slightly less hydrophobic than the L-g-PS/PS blend with a contact angle of 90.6 ± 3.9°. This can be attributed to the total content of the hydrophobic PS component being higher for the L-g-PS/PS blend. In addition to corroborating the chemical compositions and structures for the lignin, copolymer, and blend samples, the contact angle data show that the surface wettability for lignin-based polymer films can be significantly modified by the addition of a hydrophobic polymer, such as PS, (and vice versa) as either a covalently bound block copolymer or blend.

Figure 3.8 Average water contact angles for lignin, L/PS blend, L-g-PS/PS blend, and L-g-PS.
3.4 Conclusions

A novel graft copolymerization between lignin and polystyrene (PS) was successfully performed using AGET ATRP to form a lignin-graft-polystyrene (L-g-PS) copolymer. The formation of the lignin macroinitiator and subsequent successful polymerization of PS was confirmed by FTIR spectroscopy. Additionally, L-g-PS and L-g-PS/PS blend exhibited higher onset decomposition temperatures (ca. 381 and 378 °C) compared to native lignin and L/PS blend (ca. 325 and 340 °C), indicating enhanced thermal stability as confirmed by TGA analysis, making it generally a more suitable material for industrial polymer processing. The surface morphology of L-g-PS showed a diffuse microstructure appearance due to the addition of PS chains onto lignin via graft copolymerization confirmed by SEM analysis. The DSC analysis revealed that the lignin copolymer provides a higher miscibility than native lignin in blend as only a singular $T_g$ (52.56 °C) appeared for the L-g-PS/PS blend whereas two $T_g$ values (51.89 and 141.02 °C) appeared for the L/PS blend. The water contact angle measurement of L-g-PS and both blends showed a significant increase in the hydrophobic character of the polymer film due to hydrophobic PS chains presented on the film surface. This research holds promise for enhancing the sustainability and functionality of lignin copolymer and blend for bio-based food packaging materials, printing, water filtration to promote degradation though hydrolysis.
References


Chapter 4: Conclusions and Recommendations

4.1 Overall Conclusions

In this work, lignin was successfully modified via a Mannich reaction with ethylene diamine to form aminated lignin to be used as a dye-removal agent in wastewater. By modifying lignin through the phenolation reaction, the availability of phenolic hydroxyl groups was increased. Subsequently, the number of amino groups present in the aminated lignin was increased three-fold through this modification sequence. The amine groups in aminated lignin are ionizable and positively charged under certain conditions, providing faster adsorption and a larger dye adsorption capacity. In Chapter 2, aminated lignin was used to adsorb two anionic dyes, Congo red and methyl orange. It was found that aminated lignin could be used effectively to remove these anionic dyes under both acidic and basic solutions. The removal efficiency of aminated lignin was measured to be ~96% for Congo red and ~69% for methyl orange under basic conditions (pH = 9.98 for Congo red and pH = 10.06 for methyl orange). The adsorption of both dyes using aminated lignin followed a pseudo second-order adsorption kinetic model, showing that this is a chemisorption process. Moreover, after removal treatment, aminated lignin restored the pH neutrality of treated wastewater (pH 6.5-8), suitable for agriculture water supply.

In addition to modifying or adding functional groups onto lignin, different methods have been examined to valorize lignin including copolymerization and blending as described in the Chapter 1 literature review. Lignin copolymers and blends have been explored for many applications. These applications range from a sustainable material for water remediation, to a biodegradable filler in thermoplastics used for food and medical packaging, to a precursor material for the carbon fiber industry. Lignin copolymer and synthetic polymer blend displays high compatibility and dispersion interaction, leading to improved thermal and mechanical properties.
In Chapter 3, lignin was copolymerized with polystyrene via AGET ATRP to obtain a partially bio-based polymer material with enhanced thermal and hydrophobic properties. This L-g-PS copolymer was also blended with PS and compared with L/PS blend. It was found that L-g-PS/PS displayed a higher thermal stability and better compatibility between lignin and PS than L/PS blend.

4.2 Recommendations for Future Work

The findings in Chapter 2 confirmed a successful synthesis of aminated lignin and promising results for anionic dye adsorption from water solutions. However, to further enhance our understanding, instead of ethylenediamine, a longer-chain amino compound could be reacted with phenolated lignin for comparison to investigate the different removal efficiency. The control amination reaction of alkali lignin at various temperatures and solvents should also be prepared to study the impact of these parameters on the amine content in aminated lignin. Moreover, in addition to pH, the adsorption capacity of different dye concentrations using various aminated lignin contents should also be studied. Also, since the Congo red and methyl orange dyes were examined in deionized water solutions, to better model wastewater treatment, it is recommended that more realistic wastewater prepared with target dye for removal, along with other common constituents found in real wastewater—such as organic matter, inorganic salts—should be used to obtain more realistic data and adsorption efficiency.

Lignin could be copolymerized with other synthetic polymers (e.g., poly(methyl methacrylate), poly(methacrylic acid)) chosen to match a given application. Blending via a compounding/extruder should be examined—versus solution blending—as the issue of finding a compatible solvent will be eliminated and intimate mixing between the copolymers and synthetic polymers might be achieved. It is also recommended that the contact angle of PS homopolymer
should be determined and compared to other samples. Furthermore, to fully examine the application potential for the lignin copolymer and blend systems, additional mechanical testing should be carried out. Finally, the degradation potential for L-g-PS and the L-g-PS/PS and L/PS blends should be examined via enzymatic and hydrolytic degradation testing.
Appendices

Appendix A: Supplemental Information for Chapter 2

A.1 UV-Vis Spectrometry

Below are the UV-Vis spectra of alkaline lignin in deionized water, Am-PL in CR solution (at pH 3.84, 8.86 (native), 9.98), and Am-PL in MO (at pH3.88, 9.16 (native), 10.06) at different time from 0 to 96 hrs.

Figure A.1 UV-Vis spectrum of alkaline lignin in deionized water.
Figure A.2 UV-Vis Spectra of Am-PL in CR at pH 3.84 from 0 to 96 hrs.

Figure A.3 UV-Vis Spectra of Am-PL in CR at pH 8.86 from 0 to 96 hrs.
Figure A.4 UV-Vis Spectra of Am-PL in CR at pH 9.98 from 0 to 96 hrs.

Figure A.5 UV-Vis Spectra of Am-PL in MO at pH 3.88 from 0 to 96 hrs.
Figure A.6 UV-Vis Spectra of Am-PL in MO at pH 9.98 from 0 to 96 hrs.

Figure A 7 UV-Vis Spectra of Am-PL in MO at pH 10.06 from 0 to 96 hrs.
A.2 Anionic Dye Calibration Curves

Congo red and Methyl orange dye solutions were prepared each into seven concentrations (0.3, 0.05, 0.07, 0.08, 0.09, 0.10, and 0.14 mM). The maximum absorbance values of each solution concentration were analyzed via UV-Vis spectrometer.

Figure A.8 CR dye calibration curve.
**Figure A.9 MO dye calibration curve.**

The calibration graph is expected to be linear, where the $R^2 = 1$. The linear fitting equation of Congo red is $y = 0.1052x - 0.0046$, and the $R^2 = 0.987$. The linear fitting equation of Methyl orange is $y = 0.510x - 0.00278$, and the $R^2 = 0.988$

### A.3 Percentages of C, N, and O in AL, Am-AL, and Am-PL from XPS Analysis

<table>
<thead>
<tr>
<th></th>
<th>Atomic Percent (%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cls</td>
<td>NIs</td>
</tr>
<tr>
<td>AL</td>
<td>69.70</td>
<td>0</td>
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<tr>
<td>Am-AL</td>
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<td>3.10</td>
</tr>
<tr>
<td>Am-PL</td>
<td>48.80</td>
<td>9.60</td>
</tr>
</tbody>
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**Appendix B: Supplemental Information for Chapter 3**

**B.1 Dynamic Light Scattering (DLS)**

Lignin molecular weights were measured with an Anton Paar DLS Litesizer 500 instrument using aqueous lignin solutions at 3 to 5 concentrations per solution. Aqueous solutions at lignin concentrations of 0.1, 0.08, 0.06, 0.04, and 0.02 mg.mL$^{-1}$ were prepared by dissolving purified
lignin in deionized water at 70 °C. Solutions were mixed thoroughly for 15 min, placed in a quartz cuvette, and solutions kept stationary in the instrument for 5 min prior to data collection at room temperature. The resulting average molecular weight of purified lignin was $2.01 \times 10^6$ g.mol$^{-1}$ ($\pm 0.44 \times 10^6$).

Figure B.1 Mw analysis of purified lignin at various concentrations (0.02, 0.04, 0.06, 0.08, 0.10 mg.mL$^{-1}$) for 25 runs via XPS analysis
Figure B.2 Mw analysis of purified lignin at various concentrations (0.02, 0.04, 0.06, 0.10 mg.mL$^{-1}$) for 25 runs via XPS analysis

Figure B.3 Mw analysis of purified lignin at various concentrations (0.02, 0.04, 0.06 mg.mL$^{-1}$) for 25 runs via XPS analysis
B.2 Laser Diffraction

Larger particle sizes of the purified lignin were measured using a Beckman Coulter LS 13 320 laser diffraction particle size analyzer. Similar to DLS, laser diffraction measurements require the aqueous lignin solutions to be analyzed at room temperature. Lignin was dispersed in deionized water at 70 °C until a homogeneous lignin solution was obtained. Several concentrations of lignin were analyzed, with the 5.0 mg/mL concentration providing the highest scattering intensity. The mean particle size measured with laser diffraction for the purified lignin was 1.47 ± 0.23 μm.
Figure B.4 Laser diffraction of purified lignin at 10.0 mg.mL$^{-1}$ with 5 min run time
Figure B. 5 Laser diffraction of purified lignin at 5.0 mg.mL$^{-1}$ with 5 min run time
Figure B. 6 Laser diffraction of purified lignin at 1.0 mg.mL$^{-1}$ with 5 min run time
B.3 Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDX)

Figure B.7 SEM-EDX of unpurified lignin
Figure B.8 SEM-EDX of purified lignin
Figure B.9 SEM-EDX of lignin macroinitiator (L-Br)
Figure B.10 SEM-EDX of L-g-PS
B.4 FTIR of Acetylated and Purified Lignin

Acetylation of lignin was done to confirm that there were enough phenolic/aliphatic hydroxyl groups consist in the purified lignin. The lignin acetylation reaction method was described as follows:

A certain amount of lignin was dissolved in pyridine and acetic anhydride (1:1, v:v). The mixture was then stirred for 48 h at room temperature. After the reaction, the mixture was added dropwise to 300 mL of deionized water at 0 °C to precipitate the product. Lastly, the precipitated acetylated lignin was filtered, washed, and dried in a vacuum oven at 50 °C overnight to ensure it was completely dried. This reaction technique was adapted from Kim et al.26

B.5 Contact Angle of Control Samples

The controls used in this analysis are polypropylene (PP), polytetrafluoroethylene (PTFE), and Si wafer. The contact angle of PP, PTFE, and Si wafer are 95.1 ± 2.7°, 111.2 ± 2.0°, and 65.4 ±
1.7°, respectively. These values are comparable to literature values. (PP:100° and PTFE:98-130°).54,55,57

Figure B.12 Water contact angle of control samples