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Sustainable Soybean Oil And Lignin Derived Monomers And Polymers For Potential Use In Polymeric Materials

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SUSTAINABLE SOYBEAN OIL AND LIGNIN DERIVED MONOMERS AND POLYMERS FOR
POTENTIAL USE IN POLYMERIC MATERIALS

by

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Brigham Young University Idaho, 2014

Submitted in Partial Fulfillment of the Requirements

For the Degree of Master of Science in

Chemistry

College of Arts and Sciences

University of South Carolina

2018

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DEDICATION

To my entire family, my high school and undergraduate teachers, my lab mates, and all of my friends. Their support and inspiration helped me attain all of my current achievements.

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My foremost gratitude goes to my advisor, Dr. Chuanbing Tang, for giving me the opportunity to work in his research group. He has given a lot of guidance and help not only in academia but also in my personal life. Without his understanding and support, this achievement would not have been possible.

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Finally, I would like to thank all the funding supports from the University of South Carolina.

ABSTRACT

In this thesis project, high oleic soybean oil and lignin derived monomers and polymers are investigated. The properties of these monomers and polymers are characterized and discussed.

Chapter 1 details the potential impact of bio-based resources, monomers, and polymers on the environment. An introduction on polymerization techniques is given, and the overall objectives of my research are discussed.

In Chapter 2, attempts are made at modifying a soybean oil derived thermoplastic polymer into a vitrimer. The synthesis of thermoplastics is reviewed and the vitrimer trials outlined. Different scenarios that arose are examined and discussed.

Chapter 3 outlines the preparation of a supramolecular polymer based on a cationic lignin filler as well as a lignin derived polydiene. The reaction procedures and characterizations of the monomers and polymers are discussed. Higher percentages of acrylic acid in the long chain counterpart show better potential for solvent film casting. Although hot pressed films are more successful at integrating the filler, they are too brittle to test for mechanical properties. A decomposition product of lignin is then investigated as an alternative and renewable monomer source to overcome the difficulty of using organosolv lignin. The condensation reaction produces a polydiene capable of undergoing polymerization and shows promise as a renewable alternative.

Chapter 4 concludes with a summary of this work and suggestions for future research directions.

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LIST OF SYMBOLS

D	dispersity
M_n	number average molecular weight
T_g	glass transition temperature

LIST OF ABBREVIATIONS

AA.....	Acrylic Acid
AcOH.....	Acetic Acid
ADMET.....	Acyclic diene metathesis
AIBN.....	Azobisisobutyronitrile
BA.....	n-Butyl acrylate
BPO.....	Benzoyl peroxide
DBU.....	1,8-diazabicyclo [5.4.0] undec-7-ene
DCM.....	Dichloromethane
DMAP.....	4-(dimethylamino)pyridine
ECM.....	Eugenol condensation monomer
ESO.....	Epoxidized soybean oil
EtOH.....	Ethanol
GPC.....	Gel permeation chromatography
GTMAC.....	Glycidyltrimethylammonium chloride
HG2.....	Hoveyda-Grubbs 2 nd generation catalyst
HOSBO.....	High oleic soybean oil
MA.....	Methyl Acrylate
MCHAn.....	4-methylcyclohexane-1,2-dicarboxylic anhydride
mCPBA.....	meta-Chloroperoxybenzoic acid
MeOH.....	Methanol

PSBMA	Poly(soybean methacrylate)
SBMA	Soybean methacrylate monomer
SBOH	Monohydroxy fatty amide
THF	Tetrahydrofuran
Zn(acac) ₂	Zinc acetylacetonate

CHAPTER 1
GENERAL INTRODUCTION

1.1 Renewable Biomass Derived Polymers

Reducing the carbon footprint of plastics and their impact on the environment is a major concern across the world. The low cost and desirable properties of petroleum-based products have encouraged their large-scale production. Indeed, approximately 95% of disposable plastic packaging is not degradable, and as of 2015 roughly 79% of the total 6.3 billion metric tons of plastic waste has been dumped into landfills and nature.^{1,2} Concerns have also been raised on toxicity of plastics. This has driven research towards producing non-toxic, carbon-neutral, degradable and/or recyclable plastics from renewable sources. Biomass polymers have the potential to serve as a solution to these needs. The United States Department of Agriculture and the Department of Energy in cooperation with leading experts in academia and industry have set the goal to derive 25% of chemicals from biomass by 2030.³ Biomass materials are derived through two main categories: natural polymers and molecular biomass.⁴ Natural polymers such as rubber, cellulose, lignin, hemicellulose, starch, protein, chitin, and chitosan are frequently studied as petroleum alternatives; however, they are difficult and in some cases more expensive to process as well as have heterogeneous structures that give rise to inconsistent physical properties.⁵ Molecular biomass consists of small, non-repeating molecules such as plant oils, rosin acids, terpenes, terpenoids, furan, and many others that have been made into renewable monomers and polymers. Through biorefineries, these biomass molecules can be produced on an industrial scale to replace synthetic plastic precursors. Although biomass polymers can reduce the carbon footprint of plastic materials and address the degradable/renewable issue, their biggest obstacle is to overcome their higher production expenses and lower performance in properties as compared to their petroleum counterparts.

1.2 Polymerization Techniques

Free Radical Polymerization

Free radical polymerization is a type of chain growth polymerization that is the most widely practiced technique for monomers of a vinyl structure. Many biomass materials have or can be modified with unsaturated bonds that allow them to polymerize quickly through this method. They normally do not require expensive catalysts while having high conversions and yields, and can be carried out by either bulk, solution, suspension, or emulsion polymerization, making free radical polymerization more economic and just as efficient as other techniques. Free radical polymerization consists of three main steps; initiation, propagation, and termination (**Figure 1.1**). Initiation is the formation of a free radical active center which allows chain growth by sequential addition of monomer, or propagation, to occur. The polymerization terminates with irreversible destruction of the active center.

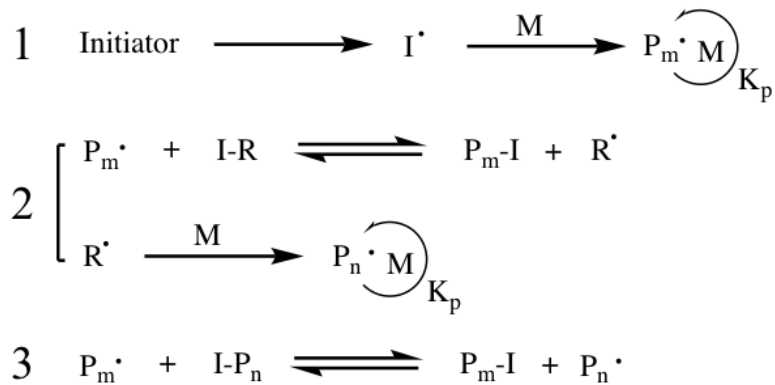


Figure 1.1 (1) Initiation, (2) propagation, and (3) termination

1.3 Research Objectives

The first objective of this work is to use dynamic covalent bonds to crosslink soybean oil derived polymers to obtain properties such as self-healing and recyclability. Two different routes were explored; the first utilizing previously reported epoxidized soybean oil polymers⁶ and a transition metal catalyst with an anhydride cross-linker (**Figure 1.2**). The second study explored disulfide and imine bond cross-linkers.

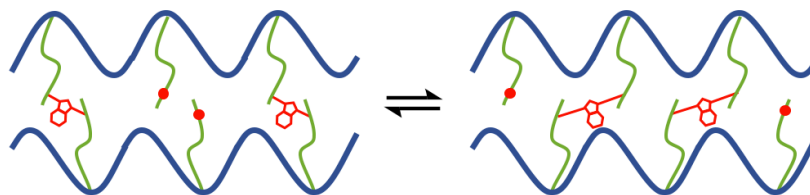


Figure 1.2 Example of soybean oil vitrimer exchange

The second objective is to use lignin as a renewable source for sustainable, biobased polymer films. One study entails the functionalization of organosolv lignin to employ a supramolecular approach to polymer wrapping with a soft, linear polymer. This was done by changing the phenolic groups in lignin to cationic groups through base catalyzed ring opening of an epoxide terminated quaternary ammonium, then using a soft acrylate-acrylic acid copolymer as the anionic polymer for chain wrapping (Figure 1.3). Due to the very limited solubility of cationic functionalized lignin, the two ionic polymers were blended together and hot pressed into films. The last study investigates the use of eugenol, a derivative of lignin, as a base unit for renewable polymers. A phenol-aldehyde condensation reaction yielded a polydiene that could be used as a monomer for polymerization.

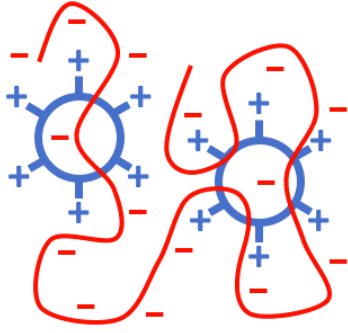


Figure 1.3 Example of supramolecular polymer wrapping

CHAPTER 2

SOYBEAN OIL DERIVED VITRIMERS

2.1 Abstract

Soybean oil derived thermoplastic polymers show promise as an alternative to petroleum-based plastics but lack reprocessability. Modification of these polymers into a vitrimer would give them beneficial self-healing and reprocessing properties while also reducing plastic waste and the carbon footprint. Two routes are studied, one through metal catalysts and the other via dynamic covalent bonds, both using the polymer that was prepared following the synthetic method on soybean-based monomer (SBMA) developed by the Tang group. The first study cures the soybean derived polymer with a zinc catalyst and an anhydride cross-linker. The second uses amine terminated sulfides to try forming dynamic disulfide and imine bonds. Solubility and compatibility issues in both studies failed to result in the formation of vitrimer.

2.2 Introduction

Plant oils are among the most important renewable resources for bio-derived chemical production. They consist of different types of triglycerides that can be synthesized into highly pure fatty acids for use as monomer feedstock. Common applications include coatings, resins, surfactants, and paint formulations. Soybean oil is the most produced plant oil and consists of oleic and linoleic acid branches (**Figure 2.1**).⁷ The ester groups allow for hydrolysis, trans-esterification and amidation, while double bonds can be used for hydrogenation, oxidation, polymerization, epoxidation, addition, and metathesis.^{8,9} High oleic soybean oil (HOSBO) has more than 70% oleic acid branches and been used as a monomer source for thermosetting resins, mendable bio-elastomers, and sustainable polyesters.^{10,11,12} It is relatively low cost, abundant, and easy for functionalization, thus a great candidate as a green alternative polymer resource.

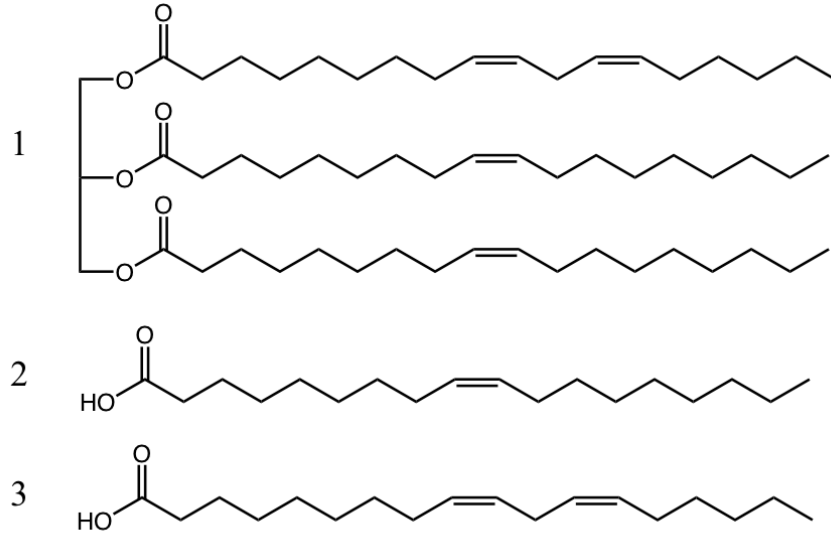


Figure 2.1 Soybean Oil (1) with Oleic (2) and linoleic (3) acid

Previous work with soybean oil derived polymers in our group has produced a variety of thermoplastics polymers.¹⁰ Without further modification, they suffer from poor tensile strength compared to petroleum derived equivalents. The unsaturated bonds in the branches allow for modification after polymerization, such as the epoxidation for thermosetting with a crosslinker. When a dynamic covalent bond is used as a crosslinker, a vitrimer with self-healing, mendability, and recycling capabilities is produced.

Vitrimers are a special class of polymers that display processing and self-healing properties similar to thermoplastics above their glass transition temperature but maintain the mechanical strength and chemical resistance of thermosets when cooled. Dynamic covalent bonds undergoing associative exchange reactions at high temperatures allow stress release, shaping, and healing to occur without the drastic drop in viscosity that appears in dissociative exchange models (**Figure 2.2**). Since the discovery of the transesterification based vitrimer by Leibler,¹³ many other dynamic covalent bond polymer networks have been created through the use of boronic acids,¹⁴ disulfides,¹⁵ imines,¹⁶ and

olefins.^{17,18} Their usefulness as a thermoset and glass like malleability of a thermoplastic can provide industries a cheaper route to complex plastic products.

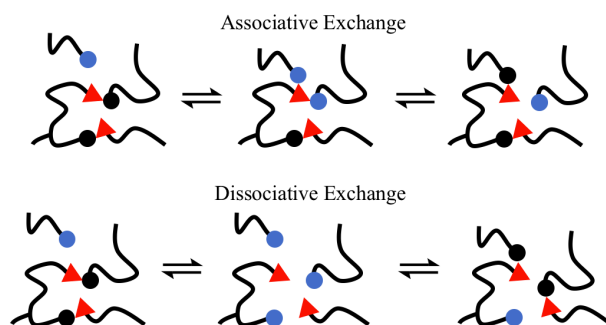


Figure 2.2 Associative and dissociative exchange networks

2.3 Experimental

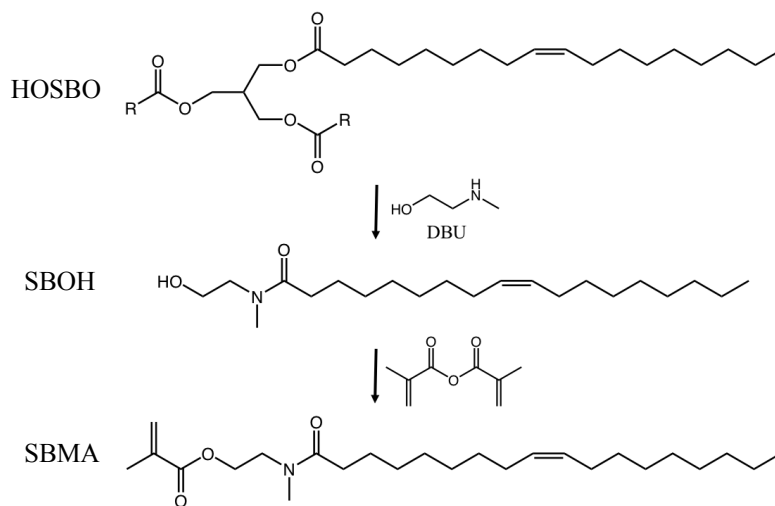
2.3.1 Materials

Plenish high oleic soy oil (HOSBO) was provided by Dupont. *N*-Methyl ethanolamine (98%, Sigma-Aldrich), sodium methoxide (5.4 M solution in methanol, 30 wt%, Acros Organics), dichloromethane (DCM, BDH), magnesium sulfate (anhydrous, Fisher Scientific), methacrylic anhydride (94%, Sigma-Aldrich), 4-(dimethylamino)pyridine (DMAP, 99%, Sigma-Aldrich), tetrahydrofuran (THF, BDH), sodium bicarbonate, azobisisobutyronitrile (AIBN, 98%, Sigma-Aldrich), methanol (MeOH, BDH), *meta*-chloroperoxybenzoic acid (*m*CPBA, 50-55%, Alfa Aesar), zinc acetylacetonate [Zn(acac)₂], 4-methylcyclohexane-1,2-dicarboxylic anhydride (MCHAn, 98%, TCI American), 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU, 99%, Alfa Aesar), terephthalaldehyde, ethanol (EtOH, 200 proof, Decon), acetic acid (AcOH, 99%, Sigma-Aldrich), cysteamine, and all other reagents were from commercial sources and used as received. Toluene was obtained from a dry still and stored over molecular sieves before use.

2.3.2 Characterization

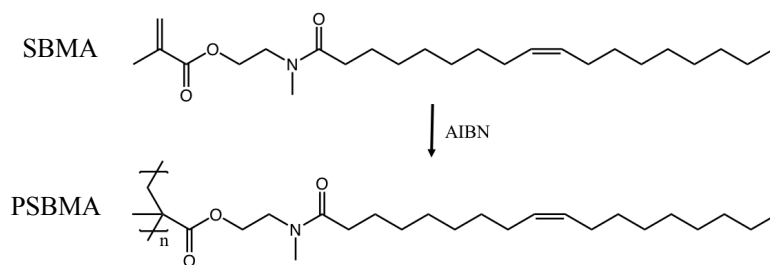
^1H NMR spectra were recorded on a Bruker Avance III HD 300 MHz spectrometer using CDCl_3 as the solvent. A Waters gel permeation chromatography (GPC) system equipped with a 1525 Binary HPLC pump, a 2414 refractive index detector, and three Styragel columns (HR1, HR3, HR5E in the effective molecular weight range of 100-5 K, 500-30 K, and 2 K-4 M, respectively) with HPLC grade THF as the eluent at 35 °C and a flow rate of 1.0 mL per minute was used to determine molecular weights and distribution of polymers. GPC samples were prepared with a concentration of ~ 5.0 mg/mL by dissolving the sample in THF and then filtering the dissolved samples through microfilters with a pore size of 0.2 μm (Teflon, 17mm Syringe Filters, National Scientific, USA). The columns were calibrated against polystyrene standards.

2.3.3 Synthesis

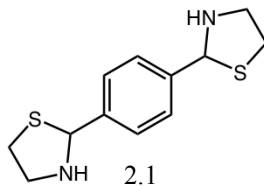


Synthesis of Soybean Methacrylate Monomer (SBMA). Based on our group's published synthesis, HOSBO (100 g, x mol) was placed into a 500 mL round bottom flask, heated to 100 °C, and purged with nitrogen for 30 minutes. The vessel was then cooled to 60 °C. 2-(methylamino) ethanol (35.6 mL, 0.443 mol) and 5.4 M sodium methoxide (1.5 mL, 1.5

wt% to oil) was added to the flask. The solution was stirred at 60 °C for 4 hours. FTIR taken to confirm completion. Contents were poured into a 2 L beaker with 200 mL DCM while stirring. The mixture was washed 3 times with brine solution, putting all the contents of the third wash into a separatory funnel. After the solution settled, the organic layer was retrieved and dried over magnesium sulfate. The monohydroxy fatty amide (SBOH) product was filtered and placed in a round bottom flask for rotary evaporation and then vacuum concentration overnight, yielding a gold colored liquid. Methacrylic anhydride (47.6 mL, 0.32 mol) and DMAP (0.367 g, 1 mol%) were added to the flask and stirred at 60 °C for 12 hours. Distilled water (10 mL) and THF (10 mL) were added and the reaction allowed to continue for another 3 hours. The solution was placed in a 1 L beaker and a sodium bicarbonate solution was slowly added and stirred for 4 hours to neutralize the acid. The contents were washed 3 times with brine solution and separated, dried with magnesium sulfate, filtered, concentrated by rotary evaporation and dried under vacuum to produce a yellow liquid. Yield 92%.



Free Radical Polymerization of SBMA. SBMA (5 g, 12.3 mmol) and AIBN (20 mg, 1 mol%) were placed in a round bottom flask with dry toluene (5 mL) and purged with nitrogen for 15 minutes. The flask was heated to 80 °C and allowed to react for 20 hours. The solution was precipitated dropwise into stirring MeOH and washed 3 times. The polymer was dried overnight under vacuum at 50 °C. 95% conversion.



Synthesis of Thiol-imine Crosslinker. Terephthalaldehyde (0.250 g, 1.86 mmol) was dissolved in an EtOH (7.5 mL) AcOH (1 mL) solution. Cysteamine (0.424 g, 3.73 mmol) was dissolved in EtOH (5 mL). The aldehyde mixture was placed in a round bottom flask and the cysteamine solution added dropwise. Contents were heated to 100 °C and refluxed for 1 hour. A white powder was filtered from the solution and air dried overnight.

2.4 Results and Discussion

The thermosets made by the Tang group from ESO and MCHAn show a range of mechanical properties from elastomers to tough plastics depending on the structure of the epoxy polymer and ratio of epoxide to anhydride.⁶ However, like other thermosets, they do not display properties of self-healing or recyclability. Dynamic cross-linking has been achieved with PSBMA and furfuryl mercaptan through retro Diels-Alder reactions.¹¹ The intent of this study was to achieve a comparable vitrimer with MCHAn and a zinc catalyst or a disulfide-amine cross-linker.

Two zinc compounds were tested for trans-esterification catalysts in crosslinked ESO and MCHAn films. Zinc acetate's difference in solubility makes it incompatible with the solvent curing process. It did not homogenize with neat ESO polymer even after prolonged heating and mixing. Conversely, Zn(acac)₂ dissolved in THF with ESO after sonication. The addition of DBU to the mixture ended with a film that failed to crosslink, as it dissolved readily in THF. This is likely due to DBU's basicity and ability to complex as a ligand with the Lewis acid nature of Zn(acac)₂. Without DBU, the film slightly swelled

in THF but did not dissolve. However, the film didn't stiffen like a cross-linked polymer should. The apparent lack of good mechanical properties in this study led to the use of dynamic covalent bonds.

Cystamine contains a central disulfide bond and primary amine ends. The disulfide could provide a metal-free dynamic covalent bond (**Figure 2.3**) and primary amines are reactive toward the epoxide sites of ESO, theoretically making cystamine a good cross-linking candidate. Its solubility, however, is limited to alcohols and dimethyl sulfoxide, making it difficult to react in the solvents used for curing films. Heating neat ESO with cystamine did not initiate a reaction to form a crosslink, as the mixture degrades before it homogenizes.

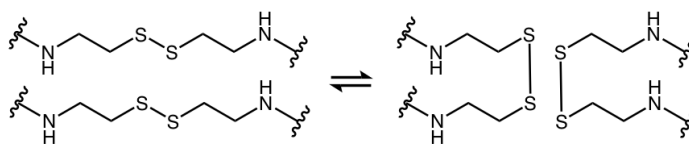


Figure 2.3 Disulfide exchange of cystamine

Cysteamine was then considered as the connecting part of a crosslink with the potential to form a dynamic imine bond. Thiol click reactions require UV irradiation, so ESO was chosen as the model polymer instead of PSBMA. To overcome the probability of the amine end reacting with the epoxide before the thiol, it was determined to synthesize the Schiff base before crosslinking. The formation of a Schiff base from the reaction of cysteamine with terephthalaldehyde and then crosslinking with ESO would be easier and less expensive than using thiol-ene click with UV irradiation and a dialdehyde.¹⁶ However, the reaction produced a white powder that was insoluble in organic solvents and did not display the characteristic peak of a thiol in the ¹H NMR (**Figure 2.4**). Literature describes

that a thiol end is very reactive with a Schiff base and the imine readily cyclizes into the thiazolidine compound 2.1 (**Figure 2.5**).¹⁹

Although the reaction of cysteamine and terephthalaldehyde did not produce a thiol terminated imine, the thiazolidine product could likely be used as a linker in thiazolidine exchange.¹⁸

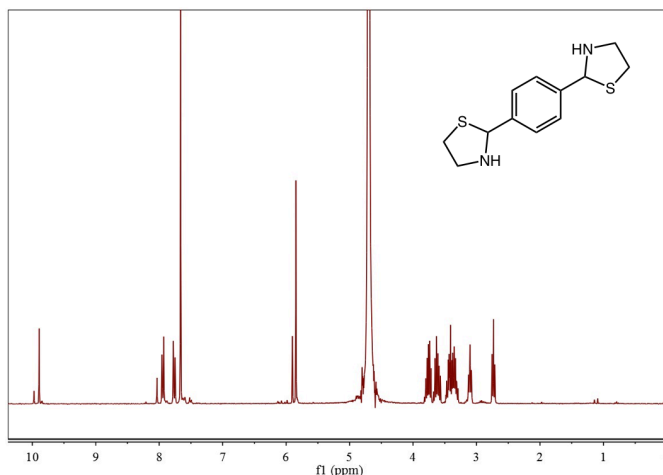


Figure 2.4 ¹H NMR spectrum of thiazolidine product

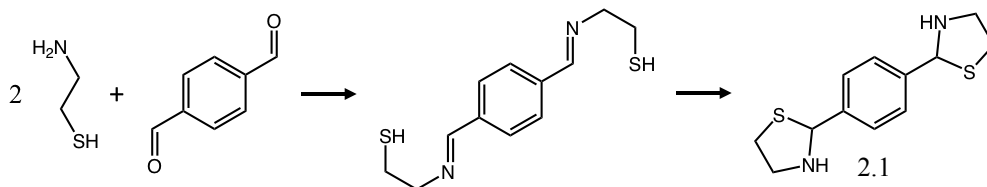


Figure 2.5 Formation of thiazolidine product

2.5 Conclusions

The incorporation of a metal catalyst into the soybean oil based thermoset did not result in a vitrimer or better mechanical properties. Attempts to make a vitrimer from a Schiff base dynamic bond were unsuccessful as the thiazolidine compound 2.1 was produced from the amino thiol reaction with an aldehyde.

CHAPTER 3

LIGNIN DERIVED SUPRAMOLECULAR AND POLYDIENE MONOMERS

3.1 Abstract

Replacing fossil fuels as a material feedstock by biomass is not only a popular research area but crucial to maintaining the wellbeing of the environment. The main challenge is to prepare a bio-renewable and sustainable product that provides comparable properties. Lignin is one of the most abundant biopolymers and is largely aromatic. As a filler, it is used to strengthen polymer composites.²⁵ In this chapter, a supramolecular polymer was prepared using a cationic lignin filler and a soft acrylic acid-acrylate copolymer. The lignin was modified by an epoxide terminated quaternary ammonium so that the linear copolymer would wrap around it via intermolecular interactions. The ratio of cationic lignin to acrylic acid was very particular to the success of film production. In order to avoid compatibility and solubility issues, a lignin derived polydiene was synthesized.

3.2 Introduction

Biomass polymers often suffer from poor mechanical properties. In order for valued applications, their mechanical strength first needs to be improved. Polymer matrices have been enhanced through the incorporation of fillers and nanocomposites such as silica nanoparticles,²⁰ clays,²¹ carbon nanotubes,²² cellulose whiskers,^{23,24} and lignin.²⁵

Lignin is an abundant and naturally occurring biopolymer that is considered the main resource for renewable aromatic compounds. As a major byproduct of the paper pulping industry, lignin is normally burnt as a fuel to produce electricity. It is often used as an additive for strengthening films and adhesives, but its low reactivity limits its use in raw form. The difficulty of utilizing lignin in industry arises from its heterogeneous structure, which is derived of three types of alcohols—*p*-coumaryl, coniferyl, and sinapyl

—connected by a variety of linkages.²⁶ The most common link is β -O-4 and is shown in **Figure 3.1**. Grafting methods have been successfully employed to synthesize lignin based renewable biocomposites for the preparation of epoxy resins.²⁷ The functionalization of lignin through techniques such as esterification, silylation, and oxidation/reduction have also been successful in modifying lignin for polymerization purposes; however, its heterogeneity results in an undesirable inconsistency in physical properties.⁵

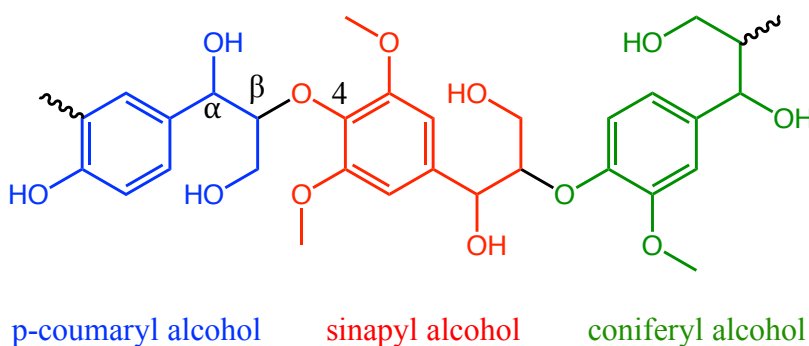


Figure 3.1 The three alcohols that constitute lignin, connected by β -O-4 links

Functionalization of lignin for supramolecular interactions can limit the variation of its physical properties by controlling the percentage of interactive sites. Supramolecular polymers employ non-covalent interactions such as hydrogen bonding, metal coordination, π - π and host-guest interactions in order to create highly organized, functional materials.^{28,29} Their reversible network-to-unit transitions often give them great capacity for self-healing, recycling, and reprocessing. Unlike molecular crystals, whose interactions are 3-dimensional, supramolecular polymers are one-dimensional due to the high directionality of their interactions. As a result, supramolecular polymers continue to have distinguishable polymeric entities in melts and solutions. Their self-assembly through these types of intermolecular forces makes supramolecular polymers inherently susceptible to external

stimuli. Heat, light, and solvent can be applied to render changes in their structures and functions dynamically reversible.³⁰

The first study in this chapter used a supramolecular approach to form polymeric materials by functionalizing lignin as a cationic filler with a soft linear copolymer as the counterpart. The resulting supramolecular interactions would create a stiff thermoplastic with the potential for mending through external stimuli. This was tested by using an epoxide terminated quaternary ammonium to functionalize the phenolic groups of lignin, while the copolymer consisted of acrylic acid with lower T_g methyl or butyl acrylate. Films were difficult to make by solvent casting, and those made by hot pressing were too brittle to be tested for mechanical properties.

Recent efforts have been directed toward the decomposition of lignin into monomeric building blocks that can be used to replace current petroleum derived monomers without the loss or inconsistency of physical properties that normally arise from using biomass polymers.^{31,32,33,34} Eugenol is a byproduct of lignin breakdown treatments as well as the main component of clove oil.^{35,36} It has been used to make bio-based polymers with consistent properties and the potential to replace petroleum derived polyesters,³⁷ thermosets,³³ and bisphenol A polymers³² at a bulk scale.

The second study in this chapter avoided the heterogeneity and solubility issues of lignin altogether by using a lignin decomposition product, eugenol, in a phenol-aldehyde condensation with hexanal. A polydiene capable of polymerization was obtained. Industries commonly use formaldehyde for resin condensations even though it is volatile and toxic, raising many health concerns for both production and use of the polymer products. Hexanal serves as a non-toxic alternative that can even be produced from

renewable sources such as sunflower oil.³⁸ The resulting lignin derived monomer is liquid at room temperature but difficult to purify.

3.3 Experimental

3.3.1 Materials

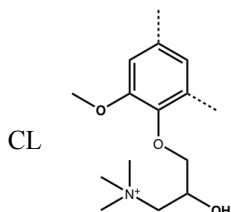
Organosolv lignin (Lignol Corporation, $M_n = 1200 \text{ g mol}^{-1}$, $D = 4.4$, phenol value = 3.2 mmol g⁻¹), potassium carbonate, glycidyltrimethylammonium chloride (GTMAC, 90%, Sigma-Aldrich), benzoyl peroxide (BPO, Fisher Scientific), 1,4-dioxane (anhydrous, 99.8%, Alfa Aesar), hexane (BDH), ethyl acetate (BDH), aluminum oxide (activated, neutral), eugenol (99%, Alfa Aesar), hexanal (98%, Alfa Aesar), hydrochloric acid, diethyl ether (anhydrous), dichloromethane (DCM, BDH), Hoveyda-Grubbs second generation catalyst (HG2, Sigma-Aldrich), ethyl vinyl ether, tetrahydrofuran (THF, BDH), and all other reagents were from commercial sources and used as received. Azobisisobutyronitrile (AIBN, 98%, Sigma-Aldrich) was recrystallized before use. Methyl acrylate (MA, stabilized, 99%, Alfa Aesar), acrylic acid (AA, stabilized, 99.5%, Acros), and n-butyl acrylate (BA, stabilized, 99%, Acros) were passed through a basic alumina column to remove inhibitor and stored for no longer than one month in a freezer at 0 °C. Spectra/Por® Biotech Cellulose Ester dialysis membranes of MWCO 500-1000D with a diameter of 10 mm were obtained from Spectrum Laboratories, Inc. and stored refrigerated in a 0.1% formaldehyde solution.

3.3.2 Characterization

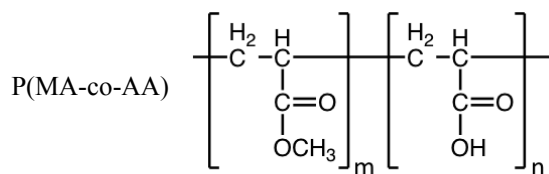
¹H NMR spectra were recorded on a Bruker Avance III HD 300 MHz spectrometer using D₂O as the solvent for cationic lignin and CDCl₃ for all other analyses. A Waters gel permeation chromatography (GPC) system equipped with a 1525 Binary HPLC pump, a

2414 refractive index detector, and three Styragel columns (HR1, HR3, HR5E in the effective molecular weight range of 100-5 K, 500-30 K, and 2 K-4 M, respectively) with HPLC grade THF as the eluent at 35 °C and a flow rate of 1.0 mL per minute was used to determine molecular weights and distribution of polymers. GPC samples were prepared with a concentration of about 5.0 mg/mL by dissolving the sample in THF and then filtering the dissolved samples through microfilters with a pore size of 0.2 µm (Teflon, 17mm Syringe Filters, National Scientific, USA). The columns were calibrated against polystyrene standards. Fourier transform infrared spectroscopy (FTIR) spectra were taken on a PerkinElmer spectrum 100 FTIR spectrometer. A Carver Laboratory Press Model C was used to prepare films of the P(MA-co-AA) and P(BA-co-AA) polymers at 150 °C to be used for the solvent free curing process.

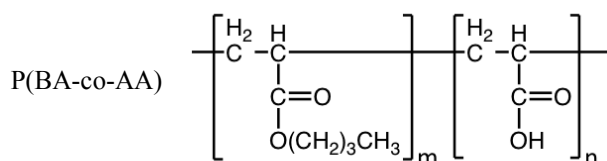
3.3.3 Synthesis



Synthesis of Cationic Lignin (CL). Potassium carbonate (1.100 g, 8.0 mmol) was dissolved in 60 mL of distilled water in a round bottom flask. Organosolv lignin (2.500 g, 8.0 mmol phenol groups) was added to the flask and stirred for 30 minutes. The flask was placed in a 60 °C oil bath stirring at 250 rpm. Glycidyltrimethylammonium chloride (1.07 mL, 8.0 mmol) was added dropwise via syringe, and allowed to react for 20 hours. The solution was cooled to room temperature and centrifuged. The dark brown liquid was dialyzed against distilled water in 1000 MWCO membranes for 2 days, changing the water three times each day. The water was boiled off and a dark brown solid was collected.



Copolymerization of Methyl Acrylate (MA) with Acrylic Acid (AA). The following procedure prepared an 80:20 wt% MA:AA copolymer. For various copolymer ratios, the same procedure was followed with the exception of different feed ratios. MA (5.05 mL, 18.6 mmol), AA (1.14 mL, 5.55 mmol), BPO (30.0 mg, 0.12 mmol), and 24 mL of anhydrous 1,4-dioxane were added to a round bottom flask and purged with nitrogen for 30 minutes. The flask was then placed in an oil bath set to 90 °C for 3 hours. The polymer solution was pipetted to a beaker and washed three times with hexane to remove unreacted monomer and initiator. After the hexane was decanted and the polymer air dried for 24 hours, the contents were placed under vacuum at room temperature for the first 24 hours then 40 °C for the second 24 hours. A soft, white polymer was obtained with 92% conversion.

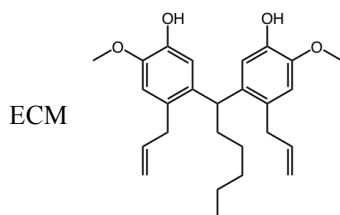


Copolymerization of Butyl Acrylate (BA) with AA. The following procedure prepared a 67:33 wt% BA:AA copolymer. Different ratios were prepared using the same procedure by changing the feed ratios accordingly. BA (5.6 mL, 39 mmol), AA (1.3 mL, 19 mmol), AIBN (4.0 mg, 0.024 mmol), and 25 mL ethyl acetate were placed in a round bottom flask. The contents were purged with nitrogen for 30 minutes. The flask was placed in an oil bath set to 77 °C for 3 hours. The polymer solution was pipetted to a beaker and washed three

times with hexane, decanting the liquid to remove unreacted monomer and initiator. After the hexane was decanted and the polymer air dried for 24 hours, the contents were placed under vacuum at room temperature for the first 24 hours then 40 °C for the second 24 hours. A tacky polymer was obtained with 94% conversion.

Solvent Free curing process. Films of P(MA-co-AA)-CL were prepared using a hot press at 150 °C and metal trips of 0.38 mm thickness. The metal strips were placed between two Teflon sheets, which was placed between the two metal hot plates. A copolymer was ground with CL in ratios of 70:30 and 95:5 wt% copolymer:CL by mortar and pestle until a fine powder was obtained. Each sample was measured out to be 0.750 g and placed in the center of the Teflon sheet between the metal strips. The press was set to 1000 lbs pressure for 30 seconds and then 5000 lbs pressure for 60 seconds. The P(MA-co-AA)-CL films obtained were very brittle.

Solvent curing of P(BA-coAA)-CL. P(BA-co-AA) (0.712 g) was dissolved in THF (7 mL). CL (0.037 g) was sonicated in MeOH (1 mL) then combined with previous mixture and stirred at 1000 rpm for 2 days. Solution transferred to Teflon mold and air dried 3 days, then under vacuum for 24 hours. A tacky, dark brown film was obtained.



Resin Condensation of Eugenol and Hexanal. Eugenol (5.58 mL, 0.036 mol) and hexanal (2.21 mL, 0.018 mol) were added to a round bottom flask with a 2.5 M HCl solution (50 mL). The flask was heated to 100 °C and allow to react for 5 hours. Conversion was checked by ¹H NMR. The cooled organic layer was extracted with diethyl ether and

dried over magnesium sulfate, then air dried for 3 hours then under vacuum overnight. Resulting monomer was a brown liquid. (MS 410 g/mol)

3.4 Results and Discussion

3.4.1 Cationization of Organosolv lignin

The procedure for synthesizing cationic organosolv lignin was adapted from reported literature.^{39,40} **Figure 3.2** shows the reaction scheme for the cationization reaction with GTMAC. Potassium carbonate was used to increase the solubility of organosolv lignin instead of sodium hydroxide because the strong hydroxide base tended to hydrolyze GTMAC and the cationic product. The base acted as a catalyst by deprotonating the phenolic hydrogens in lignin. This created and increased the availability of intermediate nucleophilic reactions sites that could interact with the epoxy group on GTMAC. The number of hydroxy groups in the organosolv lignin was previously determined and reported by our group.²⁷ The reaction proceeded through an oxirane ring-opening method to produce the GTMAC grafted cationic lignin. After the reaction, the solution is dialyzed for 2 days against distilled water, changing the eluent every 4 hours the first day and 6 hours the second day. When completed, the water was boiled off and a dark brown powder collected.

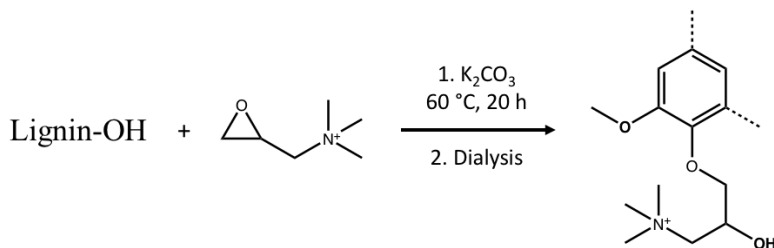


Figure 3.2 Cationization of organosolv lignin with GTMAC

The ^1H NMR spectra of unmodified (blue) and cationic (red) lignin are displayed in **Figure 3.3**. The peaks for the grafted GTMAC can be seen clearly. The methylene groups (b and d) can be seen at 3.4 ppm and 4.2 ppm, respectively. The peak at 3.5 ppm pertains to the methine group (c), whereas the peak at 3.2 ppm is associated with the trimethylammonium group (a). The solvent, D_2O , has a broad peak from about 4.6-4.8 ppm. A reduction in the aromatic region of cationic lignin is seen in both this spectrum and the work this reaction is based from.³⁹

The FTIR spectra of unmodified and cationic lignin are given in **Figure 3.4**. There is a decrease in the hydroxyl band around 3400 cm^{-1} and an increase in the intensity of the C-O-C band at 1032 cm^{-1} in the cationic lignin spectrum. Along with the new peaks for methylene groups appearing at 1466 cm^{-1} and 966 cm^{-1} , and the disappearance of the carbonyl-aromatic conjugation peak at 1700 cm^{-1} , the changes indicate successful grafting of GTMAC to lignin.

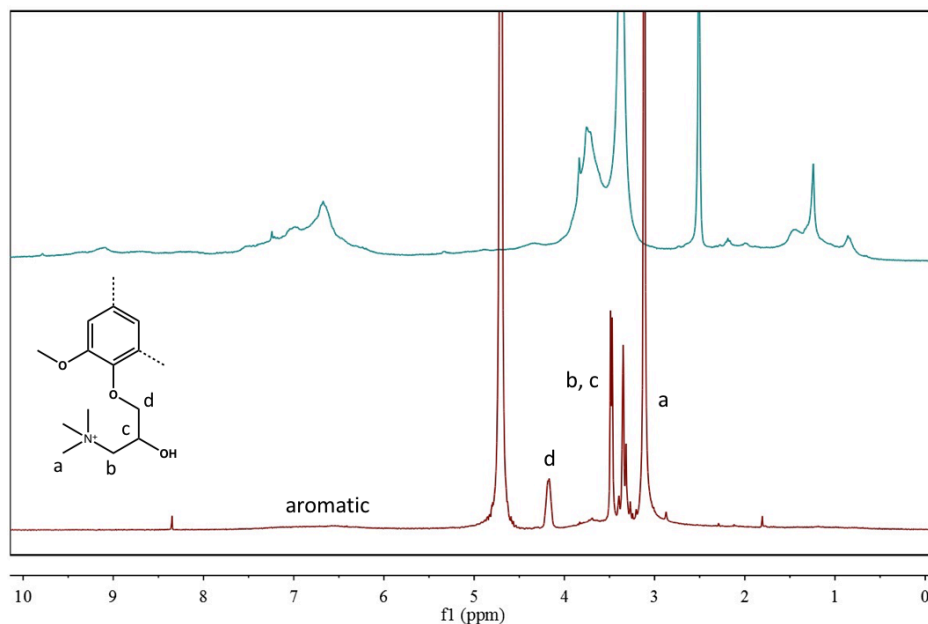


Figure 3.3 ^1H NMR spectra of (blue) unmodified and (red) cationic lignin

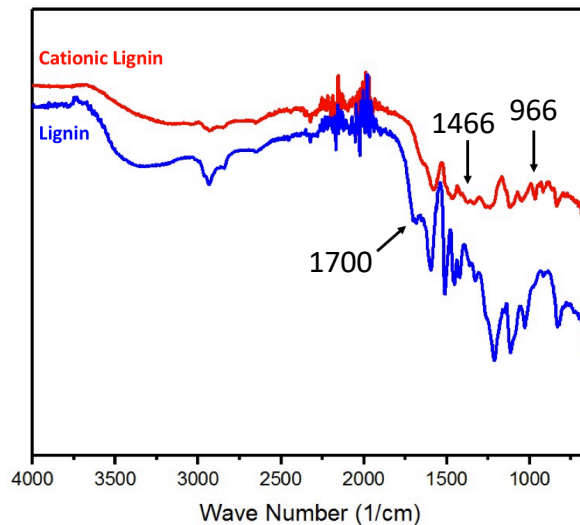


Figure 3.4 FTIR spectra of unmodified and cationic lignin

3.4.2 Lignin based Supramolecular Polymer films

In order to wrap the cationic lignin (CL) macromolecules with a supramolecular approach, a linear polymer capable of interacting with the positive ammonium groups is needed. The advantages of the (methyl/butyl) acrylate-acrylic acid copolymer are the relatively quick polymerization (**Figure 3.5**). High conversions are also obtained, as seen by the ^1H NMR spectrum (**Figure 3.6**). Acrylic acid provides the negative group while the acrylate monomer provides flexibility and lowers the T_g of the copolymer, as seen in **Table**

3.1.

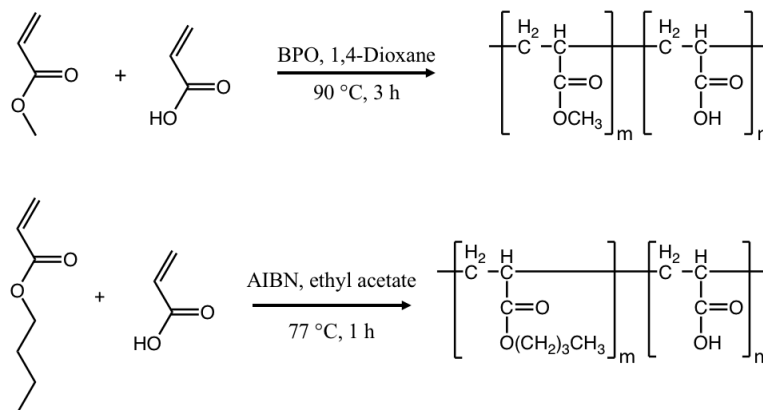


Figure 3.5 Copolymerization of MA (top) and BA (bottom) with AA

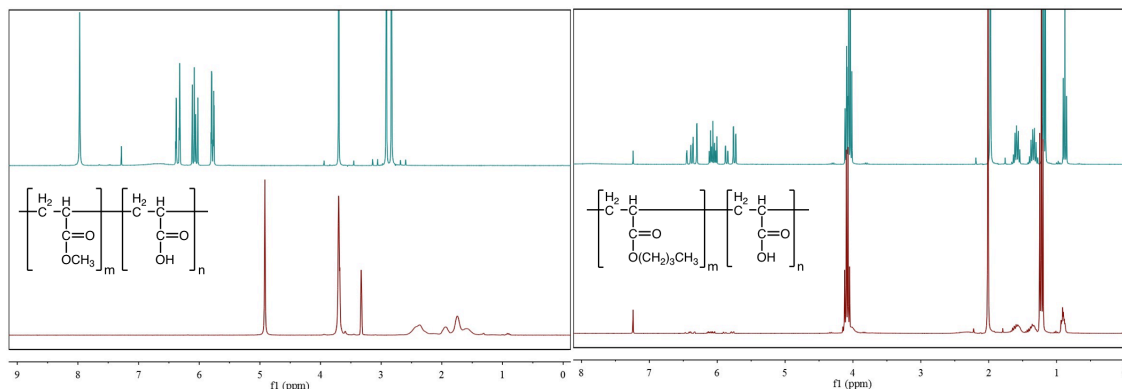


Figure 3.6 ^1H NMR spectra of (left) P(MA-co-AA) and (right) P(BA-co-AA)

Table 3.1 Acrylate-acrylic acid copolymers and their physical properties

Copolymer	Wt% AA	M_n (kDa)	D	T_g ($^{\circ}\text{C}$)
P(MA-co-AA)	10	46.3	1.7	3
P(MA-co-AA)	20	40.5	1.5	22
P(BA-co-AA)	10	60.3	1.9	-46
P(BA-co-AA)	33	117	3.2	-15

The MA based copolymers have T_g 's between 0 $^{\circ}\text{C}$ and room temperature, affording the option of hot pressing films with CL. P(BA-co-AA) copolymers were extremely tacky, and films were only viable through solvent casting.

Attempts to make films by solvent casting from CL and P(MA-co-AA) were unsuccessful due to the solubility issues of the modified lignin. CL had limited solubility in MeOH but ended up conglomerating during the drying process, as seen in **Figure 3.7**. It also trapped solvent during the curing process when a THF/ H_2O mixture was tried. The two MeOH cast films would suggest that a higher concentration of AA in the copolymer may stabilize the cationic lignin to afford a better film if the solvent is removed efficiently. With the sample of THF/ H_2O , 7 days of air drying was insufficient to remove the residual

solvent which caused the film to bubble under vacuum and become incapable of undergoing tensile testing.



Figure 3.7 Solvent cast films of CL (5 wt%) and P(MA-co-AA) in (A,B) MeOH and (C) THF/H₂O. Films differ by (A) 10% AA and (B,C) 20% AA copolymer content.

Since solvent casting was not successful, hot pressing was tried. Various blends of lignin and AA copolymer with different weight ratios were grounded by mortar and pestle into fine powder (**Figure 3.8**). A small portion of powder was placed between two metal strips within Teflon sheets and hot pressed for a short period of time. The resulting films had a better dispersion of lignin, as seen in **Figure 3.8**, yet were too brittle for any tensile testing. The stiff nature of lignin combined with the T_g of P(MA-co-AA) appears to dominate over the supramolecular interactions that would otherwise give the flexibility of films.

In order to reduce the brittleness of films, BA was substituted for MA as a way to lower the T_g for a softer copolymer. At 67 wt% BA, the polymer was too tacky for hot pressing, so an attempt was made at solvent casting in a THF/MeOH solution and 5 wt% CL. This method produced a tacky, dark brown film with much better incorporation of CL than the MeOH-cast P(MA-co-AA) (**Figure 3.9**). It appears to confirm that higher weight percent AA copolymers stabilize the CL particles due to the increase of supramolecular interactions. At 30 wt%, the lignin was again too high and macrophase separation occurred.

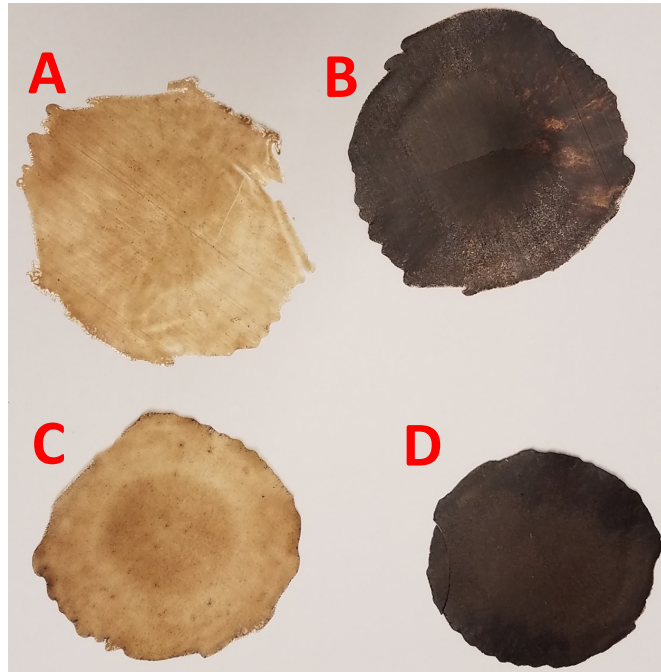
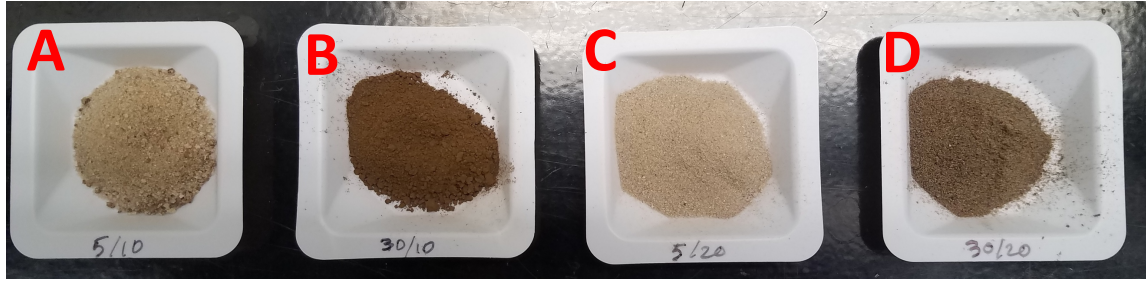


Figure 3.8 P(MA-co-AA)-CL powder (top) and films (bottom). AA copolymer content 10 wt% (A,B); 20 wt% (C,D). Lignin content 5 wt% (A,C); 30 wt% (B,D).

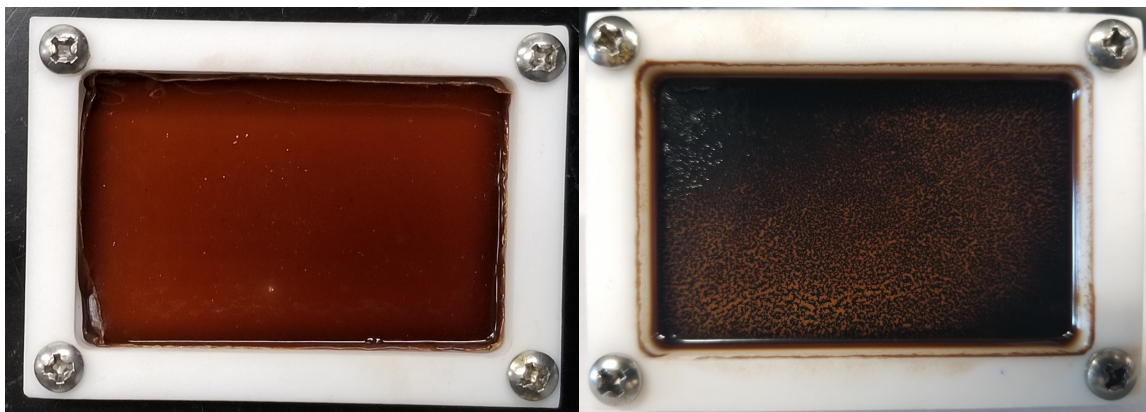


Figure 3.9 Solvent cast P(BA-co-AA)-CL film with 5 wt% (left) and 30 wt% (right) CL

If the correct ratio of AA wt% in P(BA-co-AA) with CL wt% additive is obtained, a supramolecular film is produced. Otherwise, phase separation occurs and the CL is not well incorporated into the polymer. So far, the only successful films of P(BA-co-AA)-CL were extremely tacky and unable to undergo tensile testing.

3.4.4 Lignin derived Monomer through Resin Condensation

The phenol-aldehyde condensation of eugenol and hexanal was modeled after an acid catalyzed reaction, and the overall synthesis is displayed in **Figure 3.10**.³² Hexanal links two eugenol units together via electrophilic aromatic substitution. The biphasic reaction allowed for easy extraction of the orange organic layer from the water byproduct. Attempts to remove starting material from the product were made. The monomer did not recrystallize in various solutions of hexane, toluene, heptane, diethyl ether, ethyl acetate, and acetone, as reported in literature.^{32,33,34} TLC showed multiple spots similar to eugenol that could be the differences between isomeric structures. The similarity to the starting material in polarity and solubility hindered purification by column chromatography. Drying in a vacuum overnight resulted in a dark, viscous liquid that most likely consisted of oligomers produced from monomer units linking together with unreacted hexanal.

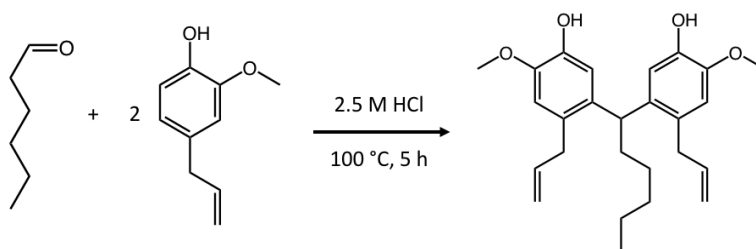


Figure 3.10 Condensation of eugenol and hexanal

The product was analyzed by ¹H NMR (**Figure 3.11**) and mass spec. The disappearance of the aldehyde peak at 9.75 ppm and shift in the adjacent methylene

hydrogens from 2.4 ppm to 1.2 ppm suggested the hexanal was almost completely used up in the reaction. Mass spec showed a prevalent peak at 410, corresponding to the molecular weight of the condensation product.

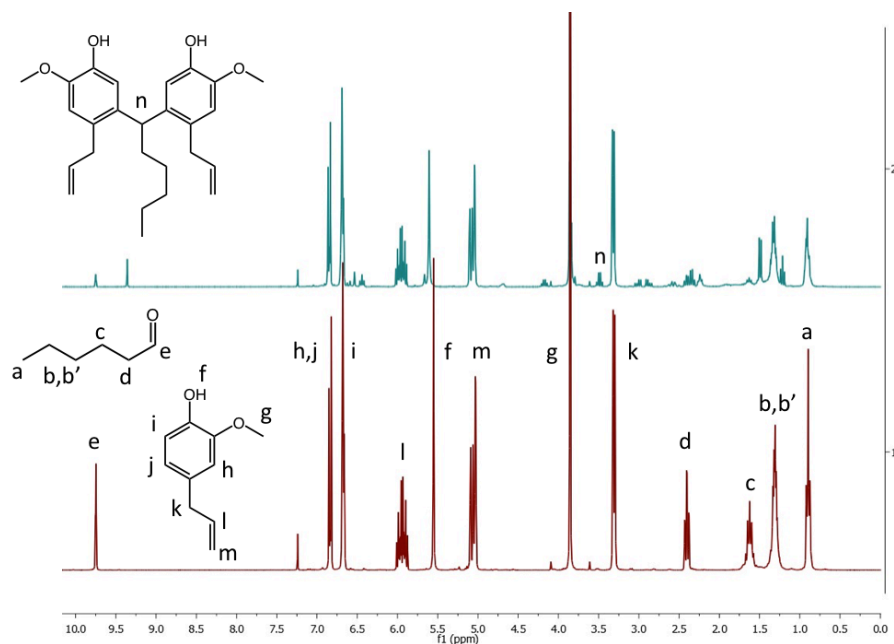


Figure 3.11 ^1H NMR spectra of (top) ECM and (bottom) eugenol and hexanal

3.5 Conclusions

The integration of cationic modified lignin with an acrylic acid-(methyl/butyl) acrylate copolymer was successful; however, the films were either too brittle or tacky for tensile testing. A viable monomer for polymerization was obtained through the phenol-aldehyde condensation of eugenol and hexanal, and the synthesized monomer could be used as a polyene or polyphenol for polymerization.

CHAPTER 4
SUMMARY AND OUTLOOK

In this thesis project, two major research goals were proposed. The first was to create a vitrimer by creating a dynamic covalent bond with a soybean oil-based polymer. The use of a metal catalyst was unsuccessful. The disulfide and imine routes were unsuccessful in creating covalent links because of differences in solubility and the formation of a thiazolidine product.

The second objective was to create a lignin derived polymer, either through a supramolecular approach or ADMET polymerization. Supramolecular films were obtained by hot pressing the higher T_g P(MA-co-AA) and solvent casting the lower T_g P(BA-co-AA) with cationic lignin. However, these films were not viable for tensile testing due to their brittle and tacky natures. The condensation of eugenol and hexanal yielded a monomer that could be used as either a polydiene or polyphenol for polymerization.

In future research, efforts could be directed toward optimizing the supramolecular films of the acrylic acid-acrylate copolymer with cationic lignin. This could be done with an acrylate monomer of low T_g and the optimal ratio of AA and CL to obtain films capable of tensile testing. One possibility would be to increase the AA fraction to 50 wt%, so higher amount of CL can be added. It could be also achieved by changing the acrylate monomer to ethyl acrylate. The eugenol-hexanal condensation product could be a very useful alternative and renewable monomer if it could be purified. The phenol group and unsaturated bond in ECM could allow diverse modifications for polymer synthesis, including a polyester by reacting with succinyl chloride, a polycarbonate by reacting with terephthaloyl chloride, or a polyene through ADMET polymerization (**Figure 4.1**).

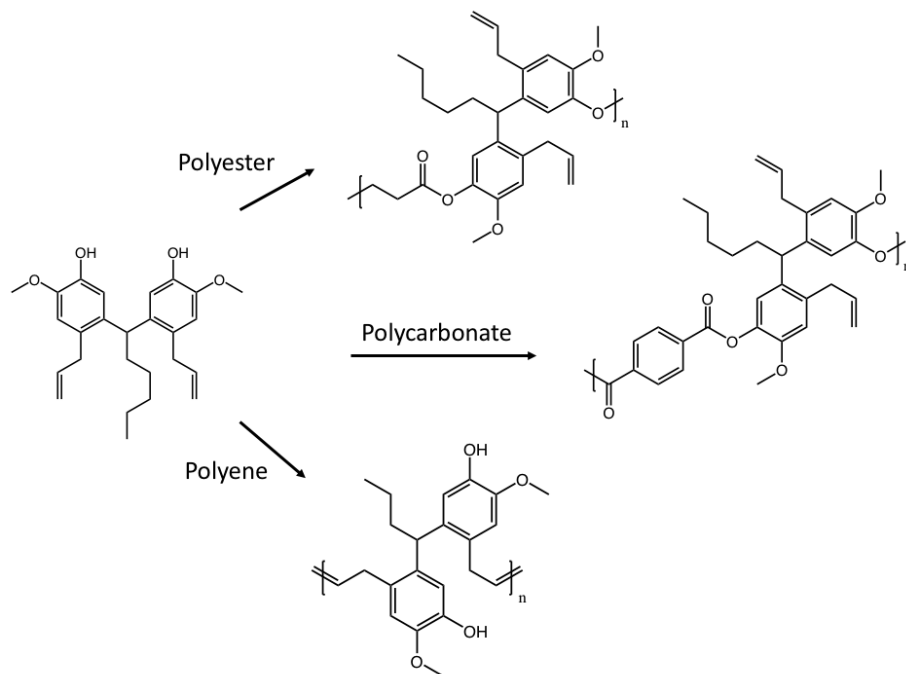


Figure 4.1 Potential polymerizations of ECM

With the need to reduce plastic waste, carbon footprint, and dependence on fossil fuels, research in renewable bio-based polymer materials continues to grow in relevance and practicality. Plant based polymers are relatively new, so there are not very many useful polymers prepared from them, yet they are gaining a lot of momentum in this field due to their potential impact as an abundant and non-toxic feedstock. Soybean and lignin derived polymer materials continue to improve in mechanical properties as they are further explored and modified in the hope that one day they could replace petroleum equivalents.

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