

Chemical Tailoring of Lignin for Functional and Sustainable Material Solutions

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners. I understand that my thesis may be made electronically available to the public.

Abstract

Lignin, being the second most abundant natural biopolymer after cellulose, constitutes between 18 wt.% and 35 wt.% of wood. Due to its abundance, sustainability, renewability, and the amenability to undergo numerous modifications through chemical reactions, there is a significant interest in lignin valorization for material applications. However, its hydrophilicity, lack of melt processability, and poor dispersibility have hindered its wide-scale application. Structural modifications are expected to counter its detrimental properties effectively. Thus, the first part of this work employed a silylation reaction to successfully modify kraft lignin and enhance its hydrophobicity for eventual incorporation in natural rubber matrix. Lignin being the hard moiety imparted mechanical strength to the composites, while NR being the soft moiety, provided it with elastomeric characteristics. The enhanced hydrophobicity enabled the specimens to better disperse in natural rubber composites, with the sample consisting of 5 wt.% modified lignin in the hydrophobic NR matrix recording a 44.4% increase in the tensile strength.

Furthermore, the incorporation of lignin in a compostable bioplastic for sustainable and biodegradable packaging materials was studied. Although petrochemical-derived and non-biodegradable plastics dominate the packaging material market, an increasing interest in sustainable alternatives is being witnessed. However, their inferior barrier properties and high cost inhibit their widespread applications. Therefore, the second part of this study investigated the use of lignin as a functional filler of a compostable bioplastic, poly (butylene adipate-co-terephthalate) (PBAT), for paper coating applications. The palmitoyl chloride esterified lignin

exhibited excellent compatibility with the PBAT polymer matrix and a comprehensive characterization recorded its enhanced dispersion in the PBAT matrix, resulting in excellent wet tensile strength and barrier properties.

In another effort to effectively valorize lignin for packaging applications, cellulose acetate and lignin blends were formulated. The inherently excellent mechanical properties, optical clarity, and compostability of pristine cellulose acetate makes it a great alternative to the single-use, petrochemical-sourced plastic materials. However, due to the lack of dimensional stability and hygroscopic behavior exhibited by cellulose acetate specimens, its applicability in the food packaging industry is limited. Therefore, the third study of this work investigated the effect of blending different concentrations of lignin (oleic acid modified and pristine) with cellulose acetate on the resulting film's morphological, barrier, mechanical, and viscoelastic properties. Moreover, the thermomechanical processed lignin-cellulose acetate sheets exhibited enhanced barrier properties (UV and moisture), better tensile properties, melt processability, and a reduction in overall moisture absorption.

Finally, the fourth part of this thesis focused on investigating the stability of lignin incorporating oil-in-water emulsions as a renewable and non-toxic alternative to organic and inorganic emulsifying agents. Three acid chlorides with varying aliphatic carbon chain lengths were employed as modifying agents. Moreover, the effect of varying pH and concentration of lignin on the stability of Pickering emulsions was studied. Post a comprehensive characterization, it was witnessed that the esterified lignin loaded emulsions outperformed the unmodified lignin stabilized Pickering emulsions. Overall, the rational and controlled

modification of lignin can make it a suitable functional and sustainable additive to various materials to achieve enhanced properties.

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Dedication

To my beloved family, the unwavering constant in my life, cherishing the memory of those we lost, embracing the present bonds, and welcoming the future generations with open hearts.

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Nomenclature

3D	Three dimensional	EA	Ethyl acetate
ACL1	Lignin isolated from industrial hardwood and non-wood residue (Bioethanol plant, USA)	ECH	Epichlorohydrin rubber
ACL2	Lignin extracted from black liquor (Kraft pulp mill, Brazil)	ESE	Emulsion solvent evaporation
ACL3	Commercial softwood kraft lignin (Indulin AT, Westvaco Corporation, USA)	FDM	Fused deposition modeling
ACL4	Commercial non wood soda lignin (Protobind 2000 ALM, India)	FTIR	Fourier transformed infrared
AM	Additive manufacturing	G'	Storage moduli constant
ASTM	American society for testing materials	G''	Loss moduli constant
atm	Standard atmospheric pressure	G _m	Gibbs free energy
BHA	benzoyl-33-hydroxyphenyl acrylate	G units	Guaiacyl units
CA	Cellulose acetate	H _m	Enthalpy of mixing
C-NMR	Carbon nuclear magnetic resonance	HCl	Hydrochloric acid
ρ	Density	H-NMR	Proton nuclear magnetic resonance
DCM	Dichloromethane	hr	Hours
DI	Deionized	H units	Hydroxy-phenyl units
DMSO-d6	Deuterated dimethyl sulfoxide	HW	Hardwood
DMF	Dimethylformamide	IR	Infrared
DNA	Deoxyribonucleic acid	ISO	International Organization for Standardization
DLS	Dynamic light scattering	KBr	Potassium bromide
% E	Elongation at break	KOH	Potassium hydroxide
E'	Storage modulus	KPS	Potassium per-sulfate
E''	Loss modulus	Lig	Unmodified Lignin

LigHC	Hexanoyl chloride modified Lignin	PMSQ	Polymethylsilsesquioxane
LNP	Lignin nanoparticles	PNIPAM	Poly(N-isopropyl acrylamide)
LNT	Lignin nanotubes	PLA	Polylactic acid
LVE	Linear viscoelastic region	psi	Pound-force per square inch
μm	Micrometer	RBF	Round-bottomed flask (RBF)
M	Molecular weight of the monomeric units	R _h	Hydrodynamic radius
mg	Milligram	RPM	Revolutions per minute
mins	Minutes	SEM	Scanning electron microscope
mL	Millimetre	S _m	Entropy of mixing
Mn	Number average molecular weight	S units	Syringyl units
MPa	Megapascal	SBS	Styrene-butadiene-styrene
Mt	Million tonnes	SLA	Stereolithography apparatus
Mt/y	Million tonnes/year	SPF	Sun Protection Factor
mV	Millivolts	SW	Softwood
OH	Hydroxyl functional groups	Δ	Solubility parameter
OP	Oxygen permeability	T _g	Glass transition temperature
OSL	Organosolv lignin	T	Absolute temperature
OWR	Oil-water ratio	T _m	Melting temperature
PAN	Polyacrylonitrile	TEPI	3-(Triethoxysilyl)propyl isocyanate
PBAT	Poly(butylene adipate-co-terephthalate)	TGA	Thermogravimetric analysis
PEDOT	poly(3,4-ethylenedioxythiophene)	UV-	Ultraviolet-
PEG	Polyethylene glycol	φ	Volume fraction
PEGMA	poly (ethylene glycol) methacrylate (PEGMA)	WCA	Water contact angle
pH	Potential of hydrogen	wt. %	Percent weight
phr	Parts per Hundred Rubber	ZDBC	Zinc (II) dibutyl dithiocarbamate
ppm	parts per million	ZnO	Zinc Oxide
PC	Palmitoyl chloride	THF	Tetrahydrofuran
PCL	Polycaprolactone	TiO ₂	Titanium (II) oxide
PDI	Polydispersity index	UTS	Ultimate tensile strength

List of Publications from PhD

- **Shorey, R.**, Gupta, A., & Mekonnen, T. H. (2021). Hydrophobic modification of lignin for rubber composites. *Industrial Crops and Products*, 174, 114189. <https://doi.org/10.1016/J.INDCROP.2021.114189>.
- **Shorey, R.**, & Mekonnen, T. H. (2022). Sustainable paper coating with enhanced barrier properties based on esterified lignin and PBAT blend. *International Journal of Biological Macromolecules*, 209, 472–484. <https://doi.org/10.1016/J.IJBIOMAC.2022.04.037>.
- **Shorey, R.**, & Mekonnen, T. H. (2023). Esterification of lignin with long chain fatty acids for the stabilization of oil-in-water Pickering emulsions. *International Journal of Biological Macromolecules*, 230, 123143. <https://doi.org/10.1016/j.ijbiomac.2023.123143>.
- Tadele, D. T., **Shorey, R.**, & Mekonnen, T. H. (2023). Fatty acid modified zein films: Effect of fatty acid chain length on the processability and thermomechanical properties of modified zein films. *Industrial Crops and Products*, 192, 116028. <https://doi.org/10.1016/J.INDCROP.2022.116028>.
- **Shorey, R.**, Mekonnen, T.H. Oleic acid decorated kraft lignin as a hydrophobic and functional filler of cellulose acetate films. (Submitted).
- **Shorey, R.**, Mekonnen, T.H. Valorization of Lignin for Advanced Material Applications: A Review (In preparation).

Chapter 1 – Introduction and Objectives

1.1. Problem statement

Conventional polymers have revolutionized human life to a great extent. From the polymer materials utilized in food packaging to running shoes and airplane parts, their applications are innumerable. Over the years, their fossil fuel origin, health and safety impacts, and the lack of environmental degradability has caused immense plastic pollution spawning serious ecological concerns. The use of synthetic polymers, such as poly(ethylene terephthalate), poly(ethylene), and poly(ethylene-co-vinyl alcohol), have led to significant environmental concerns associated with waste disposal, and in some cases safety (e.g., fluorocarbon) [1]. To mitigate the environmental damage caused by traditional plastics, the development of biodegradable, non-toxic, sustainable, and green polymeric materials is receiving substantial attention [2].

In spite of the widescale availability of numerous biodegradable polymer materials, their mass applicability is often restricted by high cost, poor mechanical and thermomechanical properties [3–5]. To address these limitations, fabrication of blends with natural macromolecules (e.g., starch, lignin, cellulose, protein, etc.) is gaining significant traction [6–10]. The composed blends exhibit better properties and superior economic feasibility.

Lignin, being the second most abundant natural biopolymer after cellulose, constitutes between 18 wt.% to 35 wt.% of available biomass. Lignin's availability in the biosphere is estimated to be 300 billion tonnes, out of which 50 to 70 million tonnes of lignin exists in the black liquor generated from the paper and pulp industry [11–14]. In a study by Dessbesell et al., the global production capacity of kraft lignin extracted from black liquor was estimated to be 265,000 t/y [15]. It possesses a unique and complex structure. Currently, the vast majority of the produced

lignin is incinerated as a low-cost fuel in power and heat generation facilities [16] and a mere 2% is employed for the manufacture of chemicals and materials, such as dispersants, adhesives, and surfactants [11].

Due to the inherent limitations of lignin, such as high polarity, inferior compatibility with polymers, poor melt flow properties, inferior thermal stability, structural complexity, and the variability of chemical structure (due to differences in lignocellulosic feedstock as well as biorefining processes), the direct utilization of lignin in materials has limited applicability [17]. To counter these limitations and enhance its utility in polymers, numerous functionalization reactions and routes have been investigated and reported in the literature [15,18–22].

This thesis work aims to valorize lignin by developing various novel functionalization routes and incorporating the modified lignin moieties in various multiphase polymer systems for material applications.

1.2. Research objectives

The primary objective of this study is to develop procedures for the valorization of lignin and its effective incorporation in materials. Unmodified lignin consists of significant hydroxyl functional groups, which impart it with high hydrophilicity. Moreover, the resultant difference in polarities between the unmodified lignin and nonpolar polymeric specimens deter lignin's uniform dispersibility in polymeric matrices. Chemically functionalized lignin moieties are expected to exhibit better dispersibility in nonpolar polymeric matrices and in turn enhance their performance and barrier properties.

Detailed research objectives have been underlined as follows:

- To investigate the effect of incorporating silylated lignin on the physico-mechanical, thermal, morphological, and barrier properties of rubber sheets
- To study the improvement in the dispersion morphology and imparted barrier properties of esterified lignin incorporated poly(butylene adipate-co-terephthalate) coating formulations for paper coating applications
- To generate an understanding on the compatibility of lignin and its modified counterpart with cellulose acetate and its impact on the hygroscopic and physico-mechanical properties of cellulose acetate films.
- To evaluate the stabilization effect of lignin in Pickering emulsions with varying dispersion medium pH and lignin loadings.

1.3. Outline

This doctoral thesis is composed of seven chapters. Each chapter aims to present the different approaches undertaken by the author to effectively valorize lignin.

Chapter 1 presents the introductory text to the work. The problem statement and the research objectives were presented. Also, the direction that subsequent chapters adhered to was outlined.

Chapter 2 reviews the literature on lignin giving a comprehensive overview of various physico-chemical modification and functionalization routes of lignin. The engineering of lignin bulk structures into micro- and nanomaterials with various morphologies for advanced material applications are covered. The most significant advances in the valorization of lignin

including lignin-incorporated sunscreen formulations, shape-memory materials, carbon fibers, additive manufacturing, Pickering emulsion stabilizers, self-healing elastomers, etc. are critically reviewed. Lastly, the perspectives for future development and opportunities for the effective valorization of lignin for material applications are discussed.

Chapter 3 covers a silylation reaction that was employed to successfully modify kraft lignin and enhance its hydrophobicity. The modification was verified by using nuclear magnetic resonance and infrared spectroscopies. The change in the wettability and dispersibility in various solvent systems indicated an increase in hydrophobicity due to the modifications. This enabled it to better disperse in natural rubber composites. Lignin being the hard moiety imparted mechanical strength, while NR being the soft moiety, provided it with elastomeric characteristics in the composites. The incorporation of 5 wt.% modified lignin in the hydrophobic NR matrix led to a 44.4% increase in the tensile strength. With higher loadings of filler in composites, an increase in elastic moduli and intensity of Payne effect were recorded. The hypothesized dispersibility improvement of the modified lignin in NR compared to its unmodified counterparts was also evident from the morphological analysis.

Chapter 4 discusses the employment of pristine and esterified lignin samples as functional fillers of poly (butylene adipate-co-terephthalate) (PBAT) based bioplastic paper coating formulations. The effects of varying concentrations of pristine and esterified lignin on the rheology, mechanical, morphology, and barrier properties of the coated paper substrate were investigated. Comprehensive characterization of esterified lignin/PBAT coatings exhibited

enhanced dispersion of the lignin fraction in the PBAT, resulting in excellent wet tensile properties and enhanced water, oil, and oxygen barrier performance.

Chapter 5 covers an investigation that employed lignin (pristine and esterified) as a functional additive of cellulose acetate matrix. The effect of varying concentrations of pristine kraft and oleic acid functionalized lignin in the cellulose acetate matrix and its effect on the resulting film's mechanical, morphological, viscoelastic, and water barrier properties was explored. Comprehensive characterization of the thermomechanical processed lignin-cellulose acetate sheets revealed reduced moisture absorption, improved UV and moisture barrier, and enhanced tensile properties with melt processability.

Chapter 6 explores the use of lignin (unmodified and esterified) specimens as an effective alternative to conventional Pickering emulsifiers. Hexanoyl chloride, decanoyl chloride, and palmitoyl chloride esterified lignin specimens were produced and their employability as Pickering emulsifiers was studied. The effects of varying the concentrations of lignin (unmodified and esterified specimens) and pH of the dispersion medium on the stability of the produced Pickering emulsions were explored. Comprehensive characterization of the esterified lignin stabilized Pickering emulsions exhibited enhanced stability, and smaller average oil droplet size, resulting in stable Pickering emulsions with high zeta potential and better flow properties.

Chapter 7 covers the concluding remarks, major contributions, short-term and long-term future projects based upon this thesis.

Chapter 2 – Literature review¹

Lignin is constituted of three monomeric units (monolignols): *p*-coumaryl, coniferyl, and sinapyl alcohols (**Figure 1**). In nature, these monolignol units undergo random radical polymerization to form complex 3D structures [16]. The complex chemical structure, poor solubility in the majority of organic solvents, numerous functional groups and structural variability due to the extraction method or the biomass source make chemical modification and characterization of lignin and its derivatives a complex task.

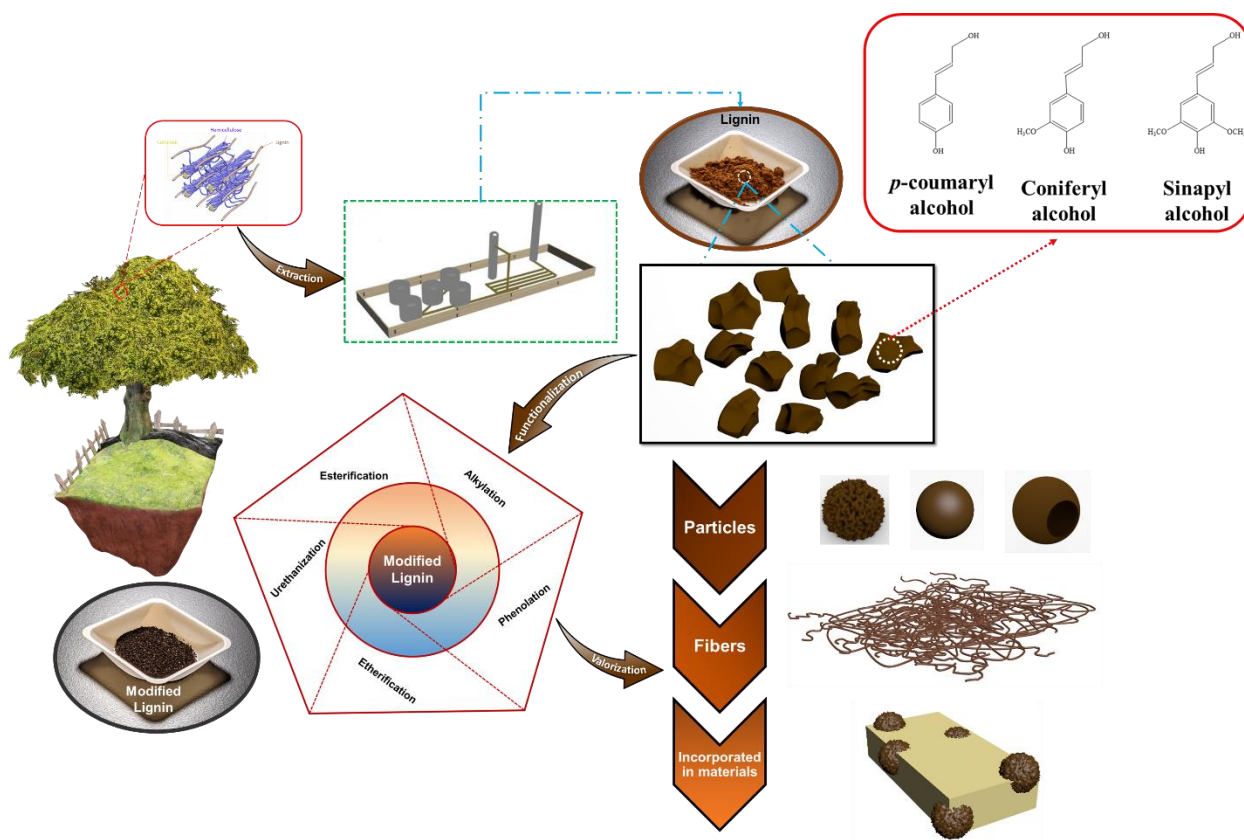


Figure 1. Valorization and functionalization of lignin

¹ A version of this chapter is in preparation to be submitted as a peer-reviewed review journal article.

Moreover, the employed extraction method dictates the sulfur content in the extracted lignin and thus creates two major types of lignin, as illustrated in **Table A 1** and **Table A 2 (Appendix A)**. The sulfur-containing lignin are comprised of kraft lignin and lignosulfonates, and their sulfur-free counterparts include soda lignin and organosolv lignin. Kraft lignin is derived from lignocellulosic biomass via kraft pulping process, thus, making it the most abundantly available type of lignin. Brown in color, kraft lignin is moderately soluble in water. As a byproduct of paper production, a vast majority of kraft lignin is burnt to supplement the energy requirements of pulp mills [16]. Lignosulfonates are typically sourced from paper and pulp industry too and are extracted using sulfite pulping process [10,16]. Contrary to the Kraft lignin, sulphonated lignin is completely soluble in water. This is due to the presence of extensive amount of sulfonate on its chemical structure [16]. Sulfur-free organosolv lignin is a product of intentional biorefinery processes [10]. In addition, soda lignin is another type of sulfur-free lignin that is typically extracted from annual plants employing soda process, which is the oldest pulping method [16].

2.1. Lignin functionalization routes

Lignin has abundant functional groups, such as hydroxyl (-OH), carboxyl (-COOH), methoxy (-OCH₃), and carbonyl (-C=O) moieties, making it amenable to various functionalization and modifications. Functionalization platforms reported in the literature includes electrochemical [17], biological [18], photochemical [19], depolymerization [20–24], and chemical [16,17,19] processes. The chemical functionalization of lignin has particularly attracted substantial

interest and could be carried out by employing various approaches, including depolymerization and fractionation, chemical modification of lignin's active moieties, and polymer grafting, as illustrated in **Figure 2** [25].

The depolymerization of lignin entails breaking down the complex three-dimensional structure of lignin to highly reactive smaller molecules [26]. Of the several routes to lignin depolymerization, hydrolytic, oxidative, and reductive depolymerization have garnered significant interest [26]. These entities could have potential value-added applications, for instance, in the synthesis of biopolymers [26].

Various chemical modification reactions of lignin to functionalize its functional groups have been studied, including alkylation, esterification, etherification, urethanization, and phenolation [25,27].

The solubility of lignin macromolecules in appropriate solvents is a critical parameter for effective modification reactions [28,29]. Conventional solvents for lignin include dimethyl sulfoxide (DMSO), toluene, acetone, ethanol, pyridine, methanol, dimethyl formamide (DMF), tetrahydrofuran (THF), chloroform, and dichloromethane [29–32]. Also, lignin moieties are known to be soluble in hot alkaline solutions [30,32,33]. Additionally, the solubility of lignin could further be improved by fractionation [29].

Esterification reactions involve the formation of an ester bond between the carboxylic acid functional group of the esterifying agent and the hydroxyl moieties of the lignin fraction. This modification route using fatty acids has been shown to produce modified lignin moieties with enhanced hydrophobicity and thermoplastic properties [27,30,31,34]. In a study by Shorey et

al., multiple activated fatty acids with varying aliphatic carbon chain lengths were employed to functionalize kraft lignin that resulted in modified lignin with enhanced hydrophobic behavior and better dispersion in nonpolar polymer matrices [30].

The urethanization of lignin translates to the formation of a urethane bond between the hydroxyl functional groups of lignin and the employed modifying agent. Silylation, which entails the addition of substituted silyl functionalities to lignin's hydroxyl moieties, is also reported. Post the silylation of lignin, the derivatized samples exhibited enhanced thermal stability, lower glass transition temperature, enhanced solubility in organic solvents, and hydrophobicity [34]. Similar results were observed in other silylation studies making it appealing in polymeric material applications [32].

The key challenges in lignin functionalization include heterogeneous structure, presence of impurities, varying solubility in various organic solvents and unique chemical reactivity of the various lignin types [35]. Another modification route for functionalizing lignin moieties is by grafting or copolymerizing foreign monomeric units onto its structure. In such a study by Sun et al., lignin was functionalized by grafting multiple monomeric units (lauryl methacrylate (LMA), and tetrahydrofurfuryl methacrylate (THFMA)) employing free-radical polymerization [36]. The functionalized lignin (Lig-*g*-P(LMA-*co*-THFMA)) was melt compounded with PLA to fabricate composites of different compositions. A significant increase (from 12% to 204%) in the elongation at break value for 20 wt.% functionalized lignin loaded composite over the baseline PLA specimen was recorded [36].

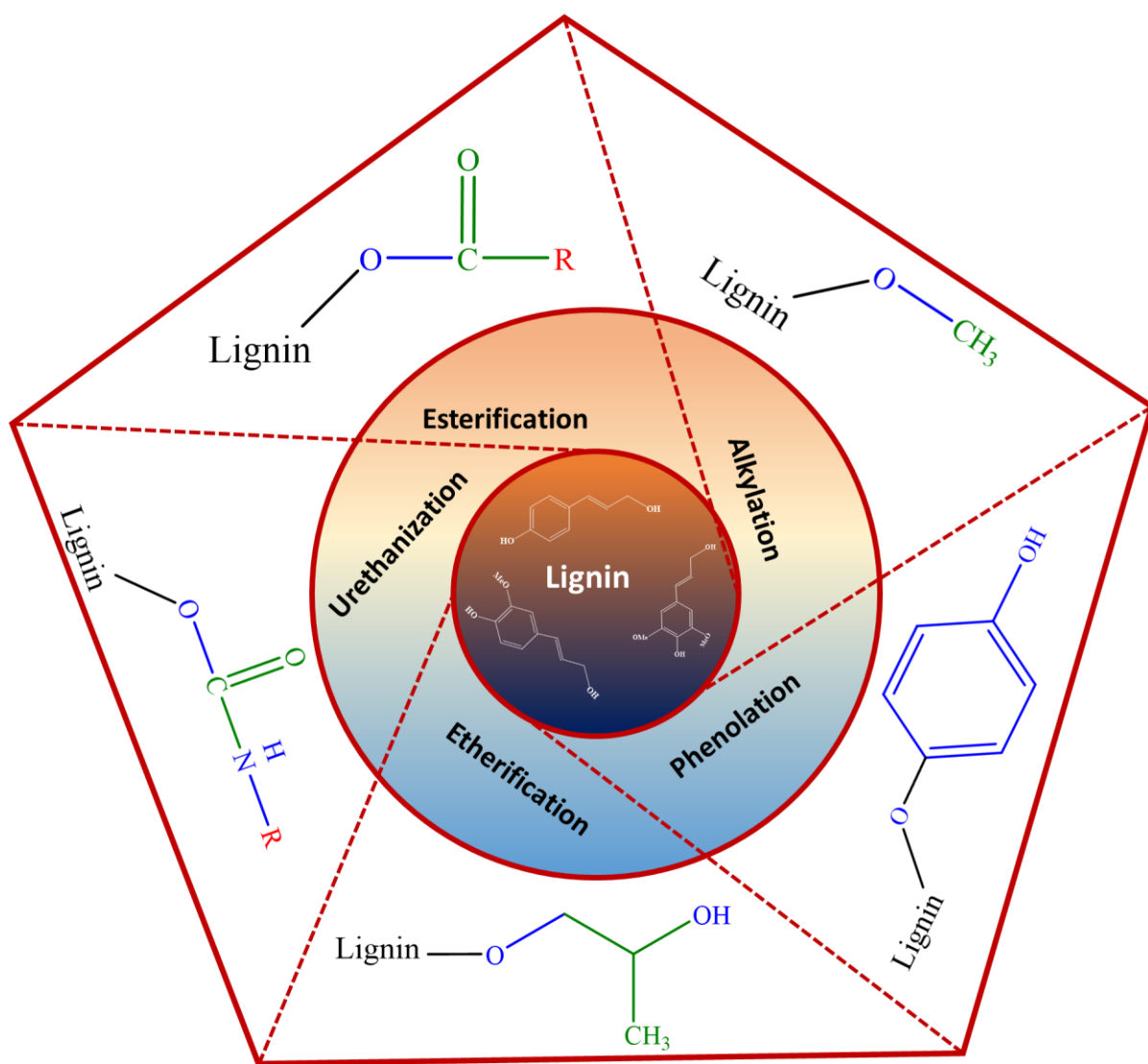


Figure 2. Chemical functionalization reactions of lignin.

2.2. Lignin engineered for multiphase and advanced material applications

In the past decade, the use of biopolymers in the design and manufacture of specialized materials with controlled structures has been witnessed. Herein, the literature on the engineering and functionalization of lignin into various structures, morphologies, shapes, and sizes for functional material applications is discussed.

2.2.1. Lignin-polymer blends for value-added applications

A polymer blend of two or more polymers entails interdiffusion amongst the constituent polymer fractions [37]. Based on the interaction (mutual miscibility) of the constituent polymers, the level of interdiffusion varies. While the polymer fractions with weak interactions have been witnessed to result in heterogeneous blends with agglomeration sites, the constituents with strong interactions exhibit homogeneity [37–40].

Lignin exhibits an inherent thermoplastic behavior caused by the inter and intramolecular hydrogen bonds [41,42]. Moreover, at high temperature it displays thermosetting behavior. This behavior is attributed to the high cross-linking reactions that lignin moieties undergo at elevated temperatures [41,43]. This results in inefficient blending of lignin specimens with other polymer materials. Effective methods of overcoming these processing limitations include addition of plasticizers and chemical modification of lignin. Blends of pristine lignin and their functionalized counterparts with various polymer materials have been reported in literature [37].

The blends of lignin with conventional polymers have been extensively researched. In a study by Sailaja et al., lignin phthalates were melt blended with low density polyethylene (LDPE) fractions [44]. Amongst various formulations, maleic anhydride grafted LDPE was added to improve interfacial adhesion, thus, acting as a compatibilizer. The resulting blend exhibited excellent thermal, mechanical, and morphological properties. Moreover, the presence of interlocked surfaces resulting from superior adhesion between the lignin moieties and the

LDPE fractions in the maleic anhydride grafted LDPE compatibilized blends was recorded [44].

In another work exploring the physical properties of lignin-polypropylene (Lig-PP) blends, the feasibility of bromododecane modified lignin was studied [45]. It was worth noting that the addition of lignin to PP enhanced its fire retardancy and toughness. For a 20 wt.% lignin loaded formulation, LOI value of 25.2 was recorded. Further increase in lignin content resulted in specimens exhibiting enhanced damping effect.

The use of lignin as a reinforcing agent in synthetic rubber matrices has been witnessed. In such a study by Košíková et al., styrene-butadiene (SBR) rubber was filled with sulfur-free lignin fractions [46]. A significant improvement in mechanical properties for lignin filled SBR composites was recorded over the baseline unfilled formulation. For instance, the 60 phr lignin loaded specimen accounted for a 94% increment in the tensile strength at break over pristine SBR specimen. The homogeneous dispersion of lignin spherical particles (100 nm) in the composite matrix were observed via scanning electron micrographs.

Furthermore, the physiochemical properties of a compostable polymer matrix (PLA) with two different lignin specimens (alkali lignin and organosolv lignin) were studied [47]. Employing different amounts of individual lignin samples and poly(lactic acid) (PLA), various blends were melt-blended employing a twin-screw extruder. Further, each type of lignin underwent acetylation. As hypothesized, the acetylated lignin samples exhibited superior compatibility with the polymer matrix than their unmodified counterparts. Moreover, the acetylated lignin

blends displayed enhanced resistance to hydrolytic degradation, thermal stability, retained tensile strength and increased elongation at break values [47].

2.2.2. Lignin microspheres and nanospheres

In recent times, polymer-based micro and nanospheres have garnered significant attention. For instance, the use of polymer microspheres and nanospheres in industrial applications, including the encapsulation and controlled release of fertilizers, pesticides, and other bioactives has been studied [48]. The surge in sustainable practices has further fueled the transition efforts from conventional plastics towards the employment of biobased and renewable polymer alternatives, such as lignin in agricultural, food, biomedical, and cosmetic controlled release applications [49,50]. The sphericity of designed micro- and nanospheres enables a homogeneous release of active substances to the surrounding environment and the facile manufacturing processes make them a favorable option for widescale applications [51].

Many routes for the fabrication of lignin micro- and nanoparticles have been reported in the literature, including emulsion inversion, antisolvent exchange, acid precipitation, chemical modification, ultrasonic irradiation, controlled drying, and a combination of multiple methods [52–58]. To fabricate lignin-based micro and/or nano particles, the employment of antisolvent exchange and acid precipitation techniques has been most prevalent [58]. In the acid precipitation technique, lignin samples are initially dissolved in alkaline solution with a pH more than 11. This is known to deprotonate hydroxyl (phenolic) and carboxylic acid moieties. Further addition of an acidic media (pH 3) protonates the hydroxyl and carboxylic acid groups thus, reducing the surface charge and in turn initiating particle precipitation [58]. On a similar

note, in the antisolvent precipitation technique, the lignin moiety is dissolved in an organic solvent (for instance THF), and with the slow addition of an antisolvent the lignin fractions form spherical colloidal particles, as illustrated in **Figure 3f**.

In a work by Sameni et al., microspheres of four types of lignin were fabricated employing a combination of the above-mentioned routes known as emulsion solvent evaporation (ESE) [48]. The four lignin samples underwent acetylation. To emphasize the dependency of ESE produced microspheres and the type of lignin on the choice of the appropriate solvent, four different lignin samples including lignin isolated from industrial hardwood and non-wood residue (Bioethanol plant, USA) (ACL1), lignin extracted from black liquor (Kraft pulp mill, Brazil) (ACL2), commercial softwood kraft lignin (Indulin AT, Westvaco Corporation, USA) (ACL3), and commercial non-wood soda lignin (Protobind 2000 ALM, India) (ACL4) were employed [48]. The first step involved the addition of two phases with opposite polarities (lignin in organic solvent (dichloromethane (DCM) or ethyl acetate (EA)) and an emulsifier (polyvinyl alcohol (PVA)) in an aqueous phase) to a container, as illustrated in **Figure 3a**. The further three steps were the emulsification of the two phases (**Figure 3b**), evaporation of the solvent phase (**Figure 3c**), and microparticle formation (**Figure 3d**).

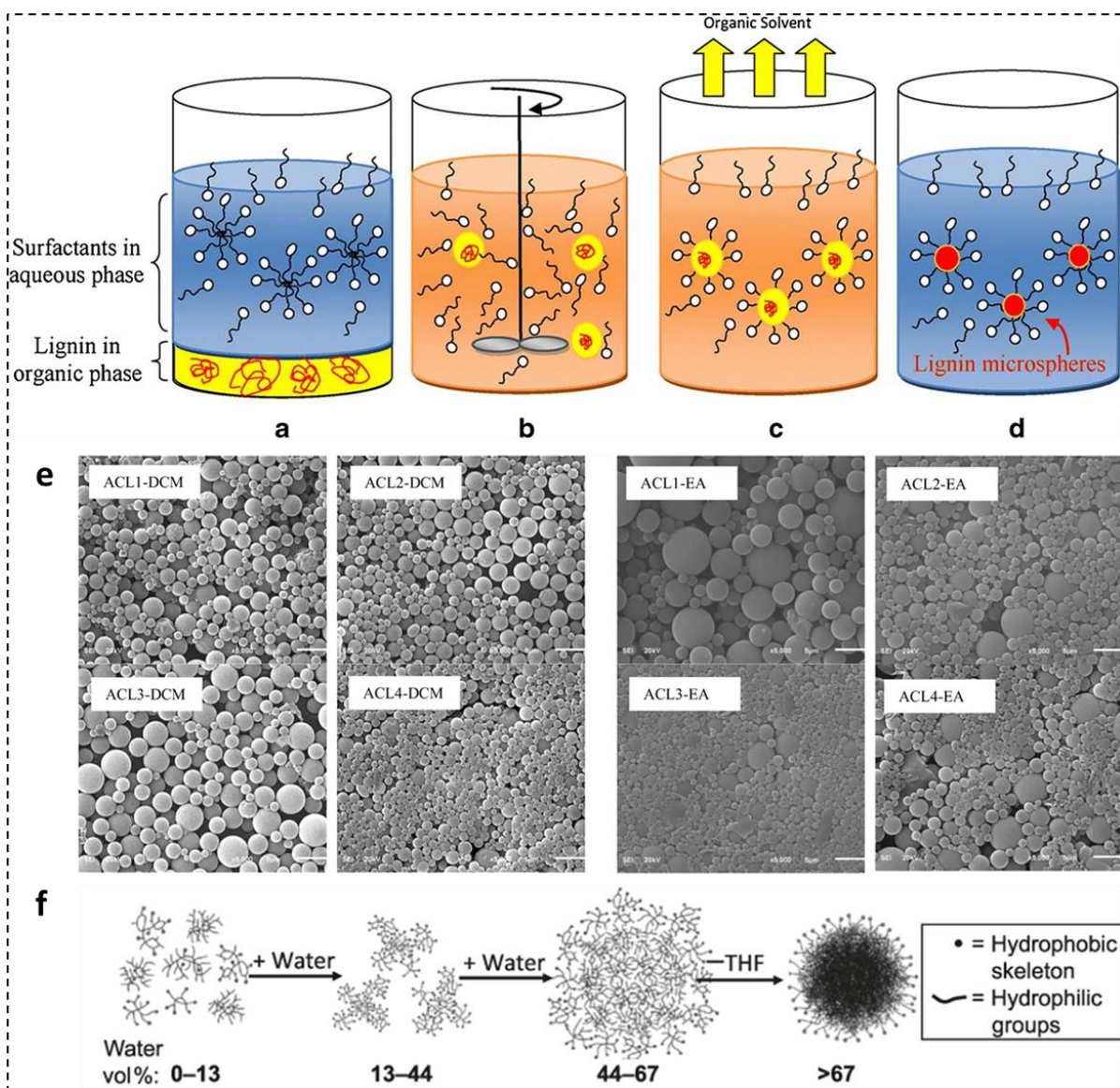


Figure 3. Four steps of ESE: a) addition of two phases with opposite polarities, b) emulsification, c) evaporation of the solvent phase, and d) microparticle formation, e) Lignin microsphere SEM micrographs, (Reproduced with permission [48]), f) Lignin microparticle formation employing solvent exchange (Reproduced with permission [59]).

Scanning electron micrographs of the prepared microparticles were recorded. As evident from **Figure 3e**, microparticle sizes ranging between 1280 nm and 1349 nm for DCM and 1313-2545 nm for EA were obtained. In another study to fabricate lignin nanoparticles, a solution of

acetylated lignin (solubilized in THF) was precipitated with an anti-solvent (H₂O). Using DLS, lignin nanoparticles with a hydrodynamic radius (R_h) of around 100 nm were recorded.

In a separate study by Saidane et al., lignin beads (micro-/nano- scale) were prepared employing epichlorohydrin as a crosslinking agent [60]. Following the reaction (scheme outlined in **Figure 4a**), smooth spherical lignin beads ranging in size between 100-800 μ m were successfully obtained (**Figure 4b**) [60]. The formulated beads underwent multiple functionalization reactions for final application in scavenging carbonyl compounds [60].

In another study, lignin beads in conjunction with treated cellulose pulp were prepared and characterized for their antimicrobial activity against *Escherichia coli* and *Staphylococcus aureus* [61]. The preparation procedure was initiated with a dispersion of lignin (up to 40%) and solvent treated (ethanol/HCl) cellulose pulp in an aqueous solution (constituting 12% urea/7% sodium hydroxide) with varying solid concentration ranges. This solution was dropped into an acidic medium to enable the lignin-cellulose bead coagulation. The inherent fluorescence of lignin was vital in observing its distribution in the obtained beads. The distribution of lignin in the fabricated beads was homogenous. Leaching of lignin fractions from the beads was recorded. While the lignin-cellulose beads did not display significant antibacterial activity against *Escherichia coli*, a significant reduction in the growth of *Staphylococcus aureus* was observed. With an increase in the lignin fraction, the growth of *S. aureus* plummeted [61].

In another work by Chen et al., the formulation of lignin beads from pine black liquor was investigated [62]. Lignin beads ranging in size from 300-450 μ m were prepared via reverse-

phase suspension polymerization. The fabricated lignin beads displayed excellent L-Lysine adsorption from aqueous media via electrostatic interaction.

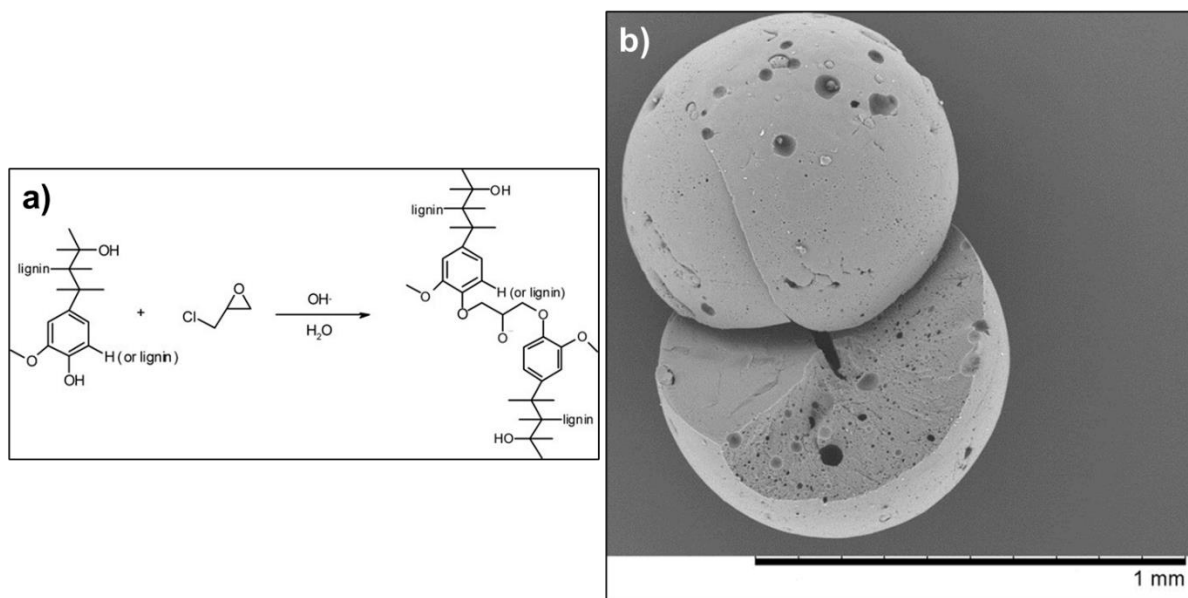


Figure 4. a) Reaction mechanism for Kraft lignin with epichlorohydrin, b) Scanning electron microscopy image of a fabricated lignin bead (Reproduced with permission [60]).

Lignin hollow nanospheres

Due to the inherent advantages of hollow nano- or macrospheres over their solid core counterparts, their application in fields like coating, drug-delivery systems, catalysis, and composite materials is gaining significant traction [63,64]. In comparison to the solid spheres, significantly higher efficiencies in drug delivery systems employing hollow nano-spheres were recorded. Thus, substantial effort in the production of hollow spheres with uniform structure, desired composition, and tailored properties have been invested [63,65,66].

To further enhance the uptake capacity of hollow spheres, a subclass of hollow spheres known as open-mouthed hollow capsules has also gained significant attention [67–70]. Various

organic polymers and inorganic oxides have been employed in the preparation of open-mouthed hollow capsules, including silica (SiO₂)[71,72], polymethylsilsesquioxane (PMSQ) [73], titanium dioxide (TiO₂) [74], polystyrene (PS) [75], polystyrene/poly(3,4-ethylenedioxythiophene) (PS/PEDOT) [76], chiral phenylacrylo-nitrile tartaric acids [77], polystyrene/poly (divinyl-benzene)[78], poly(acryamide-ethylene glycol dimethacrylate) [79]. Lignin is a new entrant material for the design and fabrication of hollow nanospheres. In a study by Xiong et al., a facile self-assembly method by dissolving enzymatically hydrolyzed lignin in THF and adding DI water to the solution was employed to fabricate lignin hollow nanospheres (**Figure 5a**) [80]. Due to π - π interactions, the layers were self-assembled from outside to inside, with the outside layer exhibiting hydrophobicity and the inside layer was hydrophilic. A positive correlation between the concentration of lignin, the thickness of the shell wall, and the diameter of the nanospheres was observed. On the flip side, with an increase in the concentration of lignin, the pore volume of nanosphere, the diameter of the single hole, and the surface area have reduced. An average particle size of around 500 nm was observed. Furthermore, an increment in the agitation speed or speed at which water is added to the system resulted in a reduction of the lignin hollow nanospheres diameter, as evidenced by the SEM micrographs in **Figure 5** [80].

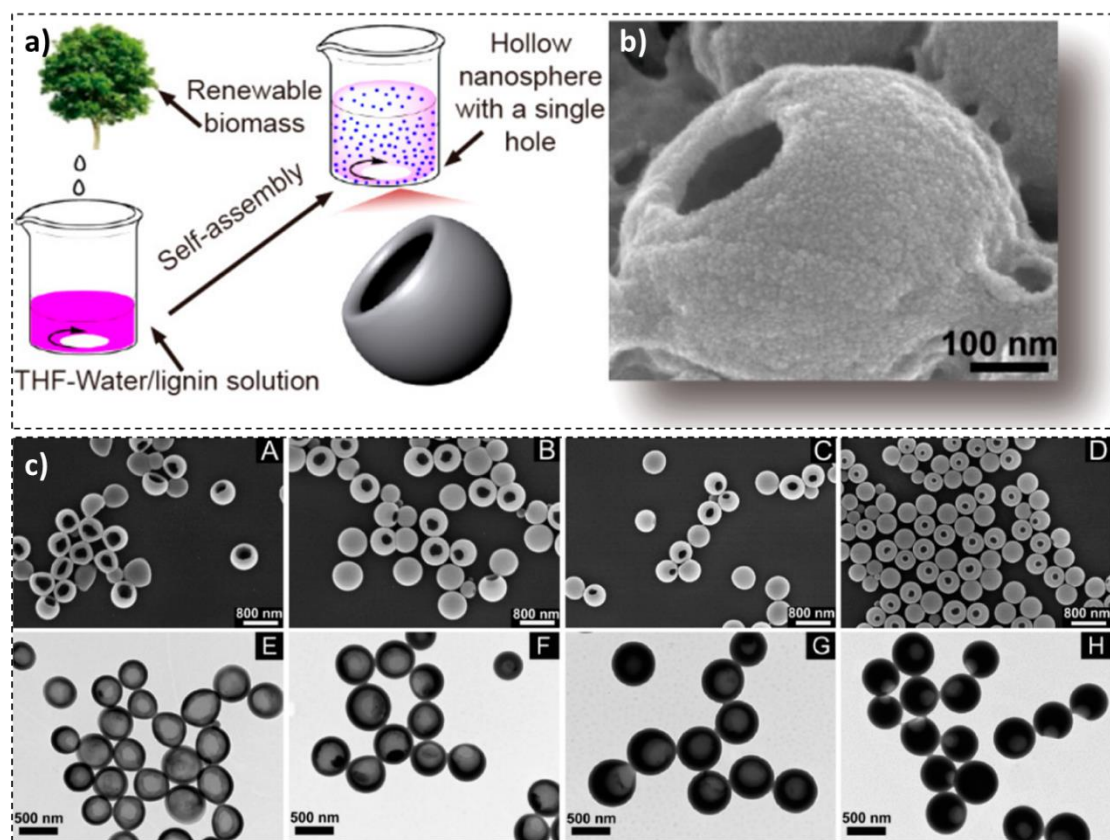


Figure 5. a) Synthesis process, b) SEM image, and c) SEM images (A–D) and TEM images (E–H) at different predropping lignin concentrations: 0.5 mg/mL (A, E), 1 mg/mL (B, F), 1.5 mg/mL (C, G), and 2 mg/mL (D, H) (Reproduced with permission [80]).

In a work by Sameni et al., the effect of process variables (mixing time, surfactant concentration, shear rate, and the organic solvent used) on the properties of lignin acetate microspheres fabrication employing ESE was studied. An average particle size between 20 and 100 μm was observed [75].

2.2.3. Lignin nanotubes and nanofibers

In a recent study by Ten et al., the use of lignin nanotubes as a gene delivery vehicle for human cells was studied [82]. With the use of lignin nanotubes (LNTs), the cytotoxicity of carbon nanotubes and the immunogenicity of viral vectors could be avoided [82]. Employing a

sacrificial alumina template, the aromatic plant cell wall (lignin) based nanotubes were synthesized. Five different lignin sources were selected for the isolation, including sorghum ((*Sorghum bicolor* (L.) Moench)), debarked stems of loblolly pine ((*Pinus taeda* L.)), debarked stems of poplar (*Populus deltoides* W. Bartram ex Humphry Marshall; POP), brown midrib6 (bmr6) and sugar cane bagasse from sugar cane (*Saccharum* spp.). As evident from the confocal micrographs (**Figure 6**), the presence of lignin nanotubes in the immortalized human cell line (HeLa) cells and the nucleus of the cell without the presence of any auxiliary agents could be observed.

In recent times, an increasing interest in the production and utilization of lignin nanofibers has been witnessed. In a work by Gao et al., surface-initiated atom-transfer radical polymerization (SI-ATRP) was employed to produce poly(N-isopropyl acrylamide)(PNIPAM) grafted softwood kraft lignin nanofiber mats [83].

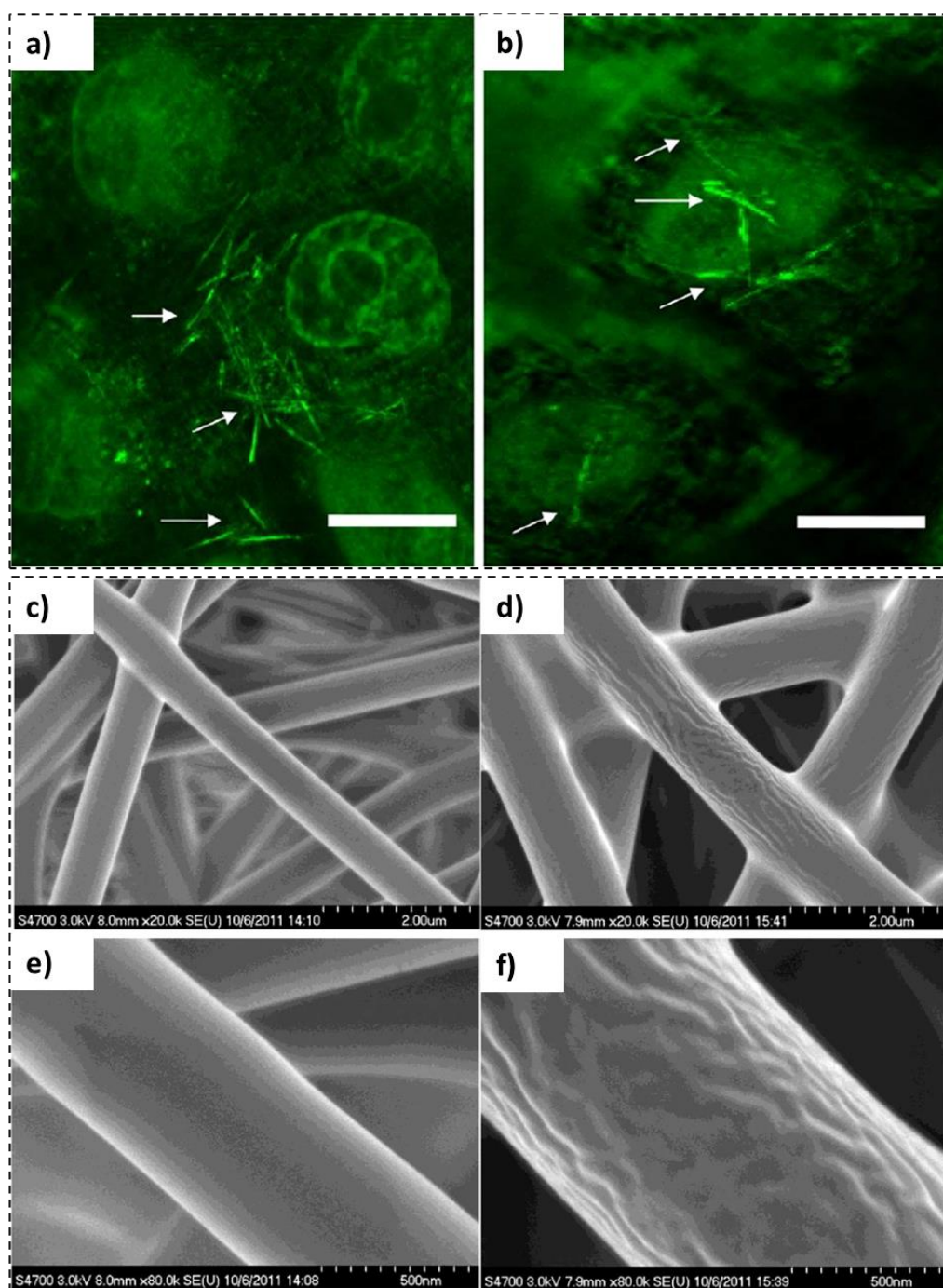


Figure 6. Confocal micrographs: a) Lignin nanotubes fabricated employing isolated pine lignin and thioglycolic acid, b) Isolated pine lignin nanotubes manufactured with NaOH (Reproduced with permission [82]), SEM micrographs: Lignin nanofibers (c, e), PNIPAM grafted lignin nanofibers (d, f) (Reproduced with permission [83]).

The nanofibers exhibited diameters between 790 to 1150 nm (**Figure 6 (c-f)**), thus, exhibiting potential applications in purification and separation devices [83,84].

2.2.4. Lignin filled composites in additive manufacturing applications

In the recent decade, technological advances have made 3D printers more accessible to the general consumer, thus, in turn fueling an interest in additive manufacturing (AM) or better known as 3D printing fabrication of materials. As illustrated in **Figure 7**, 3D printing comprises of three steps: development of a CAD model, preprocessing of the model, and additive manufacturing of the product [85].

Although the conventional fabrication materials (such as metals, conventional polymers, inorganic glasses, ceramics, and composites) are viable options for research and development at additive manufacturing's advent, their utilization at the consumer level raises sustainability concerns [86–88]. The predicted 3D printing market size between the years 2022 and 2032 is presented in **Figure 7**. In the year 2032, the global AM market size is projected to be 98.3 billion USD with a material sale potential of 900 million USD [89]. Photopolymer sales are expected to contribute the biggest fraction (350 million USD) to this value, with its primary application being in the prototyping stage and molding application. Furthermore, AM metals and polymer powders could contribute to 14%, and 25 % of the total AM material sales, respectively. The remainder of sales are expected to be associated with polymer filaments employed primarily for fused deposition modeling (FDM) [85,90]. An inclination towards the use of naturally abundant biopolymers such as lignocellulosic materials for AM feedstock has garnered significant attention [86,91–93]. Since its advent in the later part of the previous

centennial, several techniques for additive manufacturing have been developed, including stereolithography, direct ink writing, sheet lamination, binder jetting, fused deposition modeling (FDM), powder bed fusion, and vat photopolymerization [94]. Among the various additive manufacturing techniques, the stereolithography apparatus (SLA) is of particular interest.

Due to the inherent advantages of SLA such as good operator control, accuracy, and superior resolution, it can be a method of choice [95]. However, due to the ability to solely process photoreactive resins, the choice of polymer feedstock materials is relatively narrow[95]. To overcome this limitation, the development of modified photoreactive resins has been under intense investigation [96–101]. The use of traditional fillers (such as graphene oxide, carbon nanotubes, SiO₂, nano clay, sepiolite nanofibers, aluminum oxide nanowires, and TiO₂) in photoreactive resins for enhancing the tensile properties of stereolithography printed products has been recorded [97,102–106]. Although conventional fillers enhance the mechanical properties of filled products, the associated concerns are fueling a shift towards more sustainable alternatives [107].

The use of lignin as a filler in SLA-printed products are shown to enhance UV absorption [108], anti-aging properties [109] and flame retardancy [110] of 3D-printed lignin-based materials with applications in drug delivery materials [111,112] and other biomedical applications. Due to the inherent stiffness that lignin imparts to the host polymer matrix, several studies have covered its application in 3D printing materials. In a study by Sutton et al., the use of methacrylic anhydride-modified lignin in conjunction with methacrylate resin to

undergo stereolithography was explored [113]. A 300% increment in elongation at break was recorded. This was attributed to the superior dispersibility of the modified lignin (15 wt.%) in the filled matrix.

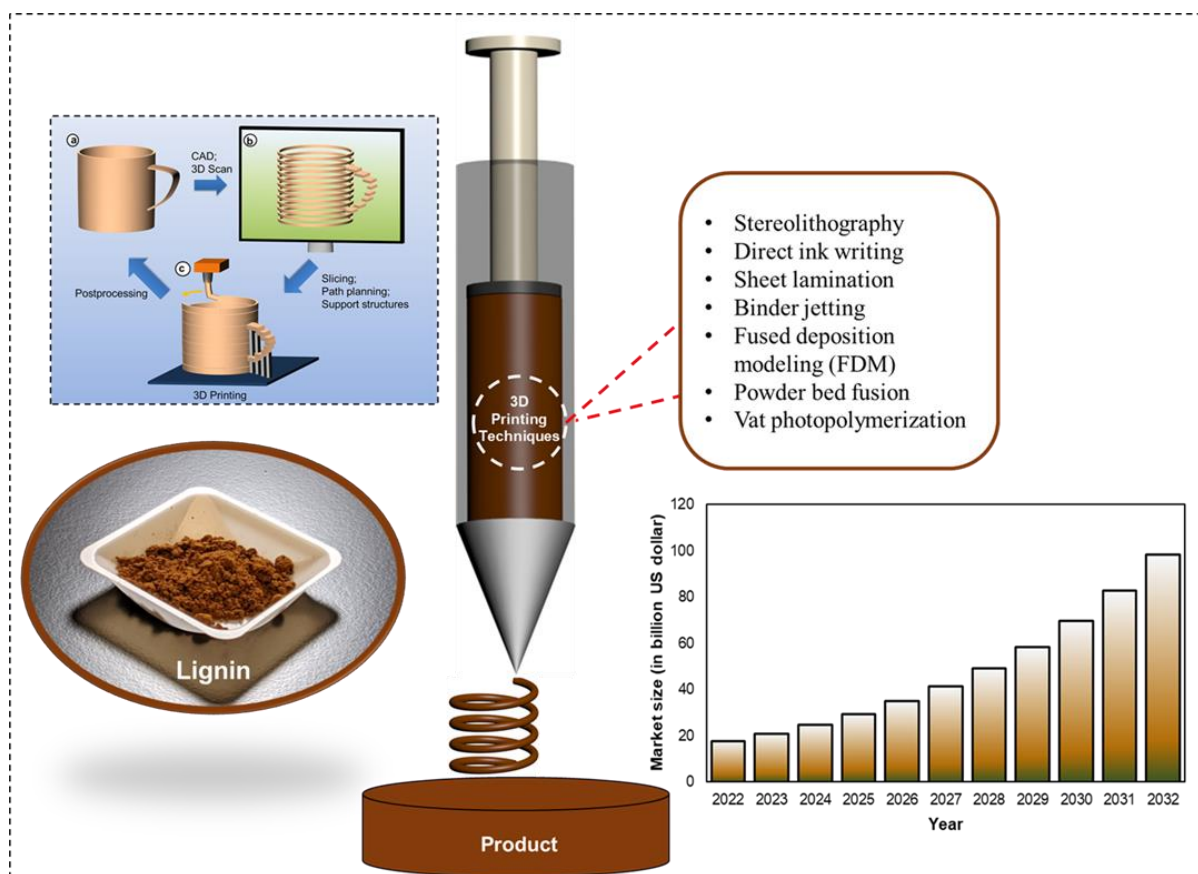


Figure 7. 3D printing representation: Fundamental steps of additive manufacturing: CAD model (development, preprocessing, and 3D printing of the product) (Reproduced with permission [85]), worldwide additive manufacturing market size (2022 to 2032) (Adapted with permission [89]).

FDM is another additive manufacturing technique that can utilize lignin as ink. In a study by Mimini et al., FDM-printed samples of PLA composites with different types of lignin (kraft lignin, organosolv lignin, and liginosulfonate) were tested for their impact and flexural strengths [114]. A minimal reduction in both flexural and impact strength values of all the specimens was recorded. In a study by Nguyen et al., FDM was employed to incorporate

hardwood lignin in a nylon 12 matrix [115]. The resultant lignin (40 wt.%) loaded specimens exhibited a tensile strength of 55 MPa with a 70% increment in Young's modulus values. This improvement in the mechanical properties was ascribed to the presence of extensive phenolic moieties in the lignin specimen and potential instances of hydrogen bonding between the lignin moieties and the amide bonds of nylon in the composite.

In another work, a similar increment in Young's modulus and a dip in tensile strength with higher loadings of pine kraft lignin in polylactide was observed [116,117]. In a separate study, the use of lignin with PLA for additive manufacturing via the fused filament fabrication technique was explored [112]. Polylactic acid pellets were coated with lignin (0-3 wt.%) and castor oil prior to extrusion at 200 °C. The produced filament underwent fused filament fabrication. The filaments exhibited antioxidant capabilities and were further used to design and fabricate meshes. The 3D-printed meshes could be utilized in wound dressing and the healthcare sector [112]. The above-mentioned studies were crucial in establishing the merits of employing lignin in additive manufacturing operations. The complexity of the systems arising due to the non-homogeneity of lignin, the lignin content of the formulations, the choice of the base polymer, and the employed additive manufacturing technique were established.

2.2.5. Utilization of Lignin as a Pickering emulsifier

In recent years, the extensive use of Pickering emulsions in cosmetic, food, and pharmaceutical industries has been witnessed [118]. The use of organic and inorganic particles for stabilization Pickering emulsions is widely practiced [119], ranging from latex [120], silica [121], and calcium carbonate [122], to laponite [123], etc. However, some of these particles have safety

and sustainability concerns. For instance, the inhalation of crystalline silica dust, which can be used as Pickering emulsifier has been proven to be a leading cause of silicosis in human beings [124]. Also, the mining operations of crystalline silica is known to be detrimental to the environment. Thus, there has been a growing interest in developing sustainable alternatives to conventional Pickering emulsifiers [125].

In a study by Shorey et al., native and esterified lignin for the stabilization of oil-in-water Pickering emulsions were studied [30]. It was observed that due to the subpar dispersibility exhibited by the unmodified lignin in solvents, unstable Pickering emulsions were produced. On the contrary, the esterified lignin (LigHC, Lig DC, and LigPC) with hydrophobic properties displayed enhanced solvent dispersion and provided outstanding stability to oil-in-water Pickering emulsions. This was substantiated by a 47 % reduction in average oil droplet size for LigHC stabilized Pickering emulsion, as displayed in **Figure 8** [30].

The use of novel Pickering emulsion formulations stabilized employing lignin nanoparticles for controlled release of trans-Resveratrol was explored [126]. In this work, the stabilization effect of alkaline lignin grafted poly(N-isopropylacrylamide) (PNIPAM) via atom transfer radical polymerization (ATRP) was studied. The fabricated nanoparticles (with diameter < 160 nm) absorbed at the interface of oil-in-water emulsions, thus, exhibiting stable Pickering emulsions with oil droplet diameter values in the vicinity of 200 μm . The stabilized Pickering emulsions exhibited stability improvement against UV radiation and exceptional controlled release performance.

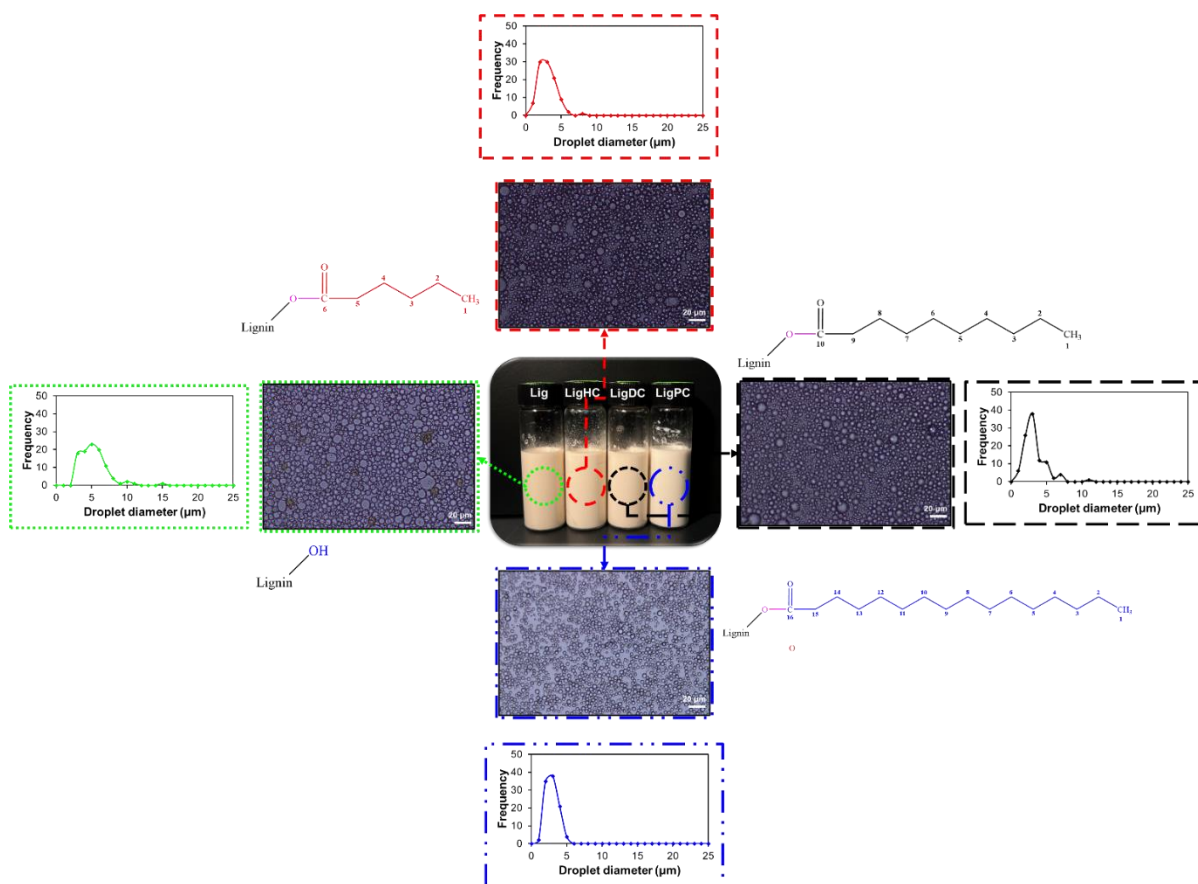


Figure 8. Optical micrographs of unmodified and esterified lignin stabilized oil-in-water Pickering emulsions (Reproduced with permission [30]).

2.2.6. Lignin-based carbon fibers and their applications

In recent times, an exponential growth in the market size of carbon fibers has been witnessed [127]. Evaluated at 2.99 billion USD in 2022, the carbon fiber market is forecasted to be worth 5.83 billion USD by 2032, with a compound annual growth rate of 6.9% [127]. Comprising of at least 92 wt.% carbon, the fibers exhibit high flexibility, low density, inertness, heat resistance, and low thermal expansion. In comparison to steel, a 10-fold increment in tensile strength at half the weight has been recorded for carbon fibers [128,129]. Due to their exceptional properties, an influx of its use has been reported in various sectors, including –

construction, automotive, aerospace, sports, oil and gas industries, etc. Amongst the various precursors available for the manufacture of carbon fibers, Polyacrylonitrile (PAN) is the most widely employed. The expensive PAN precursor (approximating 50% of the manufacturing cost) renders the carbon fibers costly for widescale industrial and commodity composite applications [130–133]. In addition, the environmental concerns posed by the use of petroleum-derived precursors have created an interest in greener, renewable, and economical carbon fiber precursors.

In recent times, the use of lignin as a carbon-fiber precursor has gained significant attention[134–137]. This is primarily due to the vast availability, high carbon content, and high post-carbonization yield exhibited by lignin [135,137]. The process of spinning carbon-fibers from lignin includes a series of processing steps – spinning (solution spinning, melt spinning, and electrospinning), pre-oxidation, and carbonization (low temperature or high temperature) (**Figure 9**) [138].

In a study by Jin et al., a tensile modulus of 98 GPa for unmodified lignin-based carbon fibers was obtained [139], which was perhaps one of the highest modulus values recorded for lignin. In this work, three fractionated–solvated lignin precursors (FSLPs) with increasing molecular weights (7200 g/mol, 13800 g/mol, and 28600 g/mol) were employed. As presented in cross-sectional SEM micrographs (**Figure 9**), the lignin carbon fibers exhibited uniform diameter (6-7 μm) with no surface deformations. These diameter values were noted to be much smaller than the values for other lignin-based carbon fibers previously reported [140,141]. Moreover, they were in close proximity to the diameter of PAN-based commercial carbon fibers [142].

PAN based carbon fibers exhibit tensile modulus values in excess of 200 GPa with some manufacturers being able to achieve tensile modulus as high as 517 GPa [143]. Although the modulus values were the highest recorded for the lignin-based carbon fibers, they were 52% lower than the tensile modulus values required for automotive industrial applications [84,139,144], indicating that there is a large gap that needs to be addressed before lignin-based carbon fibers find extensive industrial applications. Other studies on lignin-based carbon fibers are summarized in **Table A 3 (Appendix A)**.

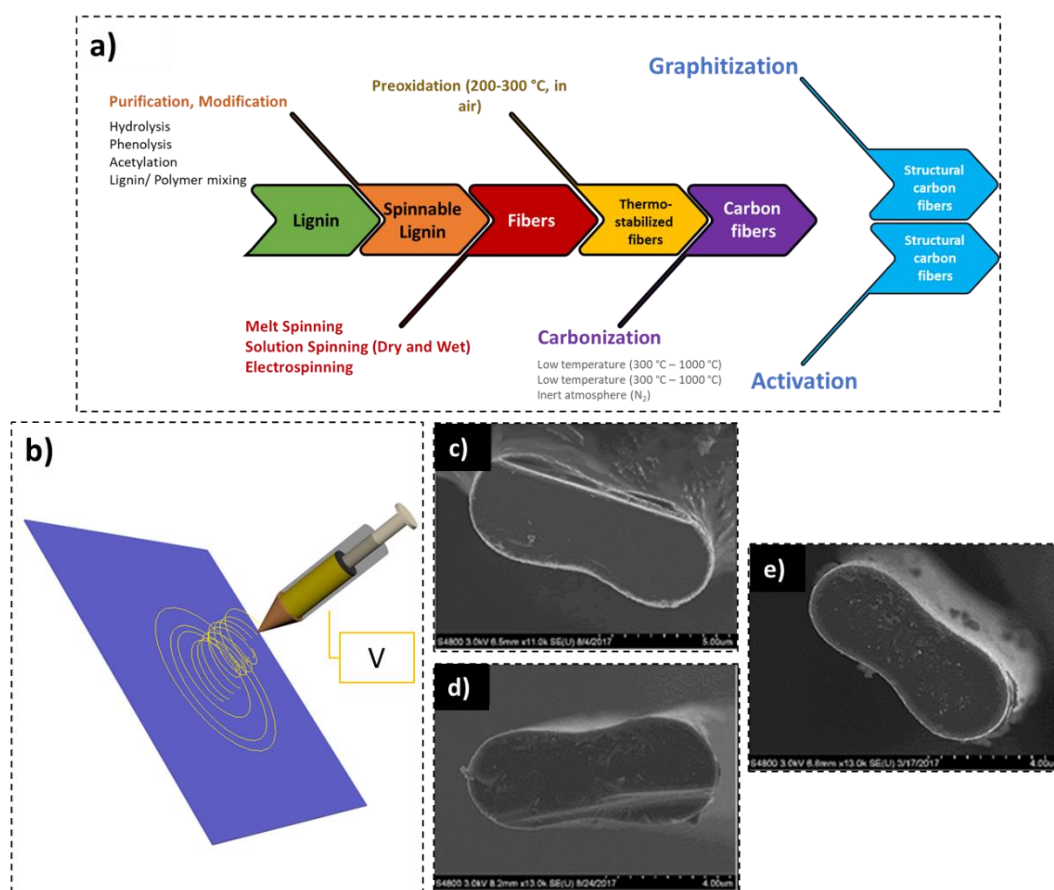


Figure 9. a) Process of spinning carbon-fibers from lignin, b) Electrospinning apparatus, Lignin carbon fibers manufactured from c) medium, d) higher, and e) highest molecular weight fractionated-solvated lignin precursors (FSLPs) (Reproduced with permission [139]).

2.2.7. Lignin-incorporated sunscreen formulations

A relationship between depleting ozone layer and increasing instances of skin cancer has been observed [145]. Skin cancer instances in excess of 82000 (6500 cases of melanoma and 76100 cases of non-melanoma skin cancer (NMSC)) were reported in Canada (2014) [146,147]. With reduced exposure to artificial and natural UV radiation, most cases of skin cancer are preventable [148,149]. The use of sunscreens as an effective UV-blocker has been widely investigated. Since their advent in the United States cosmetic market in 1928, they have been a huge commercial success [150]. Commercially available sunscreens incorporate various active ingredients (inorganic and organic) and hence vary in their respective UV-blocking mechanisms [145].

Traditionally, the use of inorganic active ingredients (including zinc oxide (ZnO), talc, titanium oxide (TiO₂), kaolin, etc.) in UV blockers are prominent [151]. These active ingredients scatter and reflect UV rays off the surface of the skin, thus, in turn preventing the sunlight from penetrating the skin. Although inorganic UV blockers mostly cover the broad UV spectrum, their inferior dispersion in cream bases and the photoreactive properties that could potentially harm cellular components make their organic counterparts an attractive and safe alternative [152–155].

On the contrary, organic UV blockers (including benzophenones, silatriazole, bisoctrizole, salicylates, ecamsule, bemotrizinol, etc.) work on the mechanism of absorbing the UV energy and converting into heat energy [156]. In numerous studies, the photostability and the synergistic effect of adding lignin to sunscreen formulations have been studied, as covered in

Table A 4 (Appendix A). There was an increment in both the sun protection factor and duration of protection against UV rays after the addition of lignin to creams and commercial sunscreen formulations [157]. In a study by Zhang et al., with progressive loadings of acetylated lignin to the substrate sunscreen lotion, a three-time increase in the SPF value (75.2 SPF) was recorded (**Figure 10**) [158]. This was attributed to the synergistic effect of the acetylated lignin in conjunction with the synthetic actives.

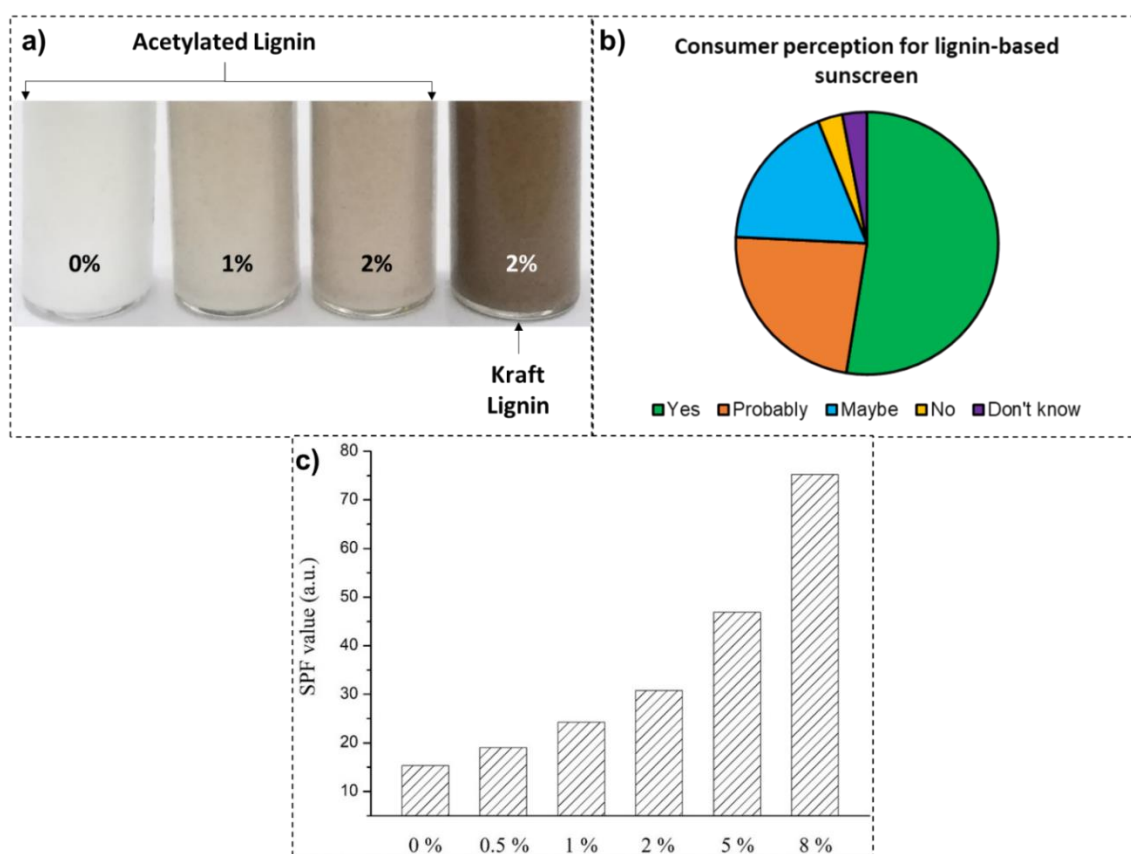


Figure 10. a) Sunscreen formulations loaded with acetylated and kraft lignin samples (Reproduced with permission [158]), b) Consumer perception to the use of lignin-based sunscreen formulations (Adapted with permission [159]), and c) Recorded SPF values at various loading concentrations of acetylated lignin (Reproduced with permission [158]).

The challenges for the mainstream application of lignin in sunscreen formulations are many, including heterogeneity of the chemical structure, dark color, broadening of the SPF value in

broad-spectrum UV blocking range, and consumer perception [160]. Fractionation of lignin with organic solvents is usually employed to remove the condensed structures, thus, increasing the dispersion in cream bases [155]. In a study by Tran et al., acetylation of the hydroxyl groups of lignin specimen lightened the color for a better appeal [161]. In a separate work by Zhang et al., the color performance of unmodified and acetylated lignin specimens in sunscreen formulations at various loadings was compared. As it is apparent from **Figure 10**, sunscreen formulations loaded with 2 wt.% of acetylated lignin demonstrated a much lighter shade than its unmodified counterpart, thus, being more acceptable to the end-consumers. Another way of lightening the lignin color is through grafting other compounds on the lignin structure, such as benzophenone [162], 2,4-benzoyl-33-hydroxyphenyl acrylate (BHA) [163], and poly(ethylene glycol) methacrylate (PEGMA) [164]. In a work by Sajinčič et al., the attitude and perception of consumers toward lignin-based sunscreen formulations were explored [159]. While the consumers in excess of 50% were willing to try lignin-based sunscreens, a mere 3% of the potential consumers refused to try them. While consumers tend to appreciate bio-sourced, healthy, and sustainable sunscreen alternatives, they are concerned about lower performance and protection. Additionally, because organic ingredients are perceived as luxurious, consumers are concerned about associated product cost.

2.2.8. Lignin-based smart materials

2.2.8.1. Shape-memory application

Shape memory polymers (SMPs) attain a temporary pre-programmed shape and return to their original shape once an external stimulus (heat, electric field, moisture, light, magnetic field,

etc.) is applied [165–169]. Recently, various applications of SMPs in biomedical, coatings, textiles, and aerospace domains have been witnessed [170,171].

In a study by Shikinaka et al., the synthesis of lignin-based SMP exhibiting a dynamic shape-recovering behavior was reported [172]. The synthesis procedure comprised mixing SESC lignin and poly(ethylene carbonate) polymers (PEC), kneading the mixture (120 °C), and compression molding (120 °C, 3-5 MPa) into films. Thermoresponsive shape-memory behavior was noted in the molded films, as presented in **Figure 11a**. The composite films were set into the original shape by application of heat (80 °C). Further cooling could straighten and fix the film shape (0–10 °C) and revert to the original shape with the reapplication of heat. The fabricated films could be remolded into different shapes many times and each shape recovery cycle undertook less than 60 seconds to the conclusion. Poly(ethylene carbonate) sheets exhibited thermosetting behavior. The shape memory characteristics of the baseline poly(ethylene carbonate) sheets were attributed to the formation of hydrogen bonds under cold conditions. The SESC lignin moieties tend to aggregate in the polymer matrix, thus, imparting dynamic shape recovery to the specimens. Thus, the synergistic movement of the polymer chains influenced by the presence of the lignin agglomerations resulted in the shape-recovery behavior of the composite films (**Figure 11b**) [172].

In a study by Liu et al., the effective use of lignin as a crosslinking agent to develop crosslinked polycaprolactone (PCL) based thermal shape memory materials was explored [173]. The multistep procedure for the synthesis of crosslinked lignin-polycaprolactone specimens is illustrated in **Figure 11c**. The process was initiated with the esterification of the lignin and

synthesis of the PCL employing bulk ring-opening polymerization. Furthermore, the obtained PCL-OH moieties underwent a modification reaction to exhibit thiol terminal functional groups. The synthesis was concluded by crosslinking the lignin and PCL moieties via a photoredox thiolene reaction. The prepared samples exhibited an ability to transition between temporary and permanent shapes, and thus, a rapid thermal shape response was recorded. A reduction in the melting temperature of the crosslinked specimen with an increase in the lignin loading was observed. Thus, lignin could be employed as an effective crosslinker in polymeric matrices [173].

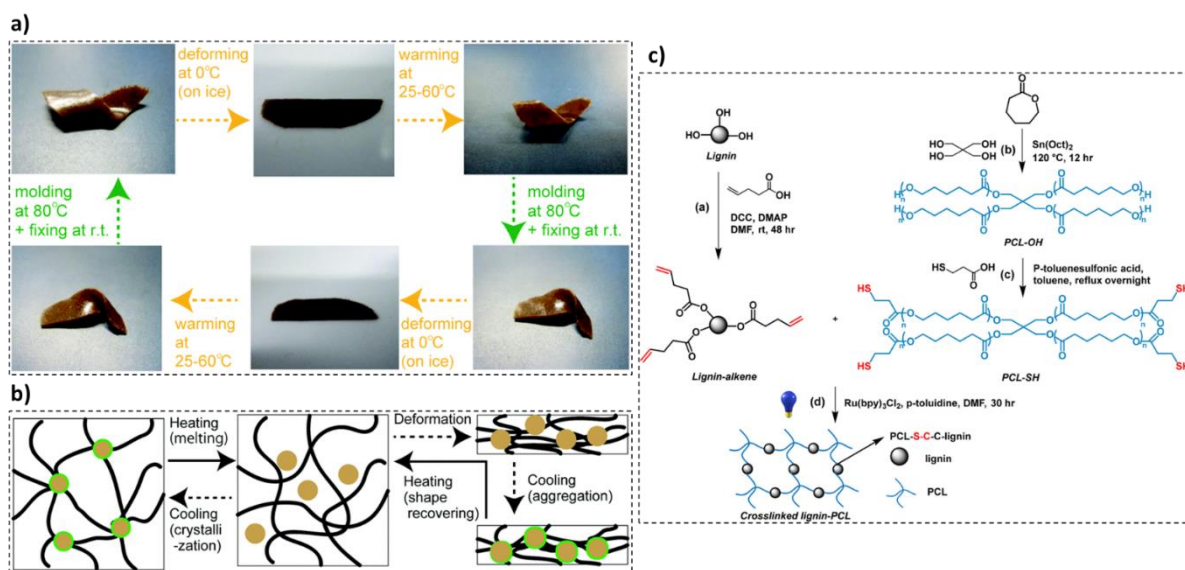


Figure 11. a) Thermoresponsive shape memory behavior exhibited by the lignin composite film (Reproduced with permission [172]), b) Molecular transformations in one shape memory-recovery cycle of lignin composite film (Reproduced with permission [172]), and c) Schematics of Lignin-PCL synthesis (Reproduced with permission [173]).

2.2.8.2. Smart hydrogels for drug-delivery applications

Hydrogels are hydrophilic polymer material with 3D network structure. Sourced from synthetic or natural resources, the polymerization process comprises of crosslinking a single or multiple monomers to obtain 3D network structures [174–176]. Due to their morphology, water retention characteristics, mechanical strength, biodegradability, and implied ability to disintegrate to non-toxic materials, interest in their applications in pharmaceutical industry has been observed [175,176].

In a study by Larrañeta et al., lignin-based hydrogels employing an esterification reaction were fabricated [177]. The synthesized lignin-poly(ethylene glycol)-poly(methyl vinyl ether-co-maleic acid) based hydrogels exhibited potential applications in medical material coatings. For lignin loaded hydrogel formulation (between 40 % and 24 %), water uptake value of up to 500 % was recorded. The formulated gels sustainable released curcumin fractions up to 4 days post loading [177]. As illustrated in **Figure 12**, lignin based photodynamic hydrogels exhibiting self-healing properties were synthesized in another work [178]. Lignin based hydrogels were synthesized and functionalized with Rose Bengal (RB) lignin-based silver nanocomplexes (L-AgNCs) (**Figure 12a** and **Figure 12b**) [178]. The hydrogels constituted of 2 to 7.5 mg/mL of lignin loadings with declining transparency for the higher loaded specimens, as displayed in **Figure 12c** [178]. 85% transmittance of the light through the hydrogels was recorded for the 2 mg/mL lignin loaded samples (**Figure 12d**) [178]. In the SEM micrographs, an extensively cross-linked and porous structure exhibited by the 2 mg/mL (**Figure 12e**) and 3 mg/mL (**Figure 12f**) hydrogel formulations was observed. In addition, the fabricated hydrogels

exhibited self-healing properties [178]. In **Figure 12g**, two dissected pieces of hydrogel self-healed upon being placed together for 30 min [178]. In another study by Ma et al., the degradability of lignin-poly (acrylic acid) based hydrogels was tested [179].

As apparent from **Figure 12 (h and j)**, significant degradation of lignin loaded hydrogel was recorded. While the lignin loaded hydrogel exhibited a well-defined structure before the initiation of degradation, post 180 days the porous structure underwent severe disintegration. On the contrary, for the baseline poly (acrylic acid) specimen no cracks or surface deformities were recorded. The deterioration of the lignin loaded sample was ascribed to the enzymatic and chemical degradation of the lignin-polymer chain covalent bonds. The 40% lignin loaded hydrogel sample lost approx. 5 % weight in 35 days, varying minimally with the type of the testing soil employed [179].

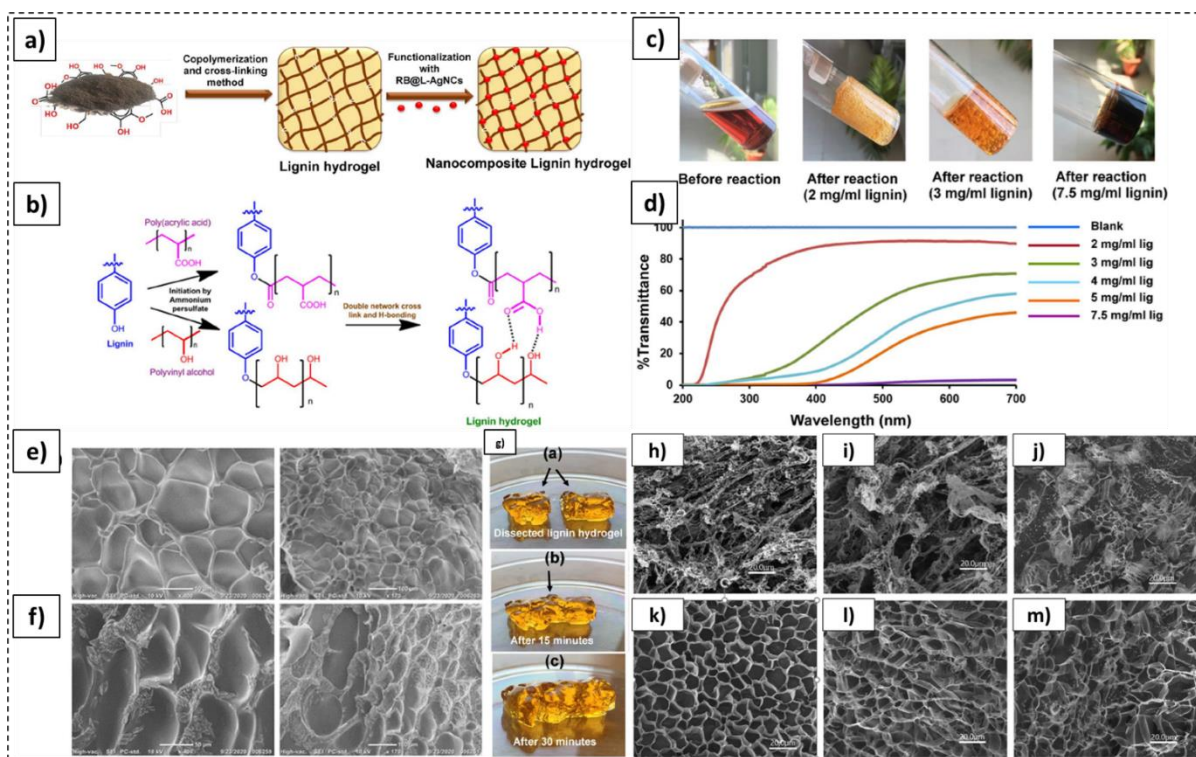


Figure 12. Lignin-based hydrogel formulations: a) Functionalization of lignin-based hydrogels, b) Lignin based hydrogel synthesis steps, c) Various lignin hydrogel formulations with different lignin loadings. d) Hydrogel transmittance, e) SEM images of 2 mg/mL lignin-based hydrogel, f) SEM images of 3 mg/mL lignin based hydrogel, g) Self-healing properties of lignin based hydrogels (Reproduced with permission [178]), SEM micrographs of hydrogel recorded post different days of degradation: 40 % lignin loaded formulation (60 PAA/40 LM) h) 0 day, i) 35 days, j) 180 days; baseline PAA degradation: k) 0 day, l) 35 days, and m) 180 days (Reproduced with permission [179]).

2.2.8.3. Use of lignin-based nano-materials for biosensing applications

Sensors possess the ability to convert input from their surrounding medium to a quantifiable output signal. On the other hand, biosensors are primarily employed in the detection of biological species [180]. Recently, the use of lignin in sensing applications (biosensors) has been witnessed. This influx in its employment in materials for sensing applications could be attributed to its biocompatibility, low cost, presence of various functional groups amenable to modification, and acceptable compatibility with numerous polymer matrices [181]. Due to the

presence of biomolecules in the system, the surrounding medium undergoes a change (temperature, pH) and thus, generates a response signal [180].

In a study by Cerrutti et al., electrical impedance spectroscopy (EIS) based immunosensors were fabricated [181]. These sensors constituted lignin and antigenic peptide on interdigitated gold electrodes and exhibited anti-p17 (HIV) antibodies detection capabilities (**Figure 13a**). The manufactured immunosensors could detect low concentrations of anti-bodies (0.1 ng/mL) for up to 2 months [181]. In a separate study, Jędrzak et al. prepared biosensors based on Silica (SiO_2)/Lignin material for glucose detection [182]. The developed SiO_2 /Lignin hybrid material underwent glucose oxidase immobilization, as presented in **Figure 13b**. Incorporating lignin into the matrix resulted in twice (25.28 mg/g) the amount of GOx immobilization than its baseline (SiO_2) counterpart. Lignin-based biosensors demonstrated high sensitivity (0.78 $\mu\text{A}/\text{M}$) and an ability to detect glucose in biological samples with great accuracy. Poly(3,4-ethylenedioxythiophene) (PEDOT) in conjunction with sulfonated lignin was incorporated as the conductive material in poly(acrylic acid) (PAA) skeleton for the fabrication of hydrogel-based wearable sensors, as illustrated in **Figure 13 (c - f)** [183]. The high sensitivity of the produced sensors was capable of detecting bodily motion, physiological signals, throat vibrations, and pulses. Potential applications in the healthcare, sport science, and speech recognition were proposed. Other developments in the domain of lignin-based sensing materials have been reported. In one such work by Wang et al., lignin-based pressure sensors for wearable electronics were developed [183]. For the prototype sensor, high sensitivity (57

kPa⁻¹) and wide working pressure range (0 to 130 kPa) were recorded, as illustrated in **Figure 13 (g – i)**.

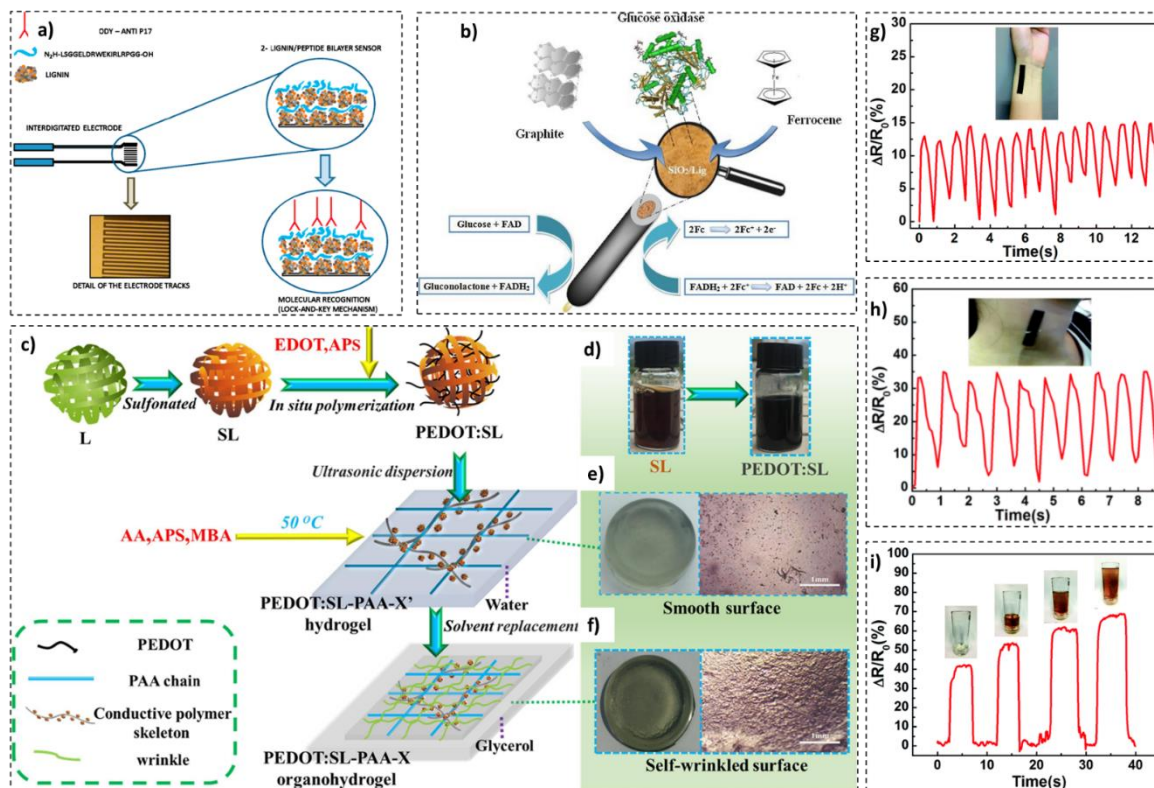


Figure 13. a) Electrical impedance spectroscopy (EIS) based immunosensors (Reproduced with permission [181]), b) Functional GOx/silica/lignin system based Carbon paste electrode (Reproduced with permission [184]), c) Synthesis of PEDOT:SL-PAA organohydrogel, d) Color change during synthesis, e) Morphology of PEDOT:SL-PAA hydrogel, f) Morphology of PEDOT:SL-PAA organohydrogel (Reproduced with permission [185]), CL/PDMS composite based wearable device: g) for wrist pulse measurement, h) for neck pulse measurement, i) Power measurement in picking up a cup (Reproduced with permission [186]).

2.2.9. Use of Lignin in self-healing elastomers

The self-healing properties exhibited by many materials stem from the presence of supramolecular interactions [187], such as π - π stacking [188], ionic interactions [189,190], hydrogen bonding [191,192], metal–ligand interactions[193,194], and host–guest interactions

[195]. These materials exhibit instantaneous self-healing properties at the expense of mechanical strength.

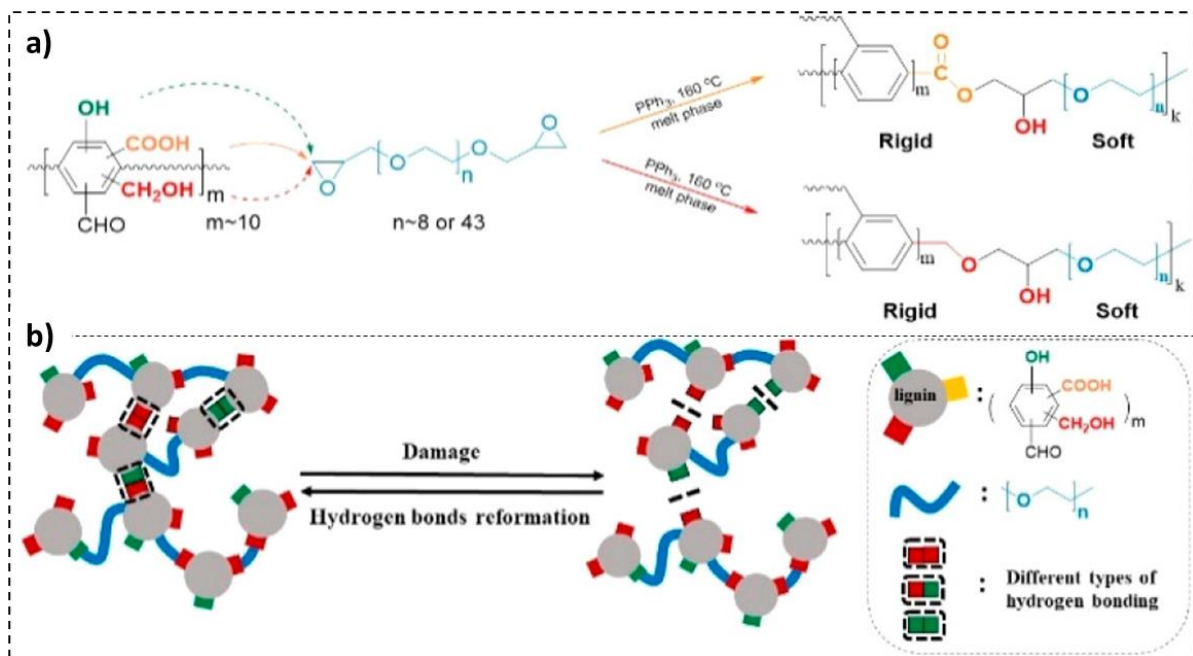


Figure 14. a) Reaction mechanism of ACN-lignin and diglycidyl ether polyethylene glycol (PEG) (melt phase), b) Illustration of the network formed by covalent and non-covalent bonds (Reproduced with permission [196]).

In a work by Cui et al., a reaction of diglycidyl ether-terminated polyethylene glycol with lignin moieties was reported [196]. The existence of covalent and hydrogen bonds in the resulting self-healing elastomers was observed, as illustrated in **Figure 14a** and **Figure 14b**. While the lignin moieties made the material stiff, the PEG soft phase fractions enabled chain movement [196]. An elastic modulus value of 86 MPa with a tensile strength of 12 MPa was recorded for the 58% lignin-loaded sample. Furthermore, the 55 wt.% lignin samples were observed to be extremely stretchable, reporting an elongation at break value exceeding 2200 %. The unfolding and sliding of polymer chains due to breakage and rejuvenation of hydrogen bonds imparted the material with high stretchability [194,196]. As represented in **Figure 15b**,

a recovery in elongation at break exceeding 50 % was recorded after 1 min for the 50 wt.% lignin-loaded samples [196]. An inverse relationship between lignin loadings and self-healing time was also noted.

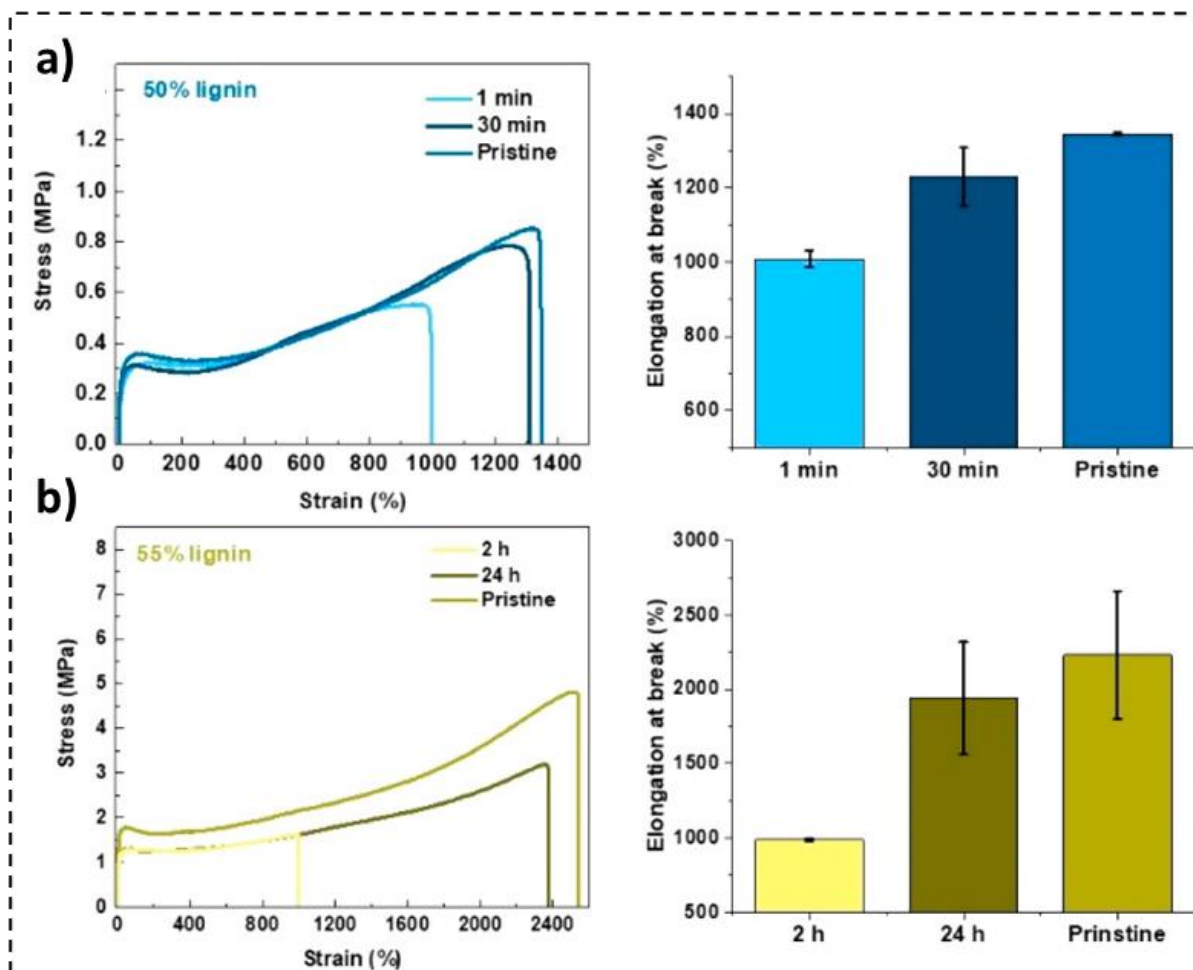


Figure 15. Tensile properties and recovery performance of a) 50% ACN-lignin (1 min and 30 min) at ambient temperature and b) 55% ACN-lignin (2 h and 24 h) exposed to 37 °C (Reproduced with permission [196]).

In another work, the preparation of lignin constituting self-healing polyurethane elastomers was discussed [197]. Good mechanical properties (tensile strength 10.77 MPa) in conjunction with self-healing properties (in excess of 93%) were observed. Moreover, the presence of

dynamic hydrogen and disulfide bonds has been correlated to superior thermal stability, mechanical properties, resistance against fatigue, and self-healing capability.

2.2.10. Antimicrobial properties of lignin for active food packaging applications

Food packaging materials predominantly employ petroleum-sourced and non-biodegradable conventional plastics. A shift towards sustainable and biodegradable packaging materials is attracting substantial interest. However, their widescale application is primarily inhibited owing to their high cost and inferior barrier and other physical properties. Thus, the use of functional fillers to counter the inherent disadvantages of virgin biopolymers is gaining significant interest. One of the crucial roles of food packaging materials is imparting defense against microbial invaders. The choice of functional fillers for antimicrobial material is not only limited by the enhancement in physical properties but also by their antimicrobial activity. Of all the functional fillers available, the employment of lignin to impart antimicrobial properties to the host packing material has been studied [198–201].

In a work by Shankar et al., the use of agar/lignin/silver nanoparticles for the fabrication of antibacterial composite sheets was studied [198]. The use of lignin as a capping and reducing agent for the preparation of silver nanoparticles was observed. Furthermore, the incorporation of lignin-capped silver nanoparticles in agar matrix via solution casting to produce composite sheets was witnessed, as evident from **Figure 16a**. With the addition of lignin, an increment in the mechanical strength, UV barrier, and water vapor barrier properties of the films was recorded, which witnessed a further improvement with the addition of silver nanoparticles. The incorporation of silver nanoparticles up to 1 wt.% in the polymer matrix exhibited clear

benefits; further increase in the concentration demonstrated detrimental effects. Antibacterial activity against *E. coli* and *L. monocytogenes* was noted in the casted films and thus, their potential application in active food packaging applications was proposed [198]. In a similar work by Hu et al., lignin-capped silver nanoparticles were incorporated on the surface of cellulose nanofibers (up to 2.9 wt.%) [199]. As evident from **Figure 16b**, the alkali lignin-containing samples exhibited no bacterial growth in comparison to the original cellulose sample.

A different approach was undertaken in a study by Yang et al., where the synergic effect of the incorporation of lignin nanoparticles (LNPs) and cellulose nanocrystals (CNCs) in a polylactic acid based (PLA and Glycidyl methacrylate (GMA) grafted PLA) matrix was investigated [201]. The antibacterial activity of binary (PLA/3LNP) and tertiary (PLA-3LNP/1CNC) melt extruded nanocomposite films against *Pseudomonas syringae* pv. tomato (Pst) was recorded [201]. With addition of 3 wt.% LNP to PLA matrix in binary nanocomposite films, the highest resistance to bacterial growth was observed. This was attributed to the antibacterial activity of lignin nanoparticles (LNPs) [201].

In another work, the incorporation of varying amounts of corncob lignin nanoparticles (0.5 wt.% to 10 wt.%) in cellulose nanofibrils for the production of cellulose composite films was studied. Superior antibacterial activity against *Escherichia coli* and *Staphylococcus aureus* was exhibited by the composite films. As evident from **Figure 16c**, the bacterial growth (*Escherichia coli* and *Staphylococcus aureus*) in the lignin-incorporated sheets was inferior to the baseline cellulose counterparts. The superior antibacterial activity of lignin-loaded sheets

against *Escherichia coli* was attributed to the presence of side chains and phenolic groups in the lignin molecular structure. Thus, the authors proposed potential application of the formulated films in antibacterial polymers [200].

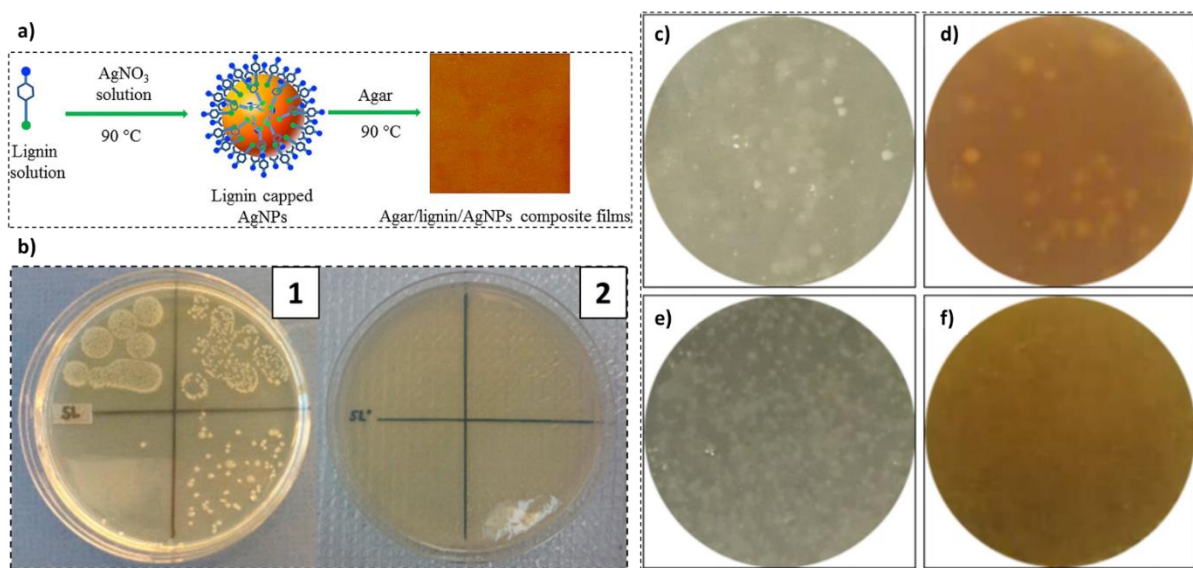


Figure 16. a) Agar/lignin/silver nanoparticle composite films synthesis procedure (Reproduced with permission [198]), b) Four diluted *E. coli* suspensions exposed (10 min) to: (1) Cell, and (2) AgNPs-AL-Cell 10 ((Reproduced with permission [199])). Antibacterial activity against *Escherichia coli* (c,d), and *Staphylococcus aureus* (e,f) of CNF (c,e) composite films, and CNF@CLNPs (d,f) composite films [200].

2.3. Summary of Chapter 2

Lignin is one of the most widely available biopolymers, thus, its effective derivation for advanced material applications is lucrative. Lignin can be distinguished on the basis of sourced-wood and extraction operation. The inherent limitation of lignin samples can be countered by functionalizing them. Of the various functionalization routes developed, chemical modification of lignin is the most widely employed. Further, the functionalized lignin moieties can be valorized in many ways. Lignin-based materials engineered at the non/microscale and their applications in various domains were extensively discussed. Further,

the influx in the use of additive manufacturing materials, properties of lignin-incorporated materials in AM, and their potential application in the healthcare sector was explored. Other valorization pathways including lignin-based carbon fibers, Pickering emulsion stabilizers, and smart materials were covered.

Lignin-incorporated sunscreen formulations were discovered to exhibit dark color. Being unappealing to potential consumers, the use of acetylated lignin demonstrated much lighter formulations. With the incorporation of a mere 8 wt.% acetylated lignin in sunscreen formulations, a 300% increment in SPF value was recorded over the baseline sunscreen formulation [158]. Furthermore, work on consumer perception of lignin indicated a vast majority of people are in favor of trying lignin-incorporated sunscreen formulations.

Another medium of valorizing lignin is its use in self-healing elastomers, where the presence of supramolecular interactions is utilized for imparting the material with self-healing properties. Moreover, the antimicrobial properties and nontoxicity of lignin fractions render it a suitable material for food packaging applications. Various studies observed positive antimicrobial activity of lignin specimens against *E. coli*, *L. monocytogenes*, *S. aureus*, etc [198–201]. Efforts in valorizing lignin at a commercial scale have been made. Borregaard, a Norwegian chemicals company have developed lignin-based products, including Dispersing agents, Emulsion stabilizers, Complexing agents, Binding agents, and Crystal growth modifiers. Another firm, Ingevity have developed proprietary lignin-based products, for instance Indulin® SA-L is a lignin-based emulsifier to especially produce anionic asphalt emulsions. Hence, the studies deliberated upon in this review were of utmost importance in

emphasizing the necessity and significance of enhancing the value of lignin for advanced material applications.

Chapter 3 – Hydrophobic modification of lignin for rubber composites²

3.1. Introduction

Although polymers have revolutionized almost every aspect of modern life – from the clothes we wear, to the cars we drive, to the adhesives in our Band-Aids – they are derived from fossil fuels and require over hundreds of years to decompose in the environment. Growing environmental concerns about their production and disposal of polymers [202,203] are driving a shift toward the development of new materials based on renewable resources (e.g., starch, lignin, and cellulose polymers), as well as the design of biodegradable, multifunctional and biocompatible polymers from natural macromolecule derivatives [204–210]. Lignin is the second most abundant natural biopolymer after cellulose, constituting anywhere from 18 to 35 wt.% of biomass, depending upon the feedstock type [211–214].

Global lignin biosphere availability is estimated to be 300 billion tonnes [215], of which approximately 100 Mt/y is produced annually [11]. 50 to 70 million tonnes of lignin exists in black liquor, a byproduct of the paper and pulp industry [12,13,216]. Dessbesell et al. estimated the global annual production capacity of kraft lignin extracted from black liquor to be 265,000 t/y in 2018 [15]. Lignin is categorized as biodegradable polymers as certain wood-rotting fungi, and some bacteria can depolymerize and mineralize it [217].

Various types of lignin exist depending on the employed extraction process. Kraft lignin, liginosulfonates, organosolv lignin, and soda lignin are the most common types of technical

² A version of this chapter has been published: Shorey, R., Gupta, A., & Mekonnen, T. H. (2021). Hydrophobic modification of lignin for rubber composites. *Industrial Crops and Products*, 174, 114189. <https://doi.org/10.1016/J.INDCROP.2021.114189>

lignin [218]. Furthermore, lignin can be produced from either soft or hardwood via dissolution or the hydrolysis of cellulose and hemicellulose at low pH resulting in an insoluble residual fraction [218–220]. Also, due to partial degradation of its molecular structure during the extraction process, commercial lignin's molecular weight and polydispersity are highly dependent on the employed process [221]. Overall, due to its abundance, sustainability, renewability, and presence of numerous functional groups that enable lignin to undergo numerous reactions, there has been a significant interest in its utilization as a feedstock for bio-aromatic chemical syntheses, such as phenols and vanillin, and the production of bio-based polymeric materials for adhesives or composites applications [222]. Currently, lignin moieties existing in black liquor from paper and pulp industry are widely used as a low-cost fuel in power and heat generation facilities [223]. The majority of extracted lignin is employed in bio aromatic chemical synthesis and bio-based polymeric materials, a small percentage of lignin is also used as fillers in paint, ink varnishes, and elastomeric matrices [26,224,225].

However, due to lignin's limitations including hydrophilicity, lack of melt processability, and poor dispersibility [226] in hydrophobic matrices like NR, structural modifications are employed. Lignin's structural modifications range from biological [227] to chemical [223,228,229], electrochemical [230], and photochemical processes [231]. Lignin-elastomer composites could generate appealing properties by combining the rigid moiety from lignin with the elastomer's soft moiety [232]. However, the lignin will be responsible for imparting the composite with tensile and tear strength and resistance to abrasion [233], the soft elastomer of NR could provide the composite with elastomeric characteristics. While the polarity mismatch

between the hydrophobic natural rubber and the -OH rich unmodified lignin typically leads to relatively poor lignin dispersion in NR, hampering its reinforcing properties [234]. Chemical modifications of lignin are attractive methods because of their efficiency, control, and various possibilities they offer.

In this work, a novel reaction for silylation of kraft lignin with the goal of reducing its hydrophilicity and enhancing its dispersion and compatibility with hydrophobic natural rubber to produce lignin-natural rubber composites was employed. Monoisocyanate functional group-containing silane, 3-(Triethoxysilyl)propyl isocyanate, was selected as the silylation agent in conjunction with tin(II) 2-ethyl hexanoate as catalyst. It was hypothesized that the high reactivity of the electrophilic carbon of the isocyanate functional group with nucleophilic oxygen of the lignin -OH moieties would result in the formation of a urethane linkage between the lignin and the silane. To evaluate the effect of the modification on the dispersion and compatibility of the lignin with natural rubber, unmodified and modified lignin samples were incorporated in casted natural rubber sheet formulations at various loading levels. Physicomechanical and morphology testing of the composites were then conducted, and results are reported.

3.2. Materials and methods

3.2.1. Materials

West Fraser Mills Ltd., Canada supplied Amallin™ LPH Kraft Lignin (average molecular mass 6,500 g/mol, pH 2.2). Stabilized natural rubber (NR) latex with 60 wt.% solid content was purchased from Chemionics Corporation, OH, USA. Sulfur (99.5%) was supplied by

Acros Organics. Methanol (99.9%), 3-(Triethoxysilyl)propyl isocyanate (TEPI, 95%), tin(II) 2-ethyl hexanoate (92.5 – 100%), potassium bromide (KBr), dimethyl sulfoxide (DMSO, 99.9%), toluene (99.9%), zinc oxide powder (ZnO), tetrahydrofuran (THF, 99.0%), potassium hydroxide (KOH) in pellet form, dimethylformamide (DMF, 99.8%), and Chloroform (99.8%) were obtained from Sigma Aldrich, USA. Zinc (II) dibutyl dithiocarbamate (ZDBC) (98 wt.%) was purchased from Fisher Scientific Inc., Canada. All the chemicals were used as received.

3.2.2. Silylation of kraft lignin

3.2.2.1. Washing and pH stabilization of Lignin

The kraft lignin employed in this study, better known as Amallin™ LPH Kraft Lignin, is precipitated by acid washing of the pulping black liquor (pH 2.2). The presence of residual sulfur, sodium, and other impurities in varying concentrations due to the production process of this kraft lignin is reported by the manufacturer [235]. To remove water-soluble impurities and residual acid the lignin was washed extensively (five times) with deionized (DI) water by dispersing it in deionized water followed by centrifugation (at 3500 for 5 min), and its pH values were recorded after each wash. The washed lignin was dried in a convection oven at 60 °C overnight (< 3 % moisture content, pH 4.8) and stored in airtight containers until further use.

3.2.2.2. Estimation of reaction parameters

The silylation of kraft lignin was carried out by employing 3-(Triethoxysilyl)propyl isocyanate(TEPI) as the silylating agent with Tin(II) 2-ethyl hexanoate as a catalyst. DMSO was chosen as the reaction medium for kraft lignin because of the excellent dispersibility of

kraft lignin in DMSO as shown in **Figure B 1d (Appendix B)**. To optimize the reaction temperature and concentration of the silylating agent, rotational rheometer studies were conducted on Haake MARS III rheometer (Thermo Scientific, United States).

First, 1 ml dispersion of 10 wt.% lignin in DMSO with 1:1 mole ratio of hydroxyl moieties of lignin to TEPI and catalyst was added to the mixture, and it was stirred for 5 min at 400 rpm. In terms of mass, 1 g of lignin and 0.89 g of TEPI was required. A zero-gap plate (1 mm) was adjusted, and the test was conducted at 80 °C at a shear rate of 100 1/s for 4200 s, followed by a 10 °C increment until a viscosity change was recorded. This study aided in optimizing the reaction temperature for the proposed modification reaction. Based on the results obtained, the subsequent study was designed to finalize the concentration of silylating agent and catalyst for a successful silylation of kraft lignin sample, where reactant mixtures with different molar ratios of TEPI (1:0.25, 1:0.5, 1:1 and 1:2) with respect to kraft lignin's hydroxyl moieties present were sheared at a constant rate of 100 1/s at 90 °C until a significant increase in viscosity was recorded. This study aided in optimizing the economic feasibility of the process.

3.2.2.3. Modification reactions

A 10 wt.% Kraft lignin solution was prepared in DMSO and sonicated for 30 min. 90 °C was selected as the reaction temperature based on the rheology study. The prepared solution was fed into a round-bottomed flask (RBF) and heated to 90 °C with constant stirring (300 rpm) and under the continuous flow of nitrogen gas in the RBF. TEPI was added dropwise with maintaining molar ratios of 0.5, 1.0, and 2.0 with respect to the hydroxyl group of lignin. Also, an excess amount of Tin(II) 2-ethyl hexanoate equivalent to half the mass of the TEPI was

added to the mixture to catalyze the reaction. Since the required catalyst level was not optimized, a higher concentration was used to ensure that the reaction proceeds as desired. The excess catalyst was washed together with the unreacted TEPI in the subsequent purification process. The reaction continued for 2.5 h and stopped after the mixture attained a jelly-like consistency. The mixture was left to cool down and was washed with methanol thrice to remove methanol soluble fractions, such as unreacted TEPI and excess catalyst [236]. Thus, the methanol insoluble fraction was isolated through the centrifuge and dried in a hot air oven at 60 °C for 36 h. The resulting silylated lignin particles were darker in color (as can be observed in **Figure B 1c**), which was subsequently ground for further application in elastomeric matrices.

3.2.2.4. Characterization of the modified lignin

Structural analysis

Thermo Scientific FTIR Nicolett 6700 was employed to record the IR spectra of lignin and silylated lignin samples at ambient temperature. Sample pellets were prepared by mixing 2 mg of lignin with 200 mg KBr and pressing using a pellet die at 7000 psi for 6 mins. The transmittance was recorded to substantiate the proposed modifications.

Carbon Solid-State NMR spectra were recorded to observe and deduce the chemical modifications resulting from the silylation of the kraft lignin specimen. The spectra were collected up to 200 ppm on a Bruker 500 MHz high-resolution NMR (Bruker-SpectroSpin 500 MHz Ultra shield, Bruker Corporation, MA).

Wettability test

To test the hydrophilicity and hydrophobicity of the kraft lignin sample and its modified counterparts, 100 mg of the unmodified and modified lignin samples were added to a 20 mL toluene-water mixture (1:1 ratio) and shaken vigorously. Since the relative polarity of both solvents are at the opposite ends of the spectrum, it was expected that the sample demonstrating hydrophilicity would disperse more towards the water, and one displaying hydrophobicity will be away from water and stay in the toluene fraction.

3.2.3. Fabrication of NR biocomposite sheets

NR-Lignin composite sheets were fabricated using a solution casting process. Measured quantities of lignin and modified lignin were solubilized in 0.3 N KOH by stirring at 300 rpm for 20 min at 100 °C on a hotplate. The solutions were left to cool down to room temperature and incorporated into the formulations as shown **Table B 1 (Appendix B)**. Three concentrations of unmodified and modified lignin (lig:TEPI::1:0.5) at 2.5, 5 and 10 wt.% were incorporated in a rubber formulation composed of NR (100 phr), Sulfur (1.5 phr), ZnO (1.3 phr), and ZDBC (0.7 phr). The lignin (modified or unmodified), sulfur (crosslinking agent), ZnO (activator), and ZDBC (accelerator) were added in 60 mL of 0.3 N KOH and stirred for 10 min at room temperature followed by 10 min sonication. The dispersion was then homogenized (Fisherbrand's Homogenizer 850) for 2 min at 10,000 rpm. A calculated amount of NR latex was then added to each formulation and stirred at 400 rpm at 40 °C for 2 h to initiate maturation. In the present study, ZnO was used as an activator for rubber curing. This

would enable the added sulphur to anchor to the rubber chains to initiate the crosslinking [237]. A baseline NR sheet without lignin was the control system for the present work and was prepared similar to the other formulations for comparison purposes. Finally, the resulting matured rubber formulations were poured into glass molds and dried for 48 h at room temperature. The dried sheets were then peeled off the glass mold and cured at 100 °C for 2 h [238].

3.2.4. Theoretical compatibility analysis

The compatibility between the NR and both unmodified and modified lignin could be analyzed based on Gibb's free energy theory [239,240].

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (3.1)$$

In Equation 3.1, ΔG_m represents Gibbs free energy of mixing, ΔH_m is the enthalpy of mixing, T and ΔS_m represent absolute temperature and entropy of mixing.

As is apparent from Equation (3.1), ΔG_m value depends upon ΔH_m and ΔS_m , where a -ve value of ΔG_m indicate the polymeric blend has undergone intimate mixing. Further, mixing enthalpy and entropy values are dependent upon their interactions, molecular weights (M), and solubility parameters. The solubility parameter dictates the cohesive properties of a material. Although a small value of mixing entropy favors polymeric phase separation, many polymeric systems have reported miscibility even with small ΔS_m values. This was primarily due to ionic interactions, π - π complex formations, charge transfer, and hydrogen bonding amongst the blended polymeric moieties [239,241].

Also, higher randomness exhibited by low molecular weight polymers results in polymeric systems with higher entropy, thus, leading to a negative Gibbs free energy and intricate mixing [241]. In the case of higher molecular weight polymeric blends, the entropy of mixing is small, primarily due to the system's inability to undergo random mixing. Thus, its value is negligible for such systems [241].

The enthalpy of mixing and individual solubility parameters of the two components of a blend are related by Equation 3.2, where δ and ϕ represent the solubility parameter and volume fraction of individual components. Further, solubility parameters were calculated by Equation 3.3, where G_m , ρ , and M represent the group molar attraction constants, density, and molecular weight of the monomer of the polymeric entity [239,240].

$$\Delta H_m = (\delta_1 - \delta_2)^2 \phi_1 \phi_2 \quad (3.2)$$

$$\delta = \frac{\rho \sum G_m}{M} \quad (3.3)$$

3.2.5. Characterization of solution cast sheets

3.2.5.1. Mechanical properties

The mechanical properties of the NR biocomposite sheets were tested on AGS-X series universal testing machine (Shimadzu, Japan) utilizing a 500 N load cell. Samples were cut from the solution cast sheets with a dog bone-shaped die, with a gauge length of 27 cm, a width of 3.12 cm (ASTM D638 type V), while the thickness of the specimen was between 1 – 1.25 mm. Samples were tested at room temperature with at least five specimens from each sheet at 500 mm/min rate.

3.2.5.2. Thermo-mechanical analysis

To record the thermo-mechanical properties of NR-lignin sheets, dynamic mechanical analysis (DMA) test employing TA Instrument's DMA Q800 was carried out. Specimens with a dimension of 12 mm x 6.5 mm were prepared, and temperature sweep test at a constant frequency of 1 Hz in a tensile mode was carried out. Samples equilibrated at -90 °C using liquid nitrogen were ramped up to 30 °C at a rate of 3 °C/min, and the storage modulus and tan delta ($\tan \delta$) were recorded and reported.

To study the filler-filler and filler-elastomer interactions, strain sweep test was conducted using TA Instrument's DMA Q800. The prepared samples with constant dimensions of 12 mm x 6.5 mm were tested at a constant frequency of 10 Hz with strain varying from 0.1 to 10%. Samples equilibrated at room temperature (27 °C) were kept at isothermal conditions for 5 minutes, and their storage modulus and strain dependence were recorded.

3.2.5.3. Morphological study

To evaluate the dispersion of the unmodified and modified lignin in the NR biocomposites, cured sheets were cryo-fractured. Their SEM images were recorded using a Scanning Electron Microscope (Zeiss FESEM 1530) at an accelerating voltage of 10.00 kV. Since the samples were non-conductive, they were gold-coated using a sputter coater prior to scanning.

3.2.5.4. Thermal analysis

Thermogravimetric analysis (TGA) was conducted to analyze the effect of modification on the thermal degradation behavior of lignin specimen – unmodified, modified and its composites,

employing TGA 2 STAR system (Mettler Toledo, Switzerland). The specimen was dried overnight at 70°C to remove the residue methanol and moisture, and 20 mg each were loaded into the ceramic crucibles for analysis. The samples were heated from 30 to 600 °C at a temperature increment of 10 °C/min. An inert environment was maintained inside the furnace with a nitrogen flow rate of 30 ml/min.

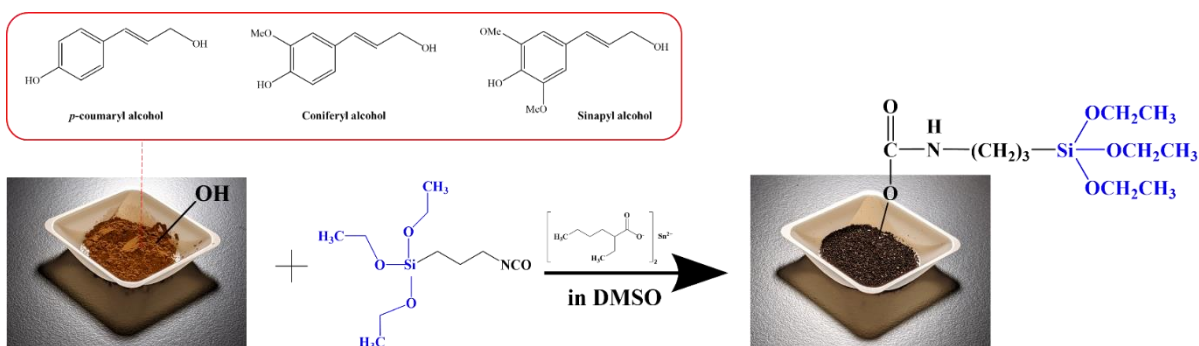
3.2.5.5. Water absorption testing

To evaluate the moisture absorption properties of the biocomposites, three strips each measuring 3 cm x 1 cm were cut from each cured sheet, and dried overnight at 80 °C in a convectional oven. The samples were then submerged in 300 mL of water, and weight change after removing excess surface water was monitored over 72 h at various time intervals.

3.3. Results and discussion

3.3.1. Silylation of lignin

The washing of lignin increased the pH from 2.2 (received samples) to 4.8. In order to improve the compatibility of lignin with a rubber matrix, it was chemically modified using a silylating agent in a solution. A dual functionalized modifying agent containing isocyanate and silane group was reacted with hydroxyl moiety of lignin to form urethane bond. The chemical reaction and plausible mechanism is shown in **Schematic 1**. The dissolution of lignin in DMSO exposed the –OH moieties of lignin to react with the electrophilic carbon of the isocyanate group of the silylating agent, ultimately forming a urethane bond.



Schematic 1. Proposed reaction mechanism

To identify the initial reaction parameters and confirm the reaction between lignin and TEPI, viscosity change was evaluated using rotational rheology analysis at incremental temperature steps. It was observed that the combination of lignin and TEPI in DMSO with the Tin(II) 2-ethyl hexanoate catalyst did not display any viscosity change for 4200 s at 80 °C. However, at 90 °C, a substantial increase in viscosity attributed to the reaction progression was recorded around 100 min mark (**Figure B 2 (Appendix B)**). In contrast, the reaction at 100 °C on the rheometer resulted in a solid product almost immediately indicating that the reaction could be too vigorous, and the viscosity could not be recorded. Thus, 90 °C was established as the optimal reaction temperature for this study.

For the concentration of the silylating agent, various molar ratios of TEPI with respect to lignin content, i.e., 0.25, 0.5, 1.0, and 2.0, were mixed, and the viscosity change was analyzed at 90 °C. Starting with a molar ratio of 1:0.25 (lignin: TEPI), no significant viscosity change was witnessed even after 1.5 h of reaction. An increase in concentrations of TEPI resulted in a substantial increase in viscosity, suggesting the occurrence of the reaction. As shown **Figure 17**, the use of 1:0.5 (lignin: TEPI) displayed a viscosity increase in 54 min.

Further increase in the concentration of the TEPI resulted in an appreciable reduction in the time required to increase the viscosity. At a molar ratio of 1:2 (-OH moiety of lignin: TEPI), the viscosity increase is noted after only 4.6 min. Moreover, the viscosity increase was dramatic. Reaction with molar ratio of 1:0.5 (-OH moiety of lignin:TEPI) utilized the least amount of TEPI, thus, it was the most economically feasible option in terms of sustainability. For the rubber composite study, lignin modified with a molar ratio 1:0.5 was employed. Overall, viscosity change indirectly provided information regarding the reaction time and temperature.

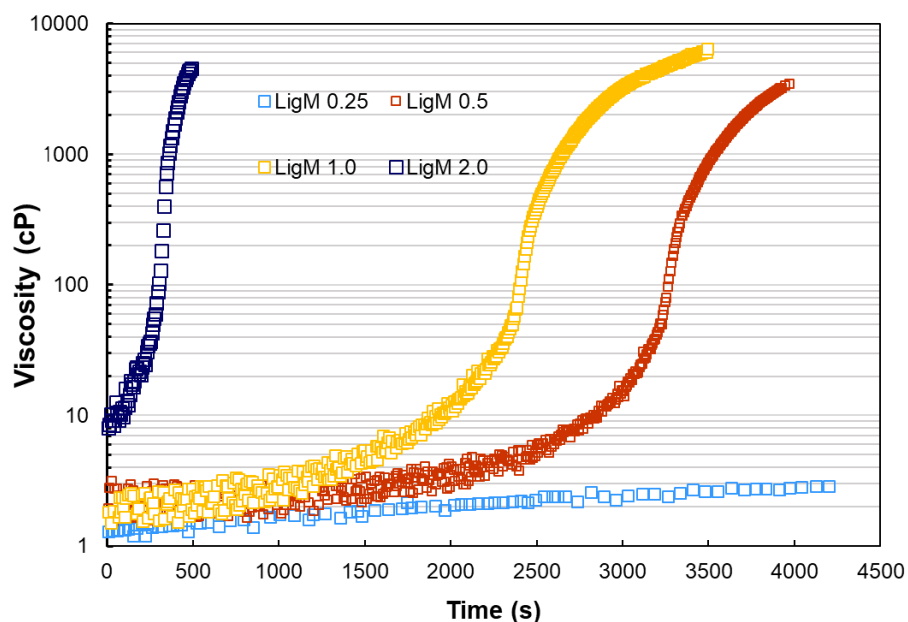


Figure 17. Variation of viscosity with varying concentration of silylating agent at 90 °C.

3.3.1.1. FTIR and NMR analysis

FTIR analysis of the baseline lignin and the modified lignin samples with various modification levels by varying the silylating agent's molar concentration are presented in **Figure 18**. The

peak at 3450 cm^{-1} was assigned to the stretching vibration of hydroxyl groups of lignin. Spectra at 2932 cm^{-1} and 2842 cm^{-1} correspond to the asymmetric and symmetric stretching vibration of C-H groups present in lignin molecules which are in coherence with the reported literature [242–246]. Peaks at 1690 cm^{-1} and 1031 cm^{-1} are associated with C=O (with urethane) and the in-plane deformation of C-H group of lignin [247].

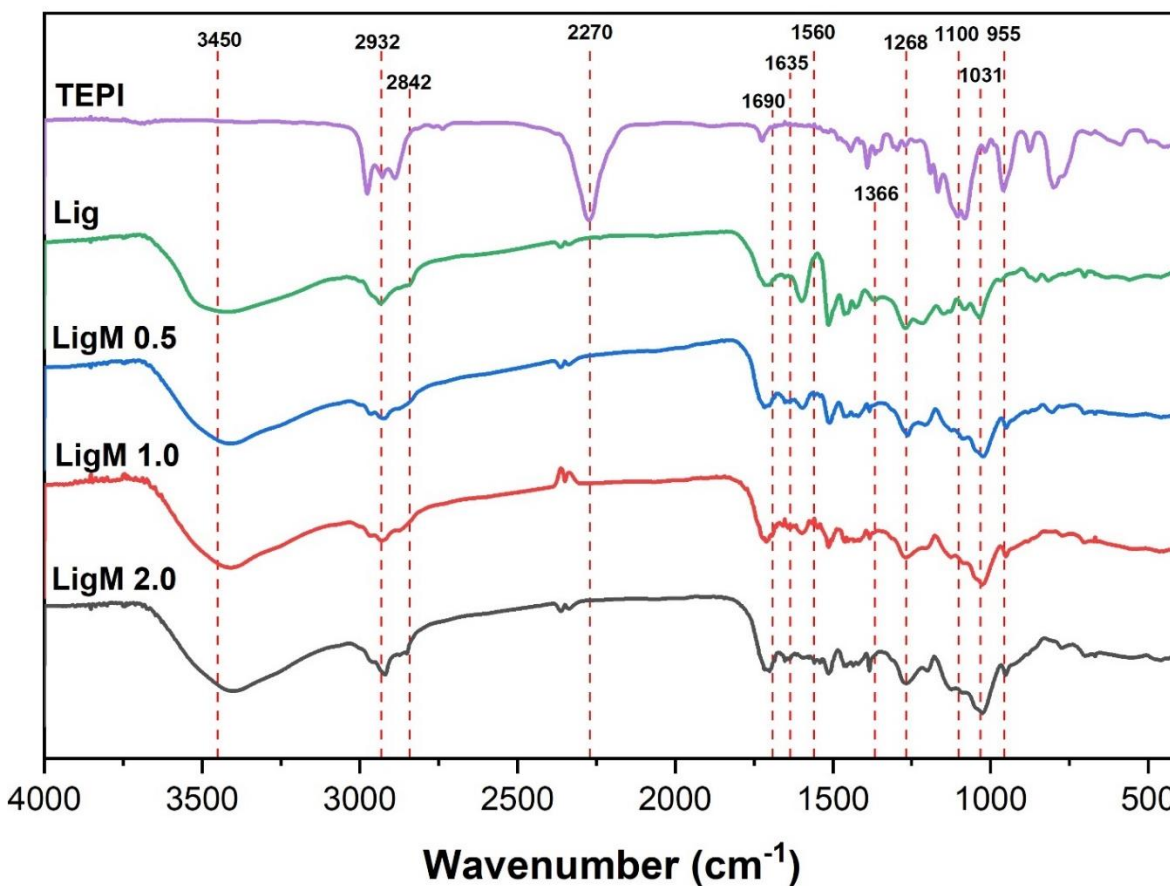


Figure 18. FTIR spectra for TEPI, unmodified lignin and modified lignin samples.

The absence of spectra at 2270 cm^{-1} in the modified lignin confirmed the complete consumption of -NCO reacting groups of TEPI by reacting with the hydroxyl groups of lignin, forming a urethane bond. The shifting of the peak at 3450 cm^{-1} also indicated the consumption

of -OH groups and the formation of -N-H groups. The generation of small shoulder peaks at 1635 cm^{-1} , 1560 cm^{-1} , 1100 cm^{-1} , and 955 cm^{-1} in the modified lignin represent the presence of C=C vibrations, N-H bending vibration from urethane functionality of modified lignin and symmetric and asymmetric stretching vibration of Si-O-C groups, respectively [245,248–252].

Furthermore, ^{13}C solid-state NMR analysis of the baseline lignin and silylated lignin was employed to confirm the bonding of TEPI to the kraft lignin, and results are displayed in **Figure 19**. ^{13}C NMR spectra of TEPI was provided by Sigma-Aldrich Co. LLC [253]. The chemical shifts at 23.5 ppm indicated the presence of C1 of the ethoxy groups of the propyltriethoxysilane pending group [254]. Chemical shift at 14.6 ppm, 23.5 ppm, and 40 ppm represent the three methylene group carbons (C2, C3 and C4) [255]. Also, characteristic peak at 56 ppm represented methoxy moieties, thus, blue region represented the presence of aliphatic carbon moieties. However, the existence of aromatic carbons was represented by the integration interval (160 – 100 ppm) [256], presented in **Figure 19** in the pink region. The most significant peaks were observed at 107 ppm and 148 ppm. A successful silylation was established by the presence of characteristic urethane signal (-NHCOO-) at 156.9 ppm [257], which was absent in the unmodified lignin was noted. The presence of a distinct peak at 175 ppm was in agreement with the findings of Serrano et al., associating the peaks to carbons with aliphatic and aromatic hydroxyl moieties [258]. With respect to the aromatic carbon peak at 148 ppm, a urethane signal (156.9 ppm) were recorded. With higher concentrations of TEPI, the urethane peak at 156.9 ppm displayed higher intensity (peak and width), accounting for a relative peak area of 0.0516 for LigM 0.5 sample and increasing to 0.2687 for LigM 2.0 with

respect to 148 ppm aromatic carbon peak. This relative increase in the area indicated higher TEPI incorporation with an increase in the TEPI loading.

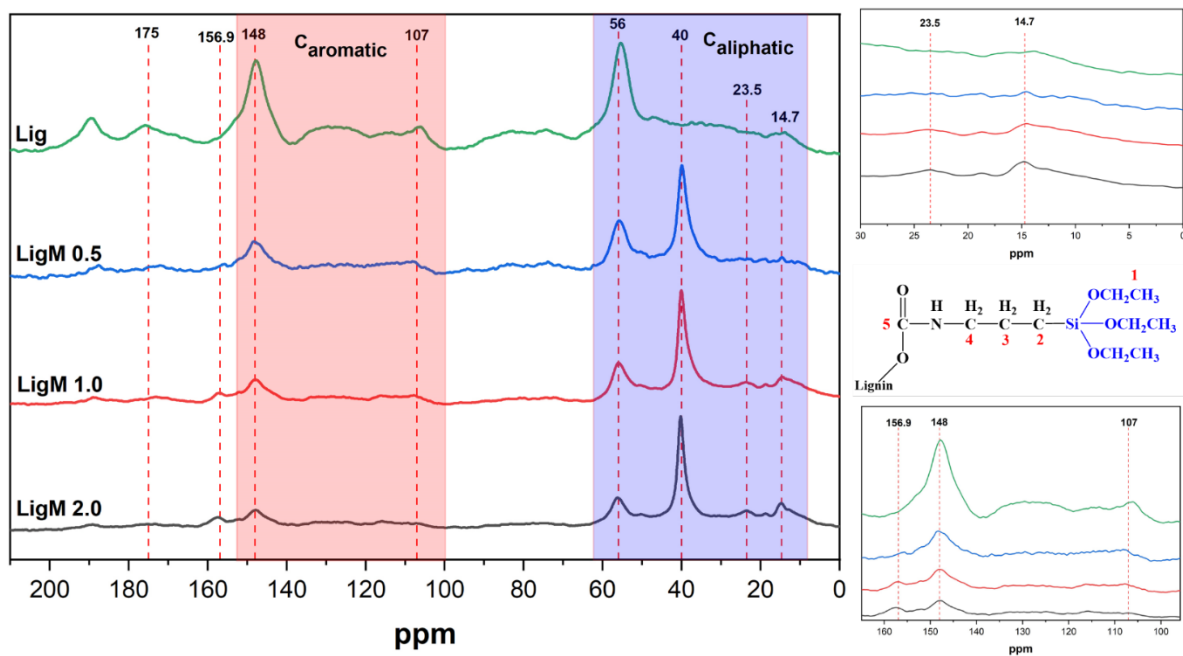


Figure 19. ^{13}C Solid Sate NMR spectra of the unmodified and modified lignin samples.

3.3.1.2. Wettability test

The wettability test was aimed at exploring the affinity of unmodified and modified lignin samples to solvents exhibiting opposite relative polarities. The study conducted in a 1:1 (v/v) ratio of water (relative polarity - 1.0) and toluene (relative polarity – 0.099), indicated that the majority of the unmodified lignin was in the water fraction represented as the region below the red line of the vial in **Figure 20**. Also, some fractions of the samples had settled at the bottom of the vial, in agreement with our expectation as a result of lignin's hydrophilicity. Moreover, a meniscus can be observed in all the samples carrying some lignin fractions due to water's surface tension and cohesive forces between the water and glass surface. No modified lignin

fractions were witnessed in the water fraction, thus signifying hydrophobicity. While the LigM 0.5 samples formed a stable layer at the toluene-water interface, the LigM 1.0 and LigM 2.0 samples were mildly dispersed in toluene with no sign of dispersion in the water phase. This could be due to an increase in hydrophobicity with a higher molar ratio of TEPI. Overall, the unmodified kraft lignin displayed more hydrophilicity than the modified lignin, which solely exhibited varying degrees of hydrophobicity depending on the modification level.

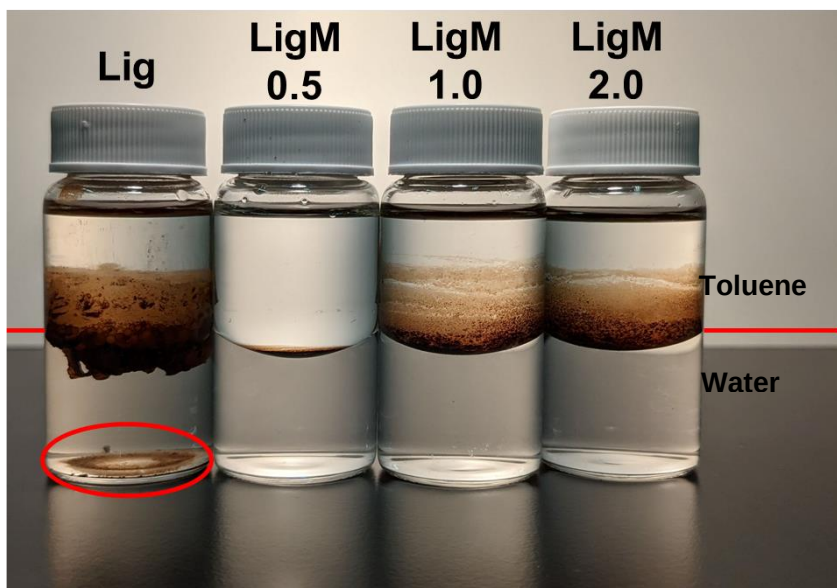


Figure 20. Wettability test of the unmodified and modified samples in 1:1 toluene water mixture.

3.3.2. Effect of silylated lignin on rubber composites

3.3.2.1. Compatibility analysis

As was discussed in the methods sections, a negative Gibbs free energy indicates intimate mixing of polymer systems. Since both NR and lignin possess high molecular weight, the

entropy contribution is considered to be negligible. Thus, Equation 3.1 reduced to the Gibbs free energy is determined by the enthalpy of mixing $\Delta G_m = \Delta H_m$ [239].

Group molar attraction constant values were calculated (NR = 1415, Lig = 8059.5, and LigM = 36043.5). The $\sum G_m$ values thus obtained, with ρ values (lignin: 1.20 g/cm³ and NR: 0.9775 g/cm³) and monomer molecular weights of NR and unmodified lignin of 68.12 g/mol, and 540.48 g/mol, respectively (as represented in **Schematic 1**), and modified lignin of 2024.7 g/mol are inserted in Equation 3.3 to calculate the individual solubility parameters. The solubility parameters (NR = 20.31, Lig = 15.21, and LigM = 18.16) were then plugged in Equation 3.2 to obtain the enthalpy of mixing values for individual lignin-NR composites. Thus, the Gibbs free energy for each individual component was obtained as presented in **Table B 2 (Appendix B)**. It was noted that the modified lignin samples invariably displayed substantially lower ΔG_m with the NR as compared to the unmodified lignin for the corresponding concentrations. This indicates that the modified lignin could form a better interaction with the NR, resulting in improved dispersion in the NR and hence better composite properties.

3.3.2.2. Mechanical properties

The rubber composites containing different amounts of modified and unmodified lignin are subjected to a tensile pull test at a constant rate. The effect of chemically modified lignin on mechanical properties of rubber composite is examined, and the ultimate tensile strength (UTS) and elongation at break (% E) are shown in **Figure 21**. UTS and % E of the baseline natural rubber (NR) material is found to be 23.6 MPa and 1017.7%. Although, an enhancement in UTS

was obtained with the addition of 2.5 wt.% modified or unmodified lignin, further increase in the loading of unmodified lignin led to reduction in UTS to ~15 MPa. This reduction in UTS is attributed to the polar functional moiety in lignin structure, which results in its poor dispersion in the hydrophobic rubber matrix [234].

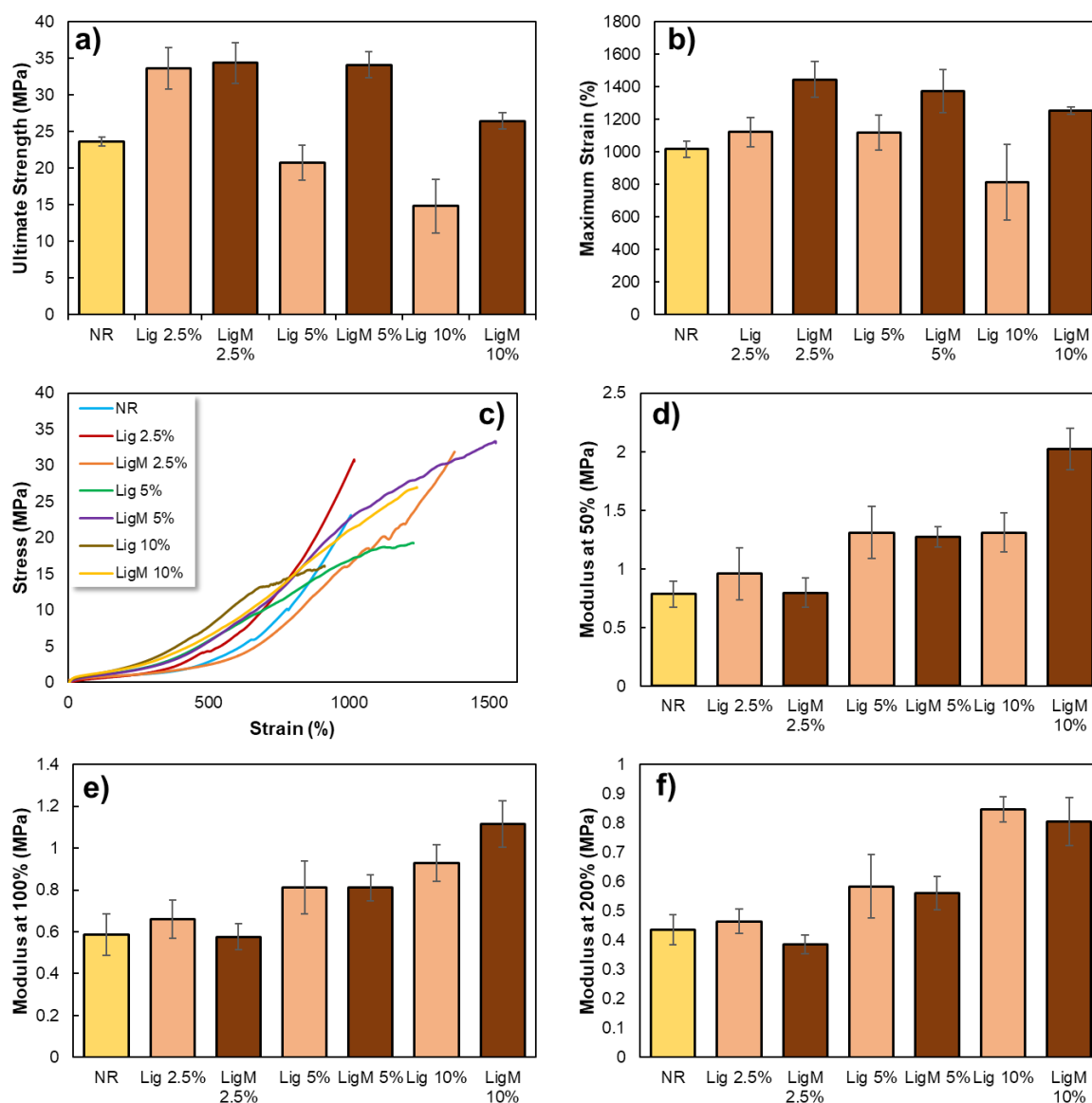


Figure 21. Tensile analysis of baseline NR and its composites with lignin and modified lignin at various concentrations, (a) ultimate strength, (b) elongation at break, (c) stress-strain plots, (d) elastic modulus at 50%, (e) elastic modulus at 100% and (f) elastic modulus at 200%.

On the contrary, the incorporation of 5 wt.% silylated lignin in the rubber matrix showed a significant improvement in UTS to ~34 MPa, i.e., a 44.4% increase compared to the unfilled NR sheet. Further increase in the content of the silylated lignin resulted in the reduction in the UTS attributed to the aggregation of lignin particles, thus, subsequently in a poor lignin-NR

interaction, leading to reduced tensile strength. It is noteworthy to mention that the composites containing 5 wt.% and 10 wt.% silylated lignin show improved UTS in comparison with their unmodified lignin counterparts. This confirms the better dispersibility of modified lignin samples imparting superior mechanical properties to the elastomeric matrices in agreement with the theoretical investigation of the compatibility of lignin with NR. Overall, the modified lignin samples exhibited enhanced tensile properties than the baseline NR or unmodified lignin composites.

The elongation at break was reduced with the addition of unmodified and modified lignin. This was ascribed to the reduced mobility of the elastomeric moieties due to the strong filler-filler interactions and incorporation of rigid lignin moiety in the matrix. Moreover, crosslinked chains cannot untangle, imparting an early breakage upon tensile pull, resulting in a decrease in the elongation at break. Similar results were observed in studies incorporating cellulose nanocrystals in elastomeric matrices, for instance, in nitrile rubber [237], styrene-butadiene rubber [259], natural rubber [233], and polychloroprene [260,261]. The reinforcing effect of cellulose nanocrystals, calcium carbonate, sago starch, and poly (α 1,3-glucan) fillers in natural rubber thin films are presented in **Appendix B (Table B 3-B 6)**.

Progressive increments in modulus values at 50%, 100% and 200% elongations were recorded and have been presented in **Figure 21**. With higher loadings of both the unmodified and modified lignin moieties in composites, an increase in the moduli (Modulus at 50%, 100%, and 200% elongation) were observed. This was partly due to incorporation of higher amounts of rigid filler in soft elastomeric matrix and also because of stronger filler-filler interactions,

as was also observed in strain sweep analysis (**Figure 23**). This was in agreement with the recorded observations on kraft lignin in polybutadiene elastomer [262]. The pristine and modified lignin may also affect the curing behavior, such as curing time and curing levels of the NR films similar to other fillers [263]. This is not covered in the present study.

3.3.2.3. Thermo-mechanical analysis

Dynamic mechanical analysis was carried out on the baseline NR sheets and their corresponding composites with lignin and silylated lignin samples. The effect of lignin on the storage modulus and $\tan \delta$ of rubber composites with a constant rise in temperature are displayed in **Figure 22**. It was witnessed that the concentration and type of lignin employed had a significant influence over its thermomechanical properties. The storage modulus (E') at low temperature indicates the glassy state of NR and its composites. The lignin-NR composites exhibited values higher than the baseline NR, indicative of better material stiffness of the composites compared to the baseline [264–266]. For the unmodified lignin-based samples, an approximate 72% improvement in the storage modulus values of Lig 2.5% and Lig 5% was recorded. The Lig 10% sample provided an almost 100 % increase in the storage modulus below glass transition temperature compared to the baseline natural rubber. LigM 5% sample recorded a 70% higher storage modulus while the other two concentrations of modified lignin-NR composites recorded about a 62% increase. This observation could be attributed to the rigidity of lignin's complex structure.

Since NR is the principal constituent in all composite samples, incorporating a low concentration of reinforcing agents (like lignin in this case) had minimal effect on its glass

transition temperature [267]. The sharp fall in storage modulus with increasing temperature indicated the relaxation of the long-crosslinked chains of NR, the midpoint of which indicated the value of glass transition temperature for the particular specimen [268–270]. Due to the cooperative motion of the elastomeric chains in the composite, dissipation of energy is induced at the temperature corresponding to the maximum value of $\tan \delta$ [271].

The intensity of $\tan \delta$ peak is a measure of the polymeric chain's mobility at the glass transition temperature [272–274]. The trend observed in **Figure 22 (b & d)** showed that increasing the lignin content from baseline NR to 2.5% samples and further to higher concentrations decreased $\tan \delta$ peak's intensity. The general understanding is that a higher $\tan \delta$ peak intensity indicates higher energy dissipation or high hysteresis and, thus, a more viscous behavior. In contrast, a lower $\tan \delta$ intensity meant a higher elastic and less viscous behavior [233]. Therefore, the observation here was in agreement with the expectation that the incorporation of lignin reduces energy dissipation.

NR and both unmodified and modified 2.5 wt.% composites exhibited a more viscous behavior. This could be attributed to the better motion of larger rubber chains over T_g as the constraint caused by the low concentration of unmodified and modified lignin composition was minimal [275,276]. The 5 and 10 wt.% samples exhibited a higher elastic and less viscous behavior than baseline NR. The Cole-Cole plot in which the loss modulus (E'') data are plotted as a function of storage modulus (E') is shown in **Figure 22 (e & f)**. It was noted that the curves resembled semi-circles, thus indicating the uniformity of the NR-lignin composites.

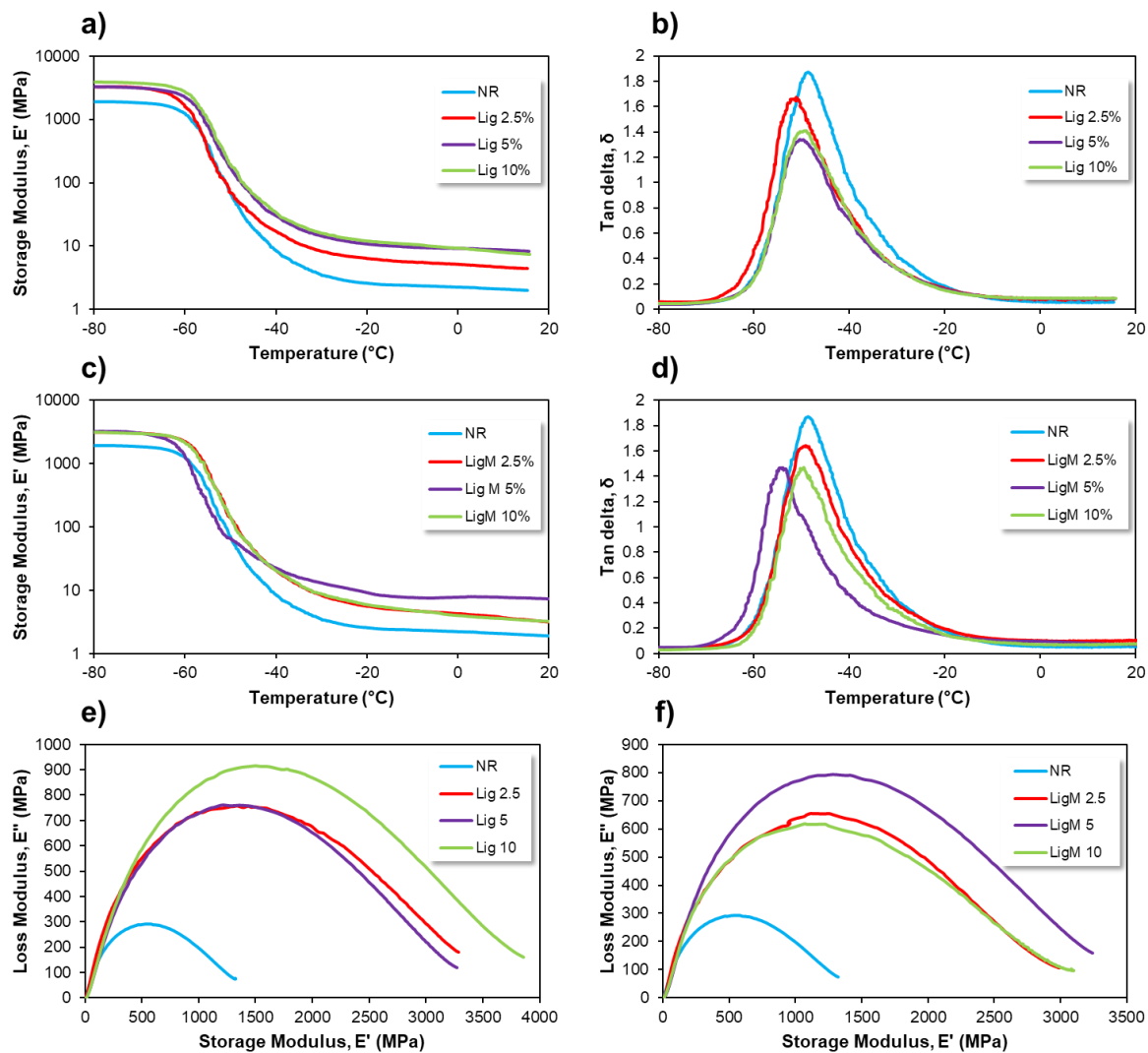


Figure 22. Dynamic Mechanical Analysis curves: (a,c) change in storage modulus, (b,d) $\tan \delta$ with respect to temperature and (e, f) cole-cole plot of composites.

Elastomeric phase interactions with lignin were studied employing strain sweep analysis, as presented in **Figure 23**. The storage modulus (E') of control system – unfilled NR showed negligible strain dependence. However, with the addition of lignin (both pristine and modified lignin), the storage modulus reduced with increasing strain rate. This was attributed to the breakage of filler-filler network with increasing strain, better referred as the Payne effect [277].

With increasing filler concentration, a greater reduction in storage modulus with increasing strain was recorded. As is evidenced by **Figure 23**, composites consisting of 2.5% and 5% lignin moieties displayed relatively lower Payne effect, in comparison to its higher lignin concentration composite counterparts irrespective of the modification. In contrast, the 10% lignin loaded composites displayed higher magnitude of Payne effect. Better dispersion or lesser instances of lignin agglomerate formations in the lightly filled elastomeric matrices as opposed to the 10%, indicated stronger rubber-lignin interactions and a weaker filler-filler interactions in agreement with the tensile results [278,279].

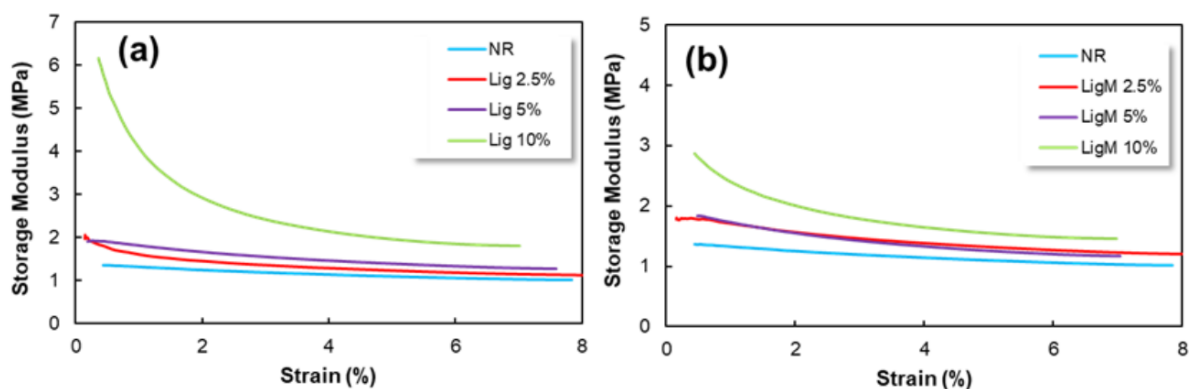


Figure 23. Strain sweep analysis: Dependence of storage modulus on dynamic strain: a) unmodified lignin-NR composites and b) modified lignin-NR composites.

3.3.3. Morphological studies

The dispersion of lignin and morphology of the NR – lignin systems are investigated using SEM, and results are presented in **Figure 24**. **Figure 24b** shows the micrograph of the cross-section (cryofractured) of the baseline NR sample. It is observed that the surface is planar with some cavities. The NR composite containing 5 wt.% unmodified and modified lignin showed good lignin dispersion. While there were some physical connections between the unmodified

lignin particles in the NR (**Figure 24d**), the modified lignin was shown as individualized particles with 0.5 – 1 μm particle size (**Figure 24c**).

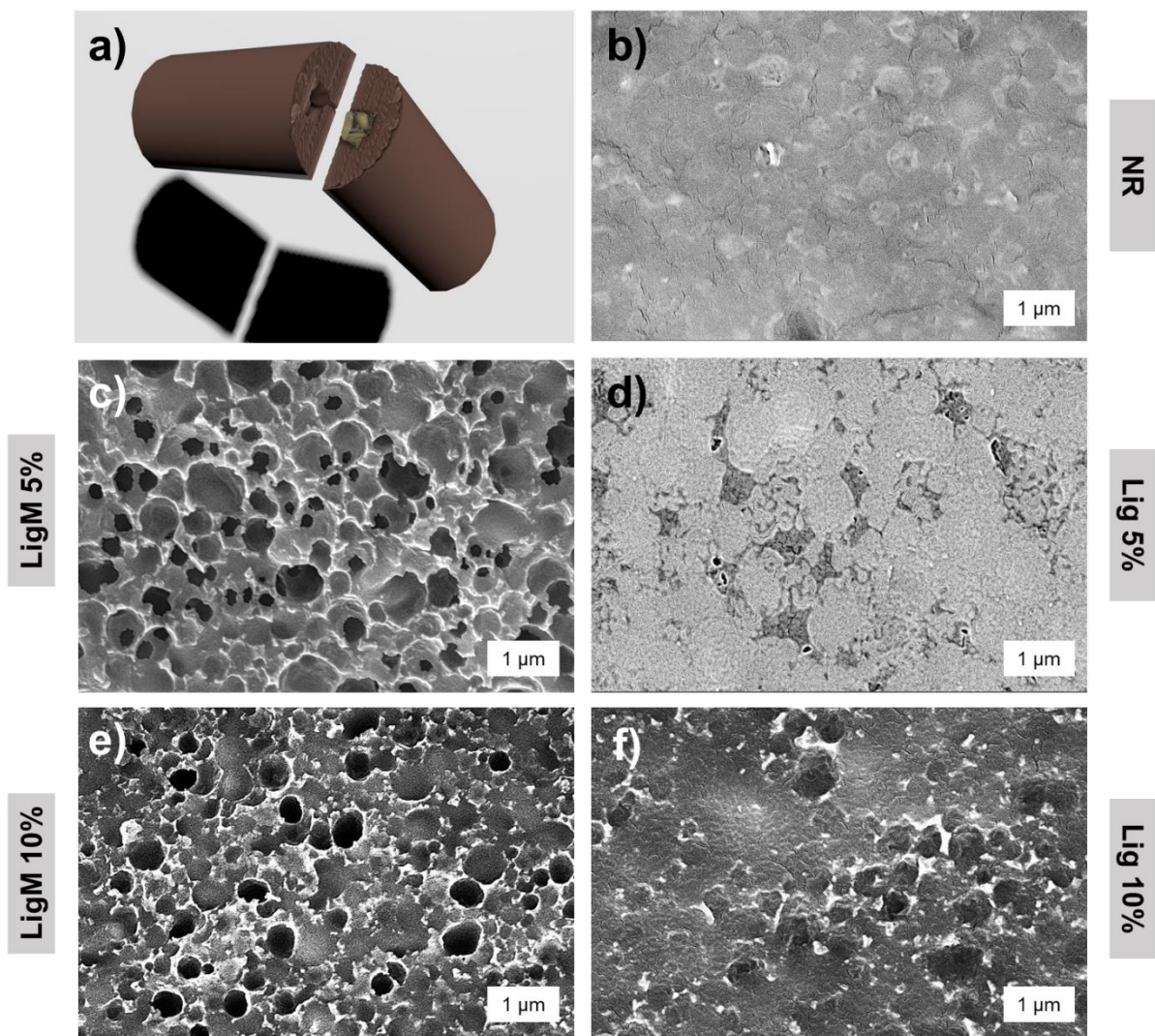


Figure 24. SEM images of baseline NR and its composites with lignin and modified lignin and cryofracture surface representation.

Moreover, the modified lignin particles are dispersed uniformly throughout the NR matrix. Visible cavities can be observed in **Figure 24c**, attributed to dislodged lignin particles during the cryofracturing process. This is similar to a bar of chocolate with nuts, whenever a piece is

broken, one half will have the nut; whereas the other half will have a cavity where the nut used to belong, as shown in **Figure 24a**. To further investigate, modified and unmodified 5% lignin - NR composite samples are leached out of their lignin fractions using hot alkali solution (KOH). Once the lignin leached out, the samples lost its brown color and were shown as a yellowish shade with a tint of brown. The SEM images of such leached samples (**Figure B 3 (a & b) (Appendix B)**) displayed porous morphology attributed to the empty space from the leached lignin. The dispersion of the porosity was in agreement with the observation shown in **Figure 24**. It can be noted that the modified samples were well dispersed, as can be seen in **Figure B 3a (Appendix B)** compared to the unmodified lignin composite as represented by **Figure B 3b (Appendix B)**. This pattern is repeated in the 10 wt% composites, with the modified lignin sample showing better dispersibility (**Figure 24e**) than the unmodified lignin sample (**Figure 24f**).

3.3.4. Water absorption

The water uptake of unmodified and modified lignin-based NR composites and the baseline NR are recorded, and results are shown in **Figure 25**. In the first 8 h, the unmodified lignin composites containing 2.5 wt%, 5 wt.% and 10 wt.% lignin surpassed the baseline NR by 7.6%, 12.9% and 58.6%, respectively. This could be attributed to the hydrophilicity of the unmodified lignin sample. The unmodified lignin is expected to associate with moisture through hydrogen-bonding [280]. Moreover, the rate of water absorption increases for the modified samples and baseline NR, flattened quicker (6 h) as opposed to the unmodified lignin-based composites. This is correlated to the hydrophobicity imparted by the modified samples to the composite.

The better dispersibility in the NR matrix could also have reduced the free volume of the NR for water uptake and retention. For instance, Ogunsona et al., reported that nanocellulose filler in acrylonitrile-butadiene rubber led to lesser free micro-voids for water sorption, thus, leading to a denser material and less water uptake [237]. Similarly, the better dispersed LigM 10 wt.% specimen displayed the least water absorption, as the well-dispersed hydrophobic modified lignin particles may have occupied more micro voids leaving behind less free volume for water to penetrate.

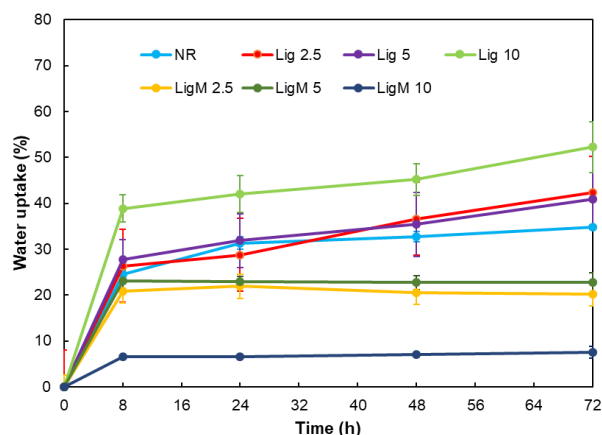


Figure 25. Water absorption analysis of unmodified and silylated lignin-natural rubber composites.

The molecular complexity and overall structural variation with changes in the production process as well as the source makes lignin a challenging material to carry out modification chemistries. While this work evaluated the potential of lignin in lightly cured rubber goods utilizing rubber latex, it did not evaluate the processability and dispersion in other common rubber processing operations by using batch mixers, roller mixers or extruders. Although this study only considered hydrophobic modification of lignin via silylation, it can be anticipated

that other chemistries could also be employed to enhance the compatibility of lignin with typically hydrophobic elastomers.

3.4. Summary of Chapter 3

In this work, lignin was successfully modified to various degrees by silylation. The modified kraft lignin was then incorporated in natural rubber through a solvent casting technique. The proposed reaction mechanism was confirmed using viscosity evaluation, spectroscopic analysis, and dispersibility studies. The wettability test confirmed the proposed substantial polarity change of the modified lignin compared to its unmodified counterparts. It was observed that the modified lignin based composite samples exhibited superior tensile properties than their unmodified counterparts. For example, 5 wt.% modified lignin sample imparted a 44.4% increase in the tensile strength of the baseline NR. The compatibility analysis, water uptake studies, and morphological analysis agreed with the polarity change of the lignin as a result of the modification providing good dispersibility of the modified lignin in the NR matrix compared to the unmodified lignin composites. Overall, the silylation modification of lignin was a straightforward process that enhanced the reinforcing capability of lignin in natural rubber. The property enhancement of NR with the modified lignin is expected to be translated into other rubber systems (e.g., styrene-butadiene rubbers).

Chapter 4 – Sustainable paper coating with enhanced barrier properties based on esterified lignin and PBAT blend³

4.1. Introduction

Petroleum sourced traditional polymers dominate the packing industry with their post-use disposal generating enormous amounts of plastic waste each year. To counter the plastic pollution, efforts are directed towards renewable and biodegradable polymeric materials, shifting their production from petroleum feedstock to renewably sourced materials [281]. Traditionally, the food packaging industry has benefited a lot from paper wraps and containers [282]. However, the use of paper in some food packaging applications is limited due to inherent challenges like poor water, oil barrier properties, and low wet tensile strength. The application of polymer coatings on cellulosic paper could effectively address such inherent limitations [1]. For instance, polyethylene coated paper is extensively used for hot beverage cups. Nevertheless, the use of synthetic polymers, such as poly(ethylene terephthalate), poly(ethylene), and poly(ethylene-co-vinyl alcohol), have led to significant environmental concerns associated with waste disposal, and in some cases safety (e.g., fluorocarbon) [1]. To mitigate the environmental damage caused by traditional plastics, the development of biodegradable, non-toxic, sustainable, and green polymeric packaging materials is receiving substantial attention [2,283–285]. Amongst the available biodegradable polymers, poly(butylene adipate-co-terephthalate) (PBAT) is a fossil fuel sourced biodegradable polymer that exhibits high flexibility and excellent moisture barrier [10]. This biodegradable polymer has

³ A version of this chapter has been published on peer-reviewed journal as a review article: Shorey, R., & Mekonnen, T. H. (2022). Sustainable paper coating with enhanced barrier properties based on esterified lignin and PBAT blend. *International Journal of Biological Macromolecules*, 209, 472–484. <https://doi.org/10.1016/J.IJBIOMAC.2022.04.037>

been used in various applications ranging from hygiene products to biomedical fields and packaging materials, such as trash bags, packaging films, and food containers [4,286–289]. Although biodegradability is a desirable attribute, its mass applicability is restricted by its high cost, poor mechanical and thermomechanical properties [3–5]. To address these limitations, selected co-blends (e.g., thermoplastic starch) and bio-fillers (e.g., cellulose, lignin, chitin) are incorporated in the PBAT to reduce the production cost and improve its properties, while maintaining its biodegradability [6–10].

Lignin is a natural polyphenolic macromolecule that constitutes 15% to 30% of the available biomass and is an appealing additive to PBAT and other sustainable polymers [290]. Despite the vast amounts of lignin produced each year by the paper and pulp industries and biorefineries, only small fraction is utilized in value-added applications, such as polymer additives, fabrication of surfactants, dispersants, and adhesives. The majority of the remaining technical lignin is utilized as a low-cost fuel [3]. With the growing interest in material sustainability, lignin valorization as a bio-filler or additive in biodegradable polymeric matrices is gaining significant attention. In previous works, lignin-loaded biopolymers such as PLA, PBAT, PEG, and PCL injection or compression molded composites have been reported [18]. The inherent limitations of lignin, such as thermal degradability, incompatibility with hydrophobic polymeric matrices, tendency to agglomerate in host matrices, and variability in its chemical structure with the feedstock sources limit its widescale applicability [291]. In order to counter these limitations, various lignin functionalization reactions have been reported in the literature [16–19,292,293].

The esterification of lignin with fatty acids has been shown to enhance its thermoplastic properties for material applications [294,295]. However, to the best of the authors' knowledge, there is no reported study on the effect of lignin on the barrier properties of paper coatings. In this work, the use of lignin as a co-blend additive of PBAT coating formulations was investigated with a focus on enhancing the barrier properties of paper coating in food packaging and wrapping applications. The study aimed at developing biodegradable alternatives to the traditional petroleum sourced waxes and polymeric film laminates in paper wrap and packaging industries. PBAT was used as the polymeric matrix in the coating formulations. Lignin was incorporated to make the resulting coating more economical and exhibit better mechanical properties. Furthermore, the inherent limitations of unmodified lignin specimen were addressed by esterifying it using an aliphatic acid chloride, palmitoyl chloride. The esterified lignin with long fatty acid chains was expected to exhibit hydrophobic characteristics, which could enhance its dispersibility in the nonpolar PBAT matrix. Consequently, the esterified lignin incorporated coatings were hypothesized to have enhanced barrier and thermo-mechanical properties. The effect of various concentrations of the incorporated lignin on the surface morphology, film-forming properties, tensile properties, water, oil, and oxygen barrier properties were studied and reported.

4.2. Materials and methods

4.2.1. Materials

The Amallin™ LPH Kraft Lignin with an average molecular weight of 6,500 g/mol and pH 2.2 was supplied by West Fraser Mills Ltd., Canada. Palmitoyl chloride (> 97%) was purchased

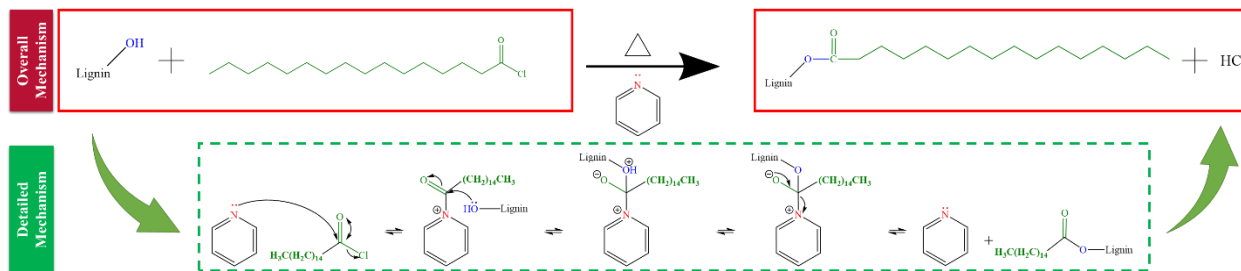
from TCI chemicals. Pyridine (99.8 %) and chloroform (99%) were obtained from Sigma-Aldrich. Kraft lignin was washed (pH 4.8), dried at 60 °C overnight (<3% moisture content) in a conventional oven, and stored in an airtight container until further use. Poly (butylene adipate-co-terephthalate) (PBAT) was purchased from T&T Industry Group Ltd, China. Semi-bleached Manilla paper substrate, 186.3 g/m² grammage, was sourced from a local stationery store (Ontario, Canada).

4.2.2. Methods

4.2.2.1. Esterification of kraft lignin with a fatty acid chloride

As demonstrated in **Schematic 2**, the modification of lignin was carried out by esterifying the –OH moieties of lignin with a long aliphatic chain containing acid chloride, palmitoyl chloride (PC) [296–298]. 10 wt. % kraft lignin was dispersed in pyridine and transferred to a round bottom flask. The flask was then immersed in silicone oil and placed on a hot plate equipped with a magnetic stirrer. The pyridine was used as a reaction medium and an acid scavenger of HCl generated as a condensation byproduct from the reaction. The dispersion was heated to 95 °C under constant agitation (400 rpm) and a measured volume of palmitoyl chloride was slowly added to the dispersion. The flask was fitted with a condenser and the reaction was allowed to run for 3 hours. Three palmitoyl chloride concentrations constituting 0.625 mL, 1.25 mL, 2.5 mL per gram of lignin were employed in the present study. The resulting products have been denoted as LigE1, LigE2, and LigE3 for the respective concentrations of palmitoyl chloride. The reaction products were subsequently precipitated with 0.1 M HCl, centrifuged (3,700 rpm for 7 min), and washed with water (three times). The complete removal of the unreacted

palmitoyl chloride was verified by the absence of its characteristic peaks in an infrared (IR) spectra of the esterified samples. The washed and esterified lignin was dried at 80 °C overnight and stored in glass vials for further characterization.



Schematic 2. Proposed reaction mechanism of kraft lignin with palmitoyl chloride.

4.2.2.2. Characterization of the esterified lignin samples

Infrared and NMR spectroscopy

The esterification reaction was characterized by Fourier transform infrared spectroscopy (*FTIR*) (Thermo Scientific Nicolett 6700) at ambient temperature. Samples for the IR analysis were prepared by mixing 2 mg of the powdered unmodified and esterified lignin with 200 mg KBr salt and pressing with a pellet die (7000 psi for 6 minutes). The *FTIR* spectra were recorded in the transmittance mode in the frequency range of 4000 to 500 cm^{-1} (128 scans).

Proton nuclear magnetic resonance ($^1\text{H-NMR}$) and carbon nuclear magnetic resonance ($^{13}\text{C-NMR}$) spectra were recorded for the control unmodified lignin and esterified lignin samples to study the induced chemical changes as a result of the reaction. Each sample weighing 2 mg was dissolved in 0.6 mL of deuterated dimethyl sulfoxide (DMSO-d_6) at room temperature

and securely sealed in 5 mm *NMR* analysis tubes. The spectra were recorded using a Bruker-SpectroSpin 500 MHz Ultra shield high-resolution *NMR* (Bruker Corporation, United States).

Thermogravimetric analysis

The effect of esterification on the thermal degradation behavior of the modified lignin samples was studied by employing a high-resolution TGA 2 STAR system (Mettler Toledo, Switzerland). The samples were dried overnight at 70 °C to remove the residual moisture and 20 mg of each sample were loaded into ceramic crucibles. The degradation analysis was carried out under an inert environment with a consistent nitrogen flow (30 mL/min) from 30 °C to 800 °C at a rate of 30 °C/min.

Zeta potential

The zeta potential (ζ -potential) of unmodified and esterified lignin samples dispersed in deionized water (0.01 wt.% concentration) was measured using a Zetasizer Nano ZS90 (Malvern Panalytical, UK). The recorded zeta potential values were an arithmetic mean of three consecutive measurements per sample.

4.2.2.3. Fabrication of lignin-PBAT based paper coatings

The coatings were formulated based on the mass ratio of lignin (unmodified and esterified (LigE2)) and PBAT, as illustrated in **Table 1**. The fabrication procedure was initiated with the solubilization of 10 wt.% PBAT in chloroform on a stir plate (400 rpm and 40 °C). Furthermore, 10 wt. % dispersion of the calculated respective lignin samples were separately dispersed in chloroform using a probe sonicator for 30 minutes. A measured quantity of the solubilized PBAT and lignin dispersion were mixed and sonicated for 10 minutes as per Table

1. The total solid concentration of the formulation was adjusted to 10 wt.% solids for all formulations by adding chloroform. Finally, a doctor blade was employed to apply a uniform coating formulation (20 μm dry thickness) on the paper substrate. The coated paper sheets were brown in color and were allowed to dry at room temperature for 24 h before testing. The coating weights of the various formulations are shown in **Table 1**.

Table 1. Composition of the coating film formulations.

Sample designation	Wt.% of lignin	Wt.% of modified lignin	Wt.% of PBAT	Wt.% of solids	Grammage of coating formulations (g/m²)
Uncoated paper	0	0	0	0	0 ^a
PBAT	0	0	100	10	13.10 $\pm$ 1.36 ^b
LigPBAT1090	10	0	90	10	12.75 $\pm$ 0.78 ^b
LigMPBAT1090	0	10	90	10	12.58 $\pm$ 2.24 ^b
LigPBAT2575	25	0	75	10	12.07 $\pm$ 0.51 ^b
LigMPBAT2575	0	25	75	10	13.95 $\pm$ 0.78 ^b
LigPBAT5050	50	0	50	10	14.81 $\pm$ 1.29 ^b
LigMPBAT5050	0	50	50	10	14.12 $\pm$ 0.51 ^b

Grammage value = mean $\pm$ standard deviation (n = 3), means with the same superscript letters within a column are not significantly different at P < 0.05 level.

4.2.2.4. Compatibility analysis

The compatibility and miscibility of lignin moieties in polymeric PBAT matrix were studied by employing a Gibbs free energy-based analysis [299,300]. The relation between Gibbs free energy (ΔG_m), the enthalpy of mixing (ΔH_m), the absolute temperature (T), and entropy of mixing (ΔS_m) is represented by Equation 4.1.

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (4.1)$$

A negative Gibbs free energy (ΔG_m) value signifies intricate mixing and compatibility between the polymeric blend components. The entropy of mixing is strongly dependent on the molecular weight of polymeric blends. A low molecular weight polymeric system will have high entropy, thus, translating to a negative value of ΔG_m and intricate mixing. On the contrary, a high molecular weight polymeric blend will not be able to undergo random mixing, thus, exhibiting a negligible entropy [301]. The enthalpy of mixing (ΔH_m) is correlated to the solubility parameter (δ) and volume fraction (ϕ) of the blend components by Equation 4.2.

$$\Delta H_m = (\delta_1 - \delta_2)^2 \phi_1 \phi_2 \quad (4.2)$$

Moreover, the solubility parameter for each component is related to the group molar attraction constant ($\sum G_m$), density (ρ) and molecular weight of the monomeric units (M), as represented in Equation 4.3 [299,302].

$$\delta = \frac{\rho \sum G_m}{M} \quad (4.3)$$

4.2.2.5. Characterization of coatings

Microscopic analysis

Optical microscopy was employed to investigate the dispersion of lignin domains (unmodified and esterified) in the PBAT matrix using BX53M polarizing optical microscope (Olympus, United States). The effect of esterification on the compatibility of the esterified samples with the polymeric matrix was recorded at 50x magnification.

The dispersibility of lignin particles and the uniformity of the lignin incorporated PBAT films on the paper surface were further studied using a Quanta FEG 250 scanning electron microscope (SEM) (FEI Company, United States). The effect of coating formulations on the surface morphology of the coated specimens was evaluated at 20 kV under vacuum.

Rheology

The viscoelastic properties of the formulated coating films were recorded employing an amplitude sweep test at 150 °C on a HAAKE Mars III rheometer (Thermo Scientific, United States). A parallel plate P20 CS L geometry with a gap of 0.2 mm between the plates was used at a frequency of 1 Hz. Before the rheometric measurements, the solution cast samples were dried overnight at 70 °C in a conventional oven.

Water contact angle (WCA)

The water contact angle (WCA) of unmodified and esterified lignin-based coating formulations was measured by utilizing a custom-built optical sessile drop system. A water droplet (5 µL) was dropped onto the specimen using a syringe pump and contact angle images were collected employing a camera (Basler scA 1000–30 fm) with high magnification and fixed focal length. The images were collected after 30 seconds at 24 °C to minimize the effect of evaporation, while enabling sufficient water contact time with the specimen. ImageJ, an image processing

program, was employed to measure the contact angle exhibited by the water droplets in contact with the coating specimens.

Cobb test: water and oil

In accordance with TAPPI T441, the coated samples were tested for water and oil absorptiveness. Three specimens were cut from separate coated sheets each having a surface area of about 10 cm². A custom-made cylinder with a depth of 1 ± 0.1 cm was filled with water. The specimen was weighed and subsequently clamped into the Cobb apparatus. The coated surface of the paper was exposed to the water for 2 minutes. The excess surface water was then removed by blotting with a paper towel and the specimen was weighed. The Cobb value was calculated using Equation 4.4.

$$Cobb\ value\ \left(\frac{g}{m^2}\right) = \frac{(m_2 - m_1) \times 10^4}{Area\ (cm^2)} \quad (4.4)$$

where m_1 and m_2 are the weight of the coated paper specimen before and post water contact, respectively. Similarly, the oil Cobb test was employed to test the oil absorption exhibited by the coated paper specimens. The coated surface was in contact with canola oil for one minute. Three measurements were recorded for each coating formulation and the mean of the recorded Cobb values have been presented.

Kit test

In compliance with TAPPI T559, the grease resistance of the coated paper specimens was evaluated using the Kit test. The test entailed exposing the coated samples to 12 different solutions (with different viscosity and surface tension). The solutions constituted of varying

concentrations of castor oil, n-heptane, and toluene. While the first Kit solution constituted entirely of castor oil, solution 12 was made up of 45 vol% of toluene and 55 vol% of n-heptane. Each specimen was exposed to the different solutions, with the highest number solution unable to leave any stain being reported as the Kit number for the specimen. Five replicates were tested for each formulation and the average is reported. Overall, the higher the Kit number was recorded, the better the grease resistance of the sample.

Mechanical properties – Dry and wet conditions

The tensile properties of the coated paper specimens were tested under dry and wet conditions on an AGS-X series universal testing machine (Shimadzu, Japan) with a 500 N load cell. Five rectangular strips (50 mm x 10 mm) of each formulation were cut from the coated sheets. The testing of samples was conducted at a strain rate of 100 mm/min, in accordance with ISO 1924-2/3.

Furthermore, the performance of the coated specimens under wet conditions was measured in accordance with ASTM D829-97. The samples were completely submerged in distilled water for 30 seconds. Subsequently, the specimens were blotted with a paper towel to remove the excess surface water and immediately tested for wet tensile strength.

Oxygen permeability

The oxygen permeability (OP) of the formulated specimens was tested utilizing a custom-made bubble flowmeter setup to distinguish between samples. It consisted of a two-chamber cartridge into which the coated samples were secured for testing. One end of the cartridge was connected to an oxygen source, thus, exposing the coated surface of the specimen to pure

oxygen. The other end was attached to a bubble flow meter and the pressure difference across the cartridge was maintained at 5 psi. To compute the flux, the time required by a bubble to travel 100 mL through the burette was recorded. The OP was then calculated by employing Equation 4.5:

$$OP = \left(\frac{V}{t.A} \right) \times \frac{l}{\Delta P} \quad (4.5)$$

Where $(V/(t.A))$ ($cc/m^2.day$) is the oxygen flux, l (m) was the thickness of coated paper specimens, and ΔP (Pa) is the pressure difference maintained across the specimen. Three specimens were tested for each coating formulation at ambient conditions and 50% RH.

4.2.2.6. Statistical analysis

A one-way ANOVA (analysis of variance) test was employed to evaluate the difference in means exhibited by the unmodified and modified lignin incorporated coated specimens. For a p value ≤ 0.05 , the difference was considered significant.

4.3. Results and discussions

4.3.1. Characterization of palmitoyl chloride esterified lignin

4.3.1.1. Structural analysis

The structural modifications incurred by the esterified lignin were characterized by employing infrared spectroscopy (*IR*) analysis. The infrared spectra of unmodified and esterified lignin samples, each illustrating different levels of modification are illustrated in **Figure 26**. The peak at 3450 cm^{-1} was assigned to the stretching vibration of hydroxyl groups (-OH) of lignin. An incremental reduction in the -OH moieties was observed in the esterified samples. This was

attributed to the use of higher concentrations of palmitoyl chloride (PC) resulting in a greater substitution of the hydroxyl moieties. Similar observations have been reported in the literature [303].

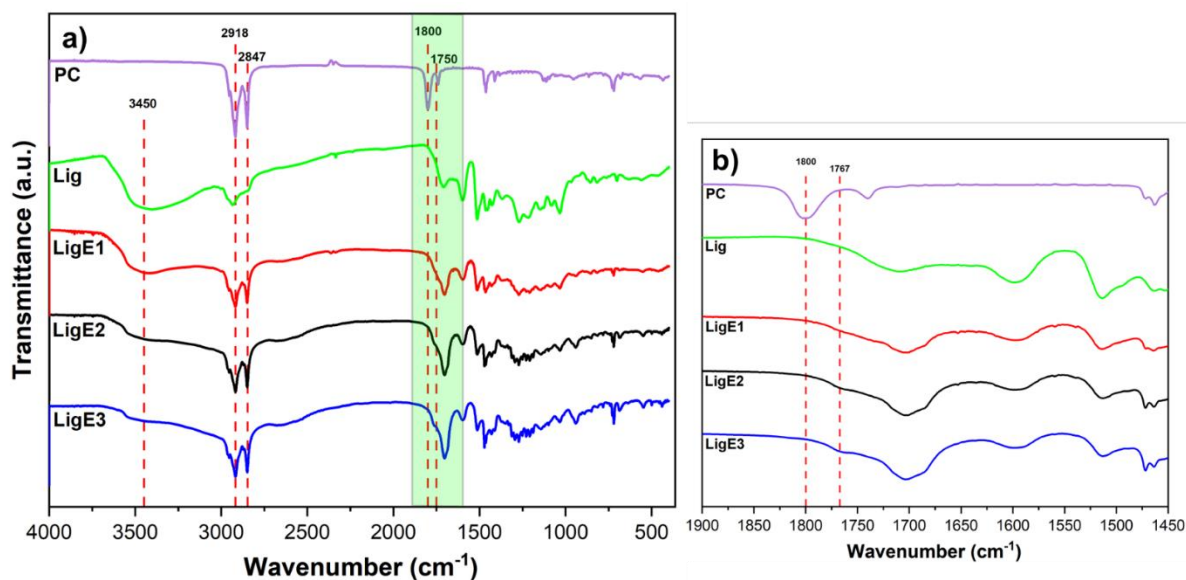


Figure 26. (a) IR spectra of palmitoyl chloride, control, and esterified lignin samples and, (b) zoomed-in view. The characteristic peaks at 2918 cm^{-1} and 2847 cm^{-1} correspond to $-\text{CH}_2$ and $-\text{CH}_3$ vibrations in palmitoyl chloride [297]. Their prominent presence in the esterified samples compared to the control lignin confirms the grafting of the aliphatic chain (**Figure 26**). As observed in **Figure 26b**, a strong transmittance peak at 1800 cm^{-1} corresponds to $-\text{COCl}$ stretching vibrations of the palmitoyl chloride. Its absence in the esterified lignin samples signified the complete removal of unreacted palmitoyl chloride with the downstream process [304]. Additional evidence of the successful esterification of the kraft lignin is the development of a new peak around 1767 cm^{-1} in the esterified samples, attributed to the presence of the ester

bond's carbonyl (C=O) group [303,305]. Overall, the *FTIR* spectra were in agreement with the proposed reaction mechanism illustrated in **Schematic 2**.

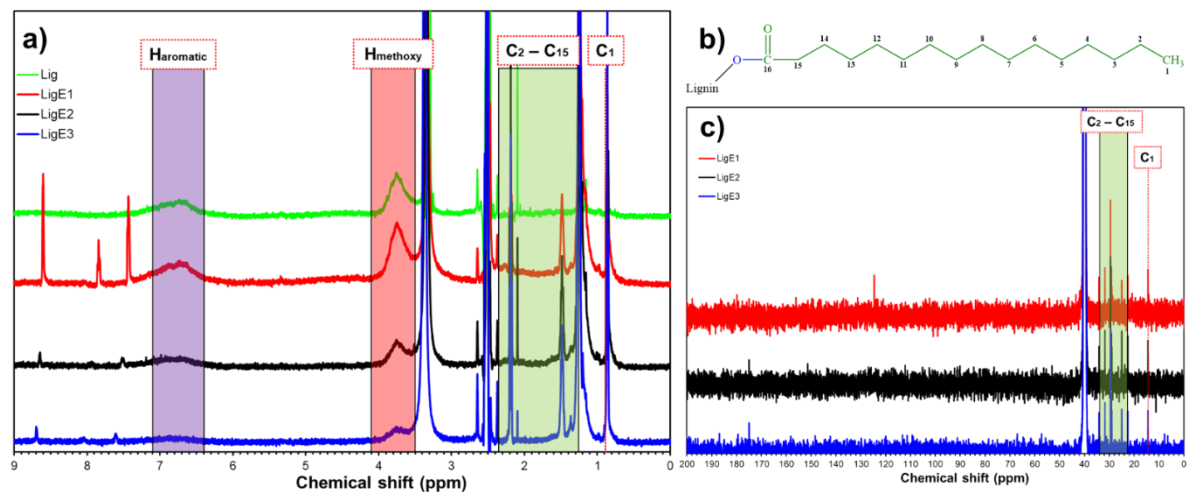


Figure 27. (a) *H*-NMR spectra of unmodified and esterified lignin specimens, (b) structural representation of esterified lignin, and (c) *C*-NMR spectra of unmodified and esterified lignin samples.

The signals noted between the regions of 7.10 to 6.40 ppm and 4.10 to 3.50 ppm corresponded to the aromatic and methoxy protons of the lignin [306]. The peak at 7.41 ppm represents vinyl protons existing on the carbon atoms besides the aromatic rings in cinnamaldehyde units and aromatic protons in benzaldehyde units [37]. Similar characteristic peaks, representing the presence of long aliphatic chains were also recorded in *C*-NMR spectra, as illustrated in **Figure 27c**. While the peak at 14.1 ppm represented the terminal methyl (–CH₃) group, the peaks between 33.9 and 22.6 were characteristics of the C2 to C15 methylene carbon atoms of the palmitic chain [308]. As shown in **Figure 26** and **Figure 27**, the sample LigE2 exhibited sufficient modification, thus, it was employed in coating formulations and henceforth has been referred to as LigM.

4.3.1.2. Thermal analysis and zeta potential

Thermogravimetric analysis was performed to study the changes imparted by the esterification on the thermal stability of the kraft lignin. The weight loss (Thermogravimetry or TG) and derivative weight loss (Derivative thermogravimetry or DTG) curves of the unmodified and esterified lignin samples were recorded from 30 to 800 °C as shown in **Figure 28a and 28b**, respectively.

Unmodified lignin exhibited superior thermal stability than its esterified counterparts. As is apparent in **Figure 28b**, rapid thermal degradation of the unmodified sample peaked at a temperature of around 401.5 °C. The same sample accounted for the highest solid residue of about 37.9 wt.% at 800 °C amongst the other esterified specimens. On the contrary, the esterified samples experienced an earlier degradation with an onset temperature of about 290 °C, while the more modified samples exhibited 5 to 7 °C higher values. For the esterified samples, two degradation peaks were recorded as shown in **Figure 28b**. The presence of these peaks was associated with the degradation of the lignin and the fatty acid chains, and this was a further evidence of the esterification of lignin. The lower thermal stability of the modified lignin and lesser residue was ascribed to the presence of long aliphatic chains, which consequently hindered the formation of H-bonds between the unreacted hydroxyl moieties [32,309]. Trinh et al. observed similar behavior while studying thermal degradation of TPS [310]. Moreover, palmitic acid is thermally less stable than lignin, as it displays severe degradation beyond 200 °C leaving behind minimal ash residue [311]. Thus, the successive reduction in the ash residue (**Figure 28a**) with an increase in the palmitoyl chloride

modification agent at higher temperature (> 400 °C) was related to the poor thermal stability of the palmitic acid grafted on the lignin structure.

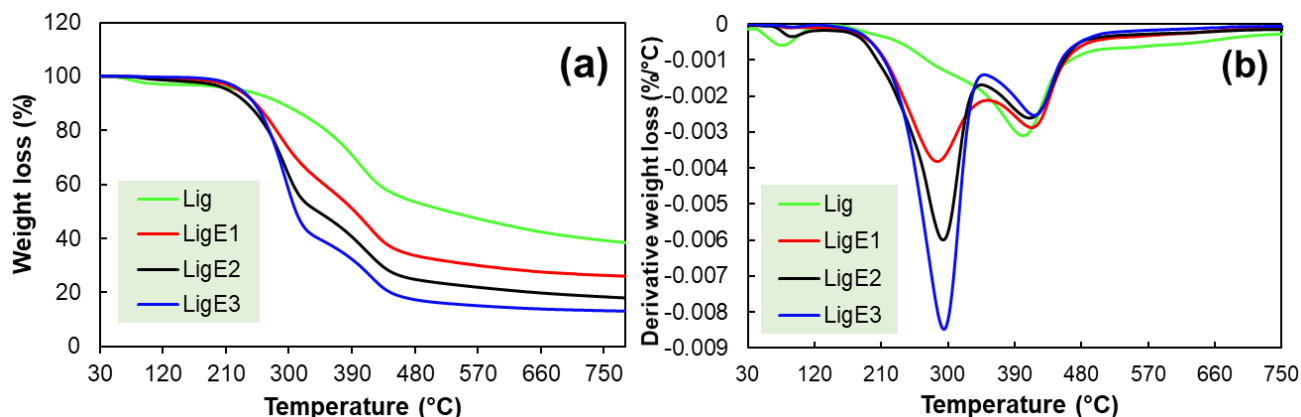


Figure 28. (a) TGA and, (b) DTG plots of unmodified and esterified lignin specimens.

The zeta potential of the unmodified and esterified lignin samples was recorded and is presented in **Table 2**.

Table 2. Zeta potential of lignin and esterified lignin samples.

Sample	ζ -potential (mV)
Lig	-55.26 ± 4.57^a
LigE1	-49.83 ± 1.21^a
LigE2	-45.30 ± 0.30^b
LigE3	-42.40 ± 0.69^c

Value = mean $\pm$ standard deviation (n = 3), means with the same superscript letters within a column are not significantly different at P < 0.05 level.

Unmodified lignin recorded a strong negative zeta potential (-55.26 mV). On the other hand, the esterified lignin samples displayed zeta potentials of -49.83, -45.30, and -42.40 mV,

respectively. The difference in the observed values were statistically significant, recording a p value < 0.05. This increase in the surface charge was credited to the carbonyl moieties of the esterified lignin, as shown in **Schematic 2**, which increased with the increase in the level of modification.

4.3.1.3. Theoretical compatibility and miscibility analysis

The interactions and compatibility between the polymeric coating constituents were studied based on their Gibbs free energy (ΔG_m). As discussed earlier, a negative ΔG_m signifies intimate mixing. The high molecular weight polymeric constituents render the entropy term (ΔS_m) negligible, thus making the Gibb's free energy (ΔG_m) equivalent to the enthalpy of mixing ΔH_m [32,300]. The group molar attraction constant ($\sum G_m$) values were obtained from the literature [32,299].

Furthermore, the solubility parameter for each constituent was calculated, substituting the respective ρ values (PBAT: 1.25 g/cm³ and lignin: 1.02 g/cm³) and the monomeric molecular weights in Equation 4.3. Putting the calculated values in Equation 4.2, the enthalpy of mixing and thus, the Gibbs free energy values for various lignin-PBAT composite sheet formulations were obtained. As evident from **Table C 6 (Appendix C)**, the modified lignin incorporated specimens exhibited lower Gibbs free energy values than their unmodified counterparts, the former signifying better compatibility and miscibility than the latter. This was attributed to the better dispersibility of the relatively nonpolar modified lignin moieties in the polymeric PBAT matrix, thus, in agreement with the finding in a previous work [32].

4.3.2. Characterization of coatings

4.3.2.1. Dispersion morphology

The compatibility and dispersibility of unmodified and esterified lignin in the PBAT matrix were further investigated with an optical microscope, and results are presented in **Figure 29 (a-e)**. As anticipated, the unmodified lignin particles agglomerated in the PBAT matrix resulting in unevenly distributed lignin moieties in the coating. This is primarily due to the inherent polarity difference between the unmodified lignin and the PBAT. On the contrary, the esterified lignin moieties were well-distributed in the polymeric PBAT phase, mainly due to the substitution of the lignin –OH moieties with the nonpolar aliphatic chains. Comparing formulations that constitute the highest fraction of lignin (LigPBAT5050) and esterified lignin (LigMPBAT5050), which was one to one weight ratio with PBAT, it was noted that the esterified lignin exhibited substantially improved dispersion and compatibility with the PBAT matrix as evidenced by the formation of a fine dispersion morphology, as shown in **Figure 29c**. The finely dispersed structure could improve reduce moisture penetration, oleophobicity, and grease resistance as noted from the Cobb and KIT tests. Similar morphology was recorded under a scanning electron microscope, as shown in **Figure 30h** and **Figure 30i**. To investigate the effect of the coating formulations on the surface morphology of the paper substrate, SEM images were collected and results are shown in **Figure 30**. As can be seen in **Figure 30a**, the surface of the uncoated paper substrate constitutes clearly visible uneven and intertwined cellulose fibers with micro-voids. The coating has filled some of the micro-voids between the fibers and formed a thin layer as seen in **Figure 30**.

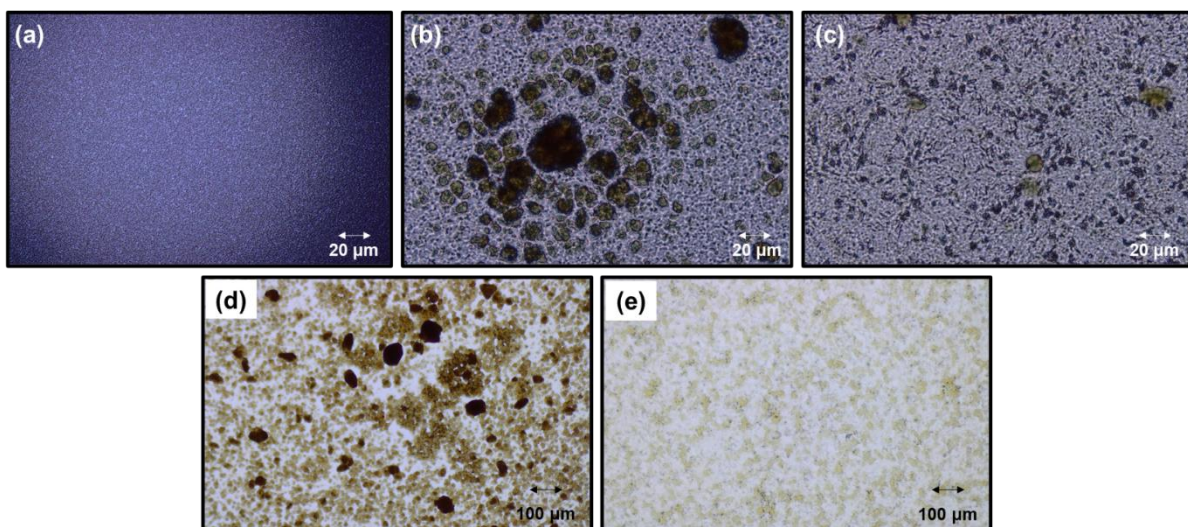


Figure 29. Optical micrographs: (a) PBAT, (b) LigPBAT1090, (c) LigMPBAT1090, (d) LigPBAT5050, and (e) LigMPBAT5050.

In the PBAT coated specimens (**Figure 30b and 30c**), a visible adhesion of the cellulosic fibers of paper can be witnessed. It was apparent from **Figure 30d** that the 10% lignin-loaded coatings did not cause severe agglomeration. As anticipated, the coating with 50% lignin (**Figure 30e and Figure 30f**) displayed considerable agglomeration of the unmodified lignin moieties. This is associated with the polarity difference between the unmodified lignin and the PBAT that led to poor compatibility [312,313]. On the contrary, the coating with a similar concentration of esterified lignin showed much better dispersion of the esterified lignin, as is apparent from the zoomed images in **Figure 30i**. This was due to the better dispersion of the hydrophobic esterified lignin in the non-polar PBAT. It is important to note that the finely dispersed structure previously observed in the LigMPBAT5050 specimen under an optical microscope was apparent in the SEM images (**Figure 30 (h and i)**) as well.

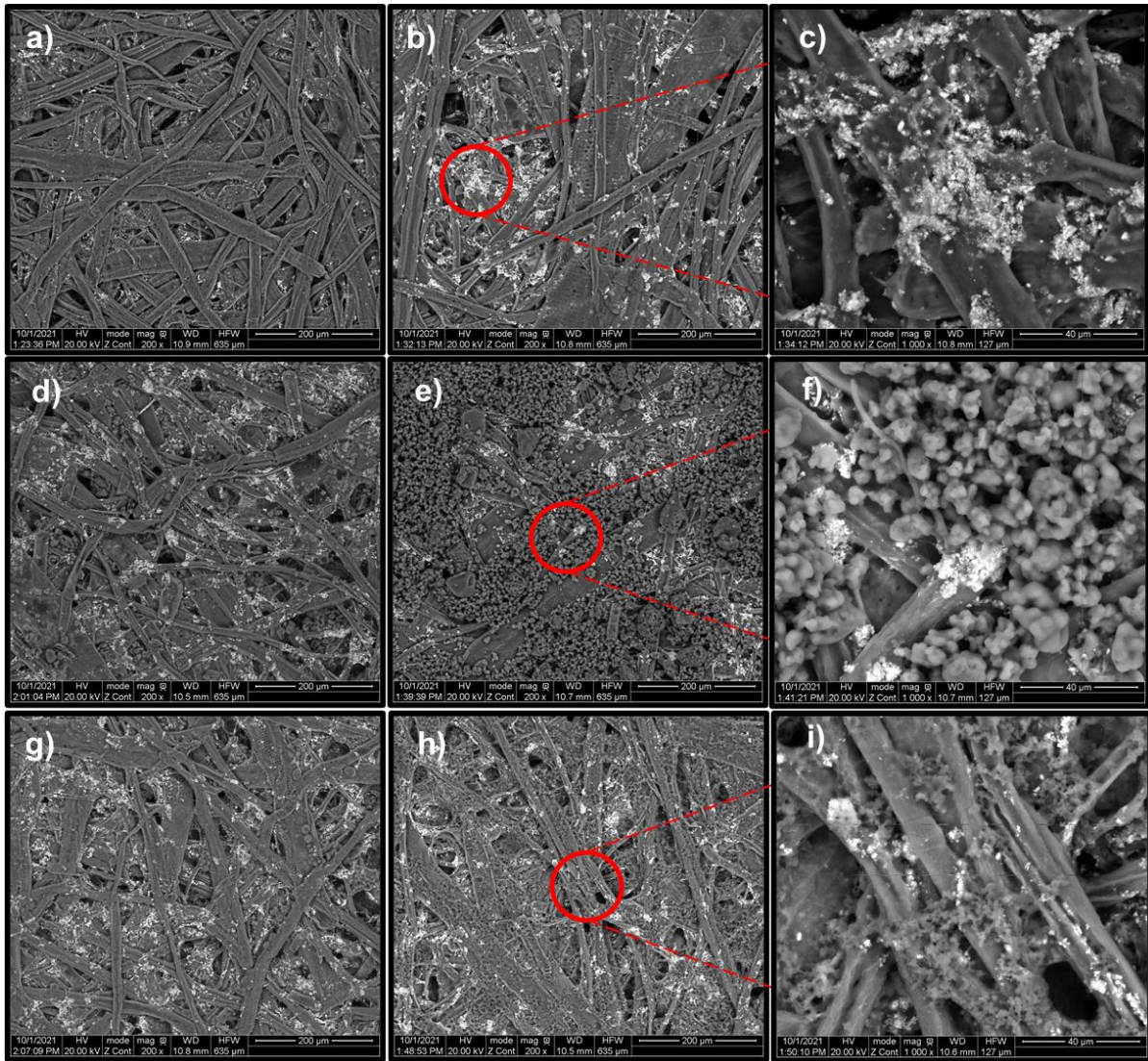


Figure 30. Scanning electron microscopy images of the surface of: (a) uncoated paper, (b) PBAT coated paper, (c) PBAT coated paper (zoomed-in view), (d) LigPBAT1090 coated paper, (e) LigPBAT5050 coated paper, (f) LigPBAT5050 coated paper (zoomed-in view), (g) LigMPBAT1090 coated paper, (h) LigMPBAT 5050 coated paper and, (i) LigMPBAT 5050 coated paper (zoomed-in view).

Observing the specimens with 60 μm coatings of LigPBAT5050 and LigMPBAT5050 (**Figure C 1 (Appendix C)**), a much more extensive covering of the cellulosic substrate than their 20 μm counterparts were recorded. The observed surface morphology for thicker coated specimens were in agreement with their thinner coated counterparts. Overall, these

observations were in line with the optical micrographs and justified the excellent water and lipid barrier property.

4.3.2.2. Rheology

An amplitude sweep test was carried out at 150 °C and a frequency of 1 Hz to determine the deformation behavior of the lignin-PBAT films in the linear viscoelastic region (LVE) [314]. **Figure 31** illustrates the effect of varying concentrations of incorporated lignin on the PBAT matrix on its viscoelastic properties with progressively increasing strain rate. The addition of lignin particles in the polymeric PBAT matrix increased the overall moduli. Overall, coating films with higher loading levels of lignin displayed greater stiffness compared to the baseline PBAT film.

The recorded amplitude sweep plots illustrate the storage (G') and loss (G'') moduli constant plateau in the LVE region. For the coating specimens with an equal ratio of lignin and PBAT (LigPBAT5050), the G' consistently exceeded the G'' in the LVE region. This behavior indicated that the formulation exhibit more elastic behavior than viscous. A study by Li et al. correlated such behaviors with the reinforcing effect of lignin in the polymeric matrices [315]. Moreover, this formulation imparted the specimen with the highest viscosity amongst all the coating formulations.

For the remainder of the samples, higher G'' values compared to G' values were recorded, indicating that the viscous component is the dominant phase at 150 °C employed for the study [314]. In accordance with the presence of smaller lignin domains in the PBAT matrix (as observed in the microscopic analysis), the samples exhibited lower viscosities.

The dynamic viscosity of the coating formulations has paramount importance in understanding the surface uniformity and flow behavior of the coating formulations. The characteristics of the suspended particles within a suspension, for instance, its shape, size, dispersion microstructure, and surface charge strongly dictate its rheological properties [316]. **Figure 31c** illustrates a positive correlation between the increasing concentration of lignin with an increase in the viscosity of the coating formulations, primarily due to the impact of lignin on the flow characteristics and restricted mobility it causes on the polymeric chains [317,318]. It is apparent that the lignin caused a shear-thinning behavior, which was more prominent at higher lignin-loading, such as the LigPBAT5050 and LigMPBAT5050 samples. Shear-thinning is a common occurrence in formulations in which solid-like materials (fillers) are incorporated in polymeric matrices [317,319,320]. Such shear-thinning behavior could be attributed to the breakdown of lignin aggregates due to the applied shear. This phenomenon is favorable in wet-coating fabrications [321,322].

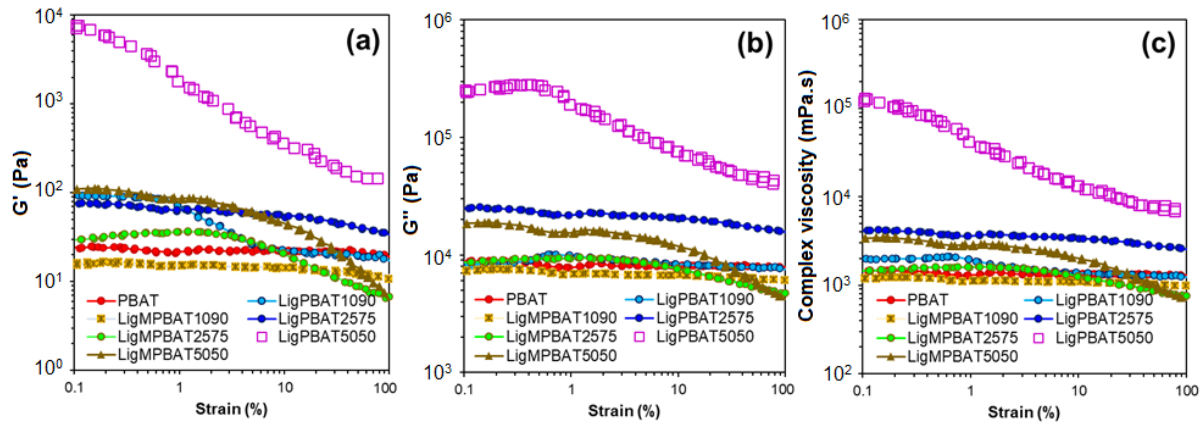


Figure 31. Viscoelastic properties of the lignin-PBAT films: (a) Storage modulus (G') vs. strain (%), (b) Loss modulus (G'') vs. strain (%) and (c) Complex viscosity vs. strain (%).

4.3.2.3. Water contact angle

The observations from the water contact angle test were used to elucidate the impact of the lignin esterification on the polarity of the fabricated composites. The smallest water contact angle was obtained for the uncoated paper sample, which was attributed to its relative hydrophilicity and porous structure. As illustrated in **Figure 32**, the addition of 50 wt.% esterified lignin to PBAT displayed a 72.6% increase in water contact angle compared to PBAT. On the contrary, the contact angle of the unmodified lignin-based composite film of similar lignin concentration showed an increase of 21.8% % in comparison to the baseline PBAT film. This increase in contact angle values over the baseline PBAT could be ascribed to change in surface morphology and superior hydrophobicity of the filled specimens [323,324]. A similar difference in contact angle was observed for films that contained lower concentrations of esterified and unmodified lignin samples. This behavior was in line with the proposed mechanism in **Schematic 2**. The decrease in hydrophilicity and increase in contact angle of the esterified lignin samples was associated with the substitution of hydroxyl moieties by the nonpolar long aliphatic chains from palmitoyl chloride [312,313,325]. The better dispersion of the highly nonpolar esterified lignin samples in the PBAT matrix could have also resulted in lesser free volume and better water repellence, as evidenced by **Figures 29 and Figure 30**. Despite the abundant –OH moieties on unmodified lignin’s structure, the composites displayed water contact angle greater than baseline PBAT film, which could be attributed to the complex aromatic rings of the lignin’s backbone structure. Moreover, undertaking an one way ANOVA test, signified the differences between the recorded water

contact angle values to be statistically significant ($p < 0.05$), as illustrated in **Table C 1 (Appendix C)**.

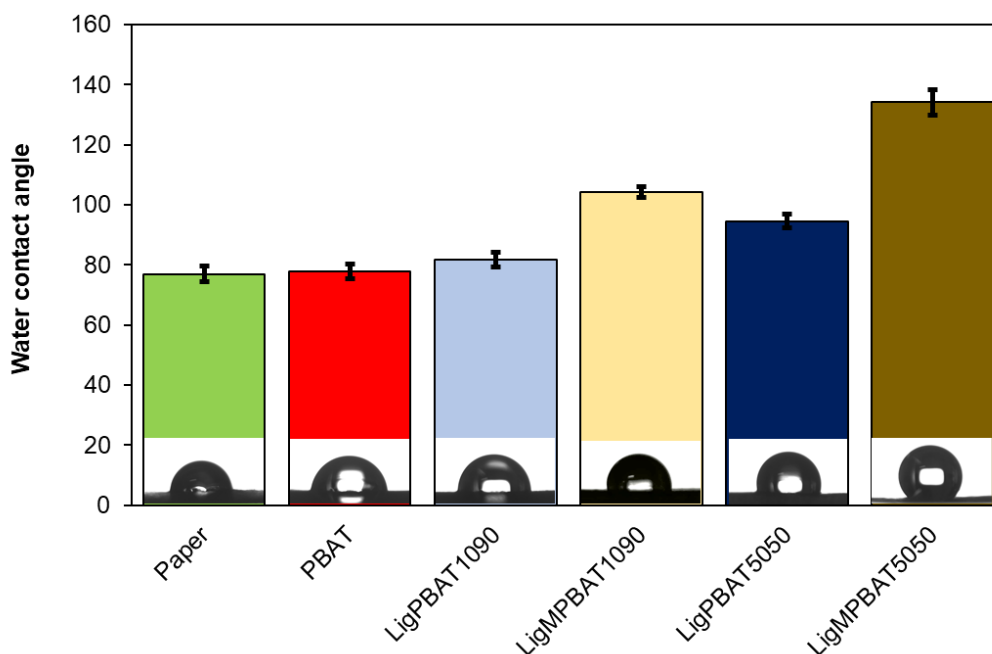


Figure 32. Water contact angle measurements for uncoated paper and coating formulations.

4.3.2.4. Cobb test: Water and oil

The water and oil Cobb test were carried out to investigate the effective hydrophobicity and oleophobicity imparted by the esterified lignin incorporation in the PBAT matrix to the respective coated paper sheets. As evidenced by **Figure 33a**, the PBAT coated sheets demonstrated a significant drop in water absorption in comparison to the base paper, with a p value ($0.000 < 0.05$), thus signifying significantly different recorded water cobb values. Further, the lignin (unmodified and modified) incorporated formulations presented statistically significantly differences in the observed water cobb values with all having $p < 0.05$ when compared with PBAT coated specimen, as illustrated in **Table C 2 (Appendix C)**. The extent

of water absorption has further reduced by approximately 40% with the addition of esterified lignin (LigMPBAT5050 (20 μm)). This could be attributed to its inherent hydrophobicity as a result of the presence of hydroxyl substituted long aliphatic chains, thus, in agreement with the water contact angle observations [326]. Moreover, the superior dispersion and uniformity exhibited by the esterified lignin-coated sheets (**Figure 29**) could reduce moisture penetration properties. In comparison, the unmodified lignin-coated specimens were ineffective in resisting water absorption, beyond 10 wt. % lignin concentration. This could be due to the abundance of polar hydroxyl moieties on lignin's structure. As illustrated in **Figure 33b**, an increase in the coating thickness decreased the water absorption significantly. The best water resistance was exhibited by 50% esterified lignin 60 μm coating (thickest coating layer), recording a water Cobb value of 4.9 g/m². **Figure 33 (c and d)** shows the oil Cobb test result, which was employed to test the oil absorption properties of the formulated paper coatings. As expected, an inverse relationship between the oil Cobb values and the oil barrier properties were noted in the studied specimens. Surely, the oil Cobb value for PBAT coating showed a 35.3% decrease in oil absorption, thus undoubtedly signifying its oil resistance with respect to the base paper. However, with an increase in the unmodified lignin concentration in the coating, the oil resistance exhibited a decrease. This was attributed to the agglomeration of the unmodified lignin moieties. On the contrary, esterified lignin comprising specimens exhibited superior oil barrier properties, the highest lipophobicity being exhibited by the samples loaded in excess of 10 wt.% esterified specimens. Moreover, an increase in the coating thickness of the specimen recorded a further decrease in its oil absorption. As expected, the maximum

lipophobicity was noted by the 60 μm thick coating composed of 50% esterified lignin-PBAT composite. Overall, these results were in-line with the lipophobicity recorded by the Kit test.

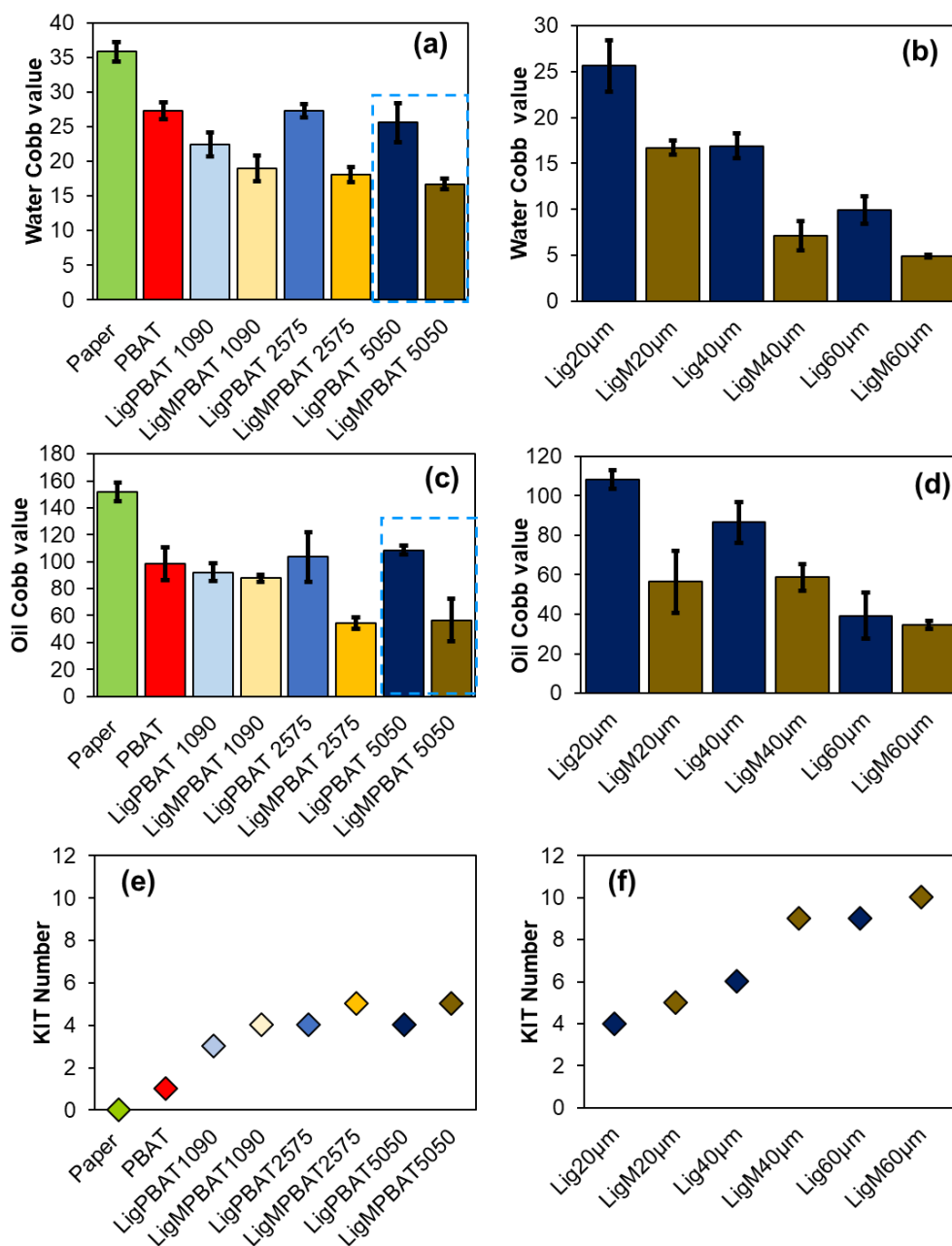


Figure 33. (a) Water Cobb test (20 μm thick-coated samples), (b) Water Cobb test (varied thickness samples of LigPBAT5050 and LigMPBAT5050), (c) Oil Cobb test (20 μm thick-coated samples), (d) Oil Cobb test (varied thickness samples of LigPBAT5050 and LigMPBAT5050), and (e) Kit test.

As recorded in **Table C 3 (Appendix C)**, most of the oil cobb values observed statistically significant difference ($p < 0.05$), with the exception of 10% lignin loaded formulation coated sheet. This could be attributed to minimal oleophobicity imparted by 10 wt.% loaded lignin moieties.

4.3.2.5. Kit test

To examine the grease resistance of the coated papers, a Kit test was performed. As illustrated by **Figure 33e**, the uncoated paper sheet failed to resist the percolation of Kit solution 1, thus, reporting the lowest Kit number. This was attributed to the irregular and highly porous surface morphology of the uncoated paper sheet. With the application of any of the coating on the base paper, the Kit number increased. This could be attributed to the formation of a tortuous path for the oil molecules. It was observed that for a constant thickness coating, esterified lignin-based samples displayed a slightly better grease resistance than their unmodified counterparts. It is essential to note that at 20 μm thickness, esterified lignin-PBAT coatings with lignin concentrations of 25 wt. % and 50 wt. % observed the highest Kit value (i.e. Kit number 5). This could be attributed to the remarkable dispersibility of the modified lignin and the resulting uniformity achieved in the paper coatings. The oleophobicity observed in thicker coating systems is attributed to enhanced coverage of the voids between the cellulose fibers in the paper substrate. Overall, the Kit numbers obtained for the various specimens were in agreement with the oil Cobb values.

4.3.2.6. Oxygen barrier properties

The barrier properties of a coating material against penetrants differ based on their interactions with the material.

While interactions with penetrants such as water vapor are highly dictated by the layer composition and its interactions with water molecules, penetrants such as lipids and oxygen are extremely responsive to the deformities and voids in the coating layer [327,328]. Oxygen permeability (*OP*) is one of the most significant packaging material properties that determine a material's potential widescale applicability. It has been widely witnessed that excessive oxygen contact is one of the main reasons for food spoilage, primarily owing to the ineffective oxygen barrier of the packaging materials. The barrier properties of the coated paper with the various PBAT – lignin formulations against oxygen permeation were tested and the results presented (**Figure 34**).

As noted from **Figure 34**, an increase in the oxygen barrier properties with the application of coatings was observed, recording a 22.1% reduction in the *OP* with the application of a 20 μm PBAT coat over the base uncoated paper sheet. This was attributed to the physical covering of micro-voids between the cellulosic fibers in the paper substrate and the semi-crystallinity of PBAT, as witnessed in **Figure 30b** and **Figure 30c**. Moreover, at higher lignin loading concentrations, the oxygen barrier properties of the specimens further improved over the pristine PBAT coated samples. This was attributed to the nonpolarity of the PBAT matrix imparting an easier passage to the nonpolar oxygen molecules [329]. Moreover, the lignin is expected to fill the free volume of the PBAT polymer, irrespective of the polarity. The lower *OP* recorded by the unmodified samples could be attributed to the presence of polar lignin

moieties interacting with the nonpolar oxygen molecules, thus, hindering the diffusion. Moreover, the better coating uniformity exhibited by higher loaded specimens imparted them with a better oxygen barrier [330].

Additionally, the esterified lignin incorporated specimens recorded even better barrier properties against oxygen. As illustrated by **Table C 4 (Appendix C)**, the differences in oxygen permeability values of the tested specimens were statistically significant ($p < 0.05$).

The 50 wt.% esterified lignin loaded specimen recorded the lowest oxygen permeability value of $1.13 \text{ cm}^3 \cdot \text{m}/(\text{m}^2 \cdot \text{day} \cdot \text{Pa})$, which was a 55.2% reduction over its unmodified counterpart. This could be resultant of superior dispersibility of the esterified specimens, as witnessed in **Figure 29, Figure 30h and, Figure 30i**, which provided optimal free volume filling to block the permeation of oxygen.

Furthermore, a 7.1% (10% lignin loading) and 29.8% (25% lignin loading) improvement in oxygen barrier properties with respect to the unmodified coatings were noted at lower concentrations of the esterified lignin coatings, as shown in **Figure 34**.

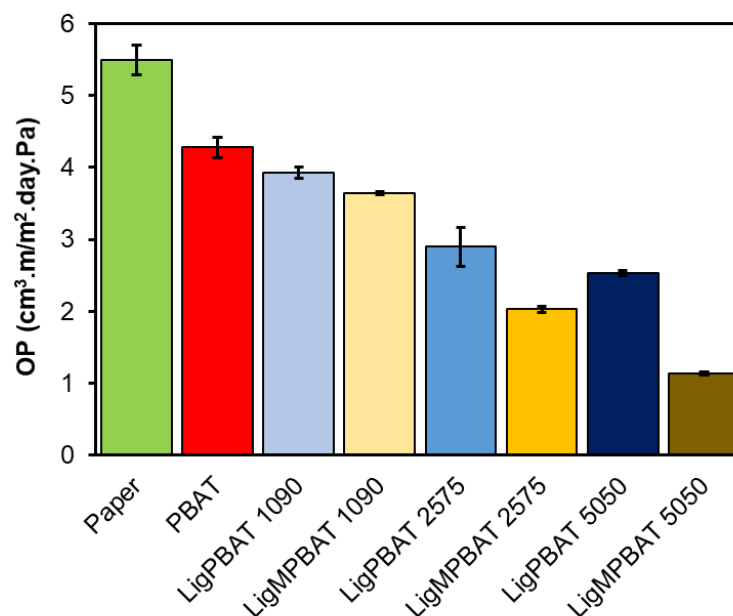


Figure 34. Oxygen Permeability (OP) values of the coating formulations.

4.3.2.7. Mechanical properties: Dry and wet conditions

To evaluate the effect of coating formulations on the tensile properties of the base paper and to investigate its physical integrity under dry and wet conditions, tensile testing of the coated films was carried out. As is evident from **Figure 35**, the tensile strength of coated paper sheets is highly dependent on the base paper [331] as a thin coating layer (20 μm) was employed in this study. Due to the adhesive nature of the polymeric coatings, they can have an additive effect on the tensile strength of the base paper. The enhanced strength can be more apparent under wet conditions where the base paper begins to disintegrate, primarily due to the disruption of non-bonded and hydrophilic cellulose fibers present in the base paper.

As illustrated in **Figure 35a**, the sample with 10 wt.% esterified lignin exhibited the highest tensile strength (60.7 MPa), which was a 24% improvement over its 10 wt.% unmodified lignin

counterpart. It is important to highlight that this was approximately 33% improvement compared to the pristine PBAT coated or uncoated paper substrate. This could be due to the good dispersibility of the esterified lignin in the PBAT matrix, as was observed in **Figure 30**. Further addition of lignin did not significantly impact the tensile properties of the paper substrate. While the tensile strength witnessed significant improvement at 10 wt.% lignin concentration, the elongation at break of coated paper sheets remained fairly constant, exhibiting values around 5% elongation. Shankar et al. reported a significant increase in the tensile strength of PBAT coated kraft paper [332]. Similar enhancement in tensile properties of paperboard coated with PLA were observed by Rhim et al. [333]. Contrary to tensile properties under dry conditions, the incorporation of esterified lignin samples into the PBAT matrix significantly improved the tensile strength of the coated specimen compared to the control paper substrate.

While the tensile strength of uncoated paper reported a substantial decrease by 87.3%, the incorporation of 25 wt.% esterified lignin in the formulation displayed a milder reduction of 54.4% from the dry specimens. These reductions were due to the disintegration of cellulosic fibers present in the uncoated paper upon submersion in water [334]. Interestingly, post water submersion, the baseline PBAT coated paper sheet exhibited a tensile strength improvement of 74.1% over the base paper. An increase in wet tensile strength with lignin concentration (both unmodified and esterified) was recorded. While the wet tensile strength of samples coated with the unmodified lignin-based formulations progressively increased from 11 MPa to 17.2 MPa with the increase in lignin concentration from 10% to 50%, the esterified samples

remained fairly constant around 19 to 20 MPa for all the formulations. Comparing the tensile strength of the PBAT coated paper versus the esterified lignin – PBAT coated paper substrate, a tensile strength improvement of up to 97% was exhibited by the esterified lignin incorporated counterpart.

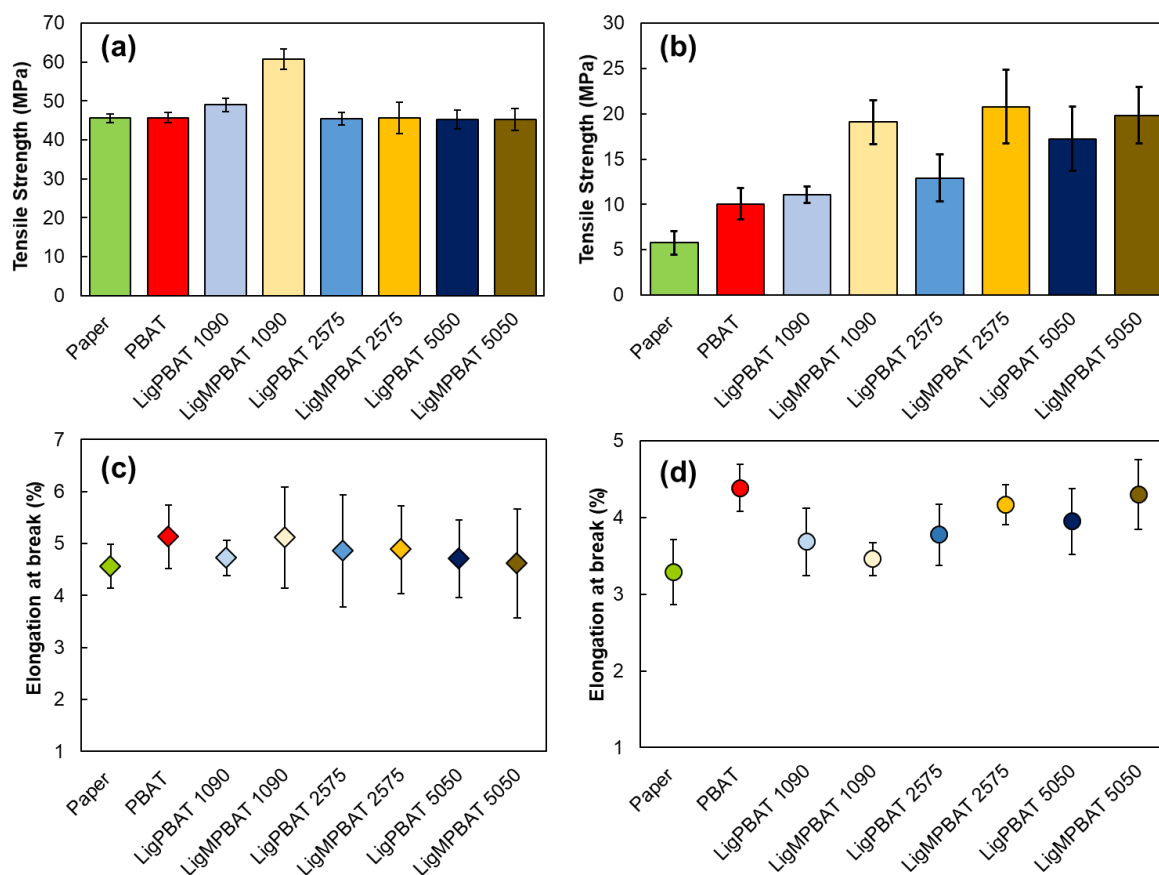


Figure 35. Tensile strength and elongation at break of paper coatings: Tensile strength: (a) dry samples, (b) wet samples, elongation at break: (c) dry samples, (d) wet samples.

The enhanced tensile properties would partially have been due to the hydrophobicity of the PBAT coating. The incorporation of a relatively nonpolar esterified lignin layer enabled the samples with added water repellence as it fills the PBAT polymer's free volume. Also, the finely dispersed esterified lignin particles in the polymeric coating could fill the micro-voids

between the cellulose fibers, thus, preventing water seepage through the pores (**Figure 29c**, **Figure 30h**, and **Figure 30i**). The recorded wet tensile strength values were in agreement with the water contact angle and water Cobb test observations. The elongation at break of the dry paper substrate was not affected with the employment of the coating layer. In the wet test, the elongation at break of the baseline paper displayed significant reduction from the dry sample (87.3%). However, under wet conditions the application of the coating helped to retain the elasticity, with the baseline PBAT and esterified lignin – PBAT based formulations displaying higher levels of elasticity retention in comparison to the dry specimens. One-way ANOVA test of dry and wet specimen concluded statistically significant differences ($p < 0.05$) with the exception of elongation at break results for dry specimen.

The analysis has been presented in **Table C 5 (Appendix C)**. Overall, the esterified lignin-based formulations exhibited great promise for simultaneous water repellence, superior tensile strength and mechanical integrity in wet conditions.

4.4. Summary of Chapter 4

The study aimed at fabricating economical, biodegradable, and sustainable alternatives to the traditional polymeric coatings for packaging applications, investigated the fabrication of lignin incorporated PBAT paper coatings. Due to the poor dispersion of lignin in hydrophobic polymers, including PBAT, an esterification modification of the lignin was employed to substitute the abundant hydroxyl moieties with long aliphatic chains. The esterified lignin exhibited enhanced dispersibility in the non-polar PBAT paper coating formulations resulting in better wet tensile strength of the coated paper. With an increase in the concentration of

esterified lignin in the coating formulations (up to 50 wt.%), appealing oxygen, oil, and moisture penetration reduction properties were recorded. An increase in the coating thickness has resulted in a further improvement in barrier properties, with the best barrier obtained using 60 μm thickness 50 wt.% esterified lignin-PBAT coatings. Overall, the fabricated paper coating films based on the esterified lignin and PBAT in this work demonstrated uniform surface morphology, better tensile properties, and remarkable barrier properties. Since both PBAT and lignin are compostable, the resulting formulation is also expected to be compostable, albeit requiring further investigation and confirmation. These characteristic properties make the formulations an appealing, sustainable material alternative for a range of paper-based food packaging and wrapping applications. The use of extrusion coating or the use of water-based dispersion systems will avoid the use of chloroform to further enhance the sustainability of the process. Potential applications of such compostable material coated papers include burger wraps, single-use lunch boxes, milk and juice containers, beverage cups, etc.

Chapter 5 – Oleic acid decorated kraft lignin as a hydrophobic and functional filler of cellulose acetate films⁴

5.1. Introduction

The synthetic and non-degradable plastics problem in our environment cannot be overstated, with the major concern of plastic waste leaching into land and waterbodies, thus, imparting harmful effects on living organisms and ecosystems. In the past decades, the domination of petroleum-sourced conventional polymers in the packaging industry has been widely recognized [335]. The dependency of the food industry on petrochemical-based plastics (e.g., polyethylene terephthalate (PET), polyethylene (PE), polystyrene (PS), polyvinyl chloride (PVC), polypropylene (PP), and polyamide (PA)) stems from their exceptional material properties and low cost [336]. Although conventional plastics have several benefits that make them popular for packaging applications (e.g., excellent barrier properties, inexpensive, mature technology), post-use disposal of these polymers contributes to significant plastic waste generation that spills into the environment. To counter the petrochemical-derived plastic waste-led environmental consequences, the valorization of renewable resource-derived macromolecules into bioplastic as alternatives to traditional polymer materials has gained substantial interest [281,337].

Potential benefits of nature-derived macromolecules include renewability, sustainability, biodegradability, non-toxicity, and extensive availability [2]. Constituting primarily cellulose, hemicellulose, and lignin moieties, lignocellulosic biomass can be a good source of nature-

⁴ A version of this chapter has been submitted for peer-reviewed publication.

derived macromolecules. Cellulose is the most abundant biopolymer, and its derivatives, such as cellulose acetate (CA), are a viable option for food packaging applications [32,335,338–340]. CA has garnered significant attention due to its compostability, transparency, good mechanical properties, and melt processability [335,341,342]. On the contrary, cellulose acetate exhibits poor UV stability and high moisture absorption resulting in inferior dimensional stability, which limits its food packaging applications [335,343,344].

Polymer blending is one of the most attractive methods to obtain new materials with excellent properties and cost structure. As such, to reduce a polymer's hydrophilicity, nonpolar materials could be incorporated into the polymer matrix. While fine dispersion of polymer blends can be achieved via optimal designing of the blending operations as well as the selection of appropriate blending partners, secondary polymer processing techniques to produce final products (e.g., injection molding, thermoforming, compression molding) could result in ineffective mixing and phase separation [345]. Moreover, the strong thermodynamic driving forces often lead to phase coalescence and/or coarsening toward a macroscopic phase-separated state with poor performance [345]. In such an effort by Rajeswari et al., seaweed-extracted carrageenan and sodium alginate were added to the cellulose acetate matrix, and significant improvements in thermal properties, morphology, and mechanical properties were recorded [335]. Lignin is another lignocellulosic derivative that could be employed to fabricate cellulose acetate composites.

Lignin is a polyphenolic macromolecule and the second most abundant biopolymer, constituting between 18 and 35 wt.% of biomass (depending on feedstock) [32,338–340]. Of

the vast amount of lignin produced by biorefineries and paper and pulp industries annually, a major fraction is burnt as inexpensive fuel [30]. Additionally, a small fraction of the produced lignin is utilized in value-added applications like fillers, adsorbents, construction, biomedical applications, surfactants, adhesives [17–19,31,294,346–350]. The extensive applicability of lignin is limited by its structural variability, hydrophilicity, non-homogeneity, tendency to agglomerate, and incomparability with nonpolar polymer matrices [295]. Thus, significant efforts are being made to chemically modify the lignin structure for its effective valorization [296–298,304,305,351,352].

The present work aims to investigate the incorporation of lignin and hydrophobically modified lignin as a blending partner of cellulose acetate to enhance the performance of cellulose acetate with a focus on sustainable food packaging material in lieu of conventional petroleum-derived plastic packaging. The employment of lignin (baseline and functionalized) as a functional additive in cellulose acetate matrix was investigated. Initially, the baseline kraft lignin sample was esterified with oleic acid due to oleic acid's bio-origin and natural abundance. The oleic acid functionalized lignin was hypothesized to exhibit non-polar characteristics, homogeneity, and compatibility with cellulose acetate matrices. The success of lignin modification reactions was validated with spectroscopy and other techniques. The impact of the lignin (unmodified and esterified) incorporation in the cellulose acetate matrix on the physicochemical properties, surface morphology, viscoelasticity, and barrier properties was systematically evaluated.

5.2. Materials and methods

5.2.1. Materials

The kraft lignin (Amallin™ LPH, low pH $\approx$ 2.2, average molecular weight = 6500 g/mol) was purchased from West Fraser Mills Ltd., Canada. Pyridine (99.8 %), p-Toluenesulfonyl chloride (reagent grade, $\geq$ 98%), oleic acid, and tetrahydrofuran (THF, ACS reagent, $\geq$ 99%) were sourced from Sigma-Aldrich (Oakville, ON, Canada). Cellulose acetate was supplied by Eastman Chemical Company, USA. The Kraft lignin sample was washed three times with distilled (DI) water and dried overnight (forced air oven, 60 °C, overnight). The dried lignin was stored in airtight containers to maintain low moisture content (<3%).

5.2.2. Methods

5.2.2.1. Lignin functionalization reactions with oleic acid

The functionalization of kraft lignin employing an oleic acid (mono-unsaturated omega-9 fatty acid) was conducted by varying one factor at a time. The factors that were evaluated were the mole ratio of hydroxyl groups of lignin to oleic acid and oleic acid to the TsCl catalyst (**Table 3**).

To carry out the reaction, 2 g of unmodified kraft lignin was dissolved in pyridine (20 mL) via sonication (20 min). This was then mixed with oleic acid – TsCl premix at different ratios (**Table 3**) under continuous stirring (300 rpm). The content was then transferred to a round bottom flask equipped with reflux and placed in an oil bath. The reaction temperature (90 °C)

and time (3 h) were selected based on preliminary experimentation and maintained similarly for all runs.

Table 3. Composition of various esterification reaction formulations

Sample ID	Mole ratio	
	Lignin (OH): Oleic acid	Oleic acid: TsCl
LigOA-1	1:3	1:1
LigOA-2	1:3	1:0.5
LigOA-3	1:3	1:0.25
LigOA-4	1:2	1:1
LigOA-5	1:1	1:1

To recover the reaction product, the generated product was precipitated with DI water followed by Soxhlet extraction to remove unreacted oleic acid. The complete removal of oleic acid was verified via FTIR and HNMR analysis of the raffinate.

5.2.2.2. Characterization of lignin modifications

Infrared (IR) spectroscopy

The successful functionalization of lignin samples was characterized and validated by Attenuated Total Reflectance-Fourier transform infrared spectroscopy (ATR-FTIR). IR spectra of the control (unmodified lignin), modified lignin samples, and modifying agent (oleic acid) were recorded using a Thermo Scientific Nicolett 6700 spectrometer at ambient conditions. The powder samples were loaded and the spectra (128 scans) were collected in the frequency range of 4000 to 500 cm^{-1} in the transmittance mode.

Proton nuclear magnetic resonance (H-NMR) spectroscopy

The H-NMR spectra of the modifying agent (oleic acid), unmodified lignin, and functionalized lignin samples were collected to evaluate the induced chemical modifications. 2 mg of each sample was dissolved in 0.6 mL of deuterated dimethyl sulfoxide (DMSO-d₆) at room temperature. The respective samples were then sealed and labeled in 5 mm NMR analysis tubes. Employing a Bruker-SpectroSpin 500 MHz Ultra shield high-resolution NMR (Bruker Corporation, United States), the H-NMR spectra were recorded.

Melt processability

The melt processability of the unmodified and modified lignin samples was tested. The specimen was compressed for 4 mins employing a compression molder (4 MT, 120 °C). The optical micrographs of the compression-molded lignin films were then collected (BX53M polarizing optical microscope, Olympus, United States). The changes in the film surface morphology were also evaluated by employing a hot stage functionality of the optical microscope (room temperature to 210 °C).

Dispersibility test

The dispersibility of the unmodified kraft lignin and oleic acid functionalized kraft lignin samples in various organic solvents was tested. Various solvents with increasing relative polarities (toluene, tetrahydrofuran, ethanol, and water) were employed. For this, 20 mg of the lignin samples were added into 10 mL of the respective solvent and sonicated for a constant time (10 minutes). It was then left undisturbed for 24 h and pictures were collected.

Contact angle measurements

The water contact (WCA) and diiodomethane (MI) contact angle of lignin-loaded sheets was measured using a custom-built optical sessile drop system. A 5 μL droplet was dropped on each respective specimen and the contact angle images were collected. Basler (scA 1000–30 fm) camera was utilized to record the contact angle images at 24 °C. To measure the contact angle values, an image processing program (ImageJ) was employed.

5.2.2.3. Theoretical model for material selection

The compatibility of unmodified and modified lignin samples with various potential polymeric matrices was studied. Gibb's free energy-based analysis was employed [299,302].

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (5.1)$$

In Equation 5.1, Gibbs free energy is represented by ΔG_m , the enthalpy of mixing is denoted by ΔH_m , the absolute temperature by T , and ΔS_m is representative of the entropy of mixing. A negative value of ΔG_m in a polymeric blend indicates intricate mixing between the components. Low molecular weight systems exhibit a high entropy and thus, a negative Gibbs free energy implying an intricate mixing between system components. In contrast, high molecular weight systems have low entropy and as a result, they typically display poor mixing[301].

$$\Delta H_m = (\delta_1 - \delta_2)^2 \phi_1 \phi_2 \quad (5.2)$$

As shown in Equation 5.2, the enthalpy of mixing is directly proportional to the volume fraction of the components (φ) and the square of solubility parameters (δ). Furthermore, the solubility parameter is proportional to the product density (ρ) and group molar attraction constant ($\sum G_m$), and inversely proportional to the molecular weight of the monomeric units (M), as described by Equation 5.3 [299,302].

$$\delta = \frac{\rho \sum G_m}{M} \quad (5.3)$$

The compatibility of unmodified and modified (esterified) lignin samples (2.5 wt.%) was compared against cellulose monoacetate (CA), poly(butylene adipate terephthalate) (PBAT), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), poly(hydroxybutyrate) (PHB), polyvinyl acetate (PVAc), and poly(vinyl alcohol) (PVOH).

Surface charge and interfacial tension

The previously recorded water and diiodomethane contact angle values were used to calculate the surface free energy values of the respective specimens employing Equation 5.4 and Equation 5.5.

$$\frac{1}{2} \gamma_w (1 + \theta_w) = [(\gamma_s^d \gamma_w^d)^{\frac{1}{2}} + (\gamma_s^p \gamma_w^p)^{\frac{1}{2}}] \quad (5.4)$$

$$\frac{1}{2} \gamma_{MI} (1 + \theta_{MI}) = [(\gamma_s^d \gamma_{MI}^d)^{\frac{1}{2}} + (\gamma_s^p \gamma_{MI}^p)^{\frac{1}{2}}] \quad (5.5)$$

From Equation 5.4 and Equation 5.5, the θ_w and θ_{MI} represent the contact angle values of water and diiodomethane exhibited by each of the respective specimens. The γ_w ($72.8 \frac{mJ}{m^2}$),

γ_{MI} ($50.8 \frac{mJ}{m^2}$), and γ_s attribute the surface energy of water, diiodomethane, and the respective sample. Furthermore, the γ_w^d ($21.8 \frac{mJ}{m^2}$), γ_{MI}^d ($49 \frac{mJ}{m^2}$), γ_w^p ($51.0 \frac{mJ}{m^2}$), and γ_{MI}^p ($1.8 \frac{mJ}{m^2}$), are representative of the surface energies with dispersive (superscript d) and polar (superscript p) components. The total surface energy is the sum of γ_s^d and γ_s^p [353].

To calculate the interfacial tension values, Owens-Wendt-Kaelble (OWK, Equation 5.6) and Wu (Equation 5.7) were used.

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2 [(\gamma_1^d \gamma_2^d)^{\frac{1}{2}} + (\gamma_1^p \gamma_2^p)^{\frac{1}{2}}] \quad (5.6)$$

$$\gamma_{12} = \gamma_1 + \gamma_2 - 4 \left(\frac{\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p} \right) \quad (5.7)$$

In Equation 5.6 and Equation 5.7, the interfacial tension between the polymer fractions was represented by γ_{12} . Further, the surface energies of lignin fractions (γ_1) and the cellulose acetate (γ_2) matrix were accounted for. The superscripts d and p were attributed to the dispersive and polar fractions of the surface energy.

5.2.2.4. *Fabrication of sheets*

In accordance with the formulations outlined in **Table 4**, a specified amount of lignin and modified lignin samples were dispersed in THF and sonicated (20 min) for dissolution. These solutions were then mixed with 10 wt.% cellulose acetate solution in THF at varying ratios to generate 2.5 wt.%, 5 wt.%, and 10 wt.% lignin and modified lignin in CA (**Table 4**). The mixtures were subsequently mixed via a magnetic stir bar on a stir plate at room temperature (200 rpm, 2 min) and cast on a petri dish to evaporate the solvent. The cast sheets were

compression molded into films at optimal temperature (170 °C) and under a compressive force (5 MT, 4 mins). To optimize the compression molding temperature of the casted sheets, a temperature sweep analysis on a rotational rheometer (HAAKE Mars III Thermo Scientific, United States) was employed. The specimen was subjected to a temperature range of 120 °C to 220 °C.

Table 4. Composition of solution cast sheets.

Sample ID	Wt.% of Cellulose Acetate	Wt.% of Unmodified Lignin	Wt.% of Modified Lignin
CA	100	-	-
Lig2.5	97.5	2.5	-
LigOA2.5	97.5	-	2.5
Lig5	95	5	-
LigOA5	95	-	5
Lig10	90	10	-
LigOA10	90	-	10

5.2.2.5. Characterization of formulated sheets

Rheology

At the optimized temperature (170 °C), the viscoelastic properties of the compression molded sheets were tested using a rotational rheometer (HAAKE Mars III rheometer, Thermo Scientific, United States). A parallel plate (P20 CS L, Plate 20 with ceramic shaft) geometry was employed to determine the linear viscoelastic region (LVE) from an amplitude sweep test (0.001% - 1%, 1 Hz). The viscoelastic properties were then tested in the LVE region by

undertaking a frequency sweep (0.01 Hz – 100 Hz) test. Prior to testing, the samples were dried overnight in a convection oven (70 °C).

Mechanical properties

The tensile properties of the compression molded sheets were evaluated using a universal tensile testing machine equipped with a 500 N load cell (AGS-X series, Shimadzu, Japan). For each formulation, at least five strips measuring 70 mm (L) × 10 mm (W) were cut from multiple compression molded sheets. Out of the strips cut for each formulation, five specimens were randomly selected and tested for their tensile properties. The testing of the randomized specimen was conducted at a strain rate of 1 mm/min.

Optical microscopy

Optical micrographs of the lignin samples (unmodified and modified) and their blends with CA matrix were recorded using BX53M polarizing optical microscope (Olympus, United States). The effect of modification on the dispersibility of the lignin moiety in the polymer matrix was captured at 10x magnification.

Moisture absorption and barrier properties of the casted sheets

The moisture uptake of the compression molded specimens was tested in an artificially maintained humid environment (99% relative humidity (RH)). Samples measuring 2 cm x 2 cm were dried overnight in a convection oven (70 °C) and placed in a desiccator and eventually transferred into a chamber adjusted to the 99% humidity environment. After 24 hr of exposure,

water uptake values were recorded. The water barrier properties of the fabricated sheets were also evaluated using the barrier cup method. For this, films were fixed in barrier cups that contained distilled water and placed inside a desiccator ($RH \leq 25\%$, room temperature). The moisture loss was monitored for 96 hours. The water vapor permeability (WVP) and water vapor transmission rate (WVTR) were calculated using Equation 5.8 and Equation 5.9.

$$WVTR = \frac{\Delta G}{A \times t} \quad (5.8)$$

$$WVP = \frac{WVTR \times l}{S(\Delta RH)} \quad (5.9)$$

Where ΔG represents the moisture loss (g), A is the exposed area of films (m^2), t is time (h), the thickness of the films was represented by l , S is the vapor pressure (saturation, $23^\circ C$), and ΔRH representing the relative humidity difference between the inside of the cup and its surrounding area [36].

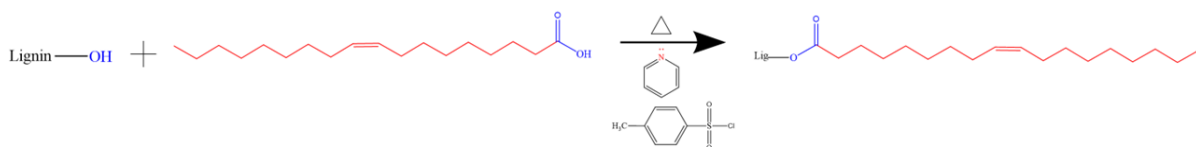
UV barrier properties

The cellulose acetate films with the unmodified and esterified lignin incorporating cellulose acetate compression molded sheets were tested for their absorbance properties between 300 nm and 800 nm. The films were cut into strips (1 cm in width) and characterized on a Cary 300 Bio UV-Visible Spectrophotometer.

5.3. Results and discussions

5.3.1. Spectroscopy analysis of lignin modification

The hypothesized functionalization reaction of kraft lignin with oleic acid is displayed in **Schematic 3**. The success of the proposed reaction was evaluated by employing infrared and nuclear magnetic resonance spectroscopic techniques.



Schematic 3. Functionalization reaction of kraft lignin with oleic acid.

The attenuated total reflectance (ATR) infrared spectra of the unmodified and functionalized lignin samples are illustrated in **Figure 36**. The stretching vibration at 3450 cm^{-1} was attributed to the presence of characteristic hydroxyl (-OH) moieties in the tested specimens. The distinctive flattening of the -OH peak in the functionalized specimen established the successful esterification of the baseline kraft lignin sample [304,354,355]. The peaks at 2918 cm^{-1} and 2847 cm^{-1} correspond to the presence of methylene (-CH₂) and methyl (-CH₃) moieties in the modifying agent (oleic acid (OA)) [356]. As observed in **Figure 36**, the evident appearance of prominent methyl and methylene peaks in the modified samples (in proportion to the unmodified sample) further signifies their successful functionalization. The development of a peak around 1710 cm^{-1} was attributed to the asymmetric carbonyl chains of the ester bond, thus, validating the successful esterification of the baseline kraft lignin [357,358].

The successful esterification of the kraft lignin (**Schematic 3**) was further validated by employing *H-NMR* spectroscopy. The *H-NMR* spectra of oleic acid, unmodified lignin, and modified lignin samples are illustrated in **Figure 37**. The prominent peak at 0.89 ppm was attributed to the presence of methyl ($-\text{CH}_3$) protons. The signals between 2.34 ppm and 1.26 ppm were representative of the long aliphatic chain protons of the oleic acid, as illustrated in **Figure 37** [308]. The distinctive presence of aliphatic carbon representing characteristic peaks in the esterified lignin spectra was observed. Their absence from the baseline kraft lignin spectra further verified the successful esterification of the modified samples, thus, synchronous with IR observations. The characteristic signals between 4.10 and 3.50 ppm signified the presence of methoxy protons of lignin [306].

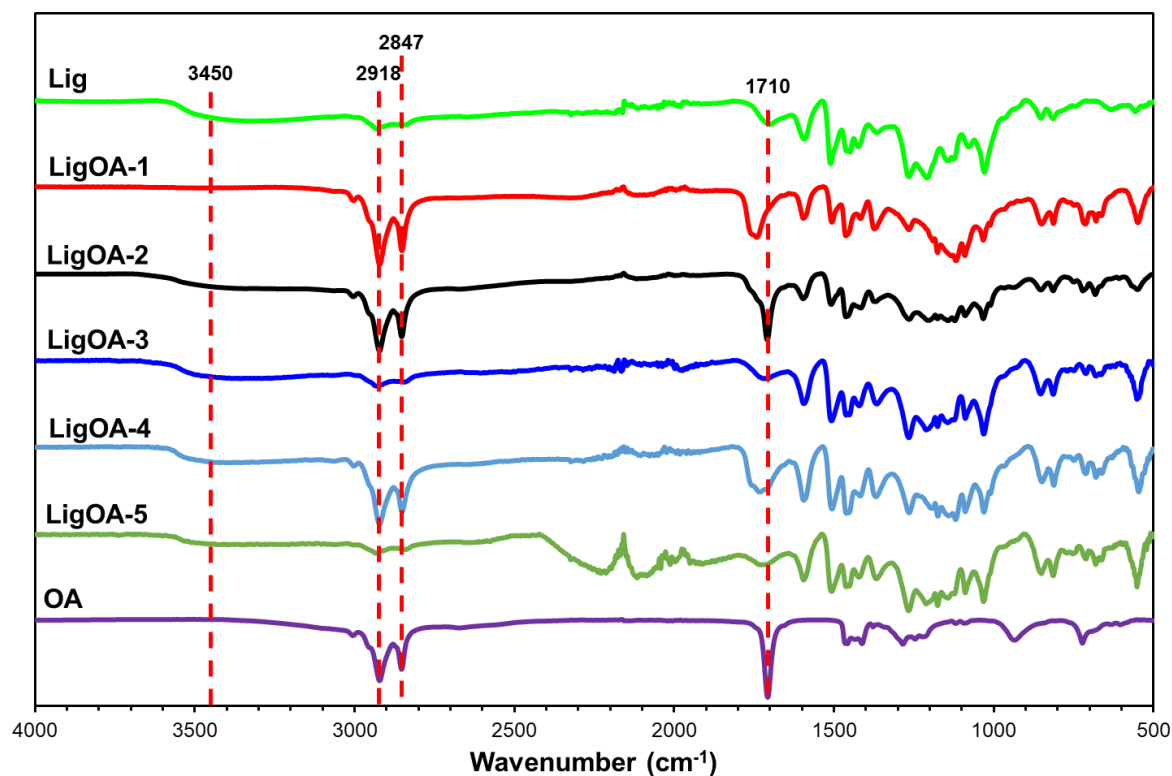


Figure 36. ATR-FTIR spectra of oleic acid, unmodified, and functionalized lignin samples.

Also, the peak at 5.34 ppm was representative of the carboxylic acid (-COOH) moieties of the oleic acid. As evident from **Figure 37**, the absence of the carboxylic acid representative peak in the esterified lignin spectra exhibited the successful removal of unreacted oleic acid fractions during post-processing steps.

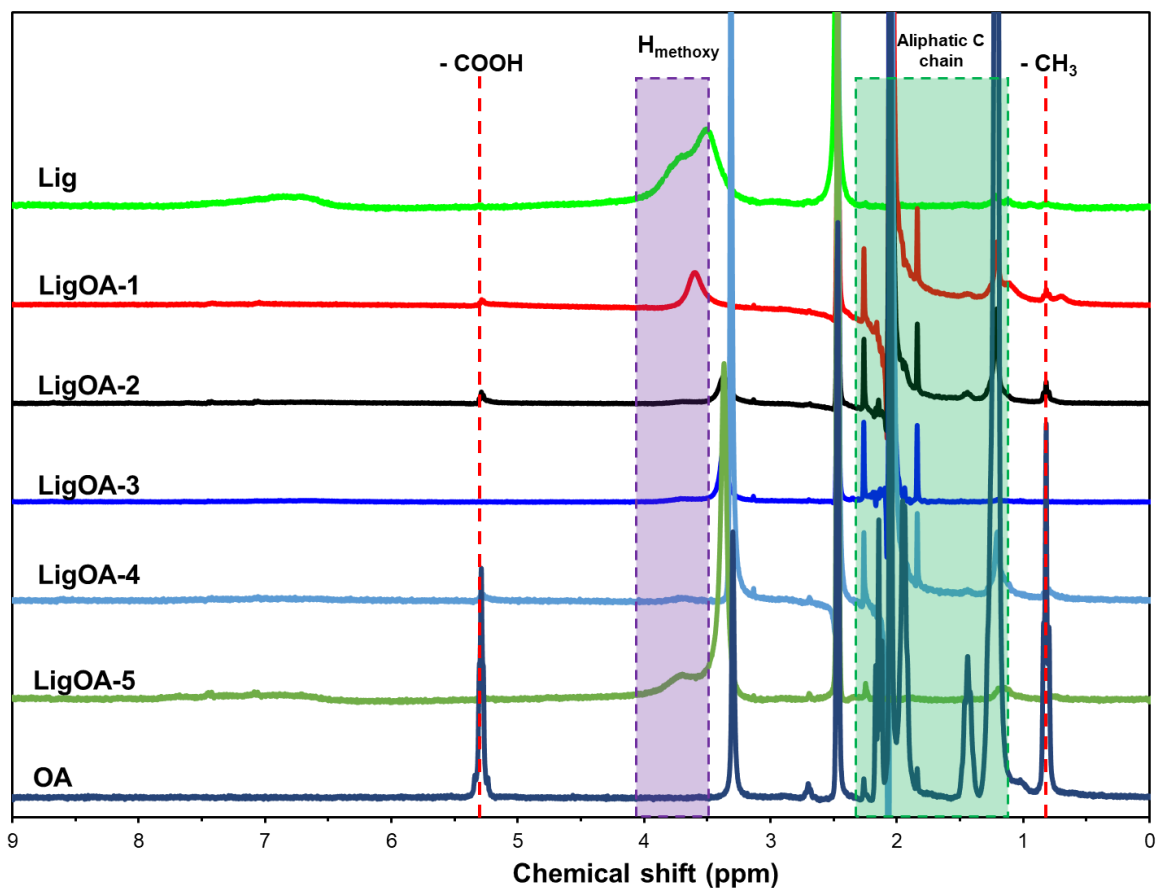


Figure 37. *HNMR* spectra of oleic acid, control, and esterified lignin specimens.

5.3.2. Melt flowability of the unmodified and esterified lignin

The melt processability of the unmodified kraft lignin specimen and functionalized lignin (LigOA-1) moieties were evaluated. Lignin samples were heated (120 °C) in a compression mold under a load of 4 MT for 4 minutes. The compression molded specimens were placed on paper (**Figure 38**) for comparative visual analysis. As is apparent from **Figure 38**, the unmodified lignin specimen did not melt apart from the fusion of particles into an opaque, self-standing, but brittle sheet (**Figure 38b**). Additionally, the sample displayed signs of heat and compression-mediated degradation, as noted from the charring.

On the contrary, the modified specimen melted under compressive forces and formed a thin, flexible film. As shown in **Figure 38c**, the compression molded modified lignin film was translucent, as the background logo image was visible with all its details. However, it has poor clarity/transparency as compared to the transparent CA film displayed in Figure 3a. Overall, the modification rendered the kraft lignin into a melt-processible material. Hence the melt processability of modified lignin samples was established. Further validation of the lignin melt processability employing hot-stage optical microscopy was conducted.



Figure 38. Melt processability and transparency of a) CA film, b) unmodified kraft lignin, and c) esterified lignin samples.

For additional evidence of lignin melt processability, the change in lignin sheet morphology was evaluated using hot-stage optical micrographs at various elevated temperatures (25 °C, 150 °C, 180°C, and 210 °C) in transmission and reflected modes. As illustrated in **Figure 39**, significant differences in the surface morphology of the baseline kraft lignin and modified lignin films were observed. While the baseline kraft lignin film displayed large lignin particle agglomerates, the modified lignin film exhibited homogeneous morphology. At 120 °C, no changes in the surface morphology of the unmodified lignin films were recorded in the transmission and reflectance mode. Heating the baseline lignin film further up to 210 °C did not impart any observable changes, with the lignin domains remaining intact. Hence, no instances of melting were observed, validating its lack of melt processability.

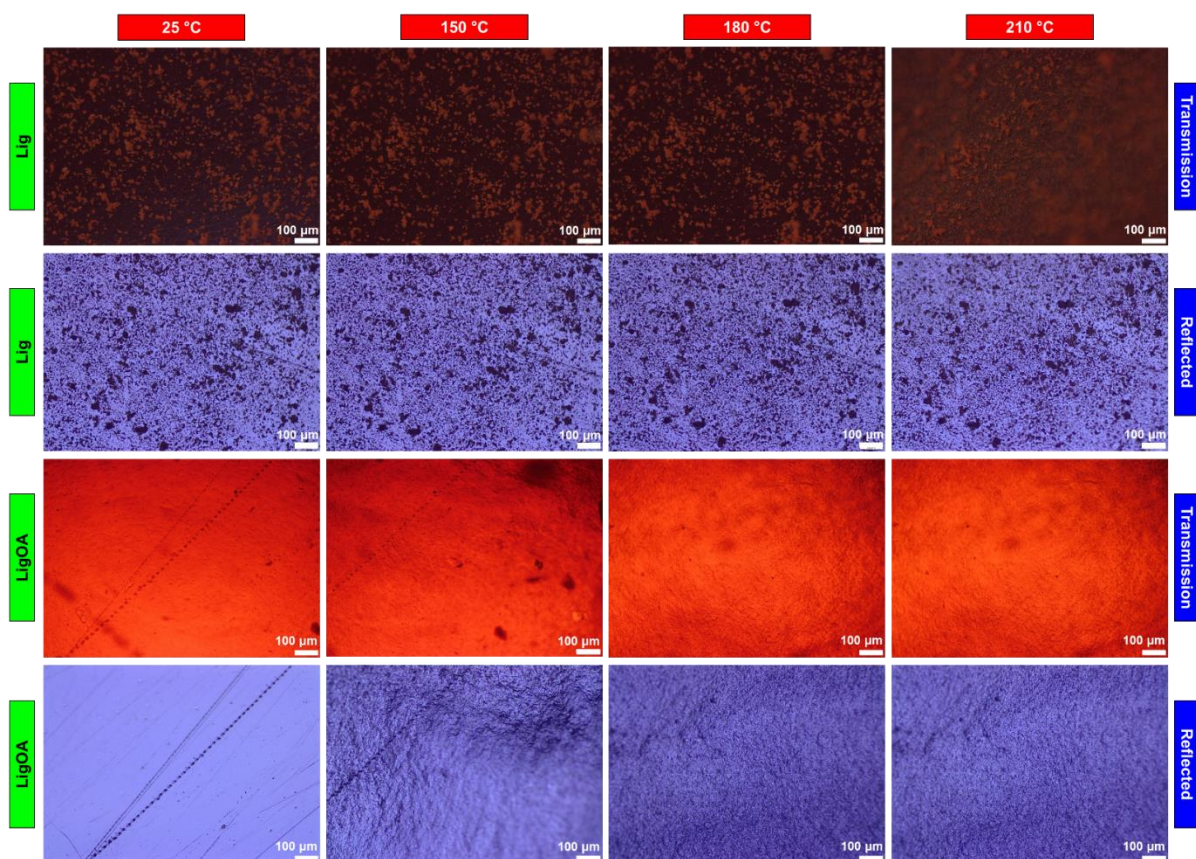


Figure 39. Hot stage optical micrographs of control and esterified lignin specimens (from room temperature (25 °C) to 210 °C).

On the other hand, the modified lignin molded film exhibited homogeneity with no visible particle aggregates at room temperature. By heating the sample to 150 °C, no significant changes to the surface morphology were observed. However, a further temperature increase to 180 °C resulted in morphology changes with visible melting conformation. Interestingly, the surface deformations on the film specimen generated during compression molding ceased to appear at 180 °C. Thus, the relatively smoother surface (at 180 °C) validated the melting behavior of the modified lignin sample. A similar trend as 180 °C was noted at 220 °C, and these observations agreed with the initial hypothesis.

5.3.3. Solvent dispersion

The dispersibility of the unmodified and modified lignin samples was tested in organic solvents with varying polarities (**Figure 40**). The employed solvents and their respective relative polarities were toluene (0.099), THF (0.207), ethanol (0.654), and water (1.000). As noted in **Figure 40**, the unmodified lignin was soluble in THF and dispersible in the rest of the solvents, thus exhibiting an affinity to both polar and nonpolar media. On the contrary, the modified lignin sample was soluble in toluene, dispersible in the THF, but insoluble in solvents with higher relative polarities (e.g., water, ethanol), thus, exhibiting a strong affinity for nonpolar solvents. This was another validation of the hydrophobic modification of lignin, demonstrating the potential compatibility of the modified lignin with the nonpolar cellulose acetate as opposed to the pristine lignin.

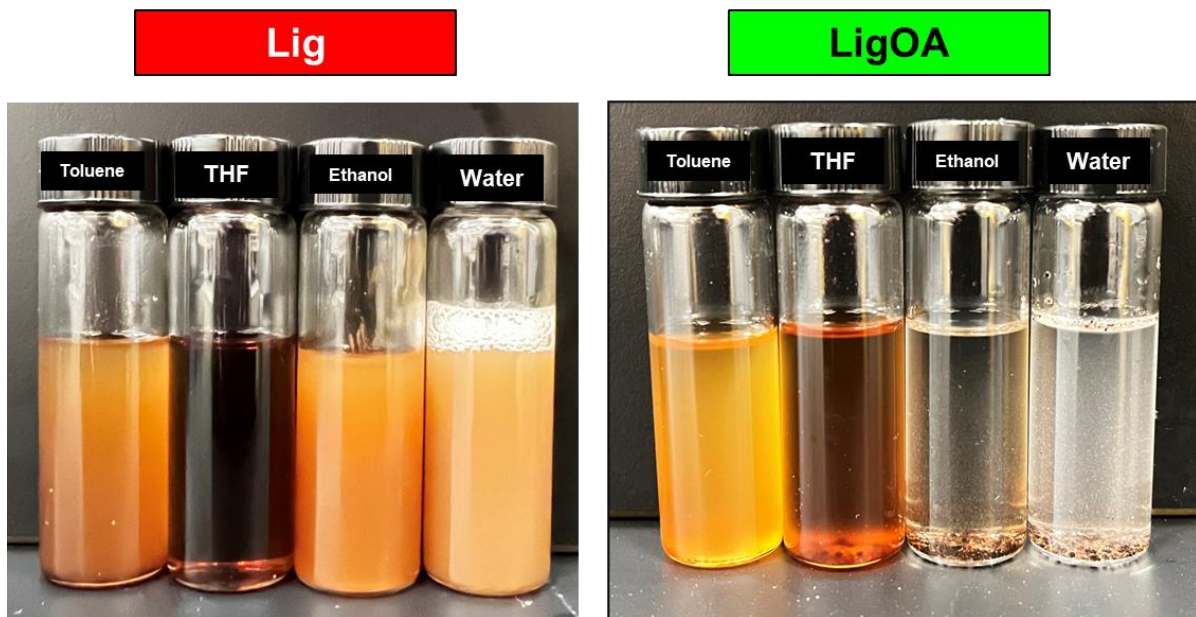


Figure 40. Dispersibility test of lignin moieties (unmodified and oleic acid functionalized) in various solvents.

5.3.4. Theoretical model for polymer phase selection

The compatibility of lignin moieties in different polymer matrices was evaluated based on their Gibbs free energy (ΔG_m). Negative Gibbs free energy is representative of the intricate mixing of the various components of the polymer systems. In the studied system, the lignin and the various polymer materials (cellulose acetate, PBAT, PHB, PHBV, PBAT, PVAc, PVOH) are all macromolecules with large molecular weights. Thus, the entropy contribution to the Gibbs free energy can be considered negligible [302]. Therefore, Equation 5.1 reduces to Equation 5.10.

$$\Delta G_m = \Delta H_m \quad (5.10)$$

The calculated Gibbs free energy values have been tabulated (**Table D 1 (Appendix D)**), using the respective density ρ values. The least ΔG_m value was obtained for the cellulose acetate-modified lignin system followed by PVAc and PVOH indicating good compatibility. On the contrary, both lignin and modified lignin displayed high ΔG_m with PHBV, PHB, and PBAT, indicating poor compatibility. Moreover, the ΔG_m values for the modified lignin-polymer compositions were lower than their unmodified lignin-polymer composition counterparts. This could be ascribed to the enhanced dispersion potential of the modified lignin in the polymer matrix compared to the baseline lignin, which could result in lignin-polymer compatibility and enhanced properties.

5.3.5. Contact angle, surface energy, and interfacial tension

The water and diiodomethane (MI) contact angles of the compression molded samples were evaluated, as illustrated in **Figure 41**.

The recorded contact angles were instrumental to further validate the hydrophobic character imparted by lignin addition to the samples. As apparent from **Figure 41**, the smallest water contact angle was recorded for the baseline cellulose acetate film. This was attributed to the polarity of cellulose acetate from the residual -OH moieties [359]. Adding 2.5 wt.% unmodified lignin to the CA matrix exhibited a 13.4 % increment in the water contact angle over the baseline cellulose acetate sample. On the contrary, the oleic acid-modified lignin-loaded samples presented a 37.9% increase in the water contact angle value. This significant improvement was ascribed to the enhanced dispersibility and hydrophobicity of the esterified lignin fractions [31,323,324].

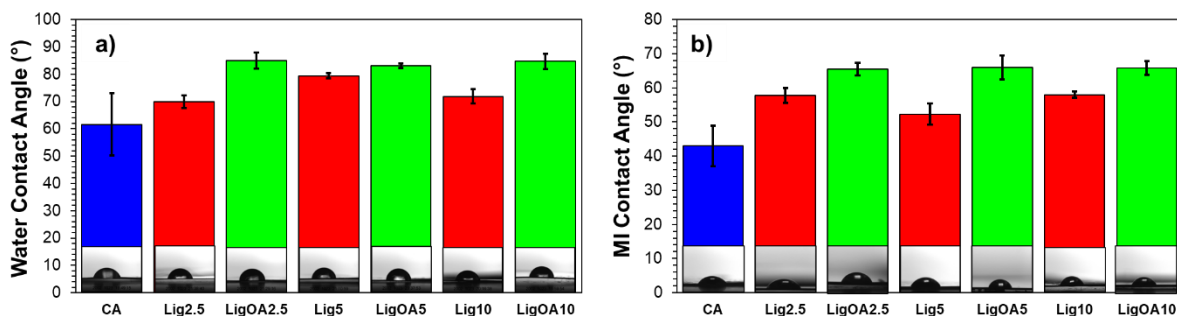


Figure 41. Contact angle values for the compression molded films: a) Water contact angles and b) Diiodomethane (MI) contact angles.

Moreover, formulations with higher lignin loading displayed a similar trend, with the unmodified specimen recording a smaller water contact angle than its oleic acid functionalized counterpart. The esterified lignin-loaded specimens exhibited higher diiodomethane (MI) contact angle values than their unmodified and baseline counterparts, as illustrated in **Figure 41**. This increase in the contact angle values could be attributed to the enhanced dispersibility

of the modified lignin moieties in the polymer matrix. As anticipated, all the esterified lignin-loaded formulations exhibited more hydrophobicity than their unmodified lignin-loaded counterparts [58]. These properties coincided with the optical micrographs, the water uptake and barrier study, and the hot-stage optical micrographs.

To further evaluate the compatibility and miscibility of the pristine and oleic acid functionalized lignin in cellulose acetate matrix, surface energy and interfacial tension values were evaluated. The interfacial properties of the lignin-cellulose acetate and functionalized lignin-cellulose acetate were estimated employing Owens-Wendt-Kaelble (OWK) and Wu's models [360,361]. As displayed in **Figure 42**, the cellulose acetate sample exhibited the highest surface energy value (37.98 mJ/m^2). In a separate study by Rbihi et al., a similar surface energy value was reported [362]. Furthermore, the surface energy of the pristine and modified lignin was observed to be 10.64 mJ/m^2 and 20.71 mJ/m^2 , respectively. The interfacial tension measurements were evaluated using the total surface tension values and their dispersive and polar components. **Figure 42** illustrates the interfacial tension of oleic acid functionalized lignin sample (LigOA) and unmodified lignin (Lig) blends with cellulose acetate were recorded. In accordance with the OWK model, interfacial tension values of 20.42 mN/m and 3.54 mN/m were recorded for the Lig-CA and LigOA-CA blends. Employing the Wu model, Lig-CA and LigOA-CA showed interfacial tension of 24.06 mN/m and 6.62 mN/m , respectively. The reduction in the interfacial tension values for the LigOA-CA blends was attributed to better compatibility between the functionalized lignin moiety and the cellulose acetate matrix, thus, indicating better miscibility and lesser instances of phase separation.

Furthermore, the lower interfacial tension could indicate enhanced mechanical properties stemming from better stress transfer between the polymer fractions [363].

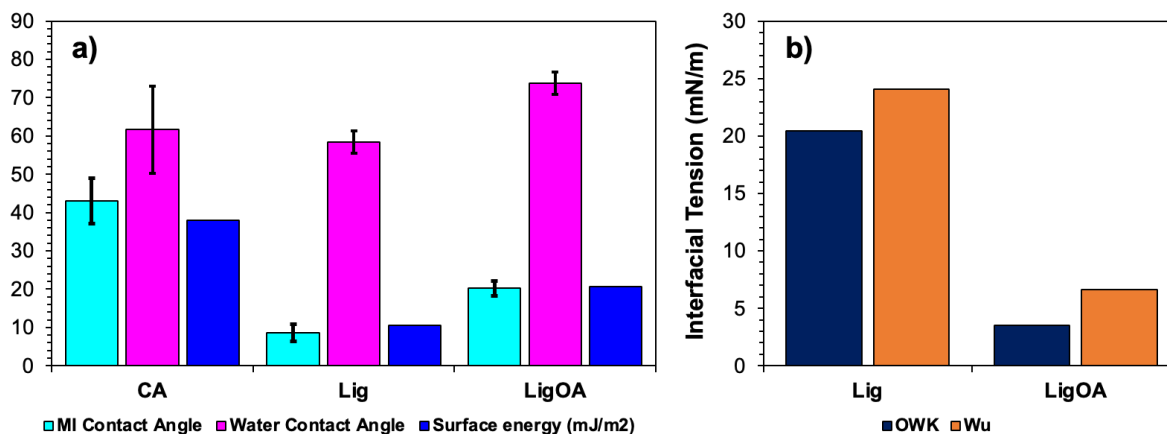


Figure 42. a) Diiodomethane (MI) contact angles, water contact angles, and surface energy values, and b) Interfacial tension values.

5.3.6. Characterization of the formulated sheets

5.3.6.1. Rheology

An amplitude sweep analysis was employed to estimate the Linear Viscoelastic region (LVE) and hence the non-destructive testing limit of the compression molded films. The effect of loading 10 wt.% lignin moieties (unmodified and esterified) on the viscoelastic properties of the cellulose acetate matrix with increasing strain rate was studied. The lignin-loaded films exhibited higher overall moduli and stiffness than the baseline cellulose acetate film (**Figure D 1 (Appendix D)**). In accordance with the G' deviation tolerance ($\pm 5\%$) dictated by ISO 6721-10 and EN/DIN EN 14770, the linearity limit of 0.01% strain was established for the present study [364].

As illustrated in **Figure 43**, the time-dependent non-destructive behavior of the molded films was tested at a strain rate of 0.01% (0.1 Hz to 100 Hz, 170 °C). The unmodified lignin-loaded formulations (for instance, Lig2.5) accounted for a higher G' value, consistently exceeding the corresponding loss moduli in the LVE region. Moreover, the baseline cellulose acetate film exhibited similar behavior. This translated to the baseline CA and the unmodified lignin-loaded samples exhibiting a more elastic behavior than viscous [31]. In a work by Li et al., similar behavior was attributed to the reinforcing effect of lignin structures in polymer matrices [315]. In addition, unmodified lignin-loaded samples recorded higher viscosity values at each concentration than their functionalized lignin-loaded counterparts likely due to strong filler-filler interactions and agglomeration sites. On the contrary, G'' values exceeded the storage moduli values for the 10 wt.% modified lignin-loaded formulation. This behavior represented a dominant viscous phase at the testing temperature [31,314]. This was synchronous to the homogeneously distributed smaller domains of modified lignin in the polymer matrix.

It is well known that the viscosity of blend formulations dictates their commercial application. As illustrated in **Figure 43c**, the complex viscosity of the lignin-cellulose acetate formulations declined at higher frequencies. This shear thinning behavior (especially at higher loadings) was attributed to the breakdown of lignin aggregates under shear [365,366]. Also, the occurrence of such shear thinning behavior in solid-filled polymer matrices has been widely observed [319,320,367]. The increment in viscosity values at higher lignin loadings could be due to the reduced polymer chain mobility caused by lignin addition [318,367]. As illustrated in **Figure 43d**, a Han curve has been plotted [368,369]. Han curve could be employed to investigate the

compatibility between polymer matrices. At different concentrations, the G' - G'' curves representing various specimens coincide, thus, exhibiting compatibility [368,369].

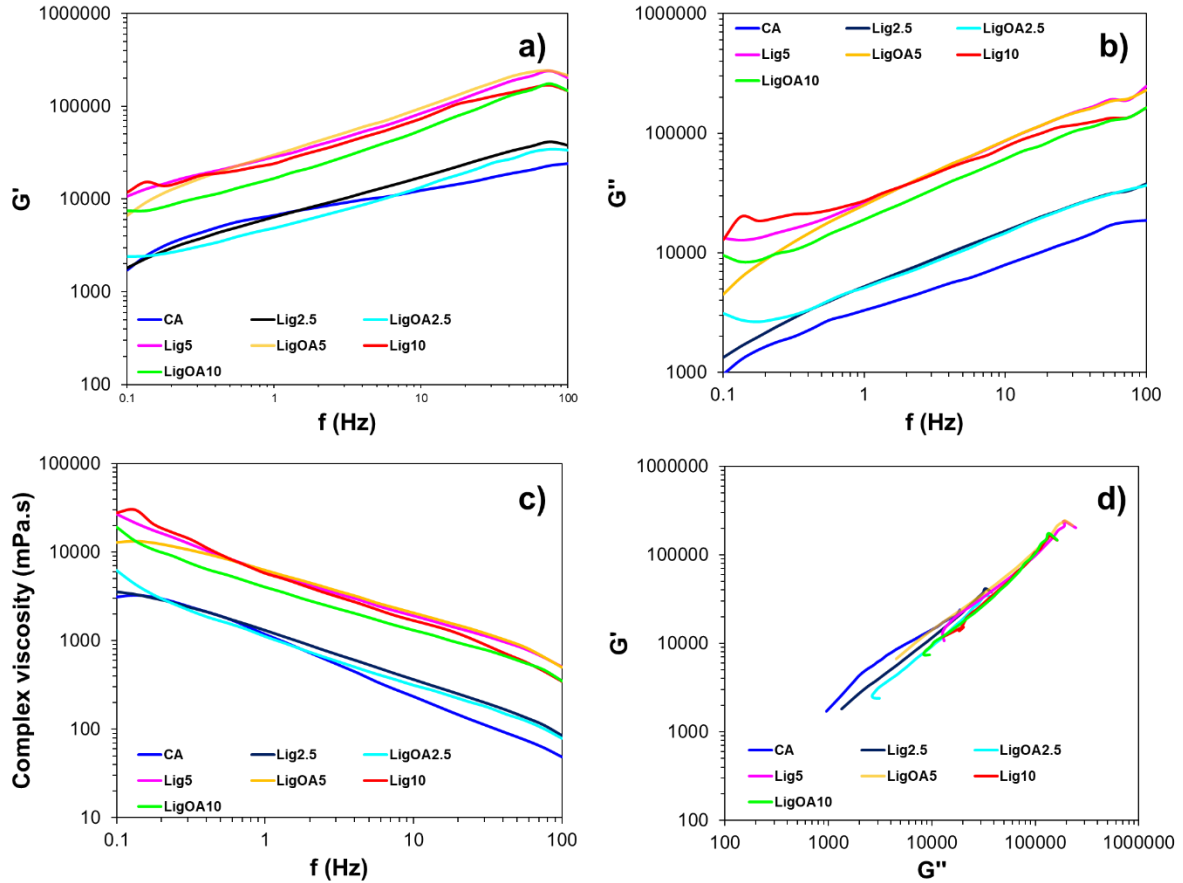


Figure 43. Frequency sweep analysis of the compression molded films: a) Storage modulus (G') vs. frequency (Hz), b) Loss modulus (G'') vs. frequency (Hz), c) Complex viscosity vs. frequency (Hz), and d) Han curve (Storage modulus (G') vs. Loss modulus (G'')).

5.3.6.2. Optical microscopy

The compatibility and homogeneity of lignin moieties in the polymer matrix were further investigated by recording optical micrographs of compression-molded polymer films, as demonstrated in **Figure 44**. As expected, unmodified lignin-loaded polymer films showed agglomeration sites and, thus, nonhomogeneous distributions. This non-homogeneity was

resultant of the polarity imparted by the extensive -OH moieties of the baseline kraft lignin specimen. Contrary to the kraft lignin blends, oleic acid-modified lignin films exhibited enhanced distribution of the lignin domain in the cellulose acetate matrix. This is primarily due to the non-polar characteristics of the modified lignin moieties and superior distribution in the polymer matrix.

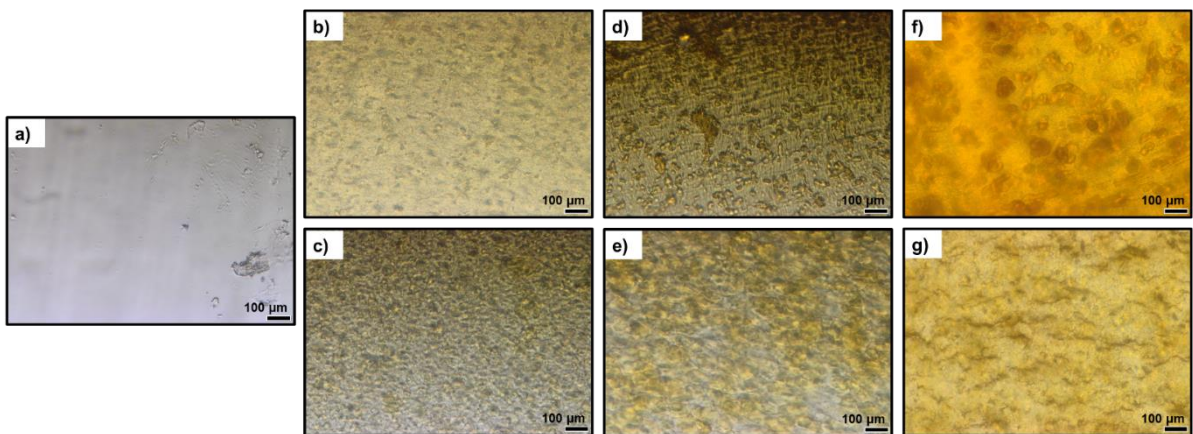


Figure 44. Optical micrographs a) CA, b) Lig2.5, c) LigOA2.5, d) Lig5, e) LigOA5, f) Lig10, and g) LigOA10. Comparing the 5 wt.% lignin (unmodified and modified) loaded sheets (Lig5 and LigOA5), it was evident that the functionalized lignin had substantially superior compatibility and fine dispersion morphology in the cellulose acetate matrix. Notably, the highest loaded samples exhibited distinctive morphologies, with the unmodified lignin domains being distinguishable from their functionalized counterpart. These observations were coherent with the initial hypothesis.

5.3.6.3. *Mechanical properties*

To investigate the effect of incorporating lignin fractions (kraft and oleic acid functionalized) on the tensile properties of the cellulose acetate films, tensile testing of the compression

molded specimens was conducted. The tensile properties of polymer composites are highly dependent on the strength of the base polymer, distribution of the filler in the host matrix, processing conditions, and their sensitivity to the surrounding environment.

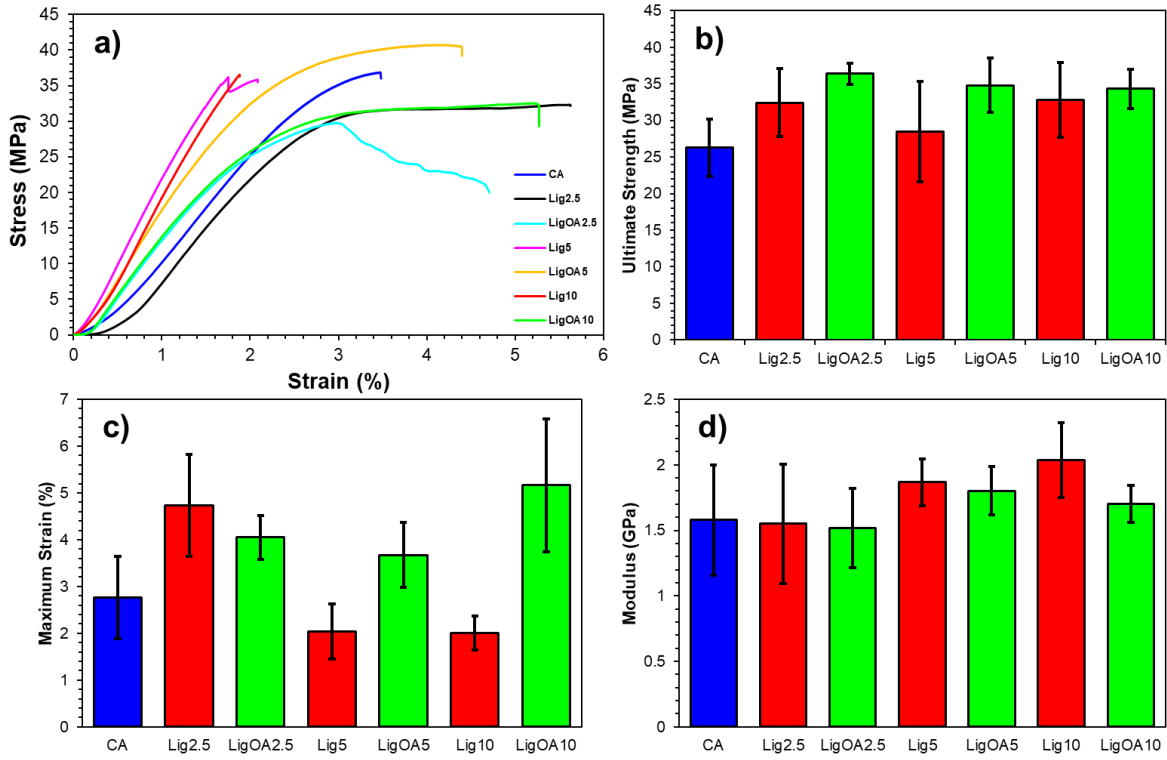


Figure 45. Mechanical properties of compression molded films at various lignin loadings: a) Stress-strain curve, b) Tensile strength, c) Elongation at break, and d) Modulus.

The specimen with 2.5 wt.% modified lignin recorded the highest tensile strength (36.4 MPa). This was a 12.4 % increment over its unmodified counterpart at the same lignin loading. Notably, the baseline cellulose acetate films exhibited a tensile strength of 26.3 MPa, thus making the 2.5 wt.% modified lignin incorporated blend's tensile strength value to be 38.4 % higher. No substantial improvement in the tensile strength of films with further addition of lignin was observed. Moreover, a slight drop in tensile strength was recorded with further

addition of lignin moieties in the CA matrix. This was attributed to instances of lignin agglomerates in the polymer matrix, as verified by the optical micrographs.

The elongation at break recorded for the unmodified and modified lignin films exhibited a decreasing trend, as illustrated in **Figure 45c**. This reduction resulted from the reduced polymer chain mobility due to the rigid aromatic lignin structure incorporation. A slight increment in modulus was recorded with the incorporation of lignin or modified lignin, as illustrated in **Figure 45d**. The modulus increase was more visible at high lignin/modified lignin incorporation (5 wt.% and 10 wt.%). This increase was ascribed to the incorporation of higher amounts of rigid material in the relatively soft CA polymer matrix in line with the reduction in elasticity.

5.3.6.4. Moisture absorption and barrier properties

The water absorptivity of the molded films was systematically investigated (24 h). The collected moisture absorption values were presented in **Figure 46a**. As anticipated, the cellulose acetate film absorbed the maximum amount of water (1.07 g/mm³). This is due to the hygroscopic behavior of the cellulose acetate film, which stems from the presence of residual -OH functional groups on its structure. In a study by Mensitieri et al., the moisture absorption behavior of cellulose acetate was categorized as sigmoidal, primarily due to its high hygroscopicity [359].

Post 24 h exposure to moisture (99% relative humidity environment), 51.4 % less moisture gain by 10 wt.% unmodified lignin-loaded composite film (Lig10) with respect to the baseline

CA film was recorded. This was attributed to a possible reduction in hydrogen bonding of water molecules to the cellulose acetate fraction due to its interactions with lignin moieties.

Moreover, a further decrease in moisture absorption was recorded for the LigOA10 specimen (**Figure 46a**). This stemmed from the enhanced dispersion of the functionalized lignin in the cellulose acetate matrix and also better hydrophobicity imparted to the blends by incorporating the nonpolar modified lignin. These observations were in agreement with the optical micrographs and contact angle measurements.

As anticipated, the maximum moisture loss was observed for the cellulose acetate films (**Figure 46b**). In comparison to the baseline CA and unmodified lignin loaded films, a 40% reduction in moisture loss was recorded for the modified lignin loaded sheets. A similar trend was observed in the water vapor permeability (WVP) values (**Figure 46c**). These observations were synchronous with the contact angle, optical microscopy, and water absorption studies.

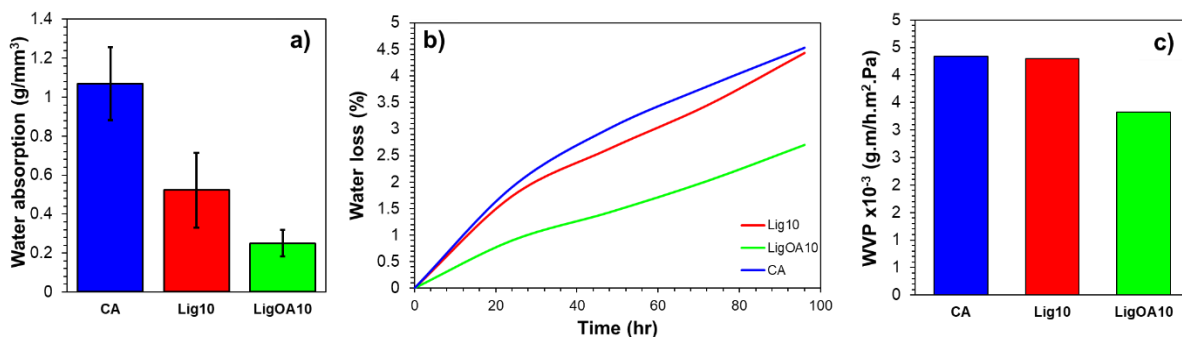


Figure 46. a) Moisture absorption, b) Moisture loss, and c) Moisture barrier properties of the compression molded specimens.

5.3.6.5. UV barrier properties

The UV barrier properties of the molded films were evaluated. As is apparent from **Figure 47**, the baseline cellulose acetate films recorded the least UV absorbance values. In a study by Orelma et al., similar observations were recorded [370]. The incorporation of lignin in its native or modified form provided a substantial improvement in the UV absorbance of the films. This is because the aromatic structure of lignin endows it with UV-absorbing properties. It is important to note that the lignin-incorporated cellulose acetate formulations exhibited high absorption in the UV spectrum. The unmodified lignin-containing sheets accounted for higher absorbance in the UV region. This could be attributed to the structural integrity of unmodified lignin compared to the modified lignin that could have been affected via the modification process. Thus, the incorporation of lignin enhanced the UV barrier properties of the resultant films, making it appealing for UV susceptible food product packaging.

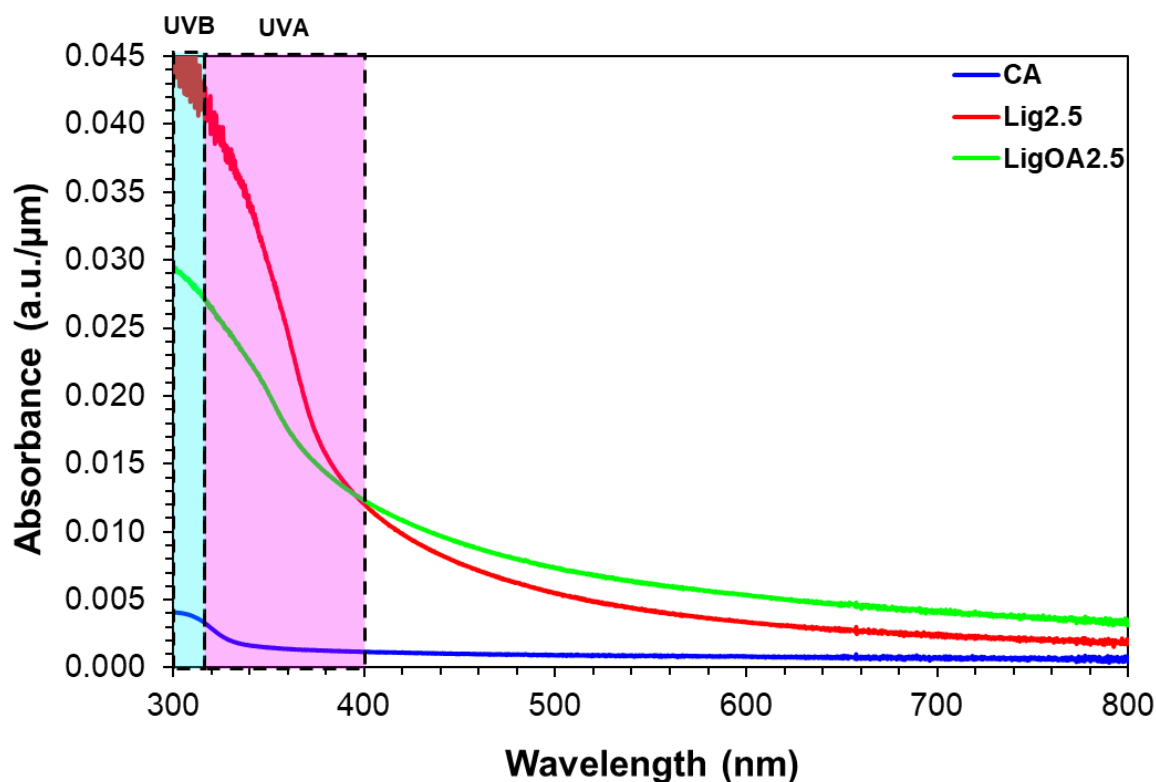


Figure 47. UV-Vis spectra of the baseline and lignin-loaded compression molded sheets.

5.4. Summary of Chapter 5

In this work, oleic acid-modified lignin was put forward as a suitable additive to cellulose acetate to fabricate a sustainable packaging film for food and other applications. The successful oleic acid esterification of lignin was validated using spectroscopic techniques, solvent dispersibility, and melt processibility evaluation. The optimized oleic acid-modified lignin (Lig-OA) displayed melt flowability, while its unmodified counterpart underwent charring upon exposure to similar thermal processing conditions. The cellulose acetate-LigOA blend films also displayed excellent thermo-mechanical processibility via compression molding with enhanced dispersion of the modified lignin in the cellulose acetate matrix. In contrast, the

unmodified lignin agglomerated in the cellulose acetate matrix, which was attributed to the polarity disparity between the cellulose acetate and the pristine lignin. With the employment of 10 wt.% modified lignin blend additive, a 77% drop in water absorption from the baseline cellulose acetate was recorded. On the other hand, the modified lignin-loaded specimen exhibited 51.4 % less moisture absorption than its unmodified counterpart. Additionally, the incorporation of lignin in cellulose acetate enhanced the UV barrier properties of the resulting films, which could have practical applications in packaging materials by preventing the degradation of UV-sensitive food or pharmaceutical components. Overall, the incorporation of functionalized lignin in cellulose acetate could diminish water absorption, enhance the moisture barrier properties, improve the UV barrier, and overall dimensional stability of the resulting films for food packaging and other material applications.

Chapter 6 – Esterification of lignin with long chain fatty acids for the stabilization of oil-in-water Pickering emulsions⁵

6.1. Introduction

Traditional surfactants have been widely recognized to deter phase inversion in emulsions. The use of certain conventional emulsifiers has raised environmental concerns [371–373]. A greener alternative to conventional surfactant-stabilized emulsions, Pickering emulsions utilize lower particle loadings of colloidal particles for effective emulsion stabilization [374]. Moreover, Pickering emulsions demonstrate superior long-term stability to their conventional surfactant-loaded counterparts. This is attributed to their irreversible adsorption at the oil-water interface, thus, avoiding the coalescence of dispersed phase droplets [373]. Thus, the development of Pickering emulsions has industrial as well as academic significance.

In recent times, the extensive use of Pickering emulsions in pharmaceutical, food, and cosmetic industries has been observed [118]. Pickering emulsions have been reported to be stabilized by both organic and inorganic particles [119], such as Calcium carbonate [122], silica [121], latex [120], LAPONOLITE [123] etc. Crystalline silica is a widely available mineral, and its mining is detrimental to the surrounding environment. In addition, breathing in of crystalline silica dust is known to cause silicosis in human beings [375]. Due to environmental and sustainability concerns, more efforts are being invested to promote the use of sustainable, renewable, biodegradable, and nontoxic alternatives to conventional Pickering emulsifiers [125]. In one

⁵ A version of this chapter has been published on peer-reviewed journal as a review article: Shorey, R., & Mekonnen, T. H. (2023). Esterification of lignin with long chain fatty acids for the stabilization of oil-in-water Pickering emulsions. *International Journal of Biological Macromolecules*, 230, 123143. <https://doi.org/10.1016/j.ijbiomac.2023.123143>

such effort, Ougiya et al. investigated the use of bacterial cellulose in stabilizing oil-in-water emulsions [376]. After cellulose, lignin is the second most abundant renewable material in nature.

Lignin, amounting to 15% to 30% of the total available biomass, is the most abundant natural phenolic biopolymer [290,377]. Each year, enormous amounts of lignin is produced as a byproduct of the biorefinery and the paper and pulp industries. While the majority share of this lignin is burnt as a low-cost fuel, a miniscule amount is valorized as adhesives, surfactants, fillers, anti-microbial agent, adsorbents, and in energy, construction, biomedical and biotechnological applications [3,378–387]. The widescale applicability of lignin is hindered by its inherent characteristics, such as the presence of extensive hydrophilic moieties, the tendency to agglomerate, variability in chemical structure with the employed extraction method and feedstock, and poor dispersibility in nonpolar mediums [291]. To effectively valorize lignin, significant efforts have been invested in modifying its chemical structure [16–19,31,32,293,348].

The presence of extensive hydroxyl (-OH) moieties on the lignin molecular structure serves as potential reaction sites. Amongst the available reaction routes, esterification of lignin is one of the viable options [294,295]. One of the considerations while choosing a fatty acid chloride for esterification of lignin specimen is the number of carbon atoms in the long-aliphatic carbon chains.

The present study aimed at developing novel sustainable and biodegradable alternatives to conventional Pickering emulsifiers and traditional surfactants. Thus, the utilization of lignin

and its esterified counterparts as a sustainable Pickering emulsifier of oil-water emulsions was investigated. Initially, the inherent limitations of the unmodified kraft lignin were addressed by esterification reactions with activated fatty acids with various aliphatic chain length. For this acid chlorides with short (hexanoyl chloride, C6), medium (decanoyl chloride, C10), and long (palmitoyl chloride, C16) aliphatic chains were employed as esterifying agents. The esterified specimens were hypothesized to exhibit enhanced dispersibility to their unmodified counterpart. The successful esterification reactions were confirmed and verified by spectroscopic and other analysis. The impact of the aliphatic chain length in the level of lignin modification and their effect in enhancing the emulsion stability was systematically evaluated. The change in the emulsion stability, oil droplet size, zeta potential, and flow properties of the prepared emulsions were also investigated in detail and reported. To the best of the authors knowledge, no previous work has attempted to study the stabilization effects of lignin esterified with various aliphatic carbon chain length fatty acids in oil-in-water emulsions while simultaneously evaluating the effect of varying pH and Pickering emulsifier concentrations on its stability.

6.2. Materials and methods

6.2.1. Materials

Kraft lignin (Amallin™ LPH, pH 2.2, and average molecular weight 6500 g/mol) was sourced from West Fraser Mills Ltd., Canada. Decanoyl chloride and Palmitoyl chloride (> 97%) were obtained from TCI chemicals. Hexanoyl chloride, Pyridine (99.8 %), Toluene (≥99.5%), and Tween 85 were purchased from Sigma-Aldrich (Oakville, ON, Canada). The Amallin™ LPH

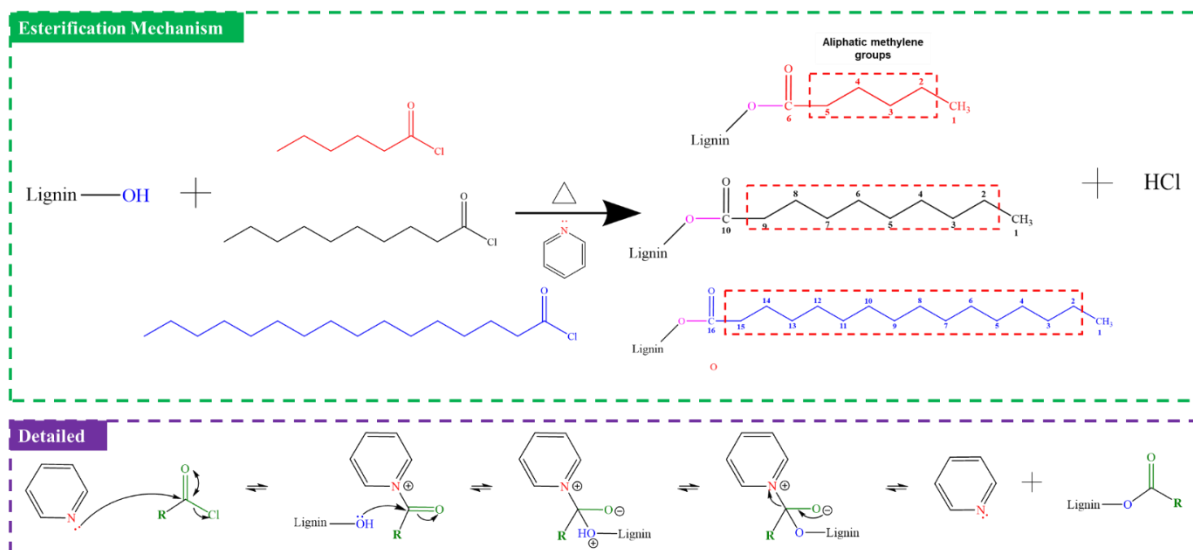
Kraft lignin was washed with DI water (thrice) and the pH has increased to 4.8, dried in a forced air oven (60 °C, overnight) and stored in an airtight container to maintain moisture content of <3% until further use.

6.2.2. Methods

6.2.2.1. *Modification of kraft lignin with various acid chlorides*

The esterification reactions of the kraft lignin (average molecular weight 6500 g/mol) were undertaken employing three fatty acid chlorides with increasing aliphatic carbon chain lengths [31,296–298]. Hexanoyl chloride, decanoyl chloride, and Palmitoyl chloride were utilized in the proposed modifications. As outlined in **Schematic 4**, the successful esterification of the supplied lignin sample entailed the grafting of long aliphatic carbon chains at the molecular sites hosting hydroxyl (–OH) moieties. A 10 wt.% solution of kraft lignin sample in pyridine was sonicated for 10 minutes and subsequently, transferred to a round bottom flask (RBF). Pyridine was employed as an acid scavenger (HCl, **Schematic 4**) and a reaction medium. The contents of the flask were heated to 95 °C in an oil bath (silicone oil) with constant stirring (400 rpm). Calculated volumes of fatty acid chlorides that provides a molar ratio of 1:1 (Lig (OH):Acid chloride) were added to the flask for each respective reaction. The reactions were monitored for 3 h, the heating source was removed, and the contents were allowed to cool down to the room temperature. The modified lignin samples were then precipitated with 0.1 M HCl and centrifuged at 3,700 rpm for 7 min. Furthermore, the products were washed with water and centrifuged (thrice). Post centrifugation, the specimens were dried in a convection oven (80 °C, overnight) and stored in glass vials. The modified samples were denoted as LigHC

(Hexanoyl chloride modified), LigDC (Decanoyl chloride modified), and LigPC (palmitoyl chloride modified). Successful esterification and complete removal of unreacted acid chlorides was verified by employing infrared (*IR*) analysis.



Schematic 4. Proposed esterification mechanism for the reaction of kraft lignin with acid chlorides of various aliphatic chain length.

6.2.2.2. Spectroscopic analysis of unmodified and esterified lignin specimens

Infrared (IR) spectroscopy

The successful esterification of kraft lignin samples was confirmed using the Fourier transform infrared (*FTIR*) spectroscopy (Nicolett 6700, Thermo Fisher Scientific, MA, United States). For the FTIR analysis, sample pellets were prepared by mixing 2 mg of the respective lignin samples with 200 mg KBr salt and pressing it at 7000 psi in an *IR* pellet die (6 minutes). The *IR* spectra (transmittance mode) were then collected in the frequency range (4000 to 500 cm^{-1} , 128 scans).

Solid-state C-NMR spectroscopy

To further verify the proposed reaction mechanism (**Schematic 4**), solid-state carbon nuclear magnetic resonance (C-NMR) spectra of the baseline and modified lignin specimens were recorded. The spectra (0 to 200 ppm) were collected on a Bruker-SpectroSpin 500 MHz Ultra shield high-resolution NMR (Bruker Corporation, MA).

6.2.2.3. Design of experiments and preparation of emulsions

A 2x2 factorial design was employed for devising the compositions of each of the unmodified

Table 5. Composition of the emulsion formulations

Type of Lignin	pH	Concentration of lignin (mg/mL)	Sample identifier
Unmodified	-1	-1	S13
	0	0	S17
	+1	-1	S5
	+1	+1	S1
	-1	+1	S9
HC modified	0	0	S18
	+1	-1	S6
	+1	+1	S2
	-1	+1	S10
	-1	-1	S14
DC modified	+1	-1	S7
	-1	+1	S11
	+1	+1	S3
	0	0	S19

	-1	-1	S15
	-1	-1	S16
	+1	-1	S8
PC modified	0	0	S20
	-1	+1	S12
	+1	+1	S4

Levels of pH = +1 (pH 9), 0 (pH 7), and -1 (pH 5); Levels of concentration = +1 (2.0 mg/mL), 0 (1.0 mg/mL), and -1 (0.5 mg/mL).

and esterified lignin stabilized Pickering emulsions using MINITAB® (Release 14.12.0). As illustrated in **Table 5**, the proposed design constitutes of two independent factors – pH and concentration of lignin samples. The high and low levels of pH were specified as pH 9 and pH 5 with the midpoint being pH 7. Similarly, the maximum and minimum lignin sample concentration used were 2 mg/mL and 0.5 mg/mL with 1 mg/mL being the defined midpoint (determined based on preliminary experimentations).

In accordance with **Table 5**, a designated amount and type of lignin sample were weighed and added to a vial. To this vial, 2 mL of Toluene (oil phase) was injected, and the contents were sonicated for 10 minutes. As specified in **Table 5**, 8 mL of the respective dispersion medium (pH 5, pH 7, or pH 9) was added dropwise to the vial. The contents were sonicated for another 10 minutes. The formed emulsions were cooled down to room temperature and further characterized.

6.2.2.4. Characterization of prepared emulsions

Type of emulsions

The type of emulsion was assessed by employing a modified version of the droplet test [351]. 1 mL of the formulated emulsion specimen was added to individual vials filled with 14 mL of

the oil phase (toluene) and the aqueous phase, respectively, and shaken (30 seconds). For an oil-in-water emulsion, the added emulsion dissolves in the continuous aqueous medium and remains separated in the nonaqueous medium and vice versa.

Stability analysis

The visual observations for the stability of the emulsions were recorded for a duration of 7 days, with photographic evidence being captured every 24 h. The resulting images were then analyzed by computing the crema index and oil fractionation.

Crema index

The creaming stability of emulsions exhibiting the creaming layer was calculated by employing Equation 6.1 [388].

$$CI (\%) = \frac{hs \times 100}{h} \quad (6.1)$$

where h_s and h are the height of the serum layer and the total emulsion height, respectively.

Fraction of oil

To further investigate the stability of prepared emulsions and measure the coalesced oil layer (in certain emulsions), the fraction of oil phase (toluene) was quantified, in accordance with the method proposed by Maaref et al. [351].

$$Fraction\ of\ oil = \frac{V_o}{V_i} \quad (6.2)$$

Where V_o is the volume of oil released and coalesced in a layer above the emulsion phase (overtime) and V_i is the initial volume of oil added to the emulsion.

Optical microscopy

To analyze the distribution of the oil droplets and lignin moieties in the prepared emulsions, their optical micrographs were recorded right after sonication. A BX53M polarizing optical microscope (Olympus, United States) was employed for the study. The effect of different aliphatic carbon chain lengths grafted on esterified lignin samples, their concentration, and the pH of the dispersion medium on the stability of formulated emulsions were investigated at 50x magnification. From the captured micrographs, the oil droplet size distribution was analyzed using ImageJ software.

Zeta potential

The zeta potential (ζ -potential) values of the baseline and esterified lignin stabilized emulsions were measured using a Zetasizer Nano ZS90 (Malvern Panalytical, UK). The samples were prepared by carrying out 100x dilution in deionized water. For each sample, an arithmetic mean of three consecutive zeta potential measurements were recorded and analyzed.

Rotational rheometry

To investigate the flow characteristics of the formulated emulsions, a rotational rheometry analysis was conducted on a HAAKE Mars III rheometer (Thermo Scientific, United States). 1 mL of the respective emulsion sample was loaded between the base plate and a parallel plate (PP35Ti) geometry with a gap of 1.0 mm. The geometry was then sheared from 0.001 1/s to 1000 1/s at 30 °C.

Comparative study

To evaluate the stability of esterified lignin stabilized emulsions in comparison to industrial grade surfactants, a stability analysis was conducted. Emulsified lignin and Tween 85 stabilized emulsions (2 mg/mL surfactant, pH 9) were prepared and subjected to rotational rheometry (0.001 1/s to 1000 1/s at 30 °C) and optical microscopy (50x). The captured micrographs were analyzed using ImageJ software.

6.2.2.5. Statistical analysis

A one-way ANOVA (analysis of variance) test was performed to investigate the difference in the average oil droplet sizes exhibited by the various prepared emulsions. For a confidence interval (CI) of 95% ($p \leq 0.05$), the difference was considered statistically significant.

6.3. Results and discussions

6.3.1. Characterization of esterified lignin specimens

6.3.1.1. Structural analysis

In accordance with **Schematic 4**, the successful modification of the baseline kraft lignin specimen was characterized by recording infrared (*IR*) spectra of the unmodified baseline, the acid chlorides, and esterified lignin samples, as illustrated in **Figure 48**. The characteristic peak at 3450 cm^{-1} corresponds to the hydroxyl (-OH) group stretching vibrations of lignin. Due to the substitution of hydroxyl moieties, weaker -OH characteristic vibrations were recorded in the esterified samples [31,303,389]. The transmittance peaks at 2918 cm^{-1} and 2847 cm^{-1} were attributed to methylene (-CH₂) and methyl (-CH₃) groups in hexanoyl chloride (**Figure 48a**) [297].

As evident from **Figure 48 (b and c)**, similar peaks were observed in the IR spectra of decanoyl and palmitoyl chloride respectively. The distinctive presence of -CH_2 and -CH_3 characteristic peaks in the esterified lignin samples relative to the baseline kraft lignin specimen verifies a successful esterification reaction.

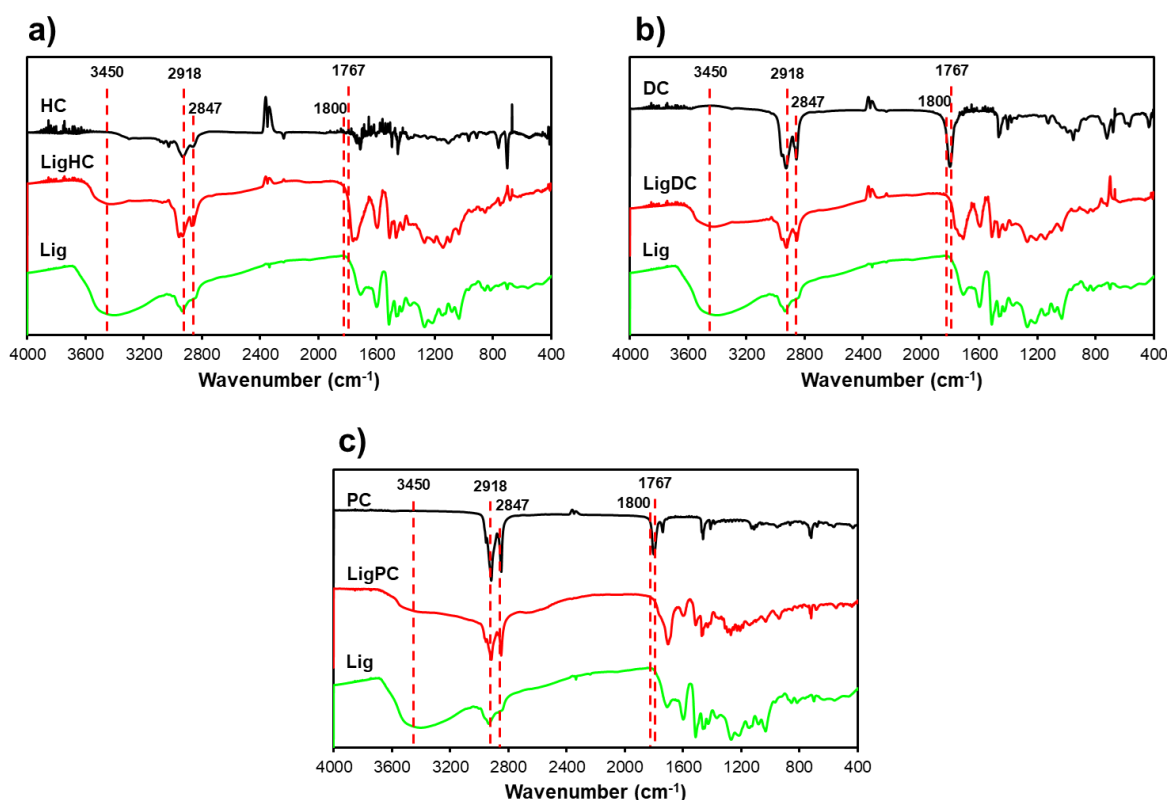


Figure 48. IR spectra of hexanoyl chloride, decanoyl chloride and palmitoyl chloride, control, and esterified lignin samples.

The stretching vibration at 1800 cm^{-1} was attributed to -COCl moieties of the fatty acid chlorides. As observed in **Figure 48**, the absence of this peak in esterified lignin specimens validated the removal of unreacted acid chlorides during the washing step [304]. The development of a peak around 1767 cm^{-1} signified the presence of carbonyl (C=O) moieties

in the esterified specimen, serving as supplementary proof of successful esterification of baseline kraft lignin [303,305]. Altogether, the IR spectra observations were in conjunction with the proposed reaction mechanism presented in **Schematic 4**.

The solid-state *C-NMR* spectra of the unmodified and esterified samples are presented in **Figure 49a**. As previously observed in the IR spectra (**Figure 48**), the appearance of peaks associated with the long-chain aliphatic carbon moieties in *C-NMR* spectra further signifies the successful esterification and grafting of the respective fatty acids on the lignin structure. The characteristic peaks between 33.9 ppm and 22.6 ppm were representative of the methylene (-CH₂) moieties of the long-aliphatic carbon chains units grafted onto the modified lignin molecules (**Figure 49b**) [308]. Also, the peak at 14.1 ppm was associated with the methyl (-CH₃) groups of the long chain aliphatic carbon moieties [31,308]. The peak associated with the carbonyl group of the esterified lignin samples was observed at 172.5 ppm [297]. At 55.7 ppm, the peak signifying the presence of methoxy (-OCH₃) moieties in the tested samples was recorded [297]. As observed from the FTIR (**Figure 48**) and C-NMR (**Figure 49**) evaluations, the esterification of baseline kraft lignin with the hexanoyl chloride (HC), decanoyl chloride (DC), and palmitoyl chloride (PC) was successful, and henceforth the respective esterified lignin samples are denoted as LigHC, LigDC, and LigPC.

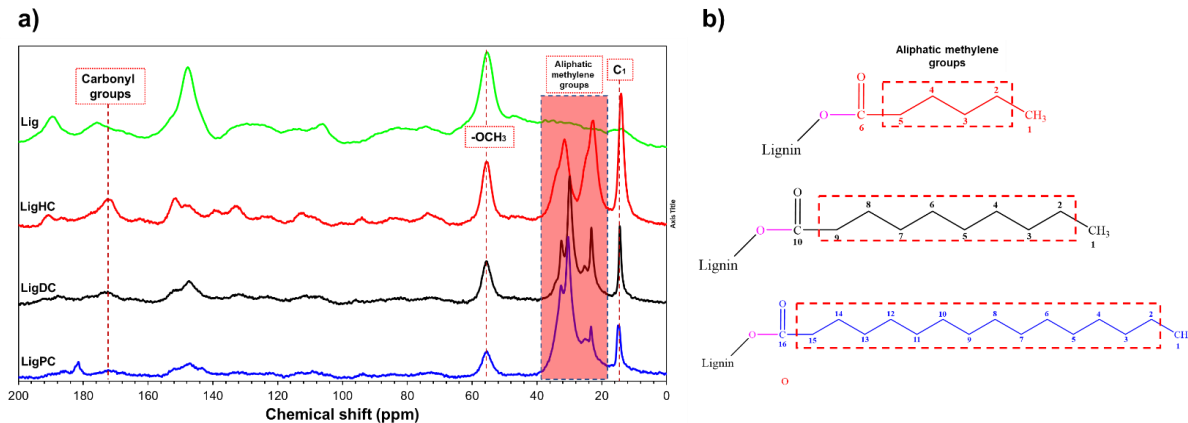


Figure 49. a) SSNMR spectra of unmodified and esterified lignin specimens, and b) chemical structure of hexanoyl, decanoyl, and palmitoyl chloride.

6.3.2. Characterization of formulated Pickering emulsions

6.3.2.1. Type of emulsion

To investigate the type of emulsions prepared, 1 mL of the Pickering emulsions were added to 14 mL of aqueous and non-aqueous phases and shaken. As illustrated in **Figure 50**, the added emulsions formed a layer above the aqueous phase and below the oil phase. This was attributed to the difference in densities of the two media. Post shaking, the emulsion samples dispersed uniformly in the aqueous phase, while it continued to exist as a separate layer in the oil phase. Thus, the emulsions were categorized as oil-in-water emulsions. These results were in coherence with the findings of Zhang et al., where the researchers indicated the presence of nonpolar oils (toluene) with partially hydrophobic particles (lignin) favored the formation of oil-in-water emulsions [351,390].

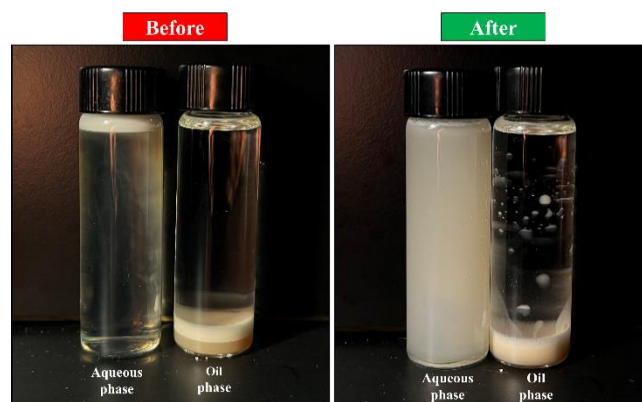


Figure 50. Droplet test for the prepared emulsions.

6.3.2.2. Effect of pH and lignin concentration on the stability of Pickering emulsions

Pickering emulsions were prepared in accordance with the formulations specified in **Table 5**. The emulsions were left undisturbed, and their images were recorded for one week, as presented in **Figure 51**, **Figure 52**, and **Figure 53**.

Stability of alkaline (pH 9) Pickering emulsions

As illustrated in **Figure 51**, visual observations were recorded for 7 days. Post 24 hours, creaming was observed in all the alkaline emulsions. In the creaming process, the density difference between the dispersed phase (oil) and the dispersion medium (water) drives a mass migration of the oil droplets to rise and concentrate to form a distinct layer [356,391]. Being a reversible process, a mild agitation can effectively redisperse the emulsion [392].

Upon visual inspection, the samples prepared in an alkaline medium (pH 9) and with a lignin concentration of 2 mg/mL exhibited superior stability than their lower pH counterparts. The emulsions formulated with the modified lignin samples exhibited higher creaming index values than their unmodified lignin counterparts (**Table E 1 (Appendix E)**). This was attributed to

the superior dispersibility of modified lignin moieties and hence better barrier against coalescence than the unmodified lignin specimen in an alkaline dispersion medium [393].

Moreover, the existence of a two-layer system, i.e. cream and serum were witnessed clearly in the unmodified lignin (Lig) emulsion (pH 9, 0.5 mg/mL). On the contrary, the emulsions made with 0.5 mg/mL of modified lignin (LigHC and LigDC) demonstrated a three-layer system, i.e. cream, emulsion, and serum [394]. This could be correlated to the better adsorption of modified lignin samples at the oil-water interface thus imparting superior stability to the modified lignin-loaded emulsions than their unmodified counterpart. Similar observations were noted in optical microscope (**Figure 54**) and Zeta potential (**Figure 58**) analysis.

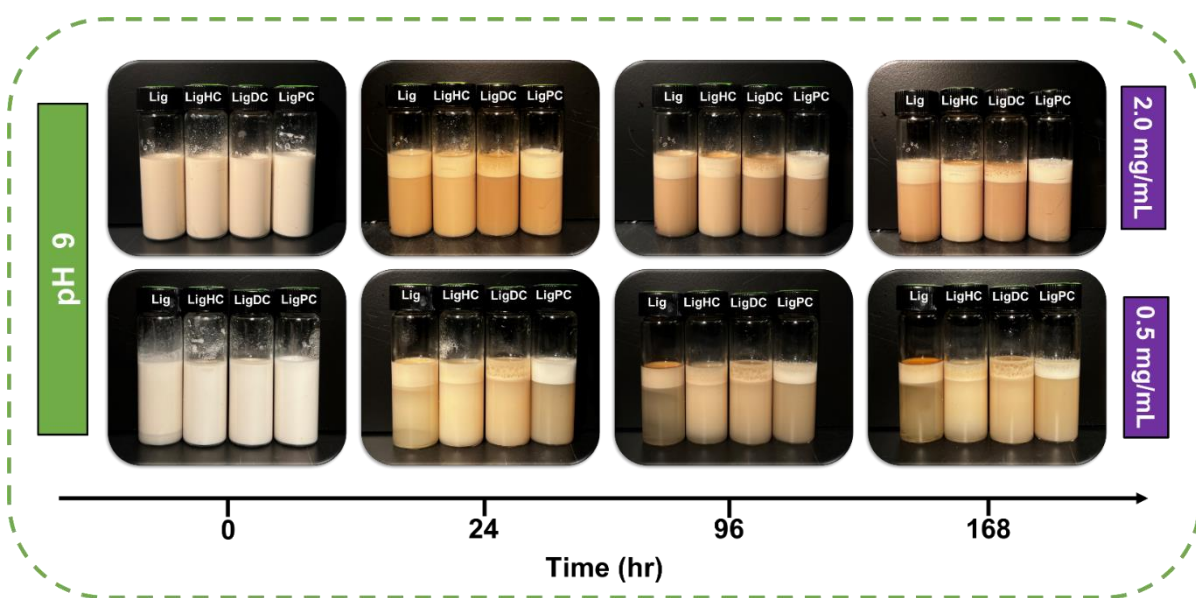


Figure 51. Effect of pH 9 and lignin concentration (2 mg/mL and 0.5 mg/mL) on the stability of prepared Pickering emulsions over 7 days.

Stability of neutral (pH 7) Pickering emulsions

The stability of Pickering emulsions at a neutral dispersion medium (pH 7) were investigated and the recorded pictures are presented in **Figure 52** that demonstrate an apparent phase separation and aggregation of the oil phase. This phenomenon was due to the stronger van der Waal attractions, resulting in film rupture and a significant increase in oil droplet sizes [391]. Moreover, agglomerations of lignin moieties could have resulted in inferior adsorption of the particles at the oil-water interface and thus, leading to the coalescence of the oil phase.

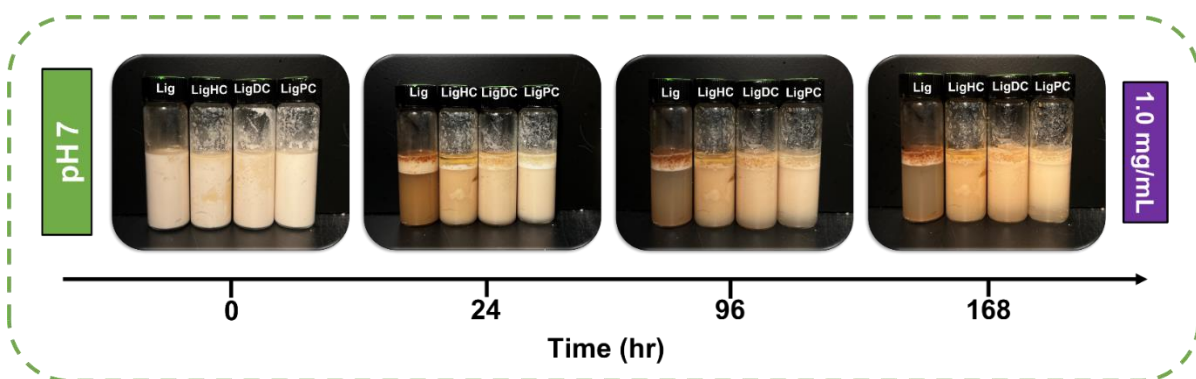


Figure 52. Effect of pH 7 and lignin concentration (1 mg/mL) on the stability of prepared Pickering emulsions over 7 days.

Stability of acidic (pH 5) Pickering emulsions

After 24 h post sonication, clear phase separation and coalescence of the oil phase was observed in acidic emulsions (**Figure 53**). Unlike the neutral emulsions, the emulsions formulated with an acidic dispersion medium exhibited a distinctive oil phase layer coalesced as a separate oil layer. This was attributed to the inferior dispersion of lignin in an acidic medium, thus, existing as agglomerated chunks. In these respective formulations, van der Waal's force of attraction would have been much stronger than the repulsive forces [391].

Thus, the barrier created by the lignin particles between the oil phase and dispersion medium would not have been sufficient to deter agglomeration. It is worth noting that distinctly coalesced oil fractions were recorded for LigHC stabilized emulsions, amounting to 0.52 and 0.55 for acidic emulsions with particle loading concentrations of 2.0 mg/mL and 0.5 mg/mL, respectively. Similarly, LigDC stabilized emulsions witnessed oil phase separation, which was less pronounced than its LigHC stabilized counterpart. Overall, the observations were in agreement with the initial hypothesis.

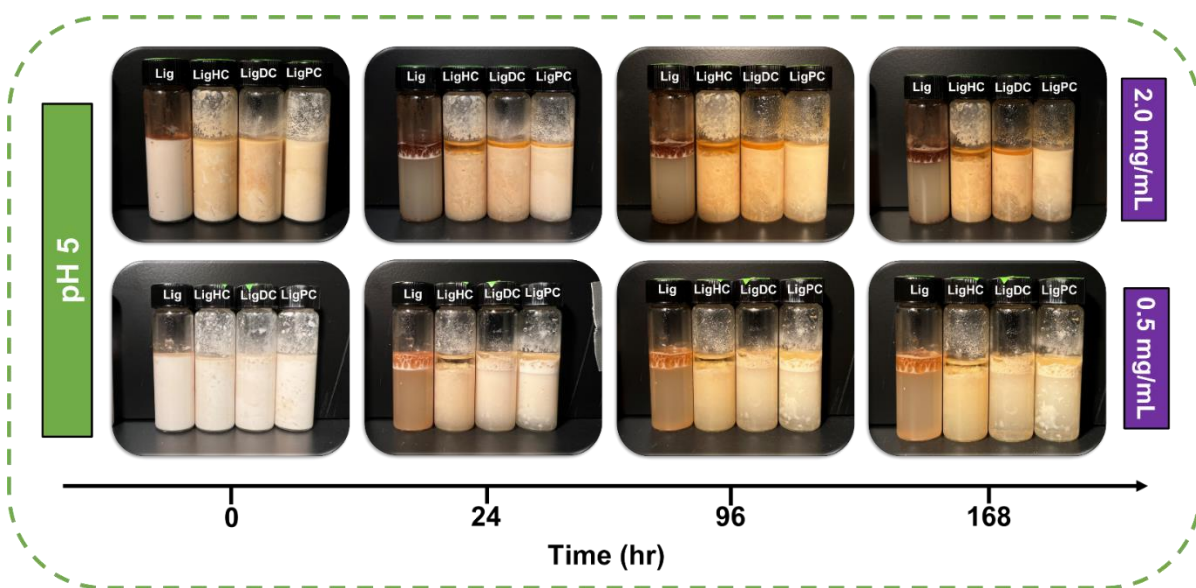


Figure 53. Effect of pH 5 and lignin concentration (2 mg/mL and 0.5 mg/mL) on the stability of prepared Pickering emulsions over 7 days.

6.3.2.3. Effect of lignin concentration and pH on the microstructure of emulsions

The stability of the prepared emulsions was further investigated via optical microscopy. The collected optical micrographs are illustrated in **Figure 54**, **Figure 56**, and **Figure 57**. As noted from **Figure 54**, the oil droplets dispersed in an alkaline dispersion medium appear to be well distributed, dispersed, and spherical with no apparent coalescence and flocculation. The

modified lignin emulsions (pH 9 and lignin concentration 2.0 mg/mL) demonstrated a smaller oil droplet size in comparison to their unmodified counterparts, as was apparent from the oil droplet size distribution (**Figure 54**). Moreover, with the addition of 2 mg/mL of LigHC, the average droplet size with respect to the unmodified lignin (Lig) samples has reduced by 47%. A similar trend was observed in the alkaline emulsions with 0.5 mg/mL of lignin samples, though the average diameter for the unmodified lignin-loaded specimen was recorded to be 5.17 μm . With a decrease in lignin concentration (from 2.0 wt.% to 0.5 wt.%), an increase in average diameter for unmodified lignin stabilized emulsions was observed. This increase was postulated to the higher lignin loadings effectively shielding the oil droplets from coalescing into bigger droplets. Similar observations in a different system were reported in the literature [354].

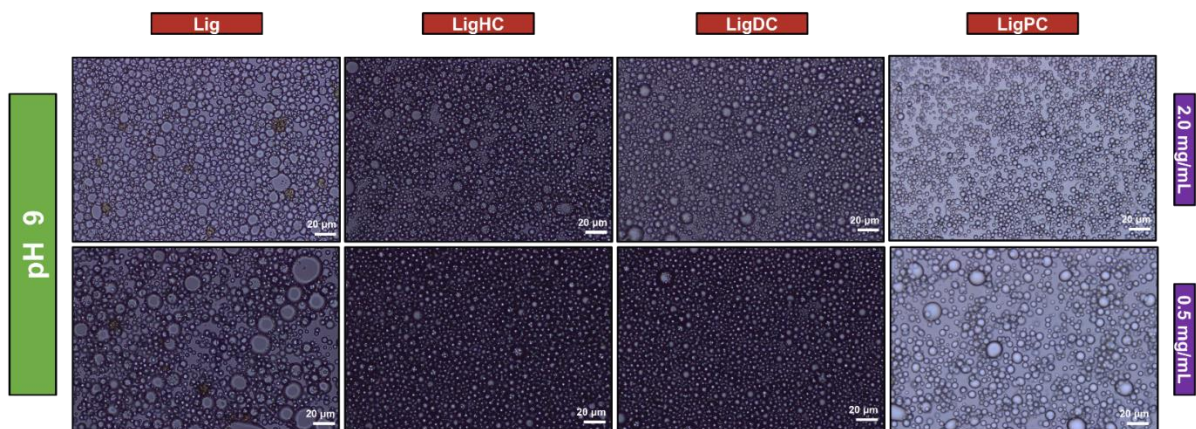


Figure 54. Optical microscopic images of alkaline Pickering emulsions.

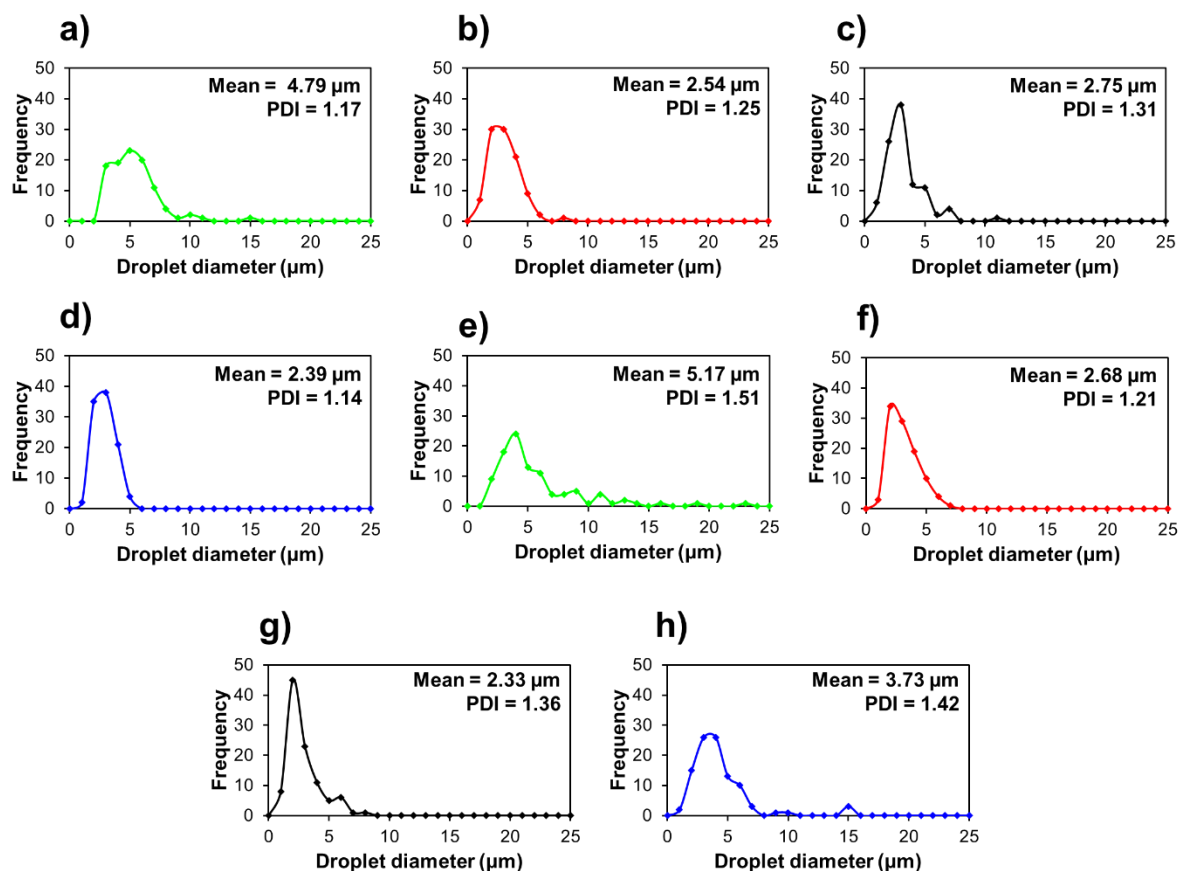


Figure 55. Droplet size distribution in alkaline (pH 9) Pickering emulsions: a) Lig (2 mg/mL), b) LigHC (2 mg/mL), c) LigDC (2 mg/mL), d) LigPC (2 mg/mL), e) Lig (0.5 mg/mL), f) LigHC (0.5 mg/mL), g) LigDC (0.5 mg/mL), and h) LigPC (0.5 mg/mL).

As evident from **Figure 56**, the unmodified lignin-loaded emulsion specimen (pH 7) recorded a 18.4% increase in average oil droplet size (5.67 μm) than its alkaline 2.0 mg/mL counterpart. Overall, significant differences between the droplet sizes of modified lignin-loaded specimens in alkaline and neutral pH were observed (**Figure 55** and **Figure E 1 (Appendix E)**). These observations were in agreement with stability analysis and recorded zeta potentials.

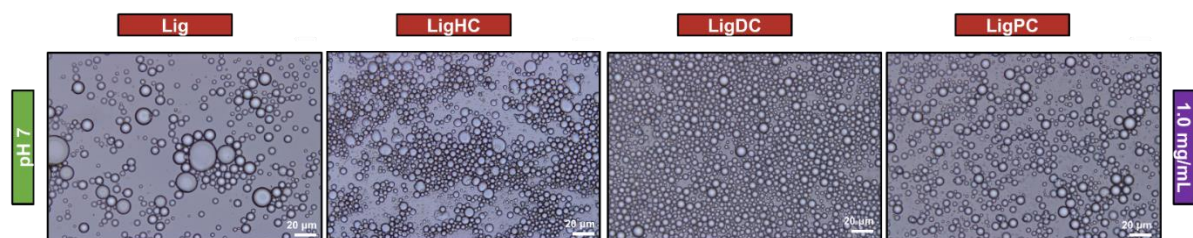


Figure 56. Optical microscopic images of neutral Pickering emulsions.

The optical micrographs of Pickering emulsions in an acidic medium are presented in **Figure 57**. Contrary to the uniformly distributed dispersed phase observed in alkaline emulsions, the distribution of oil droplets in the acidic emulsions was non-uniform. Flocculation of oil droplets was observed in 0.5 mg/mL loaded specimens, exhibiting an average diameter as high as 10.38 μm (Lig(0.5mg/mL)). Although the microscopic images were recorded right after sonication (**Figure 57**), the observed flocculation could explain the distinctive phase separations previously observed in the same specimens, post 24 hours (**Figure 53**). This could be attributed to the phenomenon of oil droplet flocculation faster to the top layer of emulsions than individual drops [355]. Also, the strong van der Waal's forces of attraction overshadowed the effect of repulsive forces, thus, leading to the coalescence of oil droplets (**Figure 53**).

Overall, the alkaline dispersion medium-based emulsions had the smallest average oil droplet size, as evidenced by the distribution curves (**Figure 55**, **Figure E 1**, **Figure E 2**, and **Figure E 3 (Appendix E)**). These observations were in agreement with visual observations from the stability test and zeta potential analysis. The recorded average oil droplet diameter values were statistically significant ($p < 0.05$). Other pH values could also be considered in follow-up studies.

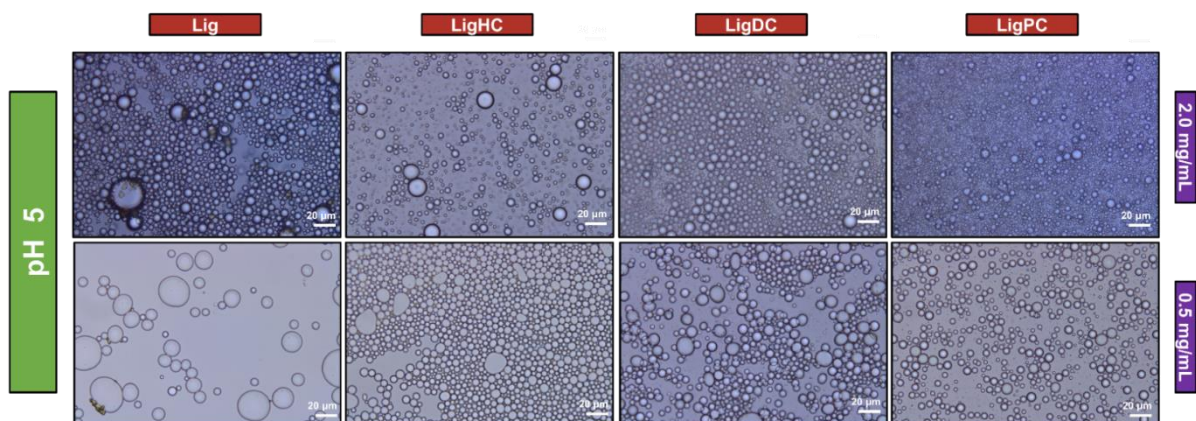


Figure 57. Optical microscopic images of acidic Pickering emulsions.

6.3.2.4. Zeta (ζ) potential analysis

The zeta potential of the prepared Pickering emulsions was measured and presented in **Figure 58**. The short and long-term stability of an emulsion can be related to its measured zeta potential values [395]. Emulsions with highly negative or positive zeta potentials are electrically stable, while the ones with lower ζ potential values tend to flocculate or coagulate. A ζ potential value lower than -30 mV and higher than 30 mV implies adequate repulsive forces for a stable dispersion [396]. This is due to the attractive forces (van der Waals) overshadowing the repulsive forces between the dispersed phase droplets [395,396]. The specimens prepared in an alkaline dispersion medium (pH 9) recorded the highest magnitude of ζ potential values respectively. For the specimen with 2.0 mg/mL of LigPC, a zeta potential of -46.60 ± 1.67 mV was recorded. Moreover, the remainder of alkaline emulsions incorporating modified lignin recorded ζ potential values lower than -30 mV, further verifying the stability analysis and lowest average oil droplet sizes observed in the optical microscopic observations.

For the emulsions with neutral (pH 7) dispersion media, ζ potential values higher than or close to -30mV were recorded. This reduction in zeta potential was attributed to the inferior dispersibility of lignin samples in a neutral medium. It is important to highlight that similar behavior was exhibited by the neutral emulsions in the stability analysis (**Figure 52**) and optical microscopy (**Figure 56**).

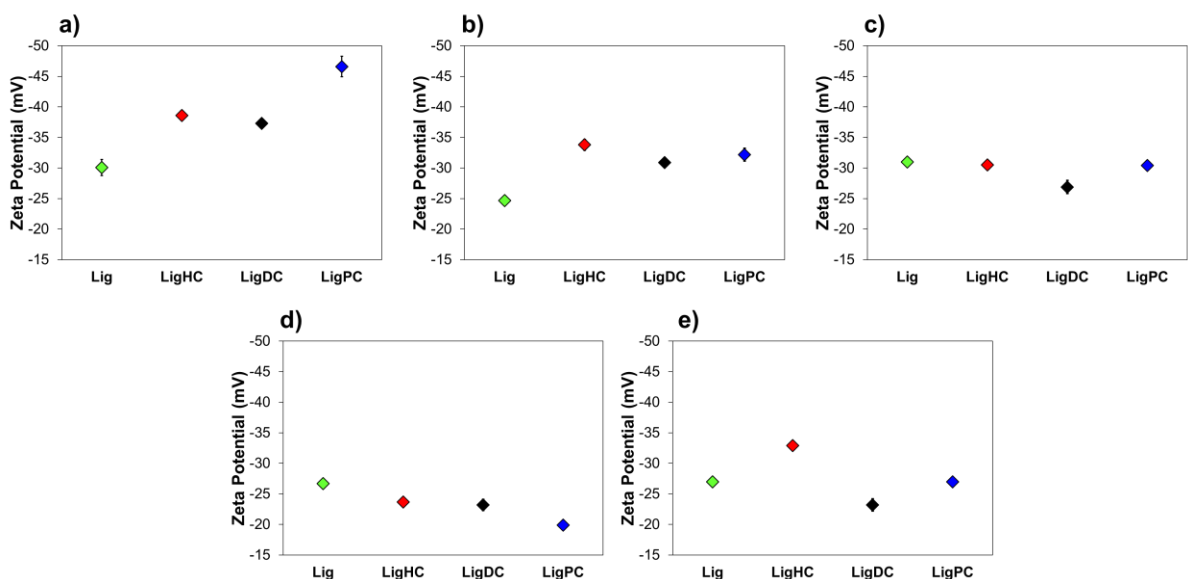


Figure 58. Zeta-potential values of prepared Pickering emulsions: a) pH 9 and 2 mg/mL Lignin particles, b) pH 9 and 0.5 mg/mL Lignin particles. c) pH 7 and 1 mg/mL Lignin particles, d) pH 5 and 2 mg/mL Lignin particles, and e) pH 5 and 0.5 mg/mL Lignin particles.

A further deterioration of stability was witnessed in acidic (pH 5) dispersion medium emulsions. For LigPC (2.0 mg/mL) emulsion, a ζ potential value of -19.9 mV was recorded. This amounted to a drop of 57.3% in ζ potential from its alkaline dispersion medium counterpart. Moreover, the majority of pH 5 Pickering emulsions recorded ζ potential values in excess of -30 mV . This was correlated to the poor dispersibility and the resulting aggregation of lignin moieties in the acidic medium, which in turn led to a poor barrier against oil droplet

coalescence. Further, the low zeta potential values for lightly loaded (0.5 mg/mL) acidic emulsions implied the dispersions were relatively unstable and prone to flocculate due to weak electrostatic repulsive forces, as observed in **Figure 57**. These observations were in agreement with the literature [351].

6.3.2.5. Rheology

To investigate the flow characteristics of the formulated emulsions, a rotational rheometry analysis was undertaken. As noted in **Figure 59**, the unmodified lignin-loaded emulsions demonstrated lower viscosity values in comparison to their modified counterparts. A sixfold increase in viscosity was recorded by modified lignin (LigPC) stabilized emulsion (pH 9, concentration: 2.0 mg/mL) over its unmodified counterpart. This was attributed to the existence of smaller oil droplets in the dispersion matrix that could amplify the specimen's resistance to shear (**Figure 54** and **Figure 55**). Moreover, the better dispersion of modified lignin moieties entails better adsorption at the oil-water interface, thus, deterring the oil droplets from coalescing into bigger droplets [373]. These observations were in-line with stability test, microscopic micrographs, and zeta potential analysis.

With increasing shear rates, the alkaline (pH 9) and neutral (pH 7) dispersion media-based emulsions exhibited shear thinning. On the contrary, a shear thickening followed by a shear thinning of acidic emulsions (pH 5) was observed. This distinctive behavior of these emulsions could be correlated with the flocculation of the dispersed phase in the dispersion medium, as previously witnessed in **Figure 57**. At lower shear rates, an aggregation of the oil droplet flocks could have resulted in a shear resisting force. This counterforce could have superseded the

shearing force, thus, in turn, leading to a minor rise in observed viscosity (shear-thickening). A further increase in shear seemed to overcome the internal resisting forces, hence, the emulsions exhibiting shear thinning behavior. Moreover, these observations were in agreement with the lower zeta (ζ) potential values recorded for the acidic emulsions (**Figure 58**).

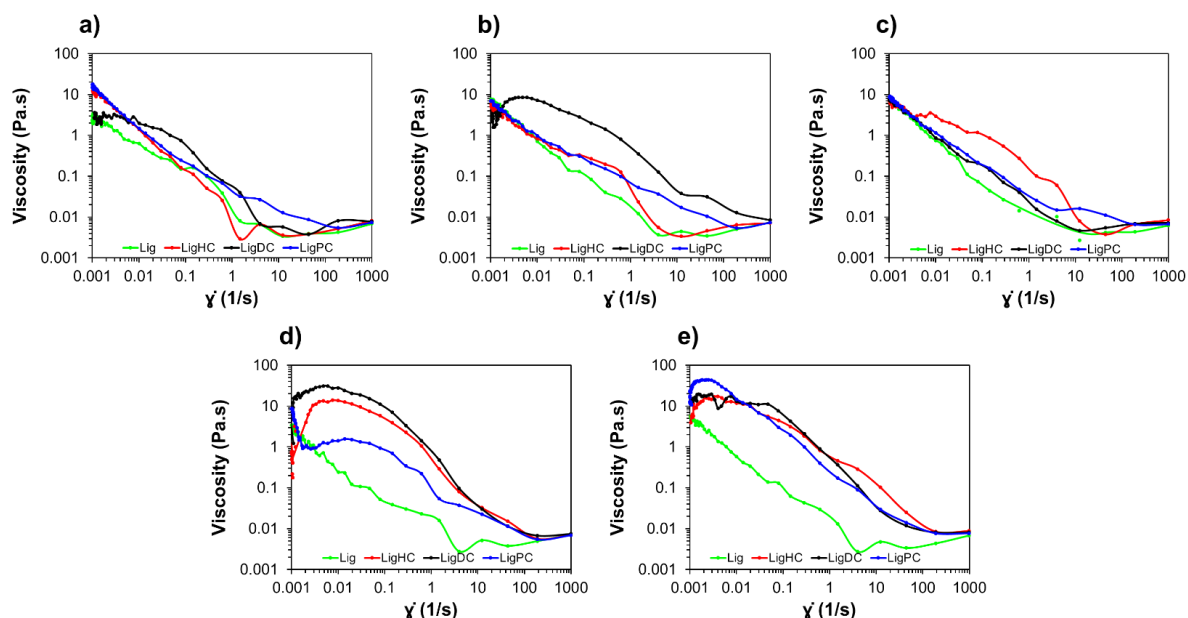


Figure 59. Rotational rheometry of prepared Pickering emulsions: a) pH 9 and 2 mg/mL Lignin particles, b) pH 9 and 0.5 mg/mL Lignin particles. c) pH 7 and 1 mg/mL Lignin particles, d) pH 5 and 2 mg/mL Lignin particles, and e) pH 5 and 0.5 mg/mL Lignin particles.

6.3.2.6. Comparative stability analysis

The emulsions stabilized with emulsified lignin (LigPC) and Tween 85 exhibited good stability (visual), as presented in **Figure 60a**. To further compare the two formulated emulsions, their flow characteristics were evaluated using rheology characteristics. As illustrated in **Figure 60b**, a higher viscosity value (in excess of 3-times) was observed for the emulsified lignin loaded emulsion over its industrial surfactant counterpart. This could be attributed to the superior shielding effect of the solid lignin particles inhibiting the oil droplets from coalescing.

Also, at the oil-water interface, the existence of probable hydrogen bonds between the unreacted hydroxyl moieties of the esterified lignin specimen could have aided in increasing its viscosity. Similar results have been previously recorded in cellulose nanocrystal-based Pickering emulsion systems [397,398].

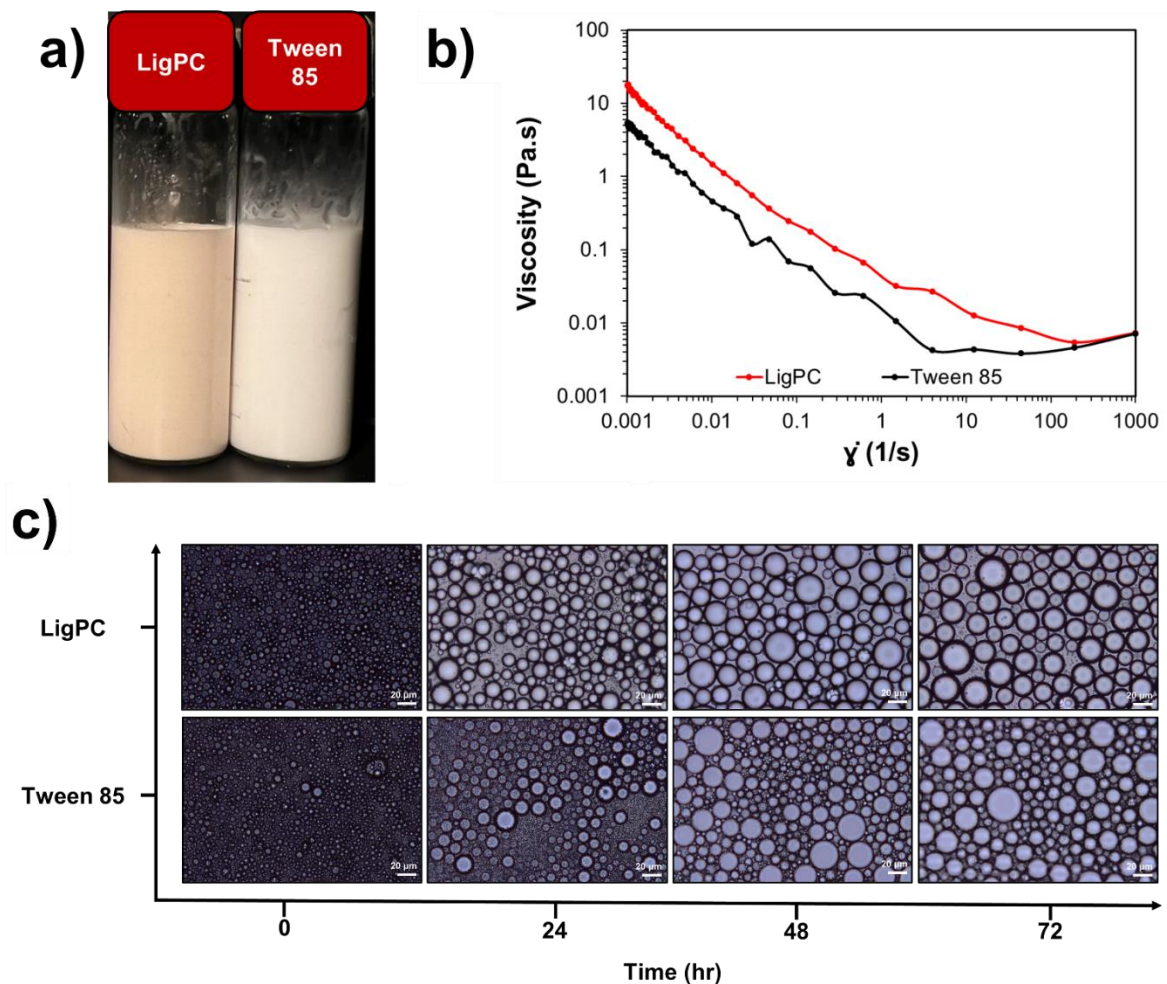


Figure 60. Comparative stability analysis: a) Visual observations of the prepared emulsions, b) Rotational rheometry of prepared Pickering emulsions, and c) Optical micrographs of the prepared emulsions (72 hours).

As evident from **Figure 60c**, the optical micrographs of the prepared emulsions were recorded for a duration of 72 h. Post sonication, the esterified lignin and Tween 85 loaded emulsions

exhibited well dispersed spherical oil droplets with no instance of flocculation or coalescence. The average droplet size of the Tween 85 stabilized emulsion specimen was recorded to be 2.02 μm , being 15.83% smaller than the value recorded for its esterified lignin counterpart. Post 24h, a minute increase in average oil droplet diameters of the formulated emulsions was witnessed. This was attributed to the coalescence of smaller oil droplets to form larger entities in the dispersion medium. After 48h, the arithmetic mean of the size of oil droplets was recorded to be 8.17 μm (LigPC) and 7.75 μm (Tween 85), accounting for a 55.92% and 50.49% increase over the previously recorded values. Lignin stabilized emulsions recorded a mere 4.03% increase in the average oil-phase particle diameter, approx. 2% lower than the oil droplet size increase exhibited by the tween 85 stabilized emulsions. Overall, it appears that the modified lignin Pickering emulsion systems displayed appealing stabilization effect not too different from the commercially available emulsifier (Tween 85).

6.4. Summary of Chapter 6

In this study, modified lignin was put forward as a sustainable and inexpensive Pickering emulsifier of oil-water emulsions. Activated fatty acids with various chain lengths were grafted on lignin to control its polarity and hence its efficacy as a Pickering emulsifier. The level of lignin modification was qualitatively evaluated using spectroscopy and solvent dispersibility analysis. Selected modified lignin samples were then employed to prepare emulsions. The properties of lignin (unmodified and modified) stabilized Pickering emulsions prepared with various stabilizer loadings and pH were characterized. In accordance with the initial hypothesis, esterified lignin loaded emulsions exhibited superior stability over the course of a

week than their unmodified lignin loaded counterparts, albeit the dependency of respective lignin moieties on the pH of the dispersion media. The alkaline emulsions exhibited superior stability in comparison to neutral and acidic emulsions, recording a 47% reduction in the average oil droplet size for LigHC emulsion in comparison to its unmodified counterpart in alkaline medium. On the contrary, the optical micrographs of neutral and acidic emulsions exhibited much larger oil droplets with instances of their apparent coalescence and flocculation. The zeta potential of alkaline samples was highly negative, while, for the, acidic emulsions higher zeta potential values were recorded. These observations were attributed to the existence of weak electrostatic repulsive forces in acidic emulsions, in-line with the poor stability witnessed. Rotational rheometry of the samples aided in confirming the superior flow properties of the modified specimen in comparison to its unmodified counterparts. In the comparative study, the esterified lignin stabilized emulsion specimen performed on-par with the conventional surfactant stabilized emulsion. Overall, the esterified lignin stabilized emulsions exhibited excellent stability and thus, our aim to design a sustainable Pickering emulsifier system was successfully achieved.

Chapter 7 – Conclusions and Future Work

7.1. Conclusions

In this doctoral thesis, various avenues for lignin functionalization and valorization for multiphase and advanced material applications were explored. In the first work, kraft lignin was successfully modified to various degrees by carrying out silylation and esterification reactions. The initial study aimed at the incorporation of silylated kraft lignin into a natural rubber matrix through a solvent casting technique. The proposed reaction mechanism was confirmed using viscosity evaluation, spectroscopic analysis, and dispersibility studies. The wettability test confirmed the proposed substantial polarity change of the modified lignin compared to its unmodified counterparts. It was observed that the modified lignin-based composite samples exhibited superior tensile properties than their unmodified counterparts. For instance, the 5 wt.% modified lignin sample imparted a 44.4% increase in the tensile strength of the baseline NR. The compatibility analysis, water uptake studies, and morphological analysis agreed with the polarity change of the lignin as a result of the silylation reaction, providing good dispersibility of the modified lignin in the NR matrix compared to the unmodified lignin samples. Overall, the silylation modification of lignin was a straightforward process that enhanced the reinforcing capability of lignin in natural rubber.

The second study aimed at fabricating economical, biodegradable, and sustainable alternatives to the traditional polymeric paper coatings for packaging applications. Due to the poor dispersion of lignin in hydrophobic polymers, including PBAT, an esterification modification of the lignin was employed to substitute the abundant hydroxyl moieties with long aliphatic

chains. The esterified lignin exhibited enhanced dispersibility in the non-polar PBAT paper coating formulations resulting in better wet tensile strength of the coated paper. With an increase in the concentration of esterified lignin in the coating formulations (up to 50 wt.%), appealing oxygen, oil, and water barrier properties were recorded. An increment in the coating thickness resulted in a further improvement in barrier properties, with the best barrier obtained using 60 μm thickness, 50 wt.% esterified lignin-PBAT coatings. Overall, the fabricated paper coating films based on the esterified lignin and PBAT in this work demonstrated uniform surface morphology, better tensile properties, and remarkable barrier properties. Since both PBAT and lignin are compostable, the resulting formulation is also expected to be compostable, albeit requiring further investigation and confirmation. These characteristic properties make the formulations an appealing, sustainable material alternative for a range of paper-based food packaging and wrapping applications. Potential applications of such compostable material coated papers include burger wraps, single-use lunch boxes, milk, and juice containers, beverage cups, etc.

The third part of the present work focused on investigating the use of oleic acid-modified lignin as a suitable additive to cellulose acetate to fabricate a sustainable packaging film for food and other applications. The successful oleic acid esterification of lignin was validated using spectroscopic techniques, solvent dispersibility, and melt processibility evaluation. The optimized oleic acid-modified lignin (Lig-OA) displayed melt flowability, while its unmodified counterpart underwent charring upon exposure to similar thermal processing conditions. The cellulose acetate-LigOA blend films also displayed excellent thermo-

mechanical processability via compression molding with enhanced dispersion of the modified lignin in the cellulose acetate matrix. In contrast, the unmodified lignin agglomerated in the cellulose acetate matrix, which was attributed to the polarity disparity between the cellulose acetate and the pristine lignin. With the employment of 10 wt.% modified lignin blend additive, a 77% drop in water absorption from the baseline cellulose acetate was recorded. On the other hand, the modified lignin-loaded specimen exhibited 51.4 % less moisture absorption than its unmodified counterpart. Additionally, the incorporation of lignin in cellulose acetate enhanced the UV barrier properties of the resulting films, which could have practical applications in packaging materials by preventing the degradation of UV-sensitive food or pharmaceutical components. Overall, the incorporation of functionalized lignin in cellulose acetate could diminish water absorption, enhance the moisture barrier properties, improve the UV barrier, and overall dimensional stability of the resulting films for food packaging and other material applications.

Finally, the modified lignin was put forward as a sustainable and inexpensive Pickering emulsifier of oil-water emulsions. Activated fatty acids with various chain lengths were grafted on lignin to control its polarity and hence its efficacy as a Pickering emulsifier. The level of lignin modification was qualitatively evaluated using spectroscopy and solvent dispersibility analysis. Selected modified lignin samples were then employed to prepare emulsions. The properties of lignin (unmodified and modified) stabilized Pickering emulsions prepared with various stabilizer loadings and pH were characterized. In accordance with the initial hypothesis, esterified lignin loaded emulsions exhibited superior stability over the course of a week than their unmodified lignin loaded counterparts, albeit the dependency of respective

lignin moieties on the pH of the dispersion media. The alkaline emulsions exhibited superior stability in comparison to neutral and acidic emulsions, recording a 47% reduction in the average oil droplet size for LigHC emulsion in comparison to its unmodified counterpart in alkaline medium. On the contrary, optical micrographs of neutral and acidic emulsions exhibited much larger oil droplets with instances of their apparent coalescence and flocculation. The zeta potential of alkaline samples was highly negative, while, for the acidic emulsions higher zeta potential values were recorded. These observations were attributed to the existence of weak electrostatic repulsive forces in acidic emulsions, in-line with the poor stability witnessed. Rotational rheometry of the samples aided in confirming the superior flow properties of the modified specimen in comparison to its unmodified counterparts. In the comparative study, the esterified lignin stabilized emulsion specimen performed on-par with the conventional surfactant stabilized emulsion. Overall, the esterified lignin stabilized emulsions exhibited excellent stability and thus, our aim to design a sustainable Pickering emulsifier system was successfully achieved. Thus, the various routes for lignin functionalization were employed for its effective employment in value added applications.

7.2. Future work

Future studies stemming from the present doctoral thesis could include short-term and long-term studies. The first short-term project should be exploring different functionalization reactions and employing them in the various valorization routes discussed in this work. Further, a comparison between the modification routes (undertaken and proposed) in the various valorization avenues covered in this work could be conducted. The use of other polymer

materials and a comprehensive comparative characterization between the various lignin-polymer blends could give further insights into their structure-property relationship. Additionally, the fractionation of lignin specimens based on molecular weight could be implemented, and thus, the fractionated specimens could be characterized for their properties, potential applications, and functionalization possibilities. Moreover, intentional hydrolysis or degradation methods to simplify the complex structure of lignin moieties, in turn obtaining lignin fraction exhibiting reduced complexity and improved reactivity could be undertaken. Lastly, the use of the novel lignin modification methods devised in this doctoral work could be further diversified to other fields such as biomedical applications, energy storage, constructional materials, etc.

The long-term investigations could be carried out to gain a deeper insight into the degradation behavior and the effects of aging on the mechanical, morphological, and barrier properties of the formulated specimens. Furthermore, the effect of environmental variables on the properties of the composites could be evaluated. Moreover, surface grafting of various monomeric units onto the lignin backbone structure to tailor its properties for composite applications could be investigated, thus, initiating another class of co-polymerized materials. In the broader perspective, more avenues for industrial scale applicability of lignin should be created. Collaborations with industrial partners for further application of lignin in products of everyday use could bring lignin the well-deserved recognition that it deserves.

References

- [1] K. Vaezi, G. Asadpour, S.H. Sharifi, Effect of coating with novel bio nanocomposites of cationic starch/cellulose nanocrystals on the fundamental properties of the packaging paper, *Polym Test.* 80 (2019) 106080. <https://doi.org/10.1016/j.polymertesting.2019.106080>.
- [2] E. Divsalar, H. Tajik, M. Moradi, M. Forough, M. Lotfi, B. Kuswandi, Characterization of cellulosic paper coated with chitosan-zinc oxide nanocomposite containing nisin and its application in packaging of UF cheese, *Int J Biol Macromol.* 109 (2018) 1311–1318. <https://doi.org/10.1016/j.ijbiomac.2017.11.145>.
- [3] S.-J. Xiong, B. Pang, S.-J. Zhou, M.-K. Li, S. Yang, Y.-Y. Wang, Q. Shi, S.-F. Wang, T.-Q. Yuan, R.-C. Sun, Economically Competitive Biodegradable PBAT/Lignin Composites: Effect of Lignin Methylation and Compatibilizer, *ACS Sustain Chem Eng.* 8 (2020) 5338–5346. <https://doi.org/10.1021/ACSSUSCHEMENG.0C00789>.
- [4] R.A. Gross, B. Kalra, Biodegradable polymers for the environment, *Science* (1979). 297 (2002) 803–807. <https://doi.org/10.1126/SCIENCE.297.5582.803/ASSET/F574722D-03B6-4ED9-9117-3EF2634AD946/ASSETS/GRAPHIC/SE3020739002.JPEG>.
- [5] M.K. Thakur, V.K. Thakur, R.K. Gupta, A. Pappu, Synthesis and Applications of Biodegradable Soy Based Graft Copolymers: A Review, *ACS Sustain Chem Eng.* 4 (2015) 1–17. <https://doi.org/10.1021/ACSSUSCHEMENG.5B01327>.
- [6] M. Mariano, N. El Kissi, A. Dufresne, Cellulose nanocrystals and related nanocomposites: Review of some properties and challenges, *J Polym Sci B Polym Phys.* 52 (2014) 791–806. <https://doi.org/10.1002/POLB.23490>.
- [7] X. Zhou, A. Mohanty, M. Misra, A New Biodegradable Injection Moulded Bioplastic from Modified Soy Meal and Poly (butylene adipate-co-terephthalate): Effect of Plasticizer and Denaturant, *J Polym Environ.* 21 (2013) 615–622. <https://doi.org/10.1007/S10924-013-0578-Y/FIGURES/8>.

- [8] R. Scaffaro, L. Botta, F. Lopresti, A. Maio, F. Sutura, Polysaccharide nanocrystals as fillers for PLA based nanocomposites, *Cellulose* 2016 24:2. 24 (2016) 447–478. <https://doi.org/10.1007/S10570-016-1143-3>.
- [9] V. Fiore, L. Botta, R. Scaffaro, A. Valenza, A. Pirrotta, PLA based biocomposites reinforced with *Arundo donax* fillers, *Compos Sci Technol.* 105 (2014) 110–117. <https://doi.org/10.1016/J.COMPSCITECH.2014.10.005>.
- [10] F. V. Ferreira, L.S. Cividanes, R.F. Gouveia, L.M.F. Lona, An overview on properties and applications of poly(butylene adipate-co-terephthalate)–PBAT based composites, *Polym Eng Sci.* 59 (2019) E7–E15. <https://doi.org/10.1002/PEN.24770>.
- [11] D.S. Bajwa, G. Pourhashem, A.H. Ullah, S.G. Bajwa, A concise review of current lignin production, applications, products and their environmental impact, *Ind Crops Prod.* 139 (2019) 111526. <https://doi.org/10.1016/J.INDCROP.2019.111526>.
- [12] H. Luo, M.M. Abu-Omar, Chemicals From Lignin, *Encyclopedia of Sustainable Technologies.* (2017) 573–585. <https://doi.org/10.1016/B978-0-12-409548-9.10235-0>.
- [13] N. Mandlekar, A. Cayla, F. Rault, S. Giraud, F. Salaün, G. Malucelli, J.-P. Guan, An Overview on the Use of Lignin and Its Derivatives in Fire Retardant Polymer Systems, *Lignin - Trends and Applications.* (2018). <https://doi.org/10.5772/INTECHOPEN.72963>.
- [14] N. Smolarski, High-value opportunities for lignin: unlocking its potential, 2012. <https://www.greenmaterials.fr/wp-content/uploads/2013/01/High-value-Opportunities-for-Lignin-Unlocking-its-Potential-Market-Insights.pdf> (accessed August 22, 2021).
- [15] L. Dessbesell, M. Paleologou, M. Leitch, R. Pulkki, C. (Charles) Xu, Global lignin supply overview and kraft lignin potential as an alternative for petroleum-based polymers, *Renewable and Sustainable Energy Reviews.* 123 (2020) 109768. <https://doi.org/10.1016/J.RSER.2020.109768>.

- [16] Chemical Modification, Properties, and Usage of Lignin, Springer US, 2002.
<https://doi.org/10.1007/978-1-4615-0643-0>.
- [17] C.S.A. Antunes, M. Bietti, M. Salamone, N. Scione, Early stages in the TiO₂-photocatalyzed degradation of simple phenolic and non-phenolic lignin model compounds, *J Photochem Photobiol A Chem.* 163 (2004) 453–462.
<https://doi.org/10.1016/j.jphotochem.2004.01.018>.
- [18] J. Pérez, J. Muñoz-Dorado, T. De La Rubia, J. Martínez, Biodegradation and biological treatments of cellulose, hemicellulose and lignin: An overview, *International Microbiology.* 5 (2002) 53–63. <https://doi.org/10.1007/s10123-002-0062-3>.
- [19] M. Kaneko, J. Nemoto, H. Ueno, N. Gokan, K. Ohnuki, M. Horikawa, R. Saito, T. Shibata, Photoelectrochemical reaction of biomass and bio-related compounds with nanoporous TiO₂ film photoanode and O₂-reducing cathode, *Electrochem Commun.* 8 (2006) 336–340.
<https://doi.org/10.1016/j.elecom.2005.12.004>.
- [20] N. Mahmood, Z. Yuan, J. Schmidt, C. Xu, Preparation of bio-based rigid polyurethane foam using hydrolytically depolymerized Kraft lignin via direct replacement or oxypropylation, *Eur Polym J.* 68 (2015) 1–9.
<https://doi.org/10.1016/J.EURPOLYMJ.2015.04.030>.
- [21] N. Mahmood, Z. Yuan, J. Schmidt, C. Xu, Production of polyols via direct hydrolysis of kraft lignin: Effect of process parameters, *Bioresour Technol.* 139 (2013) 13–20. <https://doi.org/10.1016/J.BIORTECH.2013.03.199>.
- [22] Z. Ahmad, M. Paleologou, C.C. Xu, Oxidative depolymerization of lignin using nitric acid under ambient conditions, *Ind Crops Prod.* 170 (2021) 113757.
<https://doi.org/10.1016/J.INDCROP.2021.113757>.
- [23] N. Mahmood, Z. Yuan, J. Schmidt, C.C. Xu, Hydrolytic depolymerization of hydrolysis lignin: Effects of catalysts and solvents, *Bioresour Technol.* 190 (2015) 416–419. <https://doi.org/10.1016/J.BIORTECH.2015.04.074>.

- [24] N. Mahmood, Z. Yuan, J. Schmidt, C. Xu, Depolymerization of lignins and their applications for the preparation of polyols and rigid polyurethane foams: A review, *Renewable and Sustainable Energy Reviews*. 60 (2016) 317–329.
<https://doi.org/10.1016/J.RSER.2016.01.037>.
- [25] F. Verdini, E.C. Gaudino, E. Canova, S. Tabasso, P.J. Behbahani, G. Cravotto, Lignin as a Natural Carrier for the Efficient Delivery of Bioactive Compounds: From Waste to Health, *Molecules*. 27 (2022).
<https://doi.org/10.3390/MOLECULES27113598>.
- [26] C. Xu, F. Ferdosian, *Structure and Properties of Lignin*, 2017.
https://doi.org/10.1007/978-3-662-54959-9_1.
- [27] J.J. Meister, MODIFICATION OF LIGNIN*, *Journal of Macromolecular Science, Part C: Polymer Reviews*. 42 (2002) 235–289.
<https://doi.org/10.1081/MC-120004764>.
- [28] C. Scarica, R. Suriano, M. Levi, S. Turri, G. Griffini, Lignin Functionalized with Succinic Anhydride as Building Block for Biobased Thermosetting Polyester Coatings, *ACS Sustain Chem Eng*. 6 (2018) 3392–3401.
<https://doi.org/10.1021/ACSSUSCHEMENG.7B03583>.
- [29] J. Ruwoldt, M. Tanase-Opedal, K. Syverud, Ultraviolet Spectrophotometry of Lignin Revisited: Exploring Solvents with Low Harmfulness, Lignin Purity, Hansen Solubility Parameter, and Determination of Phenolic Hydroxyl Groups, *ACS Omega*. 7 (2022) 46371–46383.
https://doi.org/10.1021/ACSOMEGA.2C04982/SUPPL_FILE/AO2C04982_SI_001.PDF.
- [30] R. Shorey, T.H. Mekonnen, Esterification of lignin with long chain fatty acids for the stabilization of oil-in-water Pickering emulsions, *Int J Biol Macromol*. 230 (2023) 123143. <https://doi.org/10.1016/j.ijbiomac.2023.123143>.
- [31] R. Shorey, T.H. Mekonnen, Sustainable paper coating with enhanced barrier properties based on esterified lignin and PBAT blend, *Int J Biol Macromol*. 209 (2022) 472–484. <https://doi.org/10.1016/J.IJBIOMAC.2022.04.037>.

- [32] R. Shorey, A. Gupta, T.H. Mekonnen, Hydrophobic modification of lignin for rubber composites, *Ind Crops Prod.* 174 (2021) 114189.
<https://doi.org/10.1016/J.INDCROP.2021.114189>.
- [33] I.A. Pearl, *The Chemistry of Lignin*, 1967.
https://books.google.ca/books/about/The_Chemistry_of_Lignin.html?id=hZZxAAAAMAAJ&redir_esc=y (accessed March 31, 2021).
- [34] P. Buono, A. Duval, P. Verge, L. Averous, Y. Habibi, New Insights on the Chemical Modification of Lignin: Acetylation versus Silylation, *ACS Sustain Chem Eng.* 4 (2016) 5212–5222.
<https://doi.org/10.1021/acssuschemeng.6b00903>.
- [35] A. Boarino, H.A. Klok, Opportunities and Challenges for Lignin Valorization in Food Packaging, Antimicrobial, and Agricultural Applications, *Biomacromolecules*. (2022).
https://doi.org/10.1021/ACS.BIOMAC.2C01385/ASSET/IMAGES/LARGE/BM2C01385_0004.JPEG.
- [36] Y. Sun, Z. Ma, X. Xu, X. Liu, L. Liu, G. Huang, L. Liu, H. Wang, P. Song, Grafting Lignin with Bioderived Polyacrylates for Low-Cost, Ductile, and Fully Biobased Poly(lactic acid) Composites, *ACS Sustain Chem Eng.* 8 (2020) 2267–2276.
https://doi.org/10.1021/ACSSUSCHEMENG.9B06593/ASSET/IMAGES/LARGE/SC9B06593_0008.JPEG.
- [37] D. Kun, B. Pukánszky, Polymer/lignin blends: Interactions, properties, applications, *Eur Polym J.* 93 (2017) 618–641.
<https://doi.org/10.1016/J.EURPOLYMJ.2017.04.035>.
- [38] I. Fortelný, D. Kamenická, J. Kovář, Effect of the viscosity of components on the phase structure and impact strength of polypropylene/ethylene-propylene elastomer blends, *Die Angewandte Makromolekulare Chemie.* 164 (1988) 125–141. <https://doi.org/10.1002/APMC.1988.051640110>.

- [39] The formation of emulsions in definable fields of flow, *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character*. 146 (1934) 501–523.
<https://doi.org/10.1098/RSPA.1934.0169>.
- [40] H.-W. Kammer, *Surface and Interfacial Tension of Polymer Melts — Thermodynamic Theory of the Interface between Immiscible Polymers*, *Zeitschrift Für Physikalische Chemie*. 258O (1977) 1149–1161.
<https://doi.org/10.1515/ZPCH-1977-258153>.
- [41] A. Sakakibara, A structural model of softwood lignin, *Wood Science and Technology* 1980 14:2. 14 (1980) 89–100. <https://doi.org/10.1007/BF00584038>.
- [42] M.N. Collins, M. Nechifor, F. Tanasă, M. Zănoagă, A. McLoughlin, M.A. Stróżyk, M. Culebras, C.A. Teacă, Valorization of lignin in polymer and composite systems for advanced engineering applications – A review, *Int J Biol Macromol*. 131 (2019) 828–849.
<https://doi.org/10.1016/J.IJBIOMAC.2019.03.069>.
- [43] S. Kubo, J.F. Kadla, Hydrogen bonding in lignin: A fourier transform infrared model compound study, *Biomacromolecules*. 6 (2005) 2815–2821.
https://doi.org/10.1021/BM050288Q/SUPPL_FILE/BM050288QSI20050421_105103.PDF.
- [44] R.R.N. Sailaja, M. V. Deepthi, Mechanical and thermal properties of compatibilized composites of polyethylene and esterified lignin, *Mater Des*. 31 (2010) 4369–4379. <https://doi.org/10.1016/J.MATDES.2010.03.046>.
- [45] F. Chen, H. Dai, X. Dong, J. Yang, M. Zhong, Physical properties of lignin-based polypropylene blends, *Polym Compos*. 32 (2011) 1019–1025.
<https://doi.org/10.1002/PC.21087>.
- [46] B. Košíková, A. Gregorová, Sulfur-free lignin as reinforcing component of styrene–butadiene rubber, *J Appl Polym Sci*. 97 (2005) 924–929.
<https://doi.org/10.1002/APP.21448>.

- [47] O. Gordobil, I. Egüés, R. Llano-Ponte, J. Labidi, Physicochemical properties of PLA lignin blends, *Polym Degrad Stab.* 108 (2014) 330–338.
<https://doi.org/10.1016/J.POLYMDEGRADSTAB.2014.01.002>.
- [48] J. Sameni, S. Krigstin, S.A. Jaffer, M. Sain, Preparation and characterization of biobased microspheres from lignin sources, *Ind Crops Prod.* 117 (2018) 58–65.
<https://doi.org/10.1016/j.indcrop.2018.02.078>.
- [49] R.M. Wilkins, Lignins as formulating agents for controlled release in agriculture, *British Polymer Journal.* 15 (1983) 177–178.
<https://doi.org/10.1002/pi.4980150407>.
- [50] S. Dubey, V. Jhelum, P.K. Patanjali, Controlled release agrochemicals formulations: A review, 2011.
<http://nopr.niscpr.res.in/handle/123456789/10970> (accessed January 27, 2023).
- [51] Asrar, (12) United States Patent(45) Date of Patent: (54) LIGNIN-BASED MICROPARTICLES FOR THE CONTROLLED RELEASE OF AGRICULTURAL ACTIVES (75) (73) (*) (21) (22) (65) (60) (51) (52) (58) A A A E A A A A A A A A A A A A A A A A 4, 2010.
<https://patents.google.com/patent/US7771749B2/en> (accessed January 27, 2023).
- [52] C. Frangville, M. Rutkevičius, A.P. Richter, O.D. Veleev, S.D. Stoyanov, V.N. Paunov, Fabrication of environmentally biodegradable lignin nanoparticles, *ChemPhysChem.* 13 (2012) 4235–4243.
<https://doi.org/10.1002/CPHC.201200537>.
- [53] I.A. Gilca, R.E. Ghitescu, A.C. Puitel, V.I. Popa, Preparation of lignin nanoparticles by chemical modification, *Iranian Polymer Journal (English Edition).* 23 (2014) 355–363. <https://doi.org/10.1007/S13726-014-0232-0>.
- [54] I.A. Gilca, V.I. Popa, C. Crestini, Obtaining lignin nanoparticles by sonication, *Ultrason Sonochem.* 23 (2015) 369–375.
<https://doi.org/10.1016/J.ULTSONCH.2014.08.021>.

- [55] R. del P. Castillo, J. Araya, E. Troncoso, S. Vinet, J. Freer, Fourier transform infrared imaging and microscopy studies of *Pinus radiata* pulps regarding the simultaneous saccharification and fermentation process, *Anal Chim Acta*. 866 (2015) 10–20. <https://doi.org/10.1016/J.ACA.2015.01.032>.
- [56] W. Yang, J.M. Kenny, D. Puglia, Structure and properties of biodegradable wheat gluten bionanocomposites containing lignin nanoparticles, *Ind Crops Prod*. 74 (2015) 348–356. <https://doi.org/10.1016/J.INDCROP.2015.05.032>.
- [57] A. Barakat, C. Gaillard, D. Lairez, L. Saulnier, B. Chabbert, B. Cathala, Supramolecular organization of heteroxylan-dehydrogenation polymers (synthetic lignin) nanoparticles, *Biomacromolecules*. 9 (2008) 487–493. <https://doi.org/10.1021/BM7009812>.
- [58] M. Ago, B.L. Tardy, L. Wang, J. Guo, A. Khakalo, O.J. Rojas, Supramolecular assemblies of lignin into nano- and microparticles, *MRS Bull*. 42 (2017) 371–378. <https://doi.org/10.1557/MRS.2017.88>.
- [59] Y. Qian, Y. Deng, X. Qiu, H. Li, D. Yang, Formation of uniform colloidal spheres from lignin, a renewable resource recovered from pulping spent liquor, *Green Chemistry*. 16 (2014) 2156–2163. <https://doi.org/10.1039/C3GC42131G>.
- [60] D. Saidane, J.C. Barbe, M. Birot, H. Deleuze, Preparation of functionalized Kraft lignin beads, *J Appl Polym Sci*. 116 (2010) 1184–1189. <https://doi.org/10.1002/APP.31659>.
- [61] K. Gabov, T. Oja, T. Deguchi, A. Fallarero, P. Fardim, Preparation, characterization and antimicrobial application of hybrid cellulose-lignin beads, *Cellulose*. 24 (2017) 641–658. <https://doi.org/10.1007/S10570-016-1172-Y/FIGURES/10>.
- [62] Adsorption of L-lysine from aqueous solution by spherical lignin beads: Kinetics and equilibrium studies :: *BioResources*, (n.d.). <https://bioresources.cnr.ncsu.edu/resources/adsorption-of-l-lysine-from-aqueous-solution-by-spherical-lignin-beads-kinetics-and-equilibrium-studies/> (accessed April 8, 2023).

- [63] F. Xiong, Y. Han, S. Wang, G. Li, T. Qin, Y. Chen, F. Chu, Preparation and Formation Mechanism of Renewable Lignin Hollow Nanospheres with a Single Hole by Self-Assembly, *ACS Sustain Chem Eng.* 5 (2017) 2273–2281. <https://doi.org/10.1021/acssuschemeng.6b02585>.
- [64] H. Hah, J. Kim, B. Jeon, S.K.-C. communications, undefined 2003, Simple preparation of monodisperse hollow silica particles without using templates, *Pubs.Rsc.Org.* (n.d.). <https://pubs.rsc.org/en/content/articlehtml/2003/cc/b301521a> (accessed January 27, 2023).
- [65] Q. Zhang, W. Wang, J. Goebel, Y.Y.-N. Today, undefined 2009, Self-templated synthesis of hollow nanostructures, Elsevier. (n.d.). <https://www.sciencedirect.com/science/article/pii/S1748013209001194> (accessed January 27, 2023).
- [66] M. Chen, L. Wu, S. Zhou, B. You, A method for the fabrication of monodisperse hollow silica spheres, *Advanced Materials.* 18 (2006) 801–806. <https://doi.org/10.1002/adma.200501528>.
- [67] S. Ding, T. Lin, Y. Wang, X. Lü, F.H.-N.J. of Chemistry, undefined 2013, New facile synthesis of TiO₂ hollow sphere with an opening hole and its enhanced rate performance in lithium-ion batteries, *Pubs.Rsc.Org.* (n.d.). <https://pubs.rsc.org/en/content/articlehtml/2013/nj/c2nj40956a> (accessed January 27, 2023).
- [68] Q. Shi, P. Zhang, Y. Li, H. Xia, D. Wang, X.T.-C. science, undefined 2015, Synthesis of open-mouthed, yolk–shell Au@ AgPd nanoparticles with access to interior surfaces for enhanced electrocatalysis, *Pubs.Rsc.Org.* (n.d.). <https://pubs.rsc.org/en/content/articlehtml/2015/sc/c5sc01088h> (accessed January 27, 2023).
- [69] X. Li, L. Zhou, Y. Wei, A.M. El-Toni, F. Zhang, D. Zhao, Anisotropic Encapsulation-Induced Synthesis of Asymmetric Single-Hole Mesoporous

- Nanocages, *J Am Chem Soc.* 137 (2015) 5903–5906.
<https://doi.org/10.1021/jacs.5b03207>.
- [70] J. Xu, A. Ma, Z. Xu, X. Liu, D. Chu, H. Xu, Synthesis of Au and Pt Hollow Capsules with Single Holes via Pickering Emulsion Strategy, *Journal of Physical Chemistry C.* 119 (2015) 28055–28060.
<https://doi.org/10.1021/acs.jpcc.5b09478>.
- [71] X. Li, L. Zhou, Y. Wei, A.M. El-Toni, F. Zhang, D. Zhao, Anisotropic Encapsulation-Induced Synthesis of Asymmetric Single-Hole Mesoporous Nanocages, *J Am Chem Soc.* 137 (2015) 5903–5906.
<https://doi.org/10.1021/jacs.5b03207>.
- [72] D. Li, Y. Chen, C. Zhang, ... S.S.-J. of M., undefined 2013, Different morphologies of silica synthesized using organic templates from the same class of chiral compounds, *Pubs.Rsc.Org.* (n.d.).
<https://pubs.rsc.org/en/content/articlehtml/2013/tb/c3tb00146f> (accessed January 27, 2023).
- [73] M.W. Chang, E. Stride, M. Edirisinghe, A new method for the preparation of monoporous hollow microspheres, *Langmuir.* 26 (2010) 5115–5121.
<https://doi.org/10.1021/la903592s>.
- [74] S. Ding, T. Lin, Y. Wang, X. Lü, F.H.-N.J. of Chemistry, undefined 2013, New facile synthesis of TiO₂ hollow sphere with an opening hole and its enhanced rate performance in lithium-ion batteries, *Pubs.Rsc.Org.* (n.d.).
<https://pubs.rsc.org/en/content/articlehtml/2013/nj/c2nj40956a> (accessed January 27, 2023).
- [75] S.H. Im, U. Jeong, Y.X.-N. materials, undefined 2005, Polymer hollow particles with controllable holes in their surfaces, *Nature.Com.* (n.d.).
<https://www.nature.com/articles/nmat1448> (accessed January 27, 2023).
- [76] S.C. Luo, J. Jiang, S.S. Liour, S. Gao, J.Y. Ying, H.H. Yu, Magnetic PEDOT hollow capsules with single holes, *Chemical Communications.* (2009) 2664–2666. <https://doi.org/10.1039/b821989c>.

- [77] D.-M. Li, Y.-S. Zheng, Single-Hole Hollow Nanospheres from Enantioselective Self-Assembly of Chiral AIE Carboxylic Acid and Amine, *J. Org. Chem.* 76 (2011) 1100–1108. <https://doi.org/10.1021/jo102206h>.
- [78] H. Minami, H. Kobayashi, M. Okubo, Preparation of Hollow Polymer Particles with a Single Hole in the Shell by SaPSeP £, *ACS Publications*. 21 (2005) 5655–5658. <https://doi.org/10.1021/la0502948>.
- [79] G. Guan, Z. Zhang, Z. Wang, B. Liu, D. Gao, C. Xie, Single-Hole Hollow Polymer Microspheres toward Specific High-Capacity Uptake of Target Species**, *Wiley Online Library*. 19 (2007) 2370–2374. <https://doi.org/10.1002/adma.200700984>.
- [80] F. Xiong, Y. Han, S. Wang, G. Li, T. Qin, Y. Chen, F. Chu, Preparation and Formation Mechanism of Renewable Lignin Hollow Nanospheres with a Single Hole by Self-Assembly, *ACS Sustain Chem Eng.* 5 (2017) 2273–2281. <https://doi.org/10.1021/acssuschemeng.6b02585>.
- [81] J. Sameni, K. Krigstin, M. Sain, Effect of Preparation Parameters on the Formation of Lignin Acetate Microspheres, *International Journal of Engineering and Innovative Technology*. 4 (2015) 2277–3754.
- [82] E. Ten, C. Ling, Y. Wang, A. Srivastava, L.A. Dempere, W. Vermerris, Lignin nanotubes as vehicles for gene delivery into human cells, *Biomacromolecules*. 15 (2014) 327–338. <https://doi.org/10.1021/bm401555p>.
- [83] G. Gao, J.I. Dallmeyer, J.F. Kadla, Synthesis of lignin nanofibers with ionic-responsive shells: Water-expandable lignin-based nanofibrous mats, *Biomacromolecules*. 13 (2012) 3602–3610. <https://doi.org/10.1021/bm301039f>.
- [84] J. Sameni, S.A. Jaffer, J. Tjong, M. Sain, Advanced Applications for Lignin Micro- and Nano-based Materials, *Current Forestry Reports*. 6 (2020) 159–171. <https://doi.org/10.1007/s40725-020-00117-4>.
- [85] S.C. Ligon, R. Liska, J. Stampfl, M. Gurr, R. Mülhaupt, Polymers for 3D Printing and Customized Additive Manufacturing, *Chem Rev.* 117 (2017) 10212–10290. <https://doi.org/10.1021/ACS.CHEMREV.7B00074>.

- [86] L.S. Ebers, A. Arya, C.C. Bowland, W.G. Glasser, S.C. Chmely, A.K. Naskar, M.P. Laborie, 3D printing of lignin: Challenges, opportunities and roads onward, *Biopolymers*. 112 (2021) e23431. <https://doi.org/10.1002/BIP.23431>.
- [87] D. Han, H. Lee, Recent advances in multi-material additive manufacturing: methods and applications, *Curr Opin Chem Eng*. 28 (2020) 158–166. <https://doi.org/10.1016/J.COCHE.2020.03.004>.
- [88] E. Sanchez-Rexach, T.G. Johnston, C. Jehanno, H. Sardon, A. Nelson, Sustainable Materials and Chemical Processes for Additive Manufacturing, *Chemistry of Materials*. 32 (2020) 7105–7119. <https://doi.org/10.1021/ACS.CHEMMATER.0C02008>.
- [89] 3D Printing Market Size To Hit USD 98.31 Billion By 2032, (n.d.). <https://www.precedenceresearch.com/3d-printing-market> (accessed May 20, 2023).
- [90] Wohlers Report 2015 - Wohlers Associates, (n.d.). <https://wohlersassociates.com/product/wohlers-report-2015/> (accessed April 12, 2023).
- [91] A. Ji, S. Zhang, S. Bhagia, C.G. Yoo, A.J. Ragauskas, 3D printing of biomass-derived composites: Application and characterization approaches, *RSC Adv*. 10 (2020) 21698–21723. <https://doi.org/10.1039/D0RA03620J>.
- [92] M.E. Lamm, L. Wang, V. Kishore, H. Tekinalp, V. Kunc, J. Wang, D.J. Gardner, S. Ozcan, Material extrusion additive manufacturing of wood and lignocellulosic filled composites, *Polymers (Basel)*. 12 (2020). <https://doi.org/10.3390/POLYM12092115>.
- [93] D. Mohan, Z.K. Teong, A.N. Bakir, M.S. Sajab, H. Kaco, Extending cellulose-based polymers application in additive manufacturing technology: A review of recent approaches, *Polymers (Basel)*. 12 (2020). <https://doi.org/10.3390/POLYM12091876>.
- [94] S. Zhang, M. Li, N. Hao, A.J. Ragauskas, Stereolithography 3D Printing of Lignin-Reinforced Composites with Enhanced Mechanical Properties, *ACS*

Omega. 4 (2019) 20197–20204.

https://doi.org/10.1021/ACSOMEGA.9B02455/ASSET/IMAGES/MEDIUM/A09B02455_M002.GIF.

- [95] X. Wang, M. Jiang, Z. Zhou, J. Gou, D. Hui, 3D printing of polymer matrix composites: A review and prospective, *Compos B Eng.* 110 (2017) 442–458. <https://doi.org/10.1016/J.COMPOSITESB.2016.11.034>.
- [96] N.B. Palaganas, J.D. Mangadlao, A.C.C. De Leon, J.O. Palaganas, K.D. Pangilinan, Y.J. Lee, R.C. Advincula, 3D printing of photocurable cellulose nanocrystal composite for fabrication of complex architectures via stereolithography, *ACS Appl Mater Interfaces.* 9 (2017) 34314–34324. <https://doi.org/10.1021/ACSAMI.7B09223>.
- [97] D. Lin, S. Jin, F. Zhang, C. Wang, Y. Wang, C. Zhou, G.J. Cheng, 3D stereolithography printing of graphene oxide reinforced complex architectures, *Nanotechnology.* 26 (2015). <https://doi.org/10.1088/0957-4484/26/43/434003>.
- [98] Y. Zhang, H. Li, X. Yang, T. Zhang, K. Zhu, W. Si, Z. Liu, H. Sun, Additive manufacturing of carbon nanotube-photopolymer composite radar absorbing materials, *Polym Compos.* 39 (2018) E671–E676. <https://doi.org/10.1002/PC.24117>.
- [99] Y.Y.C. Choong, S. Maleksaeedi, H. Eng, J. Wei, P.C. Su, 4D printing of high performance shape memory polymer using stereolithography, *Mater Des.* 126 (2017) 219–225. <https://doi.org/10.1016/J.MATDES.2017.04.049>.
- [100] M. Gurr, D. Hofmann, M. Ehm, Y. Thomann, R. Kubier, R. Mülhaupt, Acrylic nanocomposite resins for use in stereolithography and structural light modulation based rapid prototyping and rapid manufacturing technologies, *Adv Funct Mater.* 18 (2008) 2390–2397. <https://doi.org/10.1002/ADFM.200800344>.
- [101] R.J. Vora, I.A. Ashcroft, R. Hague, Investigation of stereolithography material by depth sensing indentation and differential scanning calorimetry, *Plastics, Rubber and Composites.* 36 (2007) 68–76. <https://doi.org/10.1179/174328907X171226>.

- [102] J.Z. Manapat, J.D. Mangadlao, B.D.B. Tiu, G.C. Tritchler, R.C. Advincula, High-Strength Stereolithographic 3D Printed Nanocomposites: Graphene Oxide Metastability, *ACS Appl Mater Interfaces*. 9 (2017) 10085–10093. <https://doi.org/10.1021/ACSAMI.6B16174>.
- [103] J.H. Sandoval, K.F. Soto, L.E. Murr, R.B. Wicker, Nanotailoring photocrosslinkable epoxy resins with multi-walled carbon nanotubes for stereolithography layered manufacturing, *J Mater Sci*. 42 (2007) 156–165. <https://doi.org/10.1007/S10853-006-1035-2>.
- [104] H. Eng, S. Maleksaeedi, S. Yu, Y.Y.C. Choong, F.E. Wiria, C.L.C. Tan, P.C. Su, J. Wei, 3D Stereolithography of Polymer Composites Reinforced with Orientated Nanoclay, *Procedia Eng*. 216 (2017) 1–7. <https://doi.org/10.1016/J.PROENG.2018.02.080>.
- [105] D.E. Yunus, W. Shi, S. Sohrabi, Y. Liu, Shear induced alignment of short nanofibers in 3D printed polymer composites, *Nanotechnology*. 27 (2016). <https://doi.org/10.1088/0957-4484/27/49/495302>.
- [106] L. Wang, X. Ni, The effect of the inorganic nanomaterials on the UV-absorption, rheological and mechanical properties of the rapid prototyping epoxy-based composites, *Polymer Bulletin*. 74 (2017) 2063–2079. <https://doi.org/10.1007/S00289-016-1825-X>.
- [107] A.J. Ragauskas, G.T. Beckham, M.J. Biddy, R. Chandra, F. Chen, M.F. Davis, B.H. Davison, R.A. Dixon, P. Gilna, M. Keller, P. Langan, A.K. Naskar, J.N. Saddler, T.J. Tschaplinski, G.A. Tuskan, C.E. Wyman, Lignin valorization: Improving lignin processing in the biorefinery, *Science* (1979). 344 (2014). <https://doi.org/10.1126/SCIENCE.1246843>.
- [108] S.I. FALKEHAG, J. MARTON, E. ADLER, Chromophores in Kraft Lignin, (1966) 75–89. <https://doi.org/10.1021/BA-1966-0059.CH007>.
- [109] P. Yu, H. He, Y. Jia, S. Tian, J. Chen, D. Jia, Y. Luo, A comprehensive study on lignin as a green alternative of silica in natural rubber composites, *Polym*

- Test. 54 (2016) 176–185.
<https://doi.org/10.1016/J.POLYMERTESTING.2016.07.014>.
- [110] A. De Chirico, M. Armanini, P. Chini, G. Cioccolo, F. Provasoli, G. Audisio, Flame retardants for polypropylene based on lignin, *Polym Degrad Stab.* 79 (2003) 139–145. [https://doi.org/10.1016/S0141-3910\(02\)00266-5](https://doi.org/10.1016/S0141-3910(02)00266-5).
- [111] W. Xu, X. Wang, N. Sandler, S. Willför, C. Xu, Three-Dimensional Printing of Wood-Derived Biopolymers: A Review Focused on Biomedical Applications, *ACS Sustain Chem Eng.* 6 (2018) 5663–5680.
<https://doi.org/10.1021/ACSSUSCHEMENG.7B03924>.
- [112] J. Domínguez-Robles, N.K. Martin, M.L. Fong, S.A. Stewart, N.J. Irwin, M.I. Rial-Hermida, R.F. Donnelly, E. Larrañeta, Antioxidant pla composites containing lignin for 3D printing applications: A potential material for healthcare applications, *Pharmaceutics.* 11 (2019).
<https://doi.org/10.3390/PHARMACEUTICS11040165>.
- [113] J.T. Sutton, K. Rajan, D.P. Harper, S.C. Chmely, Lignin-Containing Photoactive Resins for 3D Printing by Stereolithography, *ACS Appl Mater Interfaces.* 10 (2018) 36456–36463. <https://doi.org/10.1021/ACSAMI.8B13031>.
- [114] V. Mimini, E. Sykacek, S.N.A. Hashim, J. Holzweber, H. Hettegger, K. Fackler, A. Potthast, N. Mundigler, T. Rosenau, Compatibility of Kraft Lignin, Organosolv Lignin and Lignosulfonate With PLA in 3D Printing, *Journal of Wood Chemistry and Technology.* 39 (2019) 14–30.
<https://doi.org/10.1080/02773813.2018.1488875>.
- [115] N.A. Nguyen, S.H. Barnes, C.C. Bowland, K.M. Meek, K.C. Littrell, J.K. Keum, A.K. Naskar, A path for lignin valorization via additive manufacturing of high-performance sustainable composites with enhanced 3D printability, *Sci Adv.* 4 (2018). <https://doi.org/10.1126/SCIADV.AAT4967>.
- [116] N. Sallem-Idrissi, M. Sclavons, D.P. Debecker, J. Devaux, Miscible raw lignin/nylon 6 blends: Thermal and mechanical performances, *J Appl Polym Sci.* 133 (2016). <https://doi.org/10.1002/APP.42963>.

- [117] E. Gkartzou, E.P. Koumoulos, C.A. Charitidis, Production and 3D printing processing of bio-based thermoplastic filament, *Manuf Rev (Les Ulis)*. 4 (2017). <https://doi.org/10.1051/MFREVIEW/2016020>.
- [118] D.J. McClements, L. Bai, C. Chung, Recent Advances in the Utilization of Natural Emulsifiers to Form and Stabilize Emulsions, *Annu Rev Food Sci Technol*. 8 (2017) 205–236. <https://doi.org/10.1146/annurev-food-030216-030154>.
- [119] R. Zheng, B.P. Binks, Z. Cui, Pickering Emulsions of Hydrophilic Silica Particles and Symmetrical Organic Electrolytes, *Langmuir*. 36 (2020) 4619–4629. <https://doi.org/10.1021/acs.langmuir.0c00261>.
- [120] B.P. Binks, S.O. Lumsdon, Pickering emulsions stabilized by monodisperse latex particles: Effects of particle size, *Langmuir*. 17 (2001) 4540–4547. <https://doi.org/10.1021/la0103822>.
- [121] B.P. Binks, J. Philip, J.A. Rodrigues, Inversion of silica-stabilized emulsions induced by particle concentration, *Langmuir*. 21 (2005) 3296–3302. <https://doi.org/10.1021/la046915z>.
- [122] Z.G. Cui, K.Z. Shi, Y.Z. Cui, B.P. Binks, Double phase inversion of emulsions stabilized by a mixture of CaCO₃ nanoparticles and sodium dodecyl sulphate, *Colloids Surf A Physicochem Eng Asp*. 329 (2008) 67–74. <https://doi.org/10.1016/j.colsurfa.2008.06.049>.
- [123] N.P. Ashby, B.P. Binks, Pickering emulsions stabilised by Laponite clay particles, *Physical Chemistry Chemical Physics*. 2 (2000) 5640–5646. <https://doi.org/10.1039/b007098j>.
- [124] Our Endangered World, Is Silica Bad for the Environment?, (2022). <https://www.ourendangeredworld.com/eco/is-silica-bad-for-the-environment/> (accessed August 15, 2022).
- [125] D. Klemm, F. Kramer, S. Moritz, T. Lindström, M. Ankerfors, D. Gray, A. Dorris, Nanocelluloses: A New Family of Nature-Based Materials, *Angewandte*

- Chemie International Edition. 50 (2011) 5438–5466.
<https://doi.org/10.1002/anie.201001273>.
- [126] L. Dai, Y. Li, F. Kong, K. Liu, C. Si, Y. Ni, Lignin-based nanoparticles stabilized pickering emulsion for stability improvement and thermal-controlled release of trans-resveratrol, *ACS Sustain Chem Eng.* 7 (2019) 13497–13504.
https://doi.org/10.1021/ACSSUSCHEMENG.9B02966/SUPPL_FILE/SC9B02966_SI_001.PDF.
- [127] Carbon Fiber Market Size To Hit USD 5.83 Billion By 2032, (n.d.).
<https://www.precedenceresearch.com/carbon-fiber-market> (accessed May 22, 2023).
- [128] A.H. Wazir, L. Kakakhel, Preparation and characterization of pitch-based carbon fibers, *Xinxing Tan Cailiao/ New Carbon Materials.* 24 (2009) 83–88.
[https://doi.org/10.1016/S1872-5805\(08\)60039-6](https://doi.org/10.1016/S1872-5805(08)60039-6).
- [129] K. Sudo, K. Shimizu, A new carbon fiber from lignin, *J Appl Polym Sci.* 44 (1992) 127–134. <https://doi.org/10.1002/app.1992.070440113>.
- [130] Y. Xu, Y. Liu, S. Chen, Y. Ni, Current Overview of Carbon Fiber: Toward Green Sustainable Raw Materials, *Bioresources.* 15 (2020) 7234–7259.
https://jstatm.textiles.ncsu.edu/index.php/BioRes/article/view/BioRes_15_3_Review_Current_Overview_Carbon_Fiber (accessed April 9, 2023).
- [131] D.A. Baker, T.G. Rials, Recent advances in low-cost carbon fiber manufacture from lignin, *J Appl Polym Sci.* 130 (2013) 713–728.
<https://doi.org/10.1002/APP.39273>.
- [132] M. Zhang, W. Liu, H. Niu, D. Wu, Structure–property relationship of carbon fibers derived from polyimide/polyacrylonitrile blends, *High Perform Polym.* 31 (2019) 168–177.
https://doi.org/10.1177/0954008317753872/ASSET/IMAGES/LARGE/10.1177_0954008317753872-FIG2.JPEG.
- [133] L. Zhang, A. Aboagye, A. Kelkar, C. Lai, H. Fong, A review: carbon nanofibers from electrospun polyacrylonitrile and their applications, *Journal of Materials*

Science 2013 49:2. 49 (2013) 463–480. <https://doi.org/10.1007/S10853-013-7705-Y>.

- [134] D.A. Baker, T.G. Rials, Recent Advances in Low-Cost Carbon Fiber Manufacture from Lignin, *J. Appl. Polym. Sci.* 130 (2013) 713–728. <https://doi.org/10.1002/app.39273>.
- [135] E. Frank, L.M. Steudle, D. Ingildeev, J.M. Spörl, M.R. Buchmeiser, Carbon fibers: Precursor systems, processing, structure, and properties, *Angewandte Chemie - International Edition*. 53 (2014) 5262–5298. <https://doi.org/10.1002/anie.201306129>.
- [136] E. Frank, F. Hermanutz, M.R. Buchmeiser, Carbon fibers: Precursors, manufacturing, and properties, *Macromol Mater Eng.* 297 (2012) 493–501. <https://doi.org/10.1002/mame.201100406>.
- [137] M. Norgren, H. Edlund, Lignin: Recent advances and emerging applications, *Curr Opin Colloid Interface Sci.* 19 (2014) 409–416. <https://doi.org/10.1016/j.cocis.2014.08.004>.
- [138] Y. Xu, Y. Liu, S. Chen, Y. Ni, Current Overview of Carbon Fiber: Toward Green Sustainable Raw Materials, *Bioresources*. 15 (2020) 7234–7259. <https://doi.org/10.15376/BIORES.15.3.XU>.
- [139] J. Jin, J. Ding, A. Klett, M.C. Thies, A.A. Ogale, Carbon Fibers Derived from Fractionated-Solvated Lignin Precursors for Enhanced Mechanical Performance, *ACS Sustain Chem Eng.* 6 (2018) 14135–14142. <https://doi.org/10.1021/acssuschemeng.8b02697>.
- [140] Y. Nordström, I. Norberg, E. Sjöholm, R. Drougge, A new softening agent for melt spinning of softwood kraft lignin, *J Appl Polym Sci.* 129 (2013) 1274–1279. <https://doi.org/10.1002/APP.38795>.
- [141] L. Salmén, E. Bergnor, A.-M. Olsson, M. Åkerström, A. Uhlin, Extrusion of Softwood Kraft Lignins as Precursors for Carbon Fibres, *Bioresources*. 10 (2015) 7544–7554.

- https://jtatm.textiles.ncsu.edu/index.php/BioRes/article/view/BioRes_10_4_7544_Salmen_Extrusion_Softwood_Kraft_Lignins (accessed April 9, 2023).
- [142] X. Huang, Fabrication and Properties of Carbon Fibers, *Materials* 2009, Vol. 2, Pages 2369-2403. 2 (2009) 2369–2403. <https://doi.org/10.3390/MA2042369>.
- [143] Y. Huang, R.J. Young, Effect of fibre microstructure upon the modulus of PAN- and pitch-based carbon fibres, *Carbon* N Y. 33 (1995) 97–107. [https://doi.org/10.1016/0008-6223\(94\)00109-D](https://doi.org/10.1016/0008-6223(94)00109-D).
- [144] D.A. Baker, T.G. Rials, Recent advances in low-cost carbon fiber manufacture from lignin, *J Appl Polym Sci.* 130 (2013) 713–728. <https://doi.org/10.1002/app.39273>.
- [145] H.A. Ariyanta, E.B. Santoso, L. Suryanegara, E.T. Arung, I.W. Kusuma, M.N. Azman Mohammad Taib, M.H. Hussin, Y. Yanuar, I. Batubara, W. Fatriasari, Recent Progress on the Development of lignin as future ingredient biobased cosmetics, *Sustain Chem Pharm.* 32 (2023) 100966. <https://doi.org/10.1016/j.scp.2022.100966>.
- [146] H. Li, S. Colantonio, A. Dawson, X. Lin, J. Beecker, Sunscreen Application, Safety, and Sun Protection: The Evidence, *J Cutan Med Surg.* 23 (2019) 357–369. https://doi.org/10.1177/1203475419856611/ASSET/IMAGES/10.1177_1203475419856611-IMG2.PNG.
- [147] Canadian Cancer Society’s Advisory Committee on Cancer Statistics, *Canadian Cancer Statistics 2014: Special topic: Skin cancers*, Canadian Cancer Statistics. (2014) 1–132. [http://www.cancer.ca/~media/cancer.ca/CW/cancerinformation/cancer 101/Canadian cancer statistics/Canadian-Cancer-Statistics-2014-EN.pdf](http://www.cancer.ca/~media/cancer.ca/CW/cancerinformation/cancer%2014/Canadian%20cancer%20statistics/Canadian-Cancer-Statistics-2014-EN.pdf).
- [148] A.C. Green, G.M. Williams, V. Logan, G.M. Strutton, Reduced Melanoma After Regular Sunscreen Use: Randomized Trial Follow-Up, *Impactmelanoma.Org.* (2011). <https://doi.org/10.1200/JCO.2010.28.7078>.

- [149] B.K. Armstrong, A. Kricker, The epidemiology of UV induced skin cancer, *J Photochem Photobiol B*. 63 (2001) 8–18. [https://doi.org/10.1016/S1011-1344\(01\)00198-1](https://doi.org/10.1016/S1011-1344(01)00198-1).
- [150] P. Kullavanijaya, H.W. Lim, Photoprotection, *J Am Acad Dermatol*. 52 (2005) 937–958. <https://doi.org/10.1016/j.jaad.2004.07.063>.
- [151] M. Latha, J. Martis, V. Shobha, ... R.S.-T.J. of clinical, undefined 2013, Sunscreening agents: a review, *Ncbi.Nlm.Nih.Gov*. (n.d.). <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3543289/> (accessed January 28, 2023).
- [152] M. Morsella, N. D'Alessandro, A.E. Lanterna, J.C. Scaiano, Improving the Sunscreen Properties of TiO₂ through an Understanding of Its Catalytic Properties, *ACS Omega*. 1 (2016) 464–469. <https://doi.org/10.1021/acsomega.6b00177>.
- [153] M. Morsella, M. Giammatteo, L. Arrizza, L.T.-R. Advances, undefined 2015, Lignin coating to quench photocatalytic activity of titanium dioxide nanoparticles for potential skin care applications, *Pubs.Rsc.Org*. (n.d.). <https://pubs.rsc.org/en/content/articlehtml/2015/ra/c5ra05232g> (accessed January 28, 2023).
- [154] A. Morlando, V. Sencadas, D. Cardillo, K.K.-P. Technology, undefined 2018, Suppression of the photocatalytic activity of TiO₂ nanoparticles encapsulated by chitosan through a spray-drying method with potential for use in sunblocking, *Elsevier*. (n.d.). <https://www.sciencedirect.com/science/article/pii/S0032591018300706> (accessed January 28, 2023).
- [155] Recent Progress on the Development of lignin as future ingredient biobased cosmetics - *ScienceDirect*, (n.d.). <https://www.sciencedirect.com/science/article/pii/S2352554122003709#bib38> (accessed January 28, 2023).

- [156] K. Geoffrey, A. Mwangi, S.M.-S.P. Journal, undefined 2019, Sunscreen products: Rationale for use, formulation development and regulatory considerations, Elsevier. (n.d.).
<https://www.sciencedirect.com/science/article/pii/S1319016419301033> (accessed January 28, 2023).
- [157] S. Lee, T. Tran, J. Choi, K.W.-I. journal of biological, undefined 2019, Lignin for white natural sunscreens, Elsevier. (n.d.).
<https://www.sciencedirect.com/science/article/pii/S0141813018339266> (accessed January 28, 2023).
- [158] H. Zhang, X. Liu, S. Fu, Y. Chen, High-value utilization of kraft lignin: Color reduction and evaluation as sunscreen ingredient, *Int J Biol Macromol.* 133 (2019) 86–92. <https://doi.org/10.1016/J.IJBIOMAC.2019.04.092>.
- [159] N. Sajinčič, O. Gordobil, A. Simmons, A. Sandak, An exploratory study of consumers' knowledge and attitudes about lignin-based sunscreens and bio-based skincare products, *Cosmetics.* 8 (2021) 78.
<https://doi.org/10.3390/COSMETICS8030078/S1>.
- [160] Y. Qian, X. Zhong, Y. Li, X.Q.-I.C. and Products, undefined 2017, Fabrication of uniform lignin colloidal spheres for developing natural broad-spectrum sunscreens with high sun protection factor, Elsevier. (n.d.).
<https://www.sciencedirect.com/science/article/pii/S0926669017301450> (accessed January 28, 2023).
- [161] M. Tran, D. Phan, E.L.-G. Chemistry, undefined 2021, Review on lignin modifications toward natural UV protection ingredient for lignin-based sunscreens, *Pubs.Rsc.Org.* (n.d.).
<https://pubs.rsc.org/en/content/articlehtml/2021/xx/d1gc01139a> (accessed January 28, 2023).
- [162] Y. Wu, Y. Qian, H. Lou, D. Yang, X. Qiu, Enhancing the Broad-Spectrum Adsorption of Lignin through Methoxyl Activation, Grafting Modification, and

- Reverse Self-Assembly, *ACS Sustain Chem Eng.* 7 (2019) 15966–15973.
<https://doi.org/10.1021/acssuschemeng.9b02317>.
- [163] Y. Wu, Y. Qian, A. Zhang, H. Lou, D. Yang, X. Qiu, Light Color Dihydroxybenzophenone Grafted Lignin with High UVA/ UVB Absorbance Ratio for Efficient and Safe Natural Sunscreen, *Cite This: Ind. Eng. Chem. Res.* 59 (2020) 17057–17068. <https://doi.org/10.1021/acs.iecr.9b06970>.
- [164] D. Kai, Y. Chua, L. Jiang, C. Owh, S. Chan, X.L.-R. Advances, undefined 2016, Dual functional anti-oxidant and SPF enhancing lignin-based copolymers as additives for personal and healthcare products, *Pubs.Rsc.Org.* (n.d.).
<https://pubs.rsc.org/en/content/articlehtml/2016/ra/c6ra21433a> (accessed January 28, 2023).
- [165] N. Rapoport, Physical stimuli-responsive polymeric micelles for anti-cancer drug delivery, *Progress in Polymer Science (Oxford).* 32 (2007) 962–990.
<https://doi.org/10.1016/J.PROGPOLYMSCI.2007.05.009>.
- [166] H. Jiang, S. Kelch, A. Lendlein, Polymers move in response to light, *Advanced Materials.* 18 (2006) 1471–1475. <https://doi.org/10.1002/ADMA.200502266>.
- [167] H. Chen, H. Xia, Y. Qiu, Q.Q. Ni, Analyzing effects of interfaces on recovery rates of shape memory composites from the perspective of molecular motions, *Compos Sci Technol.* 163 (2018) 105–115.
<https://doi.org/10.1016/J.COMPSCITECH.2018.05.020>.
- [168] J. Lu, A. Arsalan, Y. Dong, Y. Zhu, C. Qian, R. Wang, C. Cuilan, Y. Fu, Q.Q. Ni, K.N. Ali, Shape memory effect and recovery stress property of carbon nanotube/waterborne epoxy nanocomposites investigated via TMA, *Polym Test.* 59 (2017) 462–469.
<https://doi.org/10.1016/J.POLYMERTESTING.2017.03.001>.
- [169] Y. Dong, H. Xia, Y. Zhu, Q.Q. Ni, Y. Fu, Effect of epoxy-graft-polyoxyethylene octyl phenyl ether on preparation, mechanical properties and triple-shape memory effect of carbon nanotube/water-borne epoxy

- nanocomposites, *Compos Sci Technol.* 120 (2015) 17–25.
<https://doi.org/10.1016/J.COMPSCITECH.2015.09.011>.
- [170] Y. Liu, H. Du, L. Liu, J. Leng, Shape memory polymers and their composites in aerospace applications: A review, *Smart Mater Struct.* 23 (2014).
<https://doi.org/10.1088/0964-1726/23/2/023001>.
- [171] J. Xu, J. Song, J. Xu, J. Song, Thermal Responsive Shape Memory Polymers for Biomedical Applications, *Biomedical Engineering - Frontiers and Challenges.* (2011). <https://doi.org/10.5772/19256>.
- [172] K. Shikinaka, Y. Funatsu, Y. Kubota, Y. Tominaga, M. Nakamura, R.R. Navarro, Y. Otsuka, Tuneable shape-memory properties of composites based on nanoparticulated plant biomass, lignin, and poly(ethylene carbonate), *Soft Matter.* 14 (2018) 9227–9231. <https://doi.org/10.1039/C8SM01683F>.
- [173] H. Liu, N. Mohsin, S. Kim, H. Chung, Lignin, a biomass crosslinker, in a shape memory polycaprolactone network, *J Polym Sci A Polym Chem.* 57 (2019) 2121–2130. <https://doi.org/10.1002/POLA.29483>.
- [174] E.S. Dragan, Design and applications of interpenetrating polymer network hydrogels. A review, *Chemical Engineering Journal.* 243 (2014) 572–590.
<https://doi.org/10.1016/J.CEJ.2014.01.065>.
- [175] M.F. Akhtar, M. Hanif, N.M. Ranjha, Methods of synthesis of hydrogels ... A review, *Saudi Pharmaceutical Journal.* 24 (2016) 554–559.
<https://doi.org/10.1016/J.JSPS.2015.03.022>.
- [176] D. Rico-García, L. Ruiz-Rubio, L. Pérez-Alvarez, S.L. Hernández-Olmos, G.L. Guerrero-Ramírez, J.L. Vilas-Vilela, Lignin-Based Hydrogels: Synthesis and Applications, *Polymers* 2020, Vol. 12, Page 81. 12 (2020) 81.
<https://doi.org/10.3390/POLYM12010081>.
- [177] E. Larrañeta, M. Imízcoz, J.X. Toh, N.J. Irwin, A. Ripolin, A. Perminova, J. Domínguez-Robles, A. Rodríguez, R.F. Donnelly, Synthesis and Characterization of Lignin Hydrogels for Potential Applications as Drug Eluting Antimicrobial Coatings for Medical Materials, *ACS Sustain Chem Eng.*

- 6 (2018) 9037–9046.
https://doi.org/10.1021/ACSSUSCHEMENG.8B01371/ASSET/IMAGES/LARGE/SC-2018-01371Z_0005.JPEG.
- [178] S. Chandna, S. Paul, R. Kaur, K. Gogde, J. Bhaumik, Photodynamic Lignin Hydrogels: A Versatile Self-Healing Platform for Sustained Release of Photosensitizer Nanoconjugates, *ACS Appl Polym Mater.* 4 (2022) 8962–8976. https://doi.org/10.1021/ACSAPM.2C01319/ASSET/IMAGES/LARGE/AP2C01319_0008.JPEG.
- [179] Y. Ma, Y. Sun, Y. Fu, G. Fang, X. Yan, Z. Guo, Swelling behaviors of porous lignin based poly (acrylic acid), *Chemosphere.* 163 (2016) 610–619. <https://doi.org/10.1016/J.CHEMOSPHERE.2016.08.035>.
- [180] A. Moreno, M.H. Sipponen, Lignin-based smart materials: a roadmap to processing and synthesis for current and future applications, *Mater Horiz.* 7 (2020) 2237–2257. <https://doi.org/10.1039/D0MH00798F>.
- [181] B.M. Cerrutti, M.L. Moraes, S.H. Pulcinelli, C. V. Santilli, Lignin as immobilization matrix for HIV p17 peptide used in immunosensing, *Biosens Bioelectron.* 71 (2015) 420–426. <https://doi.org/10.1016/J.BIOS.2015.04.054>.
- [182] A. Jędrzak, T. Rębiś, Ł. Kłapiszewski, J. Zdarta, G. Milczarek, T. Jesionowski, Carbon paste electrode based on functional GOx/silica-lignin system to prepare an amperometric glucose biosensor, *Sens Actuators B Chem.* 256 (2018) 176–185. <https://doi.org/10.1016/J.SNB.2017.10.079>.
- [183] Q. Wang, X. Pan, C. Lin, D. Lin, Y. Ni, L. Chen, L. Huang, S. Cao, X. Ma, Biocompatible, self-wrinkled, antifreezing and stretchable hydrogel-based wearable sensor with PEDOT:sulfonated lignin as conductive materials, *Chemical Engineering Journal.* 370 (2019) 1039–1047. <https://doi.org/10.1016/J.CEJ.2019.03.287>.
- [184] A. Jędrzak, T. Rębiś, Ł. Kłapiszewski, J. Zdarta, G. Milczarek, T. Jesionowski, Carbon paste electrode based on functional GOx/silica-lignin system to prepare

- an amperometric glucose biosensor, *Sens Actuators B Chem.* 256 (2018) 176–185. <https://doi.org/10.1016/J.SNB.2017.10.079>.
- [185] Q. Wang, X. Pan, C. Lin, D. Lin, Y. Ni, L. Chen, L. Huang, S. Cao, X. Ma, Biocompatible, self-wrinkled, antifreezing and stretchable hydrogel-based wearable sensor with PEDOT:sulfonated lignin as conductive materials, *Chemical Engineering Journal.* 370 (2019) 1039–1047. <https://doi.org/10.1016/J.CEJ.2019.03.287>.
- [186] B. Wang, T. Shi, Y. Zhang, C. Chen, Q. Li, Y. Fan, Lignin-based highly sensitive flexible pressure sensor for wearable electronics, *J Mater Chem C Mater.* 6 (2018) 6423–6428. <https://doi.org/10.1039/C8TC01348A>.
- [187] Y. Yang, M.W. Urban, Self-healing polymeric materials, *Chem Soc Rev.* 42 (2013) 7446–7467. <https://doi.org/10.1039/C3CS60109A>.
- [188] S. Burattini, B.W. Greenland, D.H. Merino, W. Weng, J. Seppala, H.M. Colquhoun, W. Hayes, M.E. MacKay, I.W. Hamley, S.J. Rowan, A healable supramolecular polymer blend based on aromatic π - π Stacking and hydrogen-bonding interactions, *J Am Chem Soc.* 132 (2010) 12051–12058. <https://doi.org/10.1021/JA104446R>.
- [189] S.J. Kalista, T.C. Ward, Z. Oyetunji, Self-healing of poly(ethylene-co-methacrylic acid) copolymers following projectile puncture, *Mechanics of Advanced Materials and Structures.* 14 (2007) 391–397. <https://doi.org/10.1080/15376490701298819>.
- [190] Y. Huang, M. Zhong, Y. Huang, M. Zhu, Z. Pei, Z. Wang, Q. Xue, X. Xie, C. Zhi, A self-healable and highly stretchable supercapacitor based on a dual crosslinked polyelectrolyte, *Nat Commun.* 6 (2015). <https://doi.org/10.1038/NCOMMS10310>.
- [191] P. Cordier, F. Tournilhac, C. Soulié-Ziakovic, L. Leibler, Self-healing and thermoreversible rubber from supramolecular assembly, *Nature.* 451 (2008) 977–980. <https://doi.org/10.1038/NATURE06669>.

- [192] B. Ghosh, M.W. Urban, Self-repairing oxetane-substituted chitosan polyurethane networks, *Science* (1979). 323 (2009) 1458–1460.
<https://doi.org/10.1126/SCIENCE.1167391>.
- [193] M. Burnworth, L. Tang, J.R. Kumpfer, A.J. Duncan, F.L. Beyer, G.L. Fiore, S.J. Rowan, C. Weder, Optically healable supramolecular polymers, *Nature*. 472 (2011) 334–337. <https://doi.org/10.1038/NATURE09963>.
- [194] C.H. Li, C. Wang, C. Keplinger, J.L. Zuo, L. Jin, Y. Sun, P. Zheng, Y. Cao, F. Lissel, C. Linder, X.Z. You, Z. Bao, A highly stretchable autonomous self-healing elastomer, *Nat Chem*. 8 (2016) 618–624.
<https://doi.org/10.1038/NCHEM.2492>.
- [195] K. Miyamae, M. Nakahata, Y. Takashima, A. Harada, Self-Healing, Expansion-Contraction, and Shape-Memory Properties of a Preorganized Supramolecular Hydrogel through Host-Guest Interactions, *Angewandte Chemie - International Edition*. 54 (2015) 8984–8987. <https://doi.org/10.1002/ANIE.201502957>.
- [196] M. Cui, N.A. Nguyen, P. V. Bonnesen, D. Uhrig, J.K. Keum, A.K. Naskar, Rigid Oligomer from Lignin in Designing of Tough, Self-Healing Elastomers, *ACS Macro Lett*. 7 (2018) 1328–1332.
https://doi.org/10.1021/ACSMACROLETT.8B00600/ASSET/IMAGES/LARGE/MZ-2018-00600C_0005.JPEG.
- [197] N. Sun, Z. Wang, X. Ma, K. Zhang, Z. Wang, Z. Guo, Y. Chen, L. Sun, W. Lu, Y. Liu, M. Di, Preparation and characterization of lignin-containing self-healing polyurethane elastomers with hydrogen and disulfide bonds, *Ind Crops Prod*. 174 (2021) 114178. <https://doi.org/10.1016/J.INDCROP.2021.114178>.
- [198] S. Shankar, J.W. Rhim, Preparation and characterization of agar/lignin/silver nanoparticles composite films with ultraviolet light barrier and antibacterial properties, *Food Hydrocoll*. 71 (2017) 76–84.
<https://doi.org/10.1016/J.FOODHYD.2017.05.002>.

- [199] S. Hu, Y. Lo Hsieh, Synthesis of surface bound silver nanoparticles on cellulose fibers using lignin as multi-functional agent, *Carbohydr Polym.* 131 (2015) 134–141. <https://doi.org/10.1016/J.CARBPOL.2015.05.060>.
- [200] X. Wang, S. Wang, W. Liu, S. Wang, L. Zhang, R. Sang, Q. Hou, J. Li, Facile fabrication of cellulose composite films with excellent UV resistance and antibacterial activity, *Carbohydr Polym.* 225 (2019) 115213. <https://doi.org/10.1016/J.CARBPOL.2019.115213>.
- [201] W. Yang, E. Fortunati, F. Dominici, G. Giovanale, A. Mazzaglia, G.M. Balestra, J.M. Kenny, D. Puglia, Synergic effect of cellulose and lignin nanostructures in PLA based systems for food antibacterial packaging, *Eur Polym J.* 79 (2016) 1–12. <https://doi.org/10.1016/J.EURPOLYMJ.2016.04.003>.
- [202] J.R. Jambeck, R. Geyer, C. Wilcox, T.R. Siegler, M. Perryman, A. Andrady, R. Narayan, K.L. Law, Plastic waste inputs from land into the ocean, *Science* (1979). 347 (2015) 768–771. <https://doi.org/10.1126/science.1260352>.
- [203] S.A. Miller, Sustainable polymers: Opportunities for the next decade, *ACS Macro Lett.* 2 (2013) 550–554. <https://doi.org/10.1021/mz400207g>.
- [204] O. Hauenstein, S. Agarwal, A. Greiner, Bio-based polycarbonate as synthetic toolbox, *Nat Commun.* 7 (2016) 11862.
- [205] T. Mekonnen, P. Mussone, H. Khalil, D. Bressler, Progress in bio-based plastics and plasticizing modifications, *J Mater Chem A Mater.* 1 (2013) 13379–13398. <https://doi.org/10.1039/c3ta12555f>.
- [206] R. Muthuraj, T. Mekonnen, Recent progress in carbon dioxide (CO₂) as feedstock for sustainable materials development: Co-polymers and polymer blends, *Polymer (Guildf).* 145 (2018) 348–373. <https://doi.org/10.1016/j.polymer.2018.04.078>.
- [207] G. Chen, A. Gupta, T.H. Mekonnen, Silane-modified wood fiber filled EPDM bio-composites with improved thermomechanical properties, *Compos Part A Appl Sci Manuf.* 159 (2022) 107029. <https://doi.org/10.1016/J.COMPOSITESA.2022.107029>.

- [208] C.C. Chang, B.M. Trinh, T.H. Mekonnen, Robust multiphase and multilayer starch/polymer (TPS/PBAT) film with simultaneous oxygen/moisture barrier properties, *J Colloid Interface Sci.* 593 (2021) 290–303.
<https://doi.org/10.1016/J.JCIS.2021.03.010>.
- [209] B.M. Trinh, C.C. Chang, T.H. Mekonnen, Facile fabrication of thermoplastic starch/poly (lactic acid) multilayer films with superior gas and moisture barrier properties, *Polymer (Guildf)*. 223 (2021) 123679.
<https://doi.org/10.1016/J.POLYMER.2021.123679>.
- [210] G. Chen, A. Vahidifar, S. Yu, T.H. Mekonnen, Optimization of silane modification and moisture curing for EPDM toward improved physicomechanical properties, *React Funct Polym.* 182 (2023) 105467.
<https://doi.org/10.1016/J.REACTFUNCTPOLYM.2022.105467>.
- [211] E.A.B. da Silva, M. Zabkova, J.D. Araújo, C.A. Cateto, M.F. Barreiro, M.N. Belgacem, A.E. Rodrigues, An integrated process to produce vanillin and lignin-based polyurethanes from Kraft lignin, *Chemical Engineering Research and Design*. 87 (2009) 1276–1292. <https://doi.org/10.1016/j.cherd.2009.05.008>.
- [212] F.S. Chakar, A.J. Ragauskas, Review of current and future softwood kraft lignin process chemistry, in: *Ind Crops Prod*, Elsevier, 2004: pp. 131–141.
<https://doi.org/10.1016/j.indcrop.2004.04.016>.
- [213] R. Saad, J. Hawari, Grafting of lignin onto nanostructured silica SBA-15: Preparation and characterization, *Journal of Porous Materials*. 20 (2013) 227–233. <https://doi.org/10.1007/s10934-012-9592-z>.
- [214] R.C. Pettersen, *The Chemical Composition of Wood*, n.d.
- [215] N. Smolarski, High-value opportunities for lignin: unlocking its potential, *Frost & Sullivan*. 1 (2012).
- [216] D.S. Bajwa, G. Pourhashem, A.H. Ullah, S.G. Bajwa, A concise review of current lignin production, applications, products and their environmental impact, *Ind Crops Prod*. 139 (2019) 111526.
<https://doi.org/10.1016/J.INDCROP.2019.111526>.

- [217] I.D. Reid, Biodegradation of lignin, *Canadian Journal of Botany*. 73 (1995) 1011–1018. <https://doi.org/10.1139/b95-351>.
- [218] C. Xu, F. Ferdosian, *Structure and Properties of Lignin*, 2017. https://doi.org/10.1007/978-3-662-54959-9_1.
- [219] H. Chen, *Biotechnology of lignocellulose: Theory and practice*, Springer Netherlands, 2014. <https://doi.org/10.1007/978-94-007-6898-7>.
- [220] G. Jiang, D.J. Nowakowski, A. V. Bridgwater, A systematic study of the kinetics of lignin pyrolysis, *Thermochim Acta*. 498 (2010) 61–66. <https://doi.org/10.1016/j.tca.2009.10.003>.
- [221] H. Chen, *Biotechnology of lignocellulose: Theory and practice*, Springer Netherlands, 2014. <https://doi.org/10.1007/978-94-007-6898-7>.
- [222] C.A. Cateto, M.F. Barreiro, A.E. Rodrigues, Monitoring of lignin-based polyurethane synthesis by FTIR-ATR, *Ind Crops Prod*. 27 (2008) 168–174. <https://doi.org/10.1016/j.indcrop.2007.07.018>.
- [223] *Chemical Modification, Properties, and Usage of Lignin*, Springer US, 2002. <https://doi.org/10.1007/978-1-4615-0643-0>.
- [224] M.N. Belgacem, A. Blayo, A. Gandini, Organosolv lignin as a filler in inks, varnishes and paints, *Ind Crops Prod*. 18 (2003) 145–153. [https://doi.org/10.1016/S0926-6690\(03\)00042-6](https://doi.org/10.1016/S0926-6690(03)00042-6).
- [225] C.A. Cateto, M.F. Barreiro, A.E. Rodrigues, Monitoring of lignin-based polyurethane synthesis by FTIR-ATR, *Ind Crops Prod*. 27 (2008) 168–174. <https://doi.org/10.1016/j.indcrop.2007.07.018>.
- [226] N.A. Mohamad Aini, N. Othman, M.H. Hussin, K. Sahakaro, N. Hayeemasae, Lignin as Alternative Reinforcing Filler in the Rubber Industry: A Review, *Front Mater*. 0 (2020) 329. <https://doi.org/10.3389/FMATS.2019.00329>.
- [227] J. Pérez, J. Muñoz-Dorado, T. De La Rubia, J. Martínez, Biodegradation and biological treatments of cellulose, hemicellulose and lignin: An overview,

- International Microbiology. 5 (2002) 53–63. <https://doi.org/10.1007/s10123-002-0062-3>.
- [228] G. Gellerstedt, A. Majtnerova, L. Zhang, Towards a new concept of lignin condensation in kraft pulping. Initial results, *C R Biol.* 327 (2004) 817–826. <https://doi.org/10.1016/j.crv.2004.03.011>.
- [229] J.J. Liao, N.H.A. Latif, D. Trache, N. Brosse, M.H. Hussin, Current advancement on the isolation, characterization and application of lignin, *Int J Biol Macromol.* 162 (2020) 985–1024. <https://doi.org/10.1016/J.IJBIOMAC.2020.06.168>.
- [230] C.S.A. Antunes, M. Bietti, M. Salamone, N. Scione, Early stages in the TiO₂-photocatalyzed degradation of simple phenolic and non-phenolic lignin model compounds, *J Photochem Photobiol A Chem.* 163 (2004) 453–462. <https://doi.org/10.1016/j.jphotochem.2004.01.018>.
- [231] M. Kaneko, J. Nemoto, H. Ueno, N. Gokan, K. Ohnuki, M. Horikawa, R. Saito, T. Shibata, Photoelectrochemical reaction of biomass and bio-related compounds with nanoporous TiO₂ film photoanode and O₂-reducing cathode, *Electrochem Commun.* 8 (2006) 336–340. <https://doi.org/10.1016/j.elecom.2005.12.004>.
- [232] T. Saito, R.H. Brown, M.A. Hunt, D.L. Pickel, J.M. Pickel, J.M. Messman, F.S. Baker, M. Keller, A.K. Naskar, Turning renewable resources into value-added polymer: Development of lignin-based thermoplastic, *Green Chemistry.* 14 (2012) 3295–3303. <https://doi.org/10.1039/c2gc35933b>.
- [233] T.H. Mekonnen, T. Ah-Leung, S. Hojabr, R. Berry, Investigation of the co-coagulation of natural rubber latex and cellulose nanocrystals aqueous dispersion, *Colloids Surf A Physicochem Eng Asp.* 583 (2019) 123949. <https://doi.org/10.1016/j.colsurfa.2019.123949>.
- [234] D. Barana, S.D. Ali, A. Salanti, M. Orlandi, L. Castellani, T. Hanel, L. Zoia, Influence of Lignin Features on Thermal Stability and Mechanical Properties of

- Natural Rubber Compounds, *ACS Sustain Chem Eng.* 4 (2016) 5258–5267.
<https://doi.org/10.1021/acssuschemeng.6b00774>.
- [235] West Fraser, Amallin™ Kraft Lignin Safety Data Sheet (SDS), 2020.
<https://www.westfraser.com/products/amallin-0> (accessed July 4, 2021).
- [236] T. Saito, J.H. Perkins, F. Vautard, H.M. Meyer, J.M. Messman, B. Tolnai, A.K. Naskar, Methanol fractionation of softwood Kraft lignin: Impact on the lignin properties, *ChemSusChem.* 7 (2014) 221–228.
<https://doi.org/10.1002/cssc.201300509>.
- [237] E. Ogunsona, S. Hojabr, R. Berry, T.H. Mekonnen, Nanocellulose-triggered structural and property changes of acrylonitrile-butadiene rubber films, *Int J Biol Macromol.* 164 (2020) 2038–2050.
<https://doi.org/10.1016/j.ijbiomac.2020.07.202>.
- [238] A. Adibi, J. Kim, J. Mok, C. Lenges, L. Simon, T.H. Mekonnen, Enzymatic polymerization designed alpha-1,3 glucan particle morphology as reinforcing fillers of dipped and casted rubber films, *Carbohydr Polym.* 267 (2021) 118234.
<https://doi.org/10.1016/J.CARBPOL.2021.118234>.
- [239] R. Muthuraj, M. Hajee, A.R. Horrocks, B.K. Kandola, Biopolymer blends from hardwood lignin and bio-polyamides: Compatibility and miscibility, *Int J Biol Macromol.* 132 (2019) 439–450.
<https://doi.org/10.1016/j.ijbiomac.2019.03.142>.
- [240] R. Muthuraj, M. Misra, A.K. Mohanty, Biodegradable Poly(butylene succinate) and Poly(butylene adipate-co-terephthalate) Blends: Reactive Extrusion and Performance Evaluation, *J Polym Environ.* 22 (2014) 336–349.
- [241] S.L. Ciemniecki, W.G. Glasser, Polymer Blends with Hydroxypropyl Lignin, in: UTC, 1989: pp. 452–463. <https://doi.org/10.1021/bk-1989-0397.ch035>.
- [242] T. V. Lourençon, F.A. Hansel, T.A. Da Silva, L.P. Ramos, G.I.B. De Muniz, W.L.E. Magalhães, Hardwood and softwood kraft lignins fractionation by simple sequential acid precipitation, *Sep Purif Technol.* 154 (2015) 82–88.
<https://doi.org/10.1016/j.seppur.2015.09.015>.

- [243] H. Li, A.G. McDonald, Fractionation and characterization of industrial lignins, *Ind Crops Prod.* 62 (2014) 67–76.
<https://doi.org/10.1016/j.indcrop.2014.08.013>.
- [244] R.W. Silverstein, G.C. Bassler, Spectrometric identification of organic compounds, *J Chem Educ.* 39 (1962) 546–553.
<https://doi.org/10.1021/ed039p546>.
- [245] H.Y. Yu, R. Chen, G.Y. Chen, L. Liu, X.G. Yang, J.M. Yao, Silylation of cellulose nanocrystals and their reinforcement of commercial silicone rubber, *Journal of Nanoparticle Research.* 17 (2015) 1–13.
<https://doi.org/10.1007/s11051-015-3165-4>.
- [246] M. Liu, Y. Luo, D. Jia, Facile synthesis of composite films featuring bulk superhydrophobicity, durability, and repairability for aquatic show, *Compos Sci Technol.* 197 (2020) 108231.
<https://doi.org/10.1016/J.COMPSCITECH.2020.108231>.
- [247] J.C. de Haro, L. Magagnin, S. Turri, G. Griffini, Lignin-Based Anticorrosion Coatings for the Protection of Aluminum Surfaces, *ACS Sustain Chem Eng.* 7 (2019) 6213–6222. <https://doi.org/10.1021/ACSSUSCHEMENG.8B06568>.
- [248] M. Liu, Y. Luo, D. Jia, A Robust and Versatile Continuous Super-Repellent Polymeric Film for Easy Repair and Underwater Display, *ACS Appl Mater Interfaces.* 12 (2020) 6677–6687. <https://doi.org/10.1021/ACSAMI.9B20081>.
- [249] R.B. Kasat, N.H.L. Wang, E.I. Franses, Effects of backbone and side chain on the molecular environments of chiral cavities in polysaccharide-based biopolymers, *Biomacromolecules.* 8 (2007) 1676–1685.
<https://doi.org/10.1021/bm070006h>.
- [250] L. Borum, O.C. Wilson, Surface modification of hydroxyapatite. Part II. Silica, *Biomaterials.* 24 (2003) 3681–3688. [https://doi.org/10.1016/S0142-9612\(03\)00240-0](https://doi.org/10.1016/S0142-9612(03)00240-0).

- [251] A. Pawlak, M. Mucha, Thermogravimetric and FTIR studies of chitosan blends, in: *Thermochim Acta*, Elsevier, 2003: pp. 153–166.
[https://doi.org/10.1016/S0040-6031\(02\)00523-3](https://doi.org/10.1016/S0040-6031(02)00523-3).
- [252] M. de Oliveira Taipina, M.M.F. Ferrarezi, I.V.P. Yoshida, M. do C. Gonçalves, Surface modification of cotton nanocrystals with a silane agent, *Cellulose*. 20 (2013) 217–226. <https://doi.org/10.1007/s10570-012-9820-3>.
- [253] Sigma-Aldrich Co. LLC., 3-(Triethoxysilyl)propyl isocyanate - ¹³C NMR - Spectrum -, SpectraBase. (2021).
<https://spectrabase.com/spectrum/3sbMIBOeU0Q> (accessed August 26, 2021).
- [254] Biju Francis, D.B.A. Raj, M.L. P. Reddy, Highly efficient luminescent hybrid materials covalently linking with europium(iii) complexes via a novel fluorinated β -diketonate ligand: synthesis, characterization and photophysical properties, *Dalton Transactions*. 39 (2010) 8084–8092.
<https://doi.org/10.1039/C0DT00316F>.
- [255] Biju Francis, D.B.A. Raj, M.L. P. Reddy, Highly efficient luminescent hybrid materials covalently linking with europium(iii) complexes via a novel fluorinated β -diketonate ligand: synthesis, characterization and photophysical properties, *Dalton Transactions*. 39 (2010) 8084–8092.
<https://doi.org/10.1039/C0DT00316F>.
- [256] J.C. de Haro, L. Magagnin, S. Turri, G. Griffini, Lignin-Based Anticorrosion Coatings for the Protection of Aluminum Surfaces, *ACS Sustain Chem Eng*. 7 (2019) 6213–6222. <https://doi.org/10.1021/ACSSUSCHEMENG.8B06568>.
- [257] X. Chen, X. Liu, J. Lei, L. Xu, Z. Zhao, F. Kausar, X. Xie, X. Zhu, Y. Zhang, W.Z. Yuan, Synthesis, clustering-triggered emission, explosive detection and cell imaging of nonaromatic polyurethanes, *Mol Syst Des Eng*. 3 (2018) 364–375. <https://doi.org/10.1039/C7ME00118E>.
- [258] L. Serrano, E.S. Esakkimuthu, N. Marlin, M.-C. Brochier-Salon, G. Mortha, F. Bertaud, Fast, Easy, and Economical Quantification of Lignin Phenolic

- Hydroxyl Groups: Comparison with Classical Techniques, *Energy & Fuels*. 32 (2018) 5969–5977. <https://doi.org/10.1021/ACS.ENERGYFUELS.8B00383>.
- [259] J.M. Jardin, Z. Zhang, G. Hu, K.C. Tam, T.H. Mekonnen, Reinforcement of rubber nanocomposite thin sheets by percolation of pristine cellulose nanocrystals, *Int J Biol Macromol*. 152 (2020) 428–436. <https://doi.org/10.1016/j.ijbiomac.2020.02.303>.
- [260] H. Eslami, C. Tzoganakis, T.H. Mekonnen, Constructing pristine and modified cellulose nanocrystals based cured polychloroprene nanocomposite films for dipped goods application, *Composites Part C: Open Access*. (2020). <https://doi.org/10.1016/j.jcomc.2020.100009>.
- [261] H. Eslami, C. Tzoganakis, T.H. Mekonnen, Surface graft polymerization of lactic acid from the surface of cellulose nanocrystals and applications in chloroprene rubber film composites, *Cellulose*. (2020). <https://doi.org/10.1007/s10570-020-03167-w>.
- [262] S. Hait, D. De, P. Ghosh, J. Chanda, R. Mukhopadhyay, S. Dasgupta, A. Sallat, M. Al Aiti, K.W. Stöckelhuber, S. Wießner, G. Heinrich, A. Das, Understanding the Coupling Effect between Lignin and Polybutadiene Elastomer, *Journal of Composites Science* 2021, Vol. 5, Page 154. 5 (2021) 154. <https://doi.org/10.3390/JCS5060154>.
- [263] E. Ojogbo, C. Tzoganakis, T.H. Mekonnen, Effect of extrusion, batch-mixing, and co-coagulation on the dispersion of CNCs in natural rubber - CNC nanocomposites, *Compos Part A Appl Sci Manuf*. (2021). <https://doi.org/10.1016/j.compositesa.2021.106580>.
- [264] C. Jiang, J. Bo, X. Xiao, S. Zhang, Z. Wang, G. Yan, Y. Wu, C. Wong, H. He, Converting waste lignin into nano-biochar as a renewable substitute of carbon black for reinforcing styrene-butadiene rubber, *Waste Management*. 102 (2020) 732–742.
- [265] A.K. Pandey, K. Singh, K.K. Kar, Thermo-mechanical properties of graphite-reinforced high-density polyethylene composites and its structure–property

- corelationship:, [Http://Dx.Doi.Org/10.1177/0021998316683782](http://Dx.Doi.Org/10.1177/0021998316683782). 51 (2016) 1769–1782. <https://doi.org/10.1177/0021998316683782>.
- [266] A.K. Pandey, T. Pal, R. Sharma, K.K. Kar, Study of matrix–filler interaction through correlations between structural and viscoelastic properties of carbonous-filler/polymer-matrix composites, *J Appl Polym Sci.* 137 (2020) 48660. <https://doi.org/10.1002/APP.48660>.
- [267] J. Bras, M.L. Hassan, C. Bruzesse, E.A. Hassan, N.A. El-Wakil, A. Dufresne, Mechanical, barrier, and biodegradability properties of bagasse cellulose whiskers reinforced natural rubber nanocomposites, *Ind Crops Prod.* 32 (2010) 627–633. <https://doi.org/10.1016/J.INDCROP.2010.07.018>.
- [268] W. Chonkaew, W. Minghvanish, U. Kungliean, N. Rochanawipart, W. Brostow, Vulcanization characteristics and dynamic mechanical behavior of natural rubber reinforced with silane modified silica, in: *J Nanosci Nanotechnol*, 2011: pp. 2018–2024. <https://doi.org/10.1166/jnn.2011.3563>.
- [269] V.G. Geethamma, G. Kalaprasad, G. Groeninckx, S. Thomas, Dynamic mechanical behavior of short coir fiber reinforced natural rubber composites, *Compos Part A Appl Sci Manuf.* 36 (2005) 1499–1506. <https://doi.org/10.1016/j.compositesa.2005.03.004>.
- [270] J. Datta, P. Parcheta, J. Surówka, Softwood-lignin/natural rubber composites containing novel plasticizing agent: Preparation and characterization, *Ind Crops Prod.* 95 (2017) 675–685. <https://doi.org/10.1016/j.indcrop.2016.11.036>.
- [271] M. Abdelmouleh, S. Boufi, M.N. Belgacem, A. Dufresne, Short natural-fibre reinforced polyethylene and natural rubber composites: Effect of silane coupling agents and fibres loading, *Compos Sci Technol.* 67 (2007) 1627–1639. <https://doi.org/10.1016/j.compscitech.2006.07.003>.
- [272] D.J.T. Hill, M.C.S. Perera, P.J. Pomery, H.K. Toh, Dynamic mechanical properties of networks prepared from siloxane modified divinyl benzene pre-polymers, *Polymer (Guildf).* 41 (2000) 9131–9137. [https://doi.org/10.1016/S0032-3861\(00\)00260-3](https://doi.org/10.1016/S0032-3861(00)00260-3).

- [273] J. Park, J. Eslick, Q. Ye, A. Misra, P. Spencer, The influence of chemical structure on the properties in methacrylate-based dentin adhesives, *Dental Materials*. 27 (2011) 1086–1093. <https://doi.org/10.1016/j.dental.2011.07.011>.
- [274] R. Kumar, K.K. Kar, K. Dasgupta, Superior electrical, mechanical and viscoelastic properties of CNTs coated carbon textile reinforced phenolic composite for high-performance structural applications, *J Appl Polym Sci*. 138 (2021) 49968. <https://doi.org/10.1002/APP.49968>.
- [275] R. Kumar, K.K. Kar, K. Dasgupta, Enhanced electrical, mechanical, and viscoelastic properties of carbon-carbon composites using carbon nanotubes coated carbon textile as reinforcement, *J Compos Mater*. 55 (2021) 1733–1748. <https://doi.org/10.1177/0021998320978517>.
- [276] A.K. Pandey, K. Singh, K.K. Kar, Thermo-mechanical properties of graphite-reinforced high-density polyethylene composites and its structure–property corelationship:, <Http://Dx.Doi.Org/10.1177/0021998316683782>. 51 (2016) 1769–1782. <https://doi.org/10.1177/0021998316683782>.
- [277] N. Mohamad Aini, N. Othman, M. Hussin, K. Sahakaro, N. Hayeemasae, Hydroxymethylation-Modified Lignin and Its Effectiveness as a Filler in Rubber Composites, *Processes*. 7 (2019) 315. <https://doi.org/10.3390/pr7050315>.
- [278] S. Hait, D. De, A.K. Ghosh, M. Al Aiti, P. Ghosh, J. Chanda, R. Mukhopadhyay, S. Dasgupta, S. Wießner, G. Heinrich, A. Das, Treasuring waste lignin as superior reinforcing filler in high cis-polybutadiene rubber: A direct comparative study with standard reinforcing silica and carbon black, *J Clean Prod*. 299 (2021) 126841. <https://doi.org/10.1016/J.JCLEPRO.2021.126841>.
- [279] K. Subramaniam, A. Das, F. Simon, G. Heinrich, Networking of ionic liquid modified CNTs in SSBR, *Eur Polym J*. 49 (2013) 345–352. <https://doi.org/10.1016/J.EURPOLYMJ.2012.10.023>.

- [280] C. Vudjung, U. Chaisuwan, U. Pangan, N. Chaipugdee, S. Boonyod, O. Santawitee, S. Saengsuwan, Effect of natural rubber contents on biodegradation and water absorption of Interpenetrating polymer network (IPN) hydrogel from natural rubber and cassava starch, in: *Energy Procedia*, 2014. <https://doi.org/10.1016/j.egypro.2014.07.156>.
- [281] O. Hauenstein, S. Agarwal, A. Greiner, Bio-based polycarbonate as synthetic toolbox, *Nature Communications* 2016 7:1. 7 (2016) 1–7. <https://doi.org/10.1038/ncomms11862>.
- [282] C. Setajit, C. Kongvarhodom, H. Xiao, Development of Grease Resistant Packaging Paper Using Cellulose Nanocrystals and Sodium Alginate, *Sci Adv Mater.* 12 (2019) 212–219. <https://doi.org/10.1166/sam.2020.3628>.
- [283] A. Adibi, D. Valdesueiro, L. Simon, C.P. Lenges, T.H. Mekonnen, High Barrier Sustainable Paper Coating Based on Engineered Polysaccharides and Natural Rubber, *ACS Sustain Chem Eng.* 10 (2022) 10718–10732. https://doi.org/10.1021/ACSSUSCHEMENG.2C03466/ASSET/IMAGES/MEDIUM/SC2C03466_0011.GIF.
- [284] A. Adibi, D. Valdesueiro, J. Mok, N. Behabtu, C. Lenges, L. Simon, T.H. Mekonnen, Sustainable barrier paper coating based on alpha-1,3 glucan and natural rubber latex, *Carbohydr Polym.* 282 (2022) 119121. <https://doi.org/10.1016/J.CARBPOL.2022.119121>.
- [285] A. Adibi, B.M. Trinh, T.H. Mekonnen, Recent progress in sustainable barrier paper coating for food packaging applications, *Prog Org Coat.* 181 (2023) 107566. <https://doi.org/10.1016/J.PORGCOAT.2023.107566>.
- [286] K. Van De Velde, P. Kiekens, Biopolymers: overview of several properties and consequences on their applications, *Polym Test.* 21 (2002) 433–442. [https://doi.org/10.1016/S0142-9418\(01\)00107-6](https://doi.org/10.1016/S0142-9418(01)00107-6).
- [287] J.S. Pereira da Silva, J.M. Farias da Silva, B.G. Soares, S. Livi, Fully biodegradable composites based on poly(butylene adipate-co-

- terephthalate)/peach palm trees fiber, *Compos B Eng.* 129 (2017) 117–123.
<https://doi.org/10.1016/J.COMPOSITESB.2017.07.088>.
- [288] G.F. Santana-Melo, B.V.M. Rodrigues, E. da Silva, R. Ricci, F.R. Marciano, T.J. Webster, L.M.R. Vasconcellos, A.O. Lobo, Electrospun ultrathin PBAT/nHAp fibers influenced the in vitro and in vivo osteogenesis and improved the mechanical properties of neoformed bone, *Colloids Surf B Biointerfaces.* 155 (2017) 544–552.
<https://doi.org/10.1016/J.COLSURFB.2017.04.053>.
- [289] J.G. De Castro, B.V.M. Rodrigues, R. Ricci, M.M. Costa, A.F.C. Ribeiro, F.R. Marciano, A.O. Lobo, Designing a novel nanocomposite for bone tissue engineering using electrospun conductive PBAT/polypyrrole as a scaffold to direct nanohydroxyapatite electrodeposition, *RSC Adv.* 6 (2016) 32615–32623.
<https://doi.org/10.1039/C6RA00889E>.
- [290] H. Du, W. Liu, M. Zhang, C. Si, X. Zhang, B. Li, Cellulose nanocrystals and cellulose nanofibrils based hydrogels for biomedical applications, *Carbohydr Polym.* 209 (2019) 130–144. <https://doi.org/10.1016/J.CARBPOL.2019.01.020>.
- [291] S. Sen, S. Patil, D.S. Argyropoulos, Thermal properties of lignin in copolymers, blends, and composites: a review, *Green Chemistry.* 17 (2015) 4862–4887.
<https://doi.org/10.1039/C5GC01066G>.
- [292] J.J. Liao, N.H.A. Latif, D. Trache, N. Brosse, M.H. Hussin, Current advancement on the isolation, characterization and application of lignin, *Int J Biol Macromol.* 162 (2020) 985–1024.
<https://doi.org/10.1016/J.IJBIOMAC.2020.06.168>.
- [293] G. Gellerstedt, A. Majtnerova, L. Zhang, Towards a new concept of lignin condensation in kraft pulping. Initial results, *C R Biol.* 327 (2004) 817–826.
<https://doi.org/10.1016/j.crvl.2004.03.011>.
- [294] M. Norimoto, T. Aoki, H. Hayashi, Studies on the thermoplasticization of wood, *Holzforschung.* 33 (1979) 159–166.

<https://doi.org/10.1515/HFSG.1979.33.5.159/MACHINEREADABLECITATION/RIS>.

- [295] K. Vaezi, G. Asadpour, S.H. Sharifi, Effect of coating with novel bio nanocomposites of cationic starch/cellulose nanocrystals on the fundamental properties of the packaging paper, *Polym Test.* 80 (2019) 106080. <https://doi.org/10.1016/J.POLYMERTESTING.2019.106080>.
- [296] J. Clayden, N. Greeves, S. Warren, *Organic chemistry*, 2012. https://books.google.com/books?hl=en&lr=&id=kQgu2j_ber0C&oi=fnd&pg=PP1&ots=AqP5W5Hjho&sig=tGJ-axSOayYq4aCSabBe8tHUqyg (accessed March 18, 2022).
- [297] G.K. Prakash, K.M. Mahadevan, Enhancing the properties of wood through chemical modification with palmitoyl chloride, *Appl Surf Sci.* 254 (2008) 1751–1756. <https://doi.org/10.1016/J.APSUSC.2007.07.137>.
- [298] S.J. Meek, C.L. Pitman, A.J.M. Miller, Deducing Reaction Mechanism: A Guide for Students, Researchers, and Instructors, *J Chem Educ.* 93 (2016) 275–286. https://doi.org/10.1021/ACS.JCHEMED.5B00160/SUPPL_FILE/ED5B00160_SI_002.PDF.
- [299] R. Muthuraj, M. Misra, A.K. Mohanty, Biodegradable Poly(butylene succinate) and Poly(butylene adipate-co-terephthalate) Blends: Reactive Extrusion and Performance Evaluation, *J Polym Environ.* 22 (2014) 336–349. <https://doi.org/10.1007/s10924-013-0636-5>.
- [300] R. Muthuraj, M. Hajee, A.R. Horrocks, B.K. Kandola, Biopolymer blends from hardwood lignin and bio-polyamides: Compatibility and miscibility, *Int J Biol Macromol.* 132 (2019) 439–450. <https://doi.org/10.1016/j.ijbiomac.2019.03.142>.
- [301] S.L. Ciemniecki, W.G. Glasser, Polymer Blends with Hydroxypropyl Lignin, in: *UTC*, 1989: pp. 452–463. <https://doi.org/10.1021/bk-1989-0397.ch035>.

- [302] R. Muthuraj, M. Hajee, A.R. Horrocks, B.K. Kandola, Biopolymer blends from hardwood lignin and bio-polyamides: Compatibility and miscibility, *Int J Biol Macromol.* 132 (2019) 439–450.
<https://doi.org/10.1016/J.IJBIOMAC.2019.03.142>.
- [303] K.A.Y. Koivu, H. Sadeghifar, P.A. Nousiainen, D.S. Argyropoulos, J. Sipilä, Effect of Fatty Acid Esterification on the Thermal Properties of Softwood Kraft Lignin, *ACS Sustain Chem Eng.* 4 (2016) 5238–5247.
<https://doi.org/10.1021/acssuschemeng.6b01048>.
- [304] X. Yue, P. Liu, Y. Ning, Y. Xu, Upgrading poly(butylene succinate)/wood fiber composites by esterified lignin, *Compos Interfaces.* 23 (2016) 873–885.
<https://doi.org/10.1080/09276440.2016.1175189>.
- [305] B.M. Trinh, T. Mekonnen, Hydrophobic esterification of cellulose nanocrystals for epoxy reinforcement, *Polymer (Guildf).* 155 (2018) 64–74.
<https://doi.org/10.1016/J.POLYMER.2018.08.076>.
- [306] H.D.S. Aberu, M. Freire, Methoxyl content determination of lignins by ¹H NMR, *An. Bras. Ci.* 67 (1995) 379382.
- [307] S.Y. Lin, C.W. Dence, eds., *Methods in Lignin Chemistry*, (1992).
<https://doi.org/10.1007/978-3-642-74065-7>.
- [308] S.M. Shah, P.O. Pathak, A.S. Jain, C.R. Barhate, M.S. Nagarsenker, Synthesis, characterization, and in vitro evaluation of palmitoylated arabinogalactan with potential for liver targeting, *Carbohydr Res.* 367 (2013) 41–47.
<https://doi.org/10.1016/j.carres.2012.11.025>.
- [309] B.M. Trinh, M. Smith, T.H. Mekonnen, A nanomaterial-stabilized starch-beeswax Pickering emulsion coating to extend produce shelf-life, *Chemical Engineering Journal.* 431 (2022) 133905.
<https://doi.org/10.1016/J.CEJ.2021.133905>.
- [310] B.M. Trinh, C.C. Chang, T.H. Mekonnen, Facile fabrication of thermoplastic starch/poly (lactic acid) multilayer films with superior gas and moisture barrier

- properties, *Polymer (Guildf)*. 223 (2021) 123679.
<https://doi.org/10.1016/J.POLYMER.2021.123679>.
- [311] N. Agrawal, S. Munjal, M.Z. Ansari, N. Khare, Superhydrophobic palmitic acid modified ZnO nanoparticles, *Ceram Int*. 43 (2017) 14271–14276.
<https://doi.org/10.1016/J.CERAMINT.2017.07.176>.
- [312] H.-M. Wang, B. Wang, T.-Q. Yuan, L. Zheng, Q. Shi, S.-F. Wang, G.-Y. Song, R.-C. Sun, Tunable, UV-shielding and biodegradable composites based on well-characterized lignins and poly(butylene adipate-co-terephthalate), *Green Chemistry*. 22 (2020) 8623–8632. <https://doi.org/10.1039/D0GC03284K>.
- [313] Y. Liu, S. Liu, Z. Liu, Y. Lei, S. Jiang, K. Zhang, W. Yan, J. Qin, M. He, S. Qin, J. Yu, Enhanced mechanical and biodegradable properties of PBAT/lignin composites via silane grafting and reactive extrusion, *Compos B Eng*. 220 (2021) 108980. <https://doi.org/10.1016/J.COMPOSITESB.2021.108980>.
- [314] T. Mezger, *Applied Rheology: With Joe Flow on Rheology Road*, Anton Paar, 2015.
https://scholar.google.ca/scholar?hl=en&as_sdt=0%2C5&q=Applied+Rheology+With+Joe+Flow+on+Rheology+Road&btnG= (accessed November 5, 2021).
- [315] M. Li, Y. Jia, X. Shen, T. Shen, Z. Tan, W. Zhuang, G. Zhao, C. Zhu, H. Ying, Investigation into lignin modified PBAT/thermoplastic starch composites: Thermal, mechanical, rheological and water absorption properties, *Ind Crops Prod*. 171 (2021) 113916. <https://doi.org/10.1016/J.INDCROP.2021.113916>.
- [316] C. Liu, H. Du, L. Dong, X. Wang, Y. Zhang, G. Yu, B. Li, X. Mu, H. Peng, H. Liu, Properties of Nanocelluloses and Their Application as Rheology Modifier in Paper Coating, *Ind Eng Chem Res*. 56 (2017) 8264–8273.
<https://doi.org/10.1021/ACS.IECR.7B01804>.
- [317] B. Adams, M. Abdelwahab, M. Misra, A.K. Mohanty, Injection-Molded Bioblends from Lignin and Biodegradable Polymers: Processing and Performance Evaluation, *J Polym Environ*. 26 (2018) 2360–2373.
<https://doi.org/10.1007/S10924-017-1132-0/FIGURES/8>.

- [318] A. Hosseinmardi, P.K. Annamalai, L. Wang, D. Martin, N. Amiralian, Reinforcement of natural rubber latex using lignocellulosic nanofibers isolated from spinifex grass, *Nanoscale*. 9 (2017) 9510–9519. <https://doi.org/10.1039/C7NR02632C>.
- [319] H.X. Huang, J.J. Zhang, Effects of filler–filler and polymer–filler interactions on rheological and mechanical properties of HDPE–wood composites, *J Appl Polym Sci*. 111 (2009) 2806–2812. <https://doi.org/10.1002/APP.29336>.
- [320] M.I. Aranguren, E. Mora, J. V Degroot, Effect of reinforcing fillers on the rheology of polymer melts, *Citation: Journal of Rheology*. 36 (1992) 1165. <https://doi.org/10.1122/1.550306>.
- [321] F. Grüneberger, T. Künniger, T. Zimmermann, M. Arnold, Rheology of nanofibrillated cellulose/acrylate systems for coating applications, *Cellulose* 2014 21:3. 21 (2014) 1313–1326. <https://doi.org/10.1007/S10570-014-0248-9>.
- [322] M. Mariano, N. El Kissi, A. Dufresne, Cellulose nanocrystal reinforced oxidized natural rubber nanocomposites, *Carbohydr Polym*. 137 (2016) 174–183. <https://doi.org/10.1016/J.CARBPOL.2015.10.027>.
- [323] T. Chatkitanan, N. Harnkarnsujarit, Effects of nitrite incorporated active films on quality of pork, *Meat Sci*. 172 (2021) 108367. <https://doi.org/10.1016/J.MEATSCI.2020.108367>.
- [324] P. Klinmalai, A. Srisa, Y. Laorenza, W. Katekhong, N. Harnkarnsujarit, Antifungal and plasticization effects of carvacrol in biodegradable poly(lactic acid) and poly(butylene adipate terephthalate) blend films for bakery packaging, *LWT*. 152 (2021) 112356. <https://doi.org/10.1016/J.LWT.2021.112356>.
- [325] P. Leelaphiwat, C. Pechprankan, P. Siripho, N. Bumbudsanpharoke, N. Harnkarnsujarit, Effects of nisin and EDTA on morphology and properties of thermoplastic starch and PBAT biodegradable films for meat packaging, *Food Chem*. 369 (2022) 130956. <https://doi.org/10.1016/J.FOODCHEM.2021.130956>.

- [326] P. Wongphan, M. Khowthong, T. Supatrawiporn, N. Harnkarnsujarit, Novel edible starch films incorporating papain for meat tenderization, *Food Packag Shelf Life*. 31 (2022) 100787. <https://doi.org/10.1016/J.FPSL.2021.100787>.
- [327] M. Vähä-Nissi, P. Sundberg, E. Kauppi, T. Hirvikorpi, J. Sievänen, A. Sood, M. Karppinen, A. Harlin, Barrier properties of Al₂O₃ and alucone coatings and nanolaminates on flexible biopolymer films, *Thin Solid Films*. 520 (2012) 6780–6785. <https://doi.org/10.1016/J.TSF.2012.07.025>.
- [328] E.-L. Hult, K. Koivu, J. Asikkala, J. Ropponen, P. Wrigstedt, J. Sipilä, K. Poppius-Levlin, Esterified lignin coating as water vapor and oxygen barrier for fiber-based packaging, *Holzforschung*. 67 (2013) 899–905. <https://doi.org/10.1515/HF-2012-0214>.
- [329] C.C. Chang, B.M. Trinh, T.H. Mekonnen, Robust multiphase and multilayer starch/polymer (TPS/PBAT) film with simultaneous oxygen/moisture barrier properties, *J Colloid Interface Sci*. 593 (2021) 290–303. <https://doi.org/10.1016/J.JCIS.2021.03.010>.
- [330] T. Chatkitanan, N. Harnkarnsujarit, Development of nitrite compounded starch-based films to improve color and quality of vacuum-packaged pork, *Food Packag Shelf Life*. 25 (2020) 100521. <https://doi.org/10.1016/J.FPSL.2020.100521>.
- [331] S.I. Hong, J.W. Lee, S.M. Son, Properties of polysaccharide-coated polypropylene films as affected by biopolymer and plasticizer types, *Packaging Technology and Science*. 18 (2005) 1–9. <https://doi.org/10.1002/pts.667>.
- [332] S. Shankar, J.W. Rhim, Effects of poly(butylene adipate-co-terephthalate) coating on the water resistant, mechanical, and antibacterial properties of Kraft paper, *Prog Org Coat*. 123 (2018) 153–159. <https://doi.org/10.1016/J.PORGCOAT.2018.07.002>.
- [333] J.W. Rhim, J.H. Kim, Properties of Poly(lactide)-Coated Paperboard for the Use of 1-Way Paper Cup, *J Food Sci*. 74 (2009) E105–E111. <https://doi.org/10.1111/J.1750-3841.2009.01073.X>.

- [334] N. Harnkarnsujarit, Y. Li, Structure–property modification of microcrystalline cellulose film using agar and propylene glycol alginate, *J Appl Polym Sci.* 134 (2017) 45533. <https://doi.org/10.1002/APP.45533>.
- [335] A. Rajeswari, E.J.S. Christy, E. Swathi, A. Pius, Fabrication of improved cellulose acetate-based biodegradable films for food packaging applications, *Environmental Chemistry and Ecotoxicology.* 2 (2020) 107–114. <https://doi.org/10.1016/J.ENCECO.2020.07.003>.
- [336] V. Siracusa, P. Rocculi, S. Romani, M.D. Rosa, Biodegradable polymers for food packaging: a review, *Trends Food Sci Technol.* 19 (2008) 634–643. <https://doi.org/10.1016/J.TIFS.2008.07.003>.
- [337] G. Chen, A. Gupta, T.H. Mekonnen, Effects of wood fiber loading, silane modification and crosslinking on the thermomechanical properties and thermal conductivity of EPDM biocomposite foams, *Ind Crops Prod.* 200 (2023) 116911. <https://doi.org/10.1016/J.INDCROP.2023.116911>.
- [338] F.S. Chakar, A.J. Ragauskas, Review of current and future softwood kraft lignin process chemistry, in: *Ind Crops Prod*, Elsevier, 2004: pp. 131–141. <https://doi.org/10.1016/j.indcrop.2004.04.016>.
- [339] R. Saad, J. Hawari, Grafting of lignin onto nanostructured silica SBA-15: Preparation and characterization, *Journal of Porous Materials.* 20 (2013) 227–233. <https://doi.org/10.1007/s10934-012-9592-z>.
- [340] E.A.B. da Silva, M. Zabkova, J.D. Araújo, C.A. Cateto, M.F. Barreiro, M.N. Belgacem, A.E. Rodrigues, An integrated process to produce vanillin and lignin-based polyurethanes from Kraft lignin, *Chemical Engineering Research and Design.* 87 (2009) 1276–1292. <https://doi.org/10.1016/J.CHERD.2009.05.008>.
- [341] A.K. Mohanty, A. Wibowo, M. Misra, L.T. Drzal, Development of renewable resource–based cellulose acetate bioplastic: Effect of process engineering on the performance of cellulosic plastics, *Polym Eng Sci.* 43 (2003) 1151–1161. <https://doi.org/10.1002/PEN.10097>.

- [342] M.M. Meier, L.A. Kanis, J.C. de Lima, A.T.N. Pires, V. Soldi, Poly(ϵ -caprolactone triol) as plasticizer agent for cellulose acetate films: influence of the preparation procedure and plasticizer content on the physico-chemical properties, *Polym Adv Technol.* 15 (2004) 593–600. <https://doi.org/10.1002/PAT.517>.
- [343] A.S. Abdel-Naby, S.A. Aboubshait, Cellulose acetate blends with acrylonitrile/N-phenyl maleimide copolymers morphological and thermal properties, *J Therm Anal Calorim.* 114 (2013) 1279–1286. <https://doi.org/10.1007/S10973-013-3153-9/FIGURES/6>.
- [344] A.S. Abdel-Naby, A.A. Al-Ghamdi, Chemical modification of cellulose acetate by N-(phenyl amino) maleimides: Characterization and properties, *Int J Biol Macromol.* 68 (2014) 21–27. <https://doi.org/10.1016/J.IJBIOMAC.2014.04.007>.
- [345] M. Salzano De Luna, G. Filippone, Effects of nanoparticles on the morphology of immiscible polymer blends – Challenges and opportunities, *Eur Polym J.* 79 (2016) 198–218. <https://doi.org/10.1016/J.EURPOLYMJ.2016.02.023>.
- [346] S.J. Xiong, B. Pang, S.J. Zhou, M.K. Li, S. Yang, Y.Y. Wang, Q. Shi, S.F. Wang, T.Q. Yuan, R.C. Sun, Economically Competitive Biodegradable PBAT/Lignin Composites: Effect of Lignin Methylation and Compatibilizer, *ACS Sustain Chem Eng.* 8 (2020) 5338–5346. <https://doi.org/10.1021/acssuschemeng.0c00789>.
- [347] S. Sen, S. Patil, D.S. Argyropoulos, Thermal properties of lignin in copolymers, blends, and composites: a review, *Green Chemistry.* 17 (2015) 4862–4887. <https://doi.org/10.1039/C5GC01066G>.
- [348] J.J. Liao, N.H.A. Latif, D. Trache, N. Brosse, M.H. Hussin, Current advancement on the isolation, characterization and application of lignin, *Int J Biol Macromol.* 162 (2020) 985–1024. <https://doi.org/10.1016/j.ijbiomac.2020.06.168>.

- [349] G. Gellerstedt, A. Majtnerova, L. Zhang, Towards a new concept of lignin condensation in kraft pulping. Initial results, *C R Biol.* 327 (2004) 817–826. <https://doi.org/10.1016/j.crv.2004.03.011>.
- [350] K.J. F, K.S. K, G.R. D, V.R. A, Chemical Modification, Properties, and Usage of Lignin, Springer US, 2002. <https://doi.org/10.1007/978-1-4615-0643-0>.
- [351] S. Maaref, A. Kantzas, S.L. Bryant, The effect of silanization assisted nanoparticle hydrophobicity on emulsion stability through droplet size distribution analysis, *Chem Eng Sci.* 201 (2019) 175–190. <https://doi.org/10.1016/J.CES.2019.02.034>.
- [352] L. Bai, F. Liu, X. Xu, S. Huan, J. Gu, D.J. McClements, Impact of polysaccharide molecular characteristics on viscosity enhancement and depletion flocculation, *J Food Eng.* 207 (2017) 35–45. <https://doi.org/10.1016/j.jfoodeng.2017.03.021>.
- [353] I. Charfeddine, J.C. Majesté, C. Carrot, O. Lhost, Surface tension and interfacial tension of polyolefins and polyolefin blends, *J Appl Polym Sci.* 139 (2022). <https://doi.org/10.1002/app.51885>.
- [354] Z. Wei, Q. Huang, Edible Pickering emulsions stabilized by ovotransferrin–gum arabic particles, *Food Hydrocoll.* 89 (2019) 590–601. <https://doi.org/10.1016/J.FOODHYD.2018.11.037>.
- [355] E. Dickinson, Hydrocolloids and emulsion stability, *Handbook of Hydrocolloids: Second Edition.* (2009) 23–49. <https://doi.org/10.1533/9781845695873.23>.
- [356] P.J. Wilde, Improving Emulsion Stability Through Selection of Emulsifiers and Stabilizers, *Reference Module in Food Science.* (2019). <https://doi.org/10.1016/B978-0-08-100596-5.22337-8>.
- [357] L. An, C. Si, G. Wang, C.S. Choi, Y.H. Yu, J.H. Bae, S.M. Lee, Y.S. Kim, Efficient and green approach for the esterification of lignin with oleic acid using surfactant-combined microreactors in water, *Bioresources.* 15 (2020) 89–104. <https://doi.org/10.15376/biores.15.1.89-104>.

- [358] J. Ibarra, J. Melendres, M. Almada, M.G. Burboa, P. Taboada, J. Juárez, M.A. Valdez, Synthesis and characterization of magnetite/PLGA/chitosan nanoparticles, *Mater Res Express*. 2 (2015) 095010.
<https://doi.org/10.1088/2053-1591/2/9/095010>.
- [359] G. Mensitieri, G. Scherillo, Environmental Resistance of High Performance Polymeric Matrices and Composites, *Wiley Encyclopedia of Composites*. (2012) 1–25. <https://doi.org/10.1002/9781118097298.WEOC074>.
- [360] D.K. Owens, R.C. Wendt, Estimation of the surface free energy of polymers, *J Appl Polym Sci*. 13 (1969) 1741–1747.
<https://doi.org/10.1002/APP.1969.070130815>.
- [361] S. Wu, Calculation of interfacial tension in polymer systems, *Journal of Polymer Science Part C: Polymer Symposia*. 34 (2007) 19–30.
<https://doi.org/10.1002/POLC.5070340105>.
- [362] S. Rbihi, A. Aboulouard, L. Laallam, A. Jouaiti, Contact Angle Measurements of Cellulose based Thin Film composites: wettability, surface free energy and surface hardness, *Surfaces and Interfaces*. 21 (2020) 100708.
<https://doi.org/10.1016/J.SURFIN.2020.100708>.
- [363] L. Gu, C.W. Macosko, Evaluating PE/PLA interfacial tension using ternary immiscible polymer blends, *J Appl Polym Sci*. 138 (2021) 50623.
<https://doi.org/10.1002/APP.50623>.
- [364] Amplitude sweeps :: Anton Paar Wiki, (n.d.). <https://wiki.anton-paar.com/ca-en/amplitude-sweeps/> (accessed May 28, 2023).
- [365] F. Grüneberger, T. Künniger, T. Zimmermann, M. Arnold, Rheology of nanofibrillated cellulose/acrylate systems for coating applications, *Cellulose*. 21 (2014) 1313–1326. <https://doi.org/10.1007/s10570-014-0248-9>.
- [366] M. Mariano, N. El Kissi, A. Dufresne, Cellulose nanocrystal reinforced oxidized natural rubber nanocomposites, *Carbohydr Polym*. 137 (2016) 174–183. <https://doi.org/10.1016/j.carbpol.2015.10.027>.

- [367] B. Adams, M. Abdelwahab, M. Misra, A.K. Mohanty, Injection-Molded Bioblends from Lignin and Biodegradable Polymers: Processing and Performance Evaluation, *J Polym Environ.* 26 (2018) 2360–2373. <https://doi.org/10.1007/S10924-017-1132-0/FIGURES/8>.
- [368] C. Dae Han, J.K. Kim, On the use of time-temperature superposition in multicomponent/multiphase polymer systems, *Polymer (Guildf).* 34 (1993) 2533–2539. [https://doi.org/10.1016/0032-3861\(93\)90585-X](https://doi.org/10.1016/0032-3861(93)90585-X).
- [369] M. Li, Y. Jia, X. Shen, T. Shen, Z. Tan, W. Zhuang, G. Zhao, C. Zhu, H. Ying, Investigation into lignin modified PBAT/thermoplastic starch composites: Thermal, mechanical, rheological and water absorption properties, *Ind Crops Prod.* 171 (2021) 113916. <https://doi.org/10.1016/J.INDCROP.2021.113916>.
- [370] H. Orelma, A. Hokkanen, I. Leppänen, K. Kammiovirta, M. Kapulainen, A. Harlin, Optical cellulose fiber made from regenerated cellulose and cellulose acetate for water sensor applications, *Cellulose.* 27 (2020) 1543–1553. <https://doi.org/10.1007/S10570-019-02882-3/FIGURES/6>.
- [371] L. Bai, S. Huan, W. Xiang, O.J. Rojas, Pickering emulsions by combining cellulose nanofibrils and nanocrystals: Phase behavior and depletion stabilization, *Green Chemistry.* 20 (2018) 1571–1582. <https://doi.org/10.1039/c8gc00134k>.
- [372] Y. Zhu, S. Huan, L. Bai, A. Ketola, X. Shi, X. Zhang, J.A. Ketoja, O.J. Rojas, High Internal Phase Oil-in-Water Pickering Emulsions Stabilized by Chitin Nanofibrils: 3D Structuring and Solid Foam, *ACS Appl Mater Interfaces.* 12 (2020) 11240–11251. <https://doi.org/10.1021/acsami.9b23430>.
- [373] S. Guo, X. Li, Y. Kuang, J. Liao, K. Liu, J. Li, L. Mo, S. He, W. Zhu, J. Song, T. Song, O.J. Rojas, Residual lignin in cellulose nanofibrils enhances the interfacial stabilization of Pickering emulsions, *Carbohydr Polym.* 253 (2021) 117223. <https://doi.org/10.1016/J.CARBPOL.2020.117223>.
- [374] L. Bai, S. Lv, W. Xiang, S. Huan, D.J. McClements, O.J. Rojas, Oil-in-water Pickering emulsions via microfluidization with cellulose nanocrystals: 1.

Formation and stability, *Food Hydrocoll.* 96 (2019) 699–708.

<https://doi.org/10.1016/j.foodhyd.2019.04.038>.

- [375] Is Silica Bad for the Environment?, *Our Endangered World*. (2022).
<https://www.ourendangeredworld.com/eco/is-silica-bad-for-the-environment>
(accessed December 22, 2022).
- [376] H. Ougiya, K. Watanabe, Y. Morinaga, F. Yoshinaga, Emulsion-stabilizing Effect of Bacterial Cellulose, *Biosci Biotechnol Biochem.* 61 (1997) 1541–1545. <https://doi.org/10.1271/bbb.61.1541>.
- [377] 1980- Inamuddin, R. Boddula, M.I. Ahamed, A.M. Asiri, Green adhesives : preparation, properties and applications, (n.d.).
- [378] S. Lu, D. Yang, M. Wang, M. Yan, Y. Qian, D. Zheng, X. Qiu, Pickering emulsions synergistic-stabilized by amphoteric lignin and SiO₂ nanoparticles: Stability and pH-responsive mechanism, *Colloids Surf A Physicochem Eng Asp.* 585 (2020) 124158. <https://doi.org/10.1016/J.COLSURFA.2019.124158>.
- [379] W. Li, L. Chai, B. Du, X. Chen, R.C. Sun, Full-Lignin-Based adsorbent for removal of Cr(VI) from waste water, *Sep Purif Technol.* 306 (2023) 122644. <https://doi.org/10.1016/J.SEPPUR.2022.122644>.
- [380] B. Du, L. Chai, W. Li, X. Wang, X. Chen, J. Zhou, R.C. Sun, Preparation of functionalized magnetic graphene oxide/lignin composite nanoparticles for adsorption of heavy metal ions and reuse as electromagnetic wave absorbers, *Sep Purif Technol.* 297 (2022) 121509. <https://doi.org/10.1016/J.SEPPUR.2022.121509>.
- [381] H. Li, G. Song, Paving the Way for the Lignin Hydrogenolysis Mechanism by Deuterium-Incorporated β -O-4 Mimics, *ACS Catal.* 10 (2020) 12229–12238. https://doi.org/10.1021/ACSCATAL.0C02339/ASSET/IMAGES/LARGE/CS0C02339_0003.JPEG.
- [382] A. Beaucamp, M. Muddasar, I.S. Amiinu, M. Moraes Leite, M. Culebras, K. Latha, M.C. Gutiérrez, D. Rodriguez-Padron, F. del Monte, T. Kennedy, K.M. Ryan, R. Luque, M.M. Titirici, M.N. Collins, Lignin for energy applications –

- state of the art, life cycle, technoeconomic analysis and future trends, *Green Chemistry*. 24 (2022) 8193–8226. <https://doi.org/10.1039/D2GC02724K>.
- [383] M. Stanis, Klapiszewski, M.N. Collins, T. Jesionowski, Recent progress in biomedical and biotechnological applications of lignin-based spherical nano- and microstructures: a comprehensive review, *Mater Today Chem*. 26 (2022) 101198. <https://doi.org/10.1016/J.MTCHEM.2022.101198>.
- [384] M. Culebras, M. Pishnamazi, G.M. Walker, M.N. Collins, Facile Tailoring of Structures for Controlled Release of Paracetamol from Sustainable Lignin Derived Platforms, *Molecules* 2021, Vol. 26, Page 1593. 26 (2021) 1593. <https://doi.org/10.3390/MOLECULES26061593>.
- [385] P. Jędrzejczak, M.N. Collins, T. Jesionowski, Ł. Klapiszewski, The role of lignin and lignin-based materials in sustainable construction – A comprehensive review, *Int J Biol Macromol*. 187 (2021) 624–650. <https://doi.org/10.1016/J.IJBIOMAC.2021.07.125>.
- [386] A. Beaucamp, M. Muddasar, T. Crawford, M.N. Collins, M. Culebras, Sustainable lignin precursors for tailored porous carbon-based supercapacitor electrodes, *Int J Biol Macromol*. 221 (2022) 1142–1149. <https://doi.org/10.1016/J.IJBIOMAC.2022.09.097>.
- [387] E. Chiani, A. Beaucamp, Y. Hamzeh, M. Azadfallah, A.V. Thanusha, M.N. Collins, Synthesis and characterization of gelatin/lignin hydrogels as quick release drug carriers for Ribavirin, *Int J Biol Macromol*. 224 (2023) 1196–1205. <https://doi.org/10.1016/J.IJBIOMAC.2022.10.205>.
- [388] L. Bai, F. Liu, X. Xu, S. Huan, J. Gu, D.J. McClements, Impact of polysaccharide molecular characteristics on viscosity enhancement and depletion flocculation, *J Food Eng*. 207 (2017) 35–45. <https://doi.org/10.1016/J.JFOODENG.2017.03.021>.
- [389] L. Chai, B. Du, S. Yan, W. Li, X. Chen, R. Sun, Preparation of activated lignin with high hydroxyl content using lewis acid as demethylation reagent, *Int J Biol*

- Macromol. 222 (2022) 2571–2580.
<https://doi.org/10.1016/J.IJBIOMAC.2022.10.040>.
- [390] T. Zhang, A. Davidson, S.L. Bryant, C. Huh, Nanoparticle-Stabilized Emulsions for Applications in Enhanced Oil Recovery, Proceedings - SPE Symposium on Improved Oil Recovery. 2 (2010) 1009–1026.
<https://doi.org/10.2118/129885-MS>.
- [391] T.F. Tadros, Emulsion Formation and Stability, Emulsion Formation and Stability. (2013). <https://doi.org/10.1002/9783527647941>.
- [392] T. Truong, Encyclopedia of Dairy Sciences , 3rd ed., 2022.
<https://www.sciencedirect.com/referencework/9780128187678/encyclopedia-of-dairy-sciences> (accessed July 23, 2022).
- [393] E. Melro, A. Filipe, D. Sousa, A.J.M. Valente, A. Romano, F.E. Antunes, B. Medronho, Dissolution of kraft lignin in alkaline solutions, Int J Biol Macromol. 148 (2020) 688–695.
<https://doi.org/10.1016/J.IJBIOMAC.2020.01.153>.
- [394] D.J. McClements, Stability of Food Emulsions , n.d.
[https://people.umass.edu/~mcclemen/FoodEmulsions2008/Presentations\(PDF\)/\(6\)Emulsion_Stability.pdf](https://people.umass.edu/~mcclemen/FoodEmulsions2008/Presentations(PDF)/(6)Emulsion_Stability.pdf) (accessed July 23, 2022).
- [395] G.W. Lu, P. Gao, Emulsions and Microemulsions for Topical and Transdermal Drug Delivery, in: Handbook of Non-Invasive Drug Delivery Systems, Elsevier, 2010: pp. 59–94. <https://doi.org/10.1016/B978-0-8155-2025-2.10003-4>.
- [396] E. Joseph, G. Singhvi, Multifunctional nanocrystals for cancer therapy: A potential nanocarrier, in: Nanomaterials for Drug Delivery and Therapy, Elsevier, 2019: pp. 91–116. <https://doi.org/10.1016/B978-0-12-816505-8.00007-2>.
- [397] C. Miao, M.N. Mirvakili, W.Y. Hamad, A rheological investigation of oil-in-water Pickering emulsions stabilized by cellulose nanocrystals, J Colloid

- Interface Sci. 608 (2022) 2820–2829.
<https://doi.org/10.1016/J.JCIS.2021.11.010>.
- [398] P. Ataeian, L. Aroyan, W. Parwez, K.C. Tam, Emulsions undergoing phase transition: Effect of emulsifier type and concentration, *J Colloid Interface Sci.* 617 (2022) 214–223. <https://doi.org/10.1016/J.JCIS.2022.02.140>.
- [399] S. Laurichesse, L. Avérous, Chemical modification of lignins: Towards biobased polymers, *Prog Polym Sci.* 39 (2014) 1266–1290.
<https://doi.org/10.1016/J.PROGPOLYMSCI.2013.11.004>.
- [400] A. Vishtal, P. Rousu, T. Hultholm, K. Turku, P. Paananen, J. Käyhkö, Drainage and retention enhancement of a wheat straw-containing pulp furnish using microparticle retention aids, *Bioresources.* 6 (2011) 791–806.
<https://doi.org/10.15376/BIORES.6.1.791-806>.
- [401] X. Pan, J.N. Saddler, Effect of replacing polyol by organosolv and kraft lignin on the property and structure of rigid polyurethane foam, *Biotechnol Biofuels.* 6 (2013). <https://doi.org/10.1186/1754-6834-6-12>.
- [402] J.M. Lang, U.M. Shrestha, M. Dadmun, The effect of plant source on the properties of lignin-based polyurethanes, *Front Energy Res.* 6 (2018).
<https://doi.org/10.3389/FENRG.2018.00004>.
- [403] J. Domínguez-Robles, T. Tamminen, T. Liitiä, M.S. Peresin, A. Rodríguez, A.S. Jääskeläinen, Aqueous acetone fractionation of kraft, organosolv and soda lignins, *Int J Biol Macromol.* 106 (2018) 979–987.
<https://doi.org/10.1016/J.IJBIOMAC.2017.08.102>.
- [404] J. Jin, A.A. Ogale, Carbon fibers derived from wet-spinning of equi-component lignin/polyacrylonitrile blends, *J Appl Polym Sci.* 135 (2018).
<https://doi.org/10.1002/APP.45903>.
- [405] J.F. Kadla, S. Kubo, R.A. Venditti, R.D. Gilbert, A.L. Compere, W. Griffith, Lignin-based carbon fibers for composite fiber applications, *Carbon N Y.* 40 (2002) 2913–2920. [https://doi.org/10.1016/S0008-6223\(02\)00248-8](https://doi.org/10.1016/S0008-6223(02)00248-8).

- [406] Y. Uraki, S. Kubo, N. Nigo, Y. Sano, T. Sasaya, Preparation of Carbon Fibers from Organosolv Lignin Obtained by Aqueous Acetic Acid Pulping, *Holzforschung*. 49 (1995) 343–350.
<https://doi.org/10.1515/HFSG.1995.49.4.343>/MACHINEREADABLECITATION/RIS.
- [407] S.P. Maradur, C.H. Kim, S.Y. Kim, B.H. Kim, W.C. Kim, K.S. Yang, Preparation of carbon fibers from a lignin copolymer with polyacrylonitrile, *Synth Met*. 162 (2012) 453–459.
<https://doi.org/10.1016/J.SYNTHMET.2012.01.017>.
- [408] I. Norberg, Y. Nordström, R. Drougge, G. Gellerstedt, E. Sjöholm, A new method for stabilizing softwood kraft lignin fibers for carbon fiber production, *J Appl Polym Sci*. 128 (2013) 3824–3830. <https://doi.org/10.1002/APP.38588>.
- [409] K. Sudo, K. Shimizu, A new carbon fiber from lignin, *J Appl Polym Sci*. 44 (1992) 127–134. <https://doi.org/10.1002/APP.1992.070440113>.
- [410] Y. Qian, X. Qiu, S. Zhu, Sunscreen performance of lignin from different technical resources and their general synergistic effect with synthetic sunscreens, *ACS Sustain Chem Eng*. 4 (2016) 4029–4035.
<https://doi.org/10.1021/ACSSUSCHEMENG.6B00934>/SUPPL_FILE/SC6B00934_SI_001.PDF.
- [411] Y. Qian, X. Qiu, S. Zhu, Lignin: a nature-inspired sun blocker for broad-spectrum sunscreens, 17 (2015) 320. <https://doi.org/10.1039/c4gc01333f>.
- [412] M. Bhattacharya, A.K. Bhowmick, Polymer–filler interaction in nanocomposites: New interface area function to investigate swelling behavior and Young’s modulus, *Polymer (Guildf)*. 49 (2008) 4808–4818.
<https://doi.org/10.1016/J.POLYMER.2008.09.002>.
- [413] P. Paik, K.K. Kar, Thermal degradation kinetics and estimation of lifetime of polyethylene particles: Effects of particle size, *Mater Chem Phys*. 113 (2009) 953–961. <https://doi.org/10.1016/J.MATCHEMPHYS.2008.08.075>.

- [414] P. Paik, K.K. Kar, Kinetics of thermal degradation and estimation of lifetime for polypropylene particles: Effects of particle size, *Polym Degrad Stab.* 93 (2008) 24–35. <https://doi.org/10.1016/J.POLYMDEGRADSTAB.2007.11.001>.
- [415] A. Tejado, C. Peña, J. Labidi, J.M. Echeverria, I. Mondragon, Physico-chemical characterization of lignins from different sources for use in phenol-formaldehyde resin synthesis, *Bioresour Technol.* 98 (2007) 1655–1663. <https://doi.org/10.1016/j.biortech.2006.05.042>.
- [416] R. Blanchard, E. Ogunsona, S. Hojabr, R. Berry, T. Mekonnen, E.O. Ogunsona, T.H. Mekonnen, Synergistic Crosslinking and Reinforcing Enhancement of Rubber Latex with Cellulose Nanocrystals for Glove Applications, *ACS Appl Polym Mater.* 2 (2020) 887–898. <https://doi.org/10.1021/acsapm.9b01117>.
- [417] K. Roy, Md.N. Alam, S.K. Mandal, S.C. Debnath, Silica-coated nano calcium carbonate reinforced polychloroprene rubber nanocomposites: influence of silica coating on cure, mechanical and thermal properties, *J Nanostructure Chem.* 6 (2016) 15–24. <https://doi.org/10.1007/s40097-015-0174-x>.
- [418] M.M. Afiq, A.R. Azura, Effect of sago starch loadings on soil decomposition of Natural Rubber Latex (NRL) composite films mechanical properties, *Int Biodeterior Biodegradation.* 85 (2013) 139–149. <https://doi.org/10.1016/j.ibiod.2013.06.016>.
- [419] J. López-Beceiro, A.M. Díaz-Díaz, A. Álvarez-García, J. Tarrío-Saavedra, S. Naya, R. Artiaga, The Complexity of Lignin Thermal Degradation in the Isothermal Context, *Processes* 2021, Vol. 9, Page 1154. 9 (2021) 1154. <https://doi.org/10.3390/PR9071154>.

Appendix A – Supporting information for Chapter 2

Table A 1. Various types of sulfur-free lignin and their properties.

Type of lignin	Sulfur-free lignin	
	Organosolv Lignin	Soda Lignin
Alternate names	Acetosolv lignin	Alkaline Lignin
Obtained from	Organosolv pulping process	Soda pulping process
Appearance	Powder	Crystal - powder
Raw materials	Softwood, hardwood, annual plants [86,399]	Annual plants [86,399]
Color	Brown	Black
Odor	-	-
Mn (g/mol)	500-5000 [86,399]	800-3000 [86,399]
Tg (°C)	90-110 [86,399]	140 [86,399]
Sulfur content (%)	0 [86,400]	0 [86,400]
PDI	1.5-2.5 [86,399]	2.5-3.5 [86,399]
Solubility	Organic solvents [399]	Alkali [399]
Aliphatic OH (mmol OH/g)	2.9 [86,401]	1.3 [86,402]
Phenolic OH (mmol OH/g)	2.8 [86,401]	1.6 [86,402]
Carboxylic acid (mmol/g)	0.48 [86,403]	0.7 [86,402]

Market Leaders	Nippon Paper Industries Co., Ltd., Japan Northway Lignin Chemical, Canada Domtar Corporation, US The Dallas Group of America Borregaard USA, Inc. (S/P) Liquid Lignin Company, US	Biosynth group Northway Lignin Chemicals
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Table A 2. Various types of sulfur-containing lignin and their properties.

Type of lignin	Sulfur-containing lignin	
	Kraft Lignin	Sulfonated Lignin
Alternate names	Kraft lignin powder, Alkali Lignin [235]	Lignosulfonate
Obtained from	Kraft pulping process	Sulfite pulping process
Appearance	Blocky solid to fine powder	Powder
Raw materials	Softwood, hardwood [86,399]	Softwood, hardwood [86,399]
Color	Light to dark brown	Brown/Black
Odor	Faint woody [235]	Light odor
Mn (g/mol)	1000-3000 [86,399]	15000-50000 [86,399]
Tg (°C)	150-162 [235]	130 [86,399]

Sulfur content (%)	1.2 -2.4% [86,235]	3.5-8% [86,400]
PDI	3.0-4.5 [235]	6.0-8.0 [86,399]
Solubility	Soluble in alkali, low solubility in water [235]	Completely soluble in Water [399]
Aliphatic OH (mmol OH/g)	1.5 [86,402]	5.7 [86,402]
Phenolic OH (mmol OH/g)	1.3 [86,402]	0.6 [86,402]
Carboxylic acid (mmol/g)	0.6 [86,402]	0.3 [86,402]
Market Leaders	West Fraser Timber Co. Ltd., Canada WestRock Company, US Domtar Corporation, US Stora Enso, Finland RISE, Sweden	Borregaard USA, Inc. (S/P)GREEN AGROCHEM, China Nippon Paper Industries Co., Ltd., Japan The Dallas Group of America Sappi Limited, South Africa

Table A 3. Other works on lignin-based carbon fibers

Type of Lignin	Polymer	Temperature		Tensile properties	Ref
		Thermo-stabilization	Carbonization		
Softwood kraft lignin	-	165 °C – 250 °C @ 20 °C/min, held 250 °C for 1 hr	From room temperature to 1000 °C @ 7 °C/min	Tensile modulus: 98 ± 5 GPa	[139]
Softwood kraft lignin	Equicomponent blend with PAN	300 °C @ 1 °C/min, held for 1 hr	Heated to 1200 °C @ 7 V/min and held for 1 hr	Tensile modulus: 105.7 ± 3.1 GPa	[404]
Organosolv lignin, Softwood kraft lignin	-	Heated from 12 to 180 °C/hr, held 250 °C for 1 h	1000 °C @ 180 °C/hr	Tensile modulus: 59±8 GPa	[405]
Organosolv lignin	-	250 °C @ 0.5°C/min	Heated to 1,000 °C	Modulus: 39.1 ± 13.3 GPa	[406]
Hardwood lignin	Copolymer with PAN	105 °C for 1 hr @ 1 °C/min, then heated to 280 °C for 1 hr	800 °C @ 5 °C/min	Modulus: 22.92 gf/den	[407]
Softwood kraft lignin		250 °C @ 4 °C/min, held for 30 mins	Heated to 600 °C @ 1 °C/min	-	[408]

			and to 1000 °C @ 3 °C/min		
Steam exploded lignin		Heated from 0.5 °C/min to 2.0 °C/min	Heated upto 1000 °C @ 5 °C/min	Modulus: 40.7 ± 6.3 GPa	[409]

Table A 4. The performance of lignin as a biobased sunscreen

Sunscreen formulation base	Type of Lignin	Loadings tested	SPF Value		Ref
			Before	After	
SPF 15 lotion	Eucalyptus kraft lignin	Up to 10 %	15	75.2	[158]
NIVEA moisturizing cream, Sunscreen SPF 15, and SPF 50	<u>Enzymatic hydrolysis</u> lignin and organosolv lignin	Up to 10 wt. %		47.71 ± 6.30	[160]
Pure cream	Soda Lignin	Up to 10 wt. %	0.99 ± 0.01	6.81 ± 1.15	[410]
NIVEA Pure cream	Alkali Lignin	Up to 10 wt. %	0.99 ± 0.01	5.72 ± 0.26	[411]
SPF 15 sunscreen lotion	Kraft Lignin	Up to 10 wt. %	18.22 ± 0.92	76.97 ± 6.38	[410]
Glycerin hand cream	Alkali Lignin	Up to 10 wt. %	1.06 ± 0.01	5.33 ± 0.47	
Pure cream	Kraft Lignin	Up to 10 wt. %	0.99 ± 0.01	6.33 ± 0.37	[410]
SPF 15 sunscreen lotion	Soda Lignin	Up to 10 wt. %	18.22 ± 0.92	91.61 ± 8.47	[410]

Pure cream	Organosolv Lignin	Up to 10 wt.%	0.99 ± 0.01	8.66 ± 0.25	[410]
SPF 15 sunscreen lotion	Organosolv Lignin	Up to 10 wt.%	18.22 ± 0.92	23.66 ± 1.28	[410]
Pure cream	Enzymatic- hydrolyzed lignin	Up to 10 wt.%	0.99 ± 0.01	4.20 ± 0.50	[410]
SPF 15 sunscreen lotion	Enzymatic- hydrolyzed lignin	Up to 10 wt.%	18.22 ± 0.92	20.13 ± 5.31	[410]

Appendix B – Supporting information for Chapter 3

Dispersibility test

Change in the dispersibility of the lignin sample as a result of the modification was evaluated by exposing the baseline and the modified samples in solvents with increasing relative polarity. Various levels of solvent dispersibility depending on the modification level was noted as shown in **Figure B 1d**. Samples were solubilized in Toluene (exhibiting the lowest value of relative polarity amongst all other dispersion mediums) and post sonication the unmodified lignin samples were dispersed but the solution was opaque, while the modified samples had already settled. Pristine lignin particles could be observed to have partially settled even after an hour and the following day, all the heavier fractions of the lignin sample had completely settled down while the lighter fractions floated. Similar behavior was exhibited by the lignin samples in chloroform, the sole difference being that even after 24 hours the unmodified sample didn't settle to the extent it had in toluene and also, the 0.5 TEPI ratio sample had a ring of the lignin particles floating on its surface.

In the case of DMF and DMSO, both solvents solubilized original lignin to a good extent with the lignin being uniformly dispersed, stable and the solution being clear. Similar, to the previous dispersion mediums, modified samples weren't solubilized in either of them. DMSO imparted better dispersion to lignin and even very minutely to modified lignin 0.5 sample too. Lastly, the water seemed to have dispersed the unmodified lignin sample similar to toluene thus, forming an opaque solution, with an eventual settling to the bottom of the vial. Modified samples weren't soluble in this medium too.

Thus, while, DMSO was chosen as the preferred dispersion medium for unmodified lignin samples, modified samples lacked a known dispersion medium. Then it was found that lignin could be solubilized in a hot alkali [33]. Thus, 0.3 N KOH being finalized for their dispersion, in the present study.

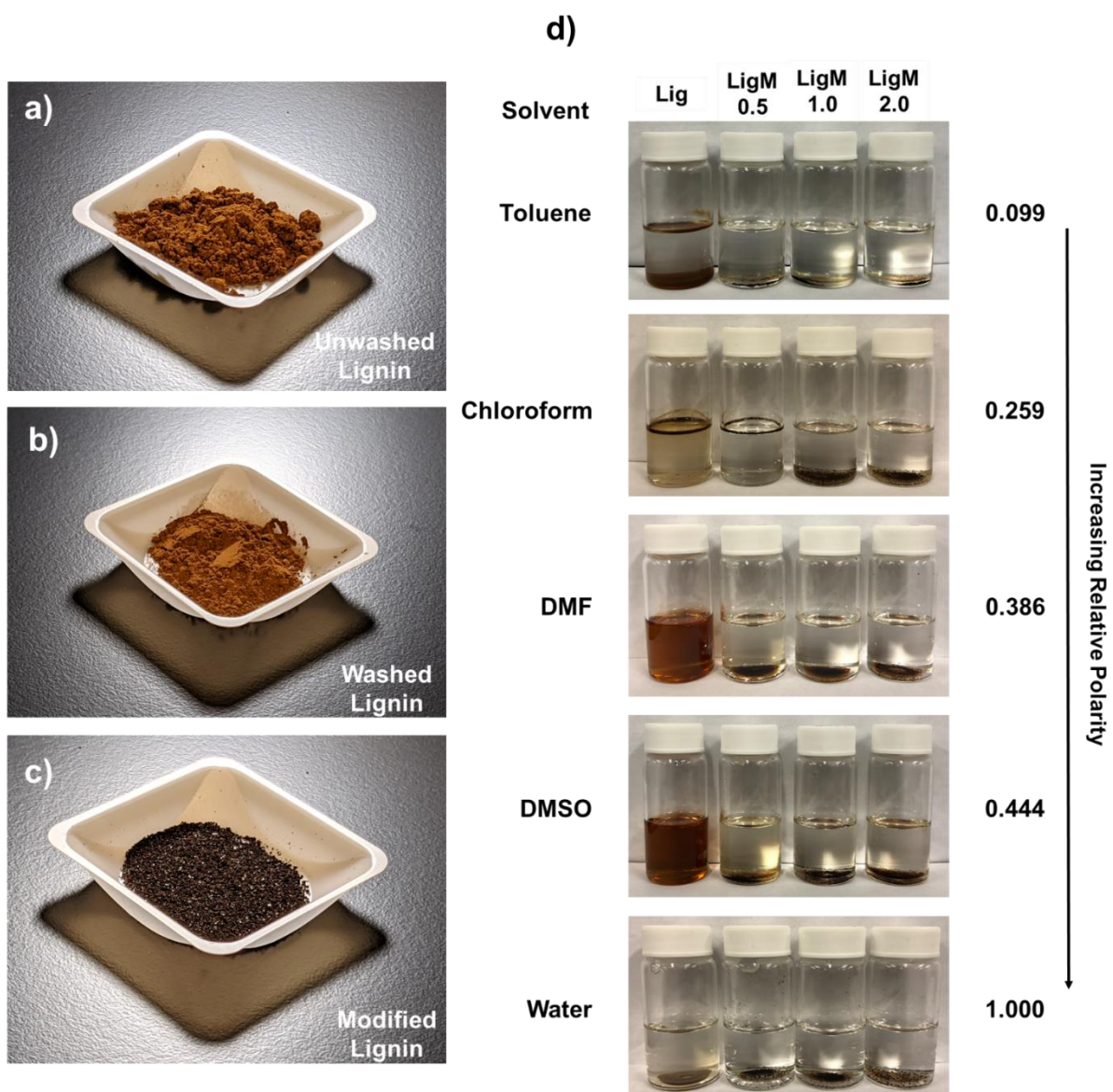


Figure B 1. (a) Unwashed lignin sample, (b) Washed lignin sample, (c) Modified lignin sample and (d) Dispersibility test of unmodified and modified lignin samples in various dispersion mediums

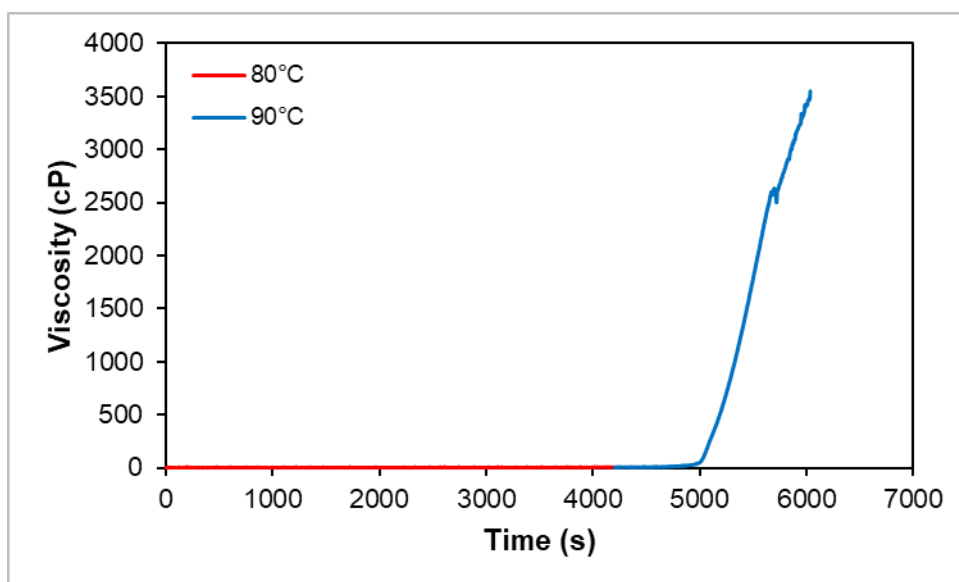


Figure B 2. Variation of viscosity with varying temperature.

Table B 1. Composition of various lignin and modified lignin formulations

Components	Concentration in each sample (phr)						
	NR	Lignin samples			Modified Lignin samples		
		Lig	Lig 5%	Lig 10%	LigM	LigM 5%	LigM
		2.5%			2.5%		10%
Lignin	-	2.5	5	10	-	-	-
Modified	-	-	-	-	2.5	5	10
Lignin							
NR	100	100	100	100	100	100	100
S	1.5	1.5	1.5	1.5	1.5	1.5	1.5
ZnO	1.3	1.3	1.3	1.3	1.3	1.3	1.3

ZDBC	0.7	0.7	0.7	0.7	0.7	0.7	0.7
KOH	60 ml of	60 ml of	60 ml of	60 ml of	60 ml of	60 ml of	60 ml of
	0.3 N	0.3 N	0.3 N	0.3 N	0.3 N	0.3 N	0.3 N
	solution	solution	solution	solution	solution	solution	solution

Table B 2. Gibbs free energy values for the composites.

Material	ΔG_m
Lig 2.5/NR	0.63
Lig 5/NR	1.24
Lig 10/NR	2.36
LigM 2.5/NR	0.11
LigM 5/NR	0.22
LigM 10/NR	0.42

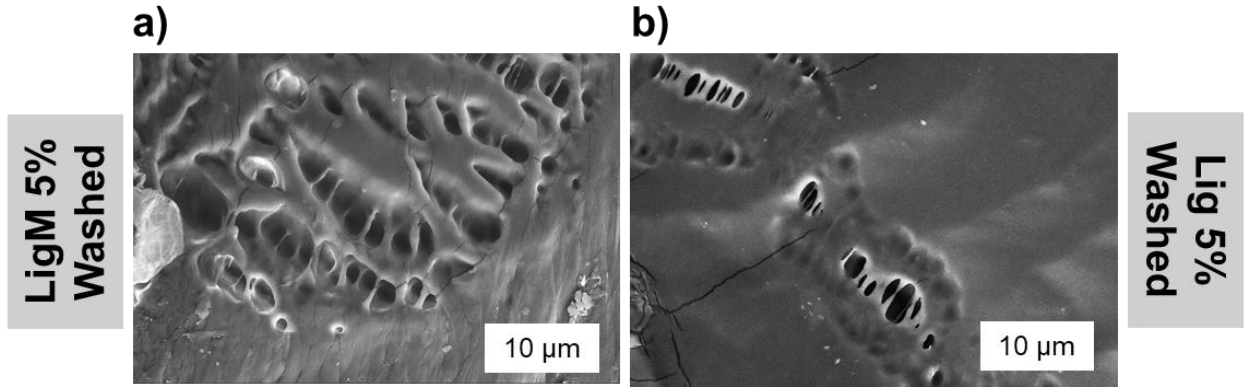


Figure B 3. Scanning electron microscope images of modified (a) and unmodified (b) 5% lignin - NR composite samples with lignin moieties having been leached out.

Guth-Gold equation

To test for the reinforcing effect of the varied filler fractions, Guth-Gold equation was employed as given by **equation S1** [412].

$$E = E_m[1 + 2.5\phi + 14.1\phi^2] \quad (\text{S1})$$

The experimental data with the predicted data have been presented in **Figure B 4 (a and b)**. The average percent deviations of the values predicted by Guth-Gold equation have been reported in **Figure B 4**. It proved to be a good fit for the unmodified samples, as evident by the reported % deviation values ranging from (0.9 to 8.5%). However, modified samples

exhibited moderate coherence with the predicted values, the deviations ranging from 8.8% to 14.1% were recorded.

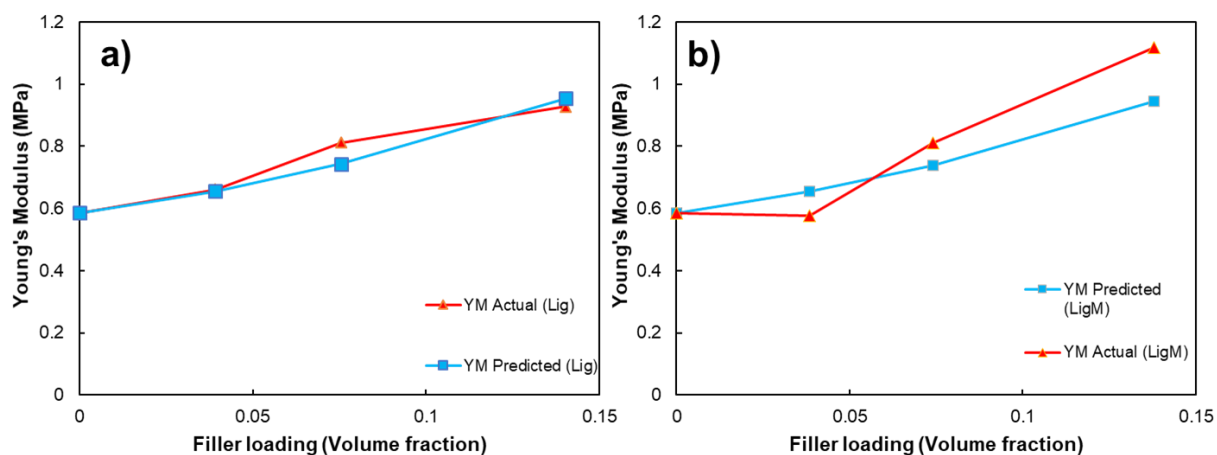


Figure B 4. Guth-Gold plot of baseline NR and its composites with (a) lignin and (b) modified lignin.

Thermal analysis

The influence of lignin and modified lignin in different concentrations on the thermal stability of the resulting composites in comparison to pure baseline NR was studied employing Thermogravimetric Analysis. The obtained TG and DTG curves of the samples present the thermal degradation behavior of the baseline NR and its composites up to 600 °C, as can be observed in **Figure B 5**. Further, the peak of derivative weight loss curves presents thermal decomposition temperatures $T_{\max}$ for the various specimen tested. As is apparent from the DTG curves, there is a single decomposition step [413]. This primarily corresponds to polymeric

chain breakdown [414] and the initiation of C-C chain bonds undergoing thermal scissions, followed by a transfer of H [415].

Further, observing the thermal decomposition temperatures in **Figure B 5**, one can observe that NR exhibited the least value of $T_{\max}$ (374.0 °C). Unmodified samples had equivalent or slightly lower values than their silylated counterparts ranging between 379.0 °C and 380.3 °C. Moreover, LigM 10% exhibited the highest $T_{\max}$ value accounting for 380.3 °C, but, the margin was insignificant. It was deduced that the addition of lignin and modified lignin to the NR matrix did not significantly impact its thermal stability. The plausible explanation was that the lower concentrations of lignin (unmodified and modified) incorporated in the elastomeric matrices were unable to impact the thermal properties of the composites, significantly.

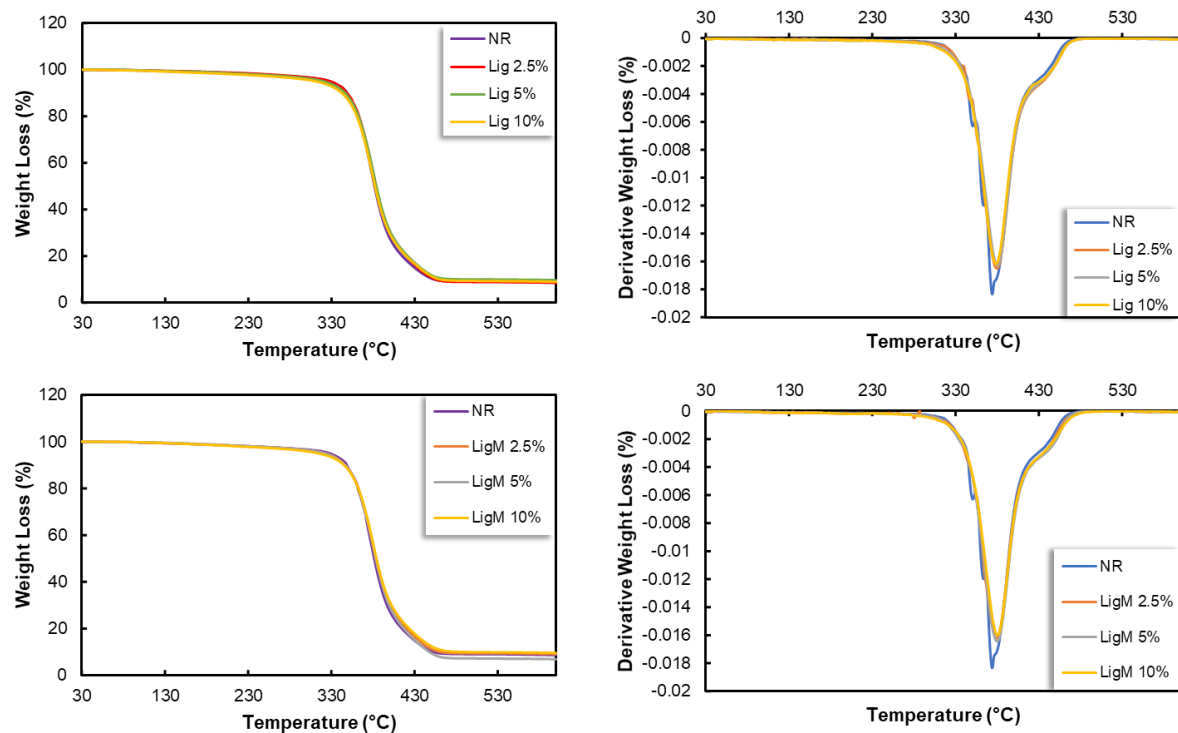


Figure B 5. Thermogravimetric analysis of baseline NR and its composites with lignin and modified lignin

Comparison of tensile properties of various fillers

Table B 3. Effect of cellulose nanocrystals content on properties of natural rubber latex film [416].

CNC Concentration in NR (phr)	Tensile Strength (MPa)	Modulus at 50 % (KPa)	Modulus at 100% (KPa)
0	2.2±0.10	3.1±0.3	1.1±0.3
0.5	2.8±0.07	5.7±0.1	1.2±0.1
1.5	2.8±0.20	7.2±0.3	3.7±0.2
3	3.7±0.10	9±0.4	4.7±0.4
5	7±0.05	11.3±0.1	6±0.1

Table B 4. Effect of calcium carbonate content on physical properties of natural rubber latex film [417].

Calcium Carbonate Concentration in NR (%)	Tensile Strength (MPa)	Elongation at break (%)	Tear Strength (KN/m)
0	18.8	2000	48.1
5	24.4	1960	65.0
10	24.8	1720	70.0

Table B 5. Effect of sago starch content on physical properties of natural rubber latex film [418].

Sago Starch Concentration in NR (phr)	Tensile Strength (MPa)	Elongation at break (%)	Modulus at 100% (KPa)	Tear Strength (N/mm)
0	22.79	1308.1	0.45	53.98
5	18.24	1192.1	0.47	57.80
10	20.73	1230.77	0.47	61.40

Table B 6. Effect of poly(alpha 1,3) glucan on the physical properties of natural rubber latex[238]

Sago Starch Concentration in NR (phr)	Tensile Strength (MPa)	Elongation at break (%)	Modulus at 100% (MPa)	Tear Strength (kN/m)
0	3.1	724.3	0.47	2.5
1	5.7	712.8	0.45	3.6
3	5.4	648.6	0.50	4.2
5	6.6	616.5	0.58	11.8
7.25	8.2	554.6	0.70	30.1
10	6.4	522.5	0.68	36.7

Appendix C – Supporting information for Chapter 4

Table C 1. One-way ANOVA of water contact angle values of baseline paper and coating formulation films.

Sample	WCA (°)
Paper	77.05 ± 2.47 ^a
PBAT	77.73 ± 2.45 ^a
LigPBAT1090	81.74 ± 2.37 ^a
LigMPBAT1090	104.24 ± 1.75 ^b
LigPBAT5050	94.66 ± 2.31 ^c
LigMPBAT5050	134.17 ± 4.26 ^d

Value = mean ± standard deviation (n = 3), ^{a-d}means with the same superscript letters within a column are not significantly different at P < 0.05 level.

Table C 2. One-way ANOVA of the Water Cobb values of baseline paper and coated sheets.

Sample	Water Cobb value
Paper	35.82 ± 1.38 ^a
PBAT	27.30 ± 1.15 ^b
LigPBAT1090	22.43 ± 1.76 ^c
LigMPBAT1090	19.00 ± 1.88 ^d
LigPBAT2575	27.27 ± 0.97 ^b
LigMPBAT2575	18.05 ± 1.08 ^d

LigPBAT5050 (20 µm)	25.60 ± 2.83 ^b
LigMPBAT5050 (20 µm)	16.70 ± 0.78 ^e
LigPBAT5050 (40 µm)	16.90 ± 1.38 ^e
LigMPBAT5050 (40 µm)	7.17 ± 1.59 ^f
LigPBAT5050 (60 µm)	9.93 ± 1.50 ^f
LigMPBAT5050 (60 µm)	4.93 ± 0.15 ^f

Value = mean ± standard deviation (n = 3), ^{a-f}means with the same superscript letters within a column are not significantly different at P < 0.05 level.

Table C 3. One-way ANOVA of the Oil Cobb values of baseline paper and coated sheets.

Sample	Water Cobb value
Paper	155.83 ± 6.67 ^a
PBAT	98.25 ± 12.23 ^b
LigPBAT1090	92.13 ± 6.47 ^b
LigMPBAT1090	87.60 ± 2.33 ^b
LigPBAT2575	103.53 ± 18.33 ^b
LigMPBAT2575	54.33 ± 4.58 ^c
LigPBAT5050 (20 µm)	108.57 ± 3.43 ^b
LigMPBAT5050 (20 µm)	56.46 ± 15.75 ^c
LigPBAT5050 (40 µm)	86.47 ± 10.14 ^b

LigMPBAT5050 (40 μm)	58.65 ± 6.58 ^c
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LigPBAT5050 (60 μm)	39.13 ± 11.65 ^d
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LigMPBAT5050 (60 μm)	34.77 ± 2.00 ^d
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Value = mean ± standard deviation (n = 3), ^{a-d}means with the same superscript letters within a column are not significantly different at P < 0.05 level.

Table C 4. One-way ANOVA of the Oxygen permeability values of baseline paper and coated sheets.

Sample	Oxygen permeability value (cm ³ .m/m ² .day.Pa)
Paper	5.49 ± 0.21 ^a
PBAT	4.28 ± 0.15 ^b
LigPBAT1090	3.92 ± 0.08 ^c
LigMPBAT1090	3.65 ± 0.02 ^c
LigPBAT2575	2.89 ± 0.27 ^e
LigMPBAT2575	2.03 ± 0.04 ^f
LigPBAT5050	2.53 ± 0.04 ^g
LigMPBAT5050	1.13 ± 0.02 ^h

Value = mean ± standard deviation (n = 3), ^{a-h}means with the same superscript letters within a column are not significantly different at P < 0.05 level.

Table C 5. One-way ANOVA of the dry and wet tensile properties of baseline paper and coated sheets.

Sample	Dry Tensile Strength (MPa)	Wet Tensile strength (MPa)	Wet Elongation at break (%)
Paper	5.49 ± 0.21 ^a	5.77 ± 1.28 ^a	3.29 ± 0.42 ^a
PBAT	4.28 ± 0.15 ^b	10.05 ± 1.73 ^b	4.39 ± 0.30 ^b
LigPBAT1090	3.92 ± 0.08 ^c	11.04 ± 0.91 ^b	3.69 ± 0.44 ^a
LigMPBAT1090	3.65 ± 0.02 ^d	19.09 ± 2.41 ^c	3.45 ± 0.22 ^a
LigPBAT2575	2.89 ± 0.27 ^e	12.91 ± 2.59 ^b	3.78 ± 0.40 ^a
LigMPBAT2575	2.03 ± 0.04 ^f	20.76 ± 4.06 ^c	4.17 ± 0.26 ^b
LigPBAT5050	2.53 ± 0.04 ^e	17.23 ± 3.56 ^c	3.95 ± 0.43 ^a
LigMPBAT5050	1.13 ± 0.02 ^g	19.84 ± 3.09 ^c	4.31 ± 0.46 ^b

Value = mean ± standard deviation (n = 5), ^{a-g}means with the same superscript letters within a column are not significantly different at P < 0.05 level.

Table C 6. Gibbs free energy values for the composites.

Material	ΔG_m
LigPBAT1090	0.82
LigMPBAT1090	0.02
LigPBAT2575	1.81
LigMPBAT2575	0.04

LigPBAT5050 2.67

LigMPBAT5050 0.06

Gibbs free values ($\sum G_m$): Lig = 8059.5, LigM = 36661.5, and PBAT = 6154.

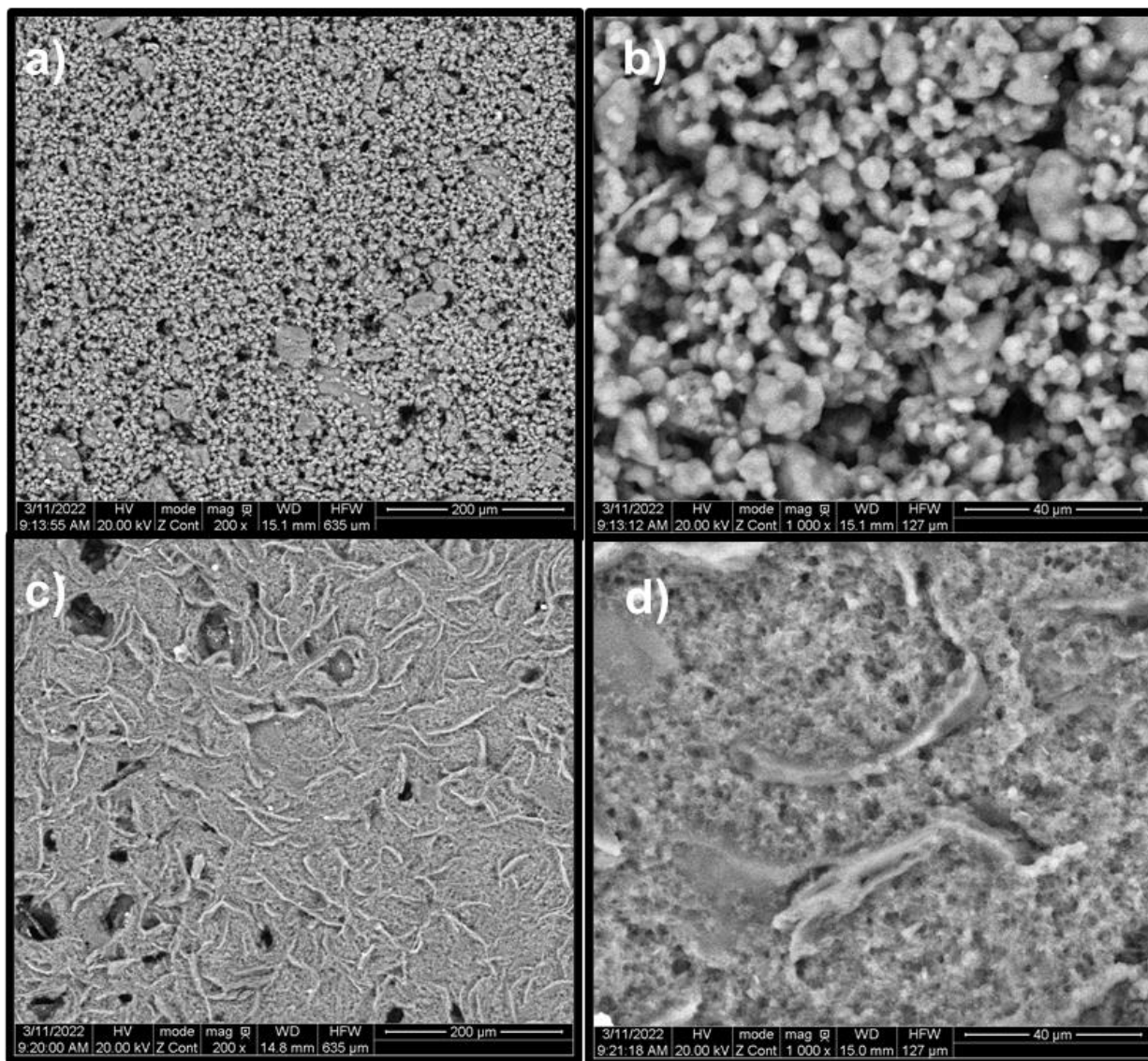


Figure C 1. Scanning electron microscopy images of the surface of: (a) LigPBAT5050 coated paper (60 μm), (b) LigPBAT5050 coated paper (60 μm) (zoomed-in view), (c) LigMPBAT5050 coated paper (60 μm) and, (d) LigMPBAT5050 coated paper (60 μm) (zoomed-in view).

Appendix D – Supporting information for Chapter 5

Table D 1. Gibbs free energy values for the lignin samples with respect to different polymer materials.

Material	ΔG_m
Lig-CA	0.023
LigOA-CA	0.090
Lig-PBAT	2.203
LigOA-PBAT	1.064
Lig-PHBV	2.494
LigOA-PHBV	1.268
Lig-PHB	2.549
LigOA-PHB	1.307
Lig-PVAc	2.074
LigOA-PVAc	0.973
Lig-PVOH	0.884
LigOA-PVOH	0.235

Gibbs free values ($\sum G_m$): Lig = 8059.5, and LigM = 24559.5.

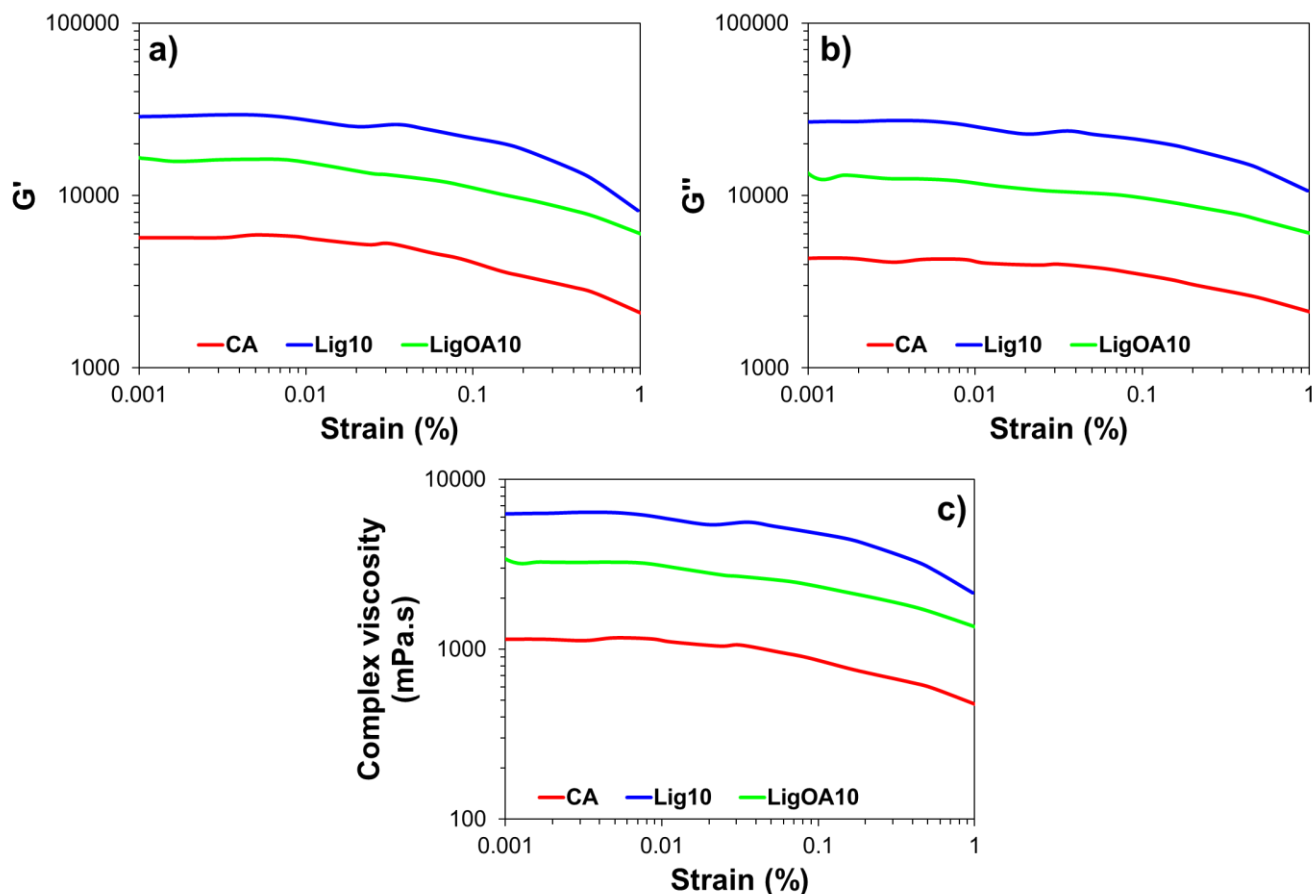


Figure D 1. Amplitude sweep analysis: a) Storage modulus vs strain, b) loss modulus vs strain, and c) complex viscosity vs strain

Optimization of compression molding temperature

The identification and optimization of compression molding temperature were undertaken by employing a rheology temperature sweep analysis (120 °C to 220 °C at 10 °C/min). The viscosity change of cellulose acetate film with increasing temperature was evaluated (**Figure D 2**). At 120 °C, a high viscosity value amounting to ~14560 Pas was recorded. At a heating rate of 10 °C/min, the specimen recorded a viscosity of ~8726 Pas at 149.2 °C. The sample exhibited shear thinning with a further reduction in the viscosity to ~2167 Pas at 170 °C. Thus,

the cellulose acetate film recorded an 85.12 % decrease in the complex viscosity relative to the initial temperature of 120 °C. In a work exploring the complexity of the thermal degradation of lignin, the onset of lignin degradation was recorded (at 200 °C) [419]. At 170 °C, a significant reduction in viscosity value was obtained and to avoid lignin degradation at temperatures closer to 200 °C, 170 °C was employed as the compression molding temperature.

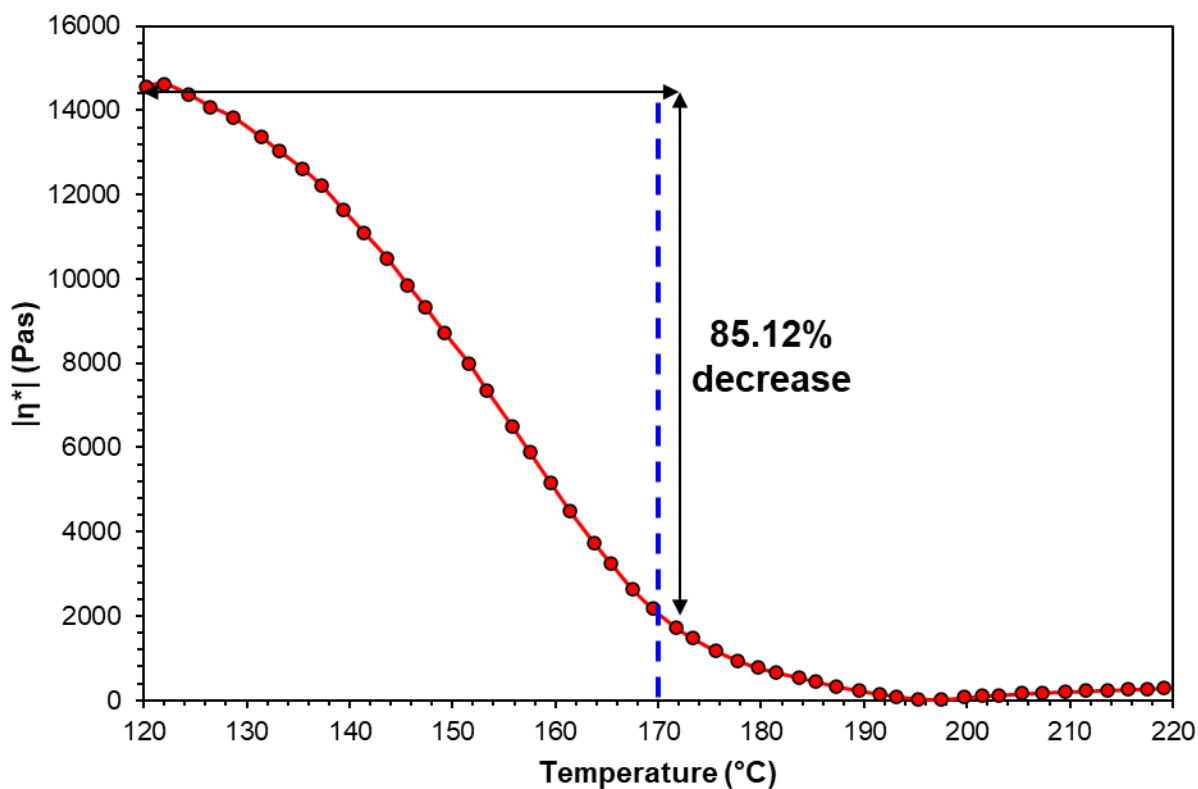


Figure D 2. Temperature sweep analysis for compression molding temperature optimization

Appendix E – Supporting information for Chapter 6

Table E 1. Creaming index values of the formulated emulsions

Sample	CI (%)
S5	72.93
S6	77.59
S7	76.51
S8	74.19
S9	75.59
S10	78.75
S11	78.40
S12	79.83

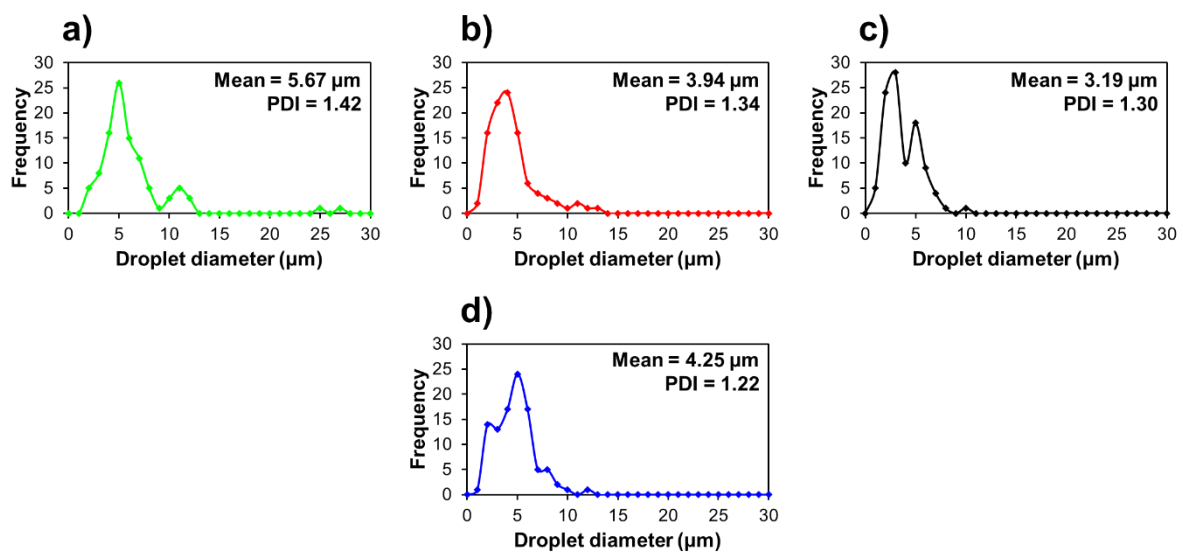


Figure E 1. Droplet size distribution in neutral (pH 7) Pickering emulsions a) Lig (1.0 mg/mL), b) LigHC (1.0 mg/mL), c) LigDC (1.0 mg/mL), and d) LigPC (1.0 mg/mL).

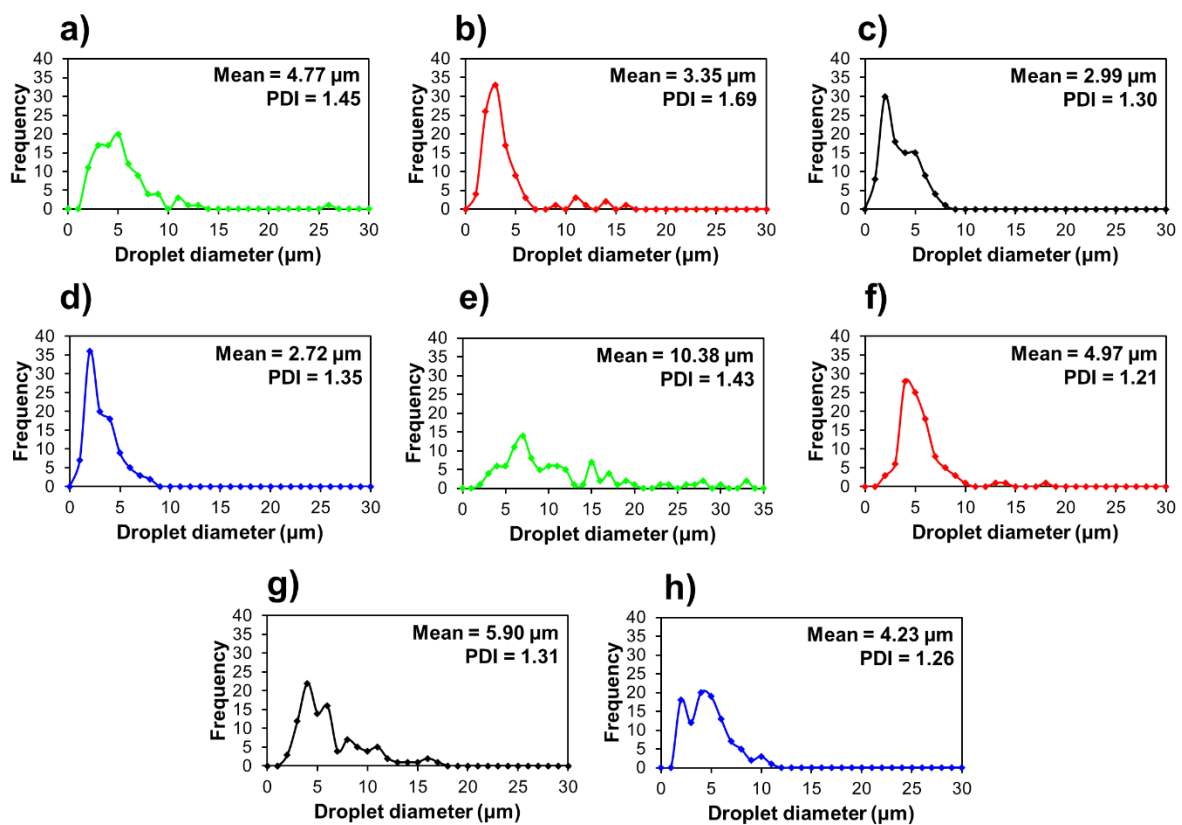


Figure E 2. Droplet size distribution in acidic (pH 5) Pickering emulsions: a) Lig (2 mg/mL), b) LigHC (2 mg/mL), c) LigDC (2 mg/mL), d) LigPC (2 mg/mL), e) Lig (0.5 mg/mL), f) LigHC (0.5 mg/mL), g) LigDC (0.5 mg/mL), and h) LigPC (0.5 mg/mL).

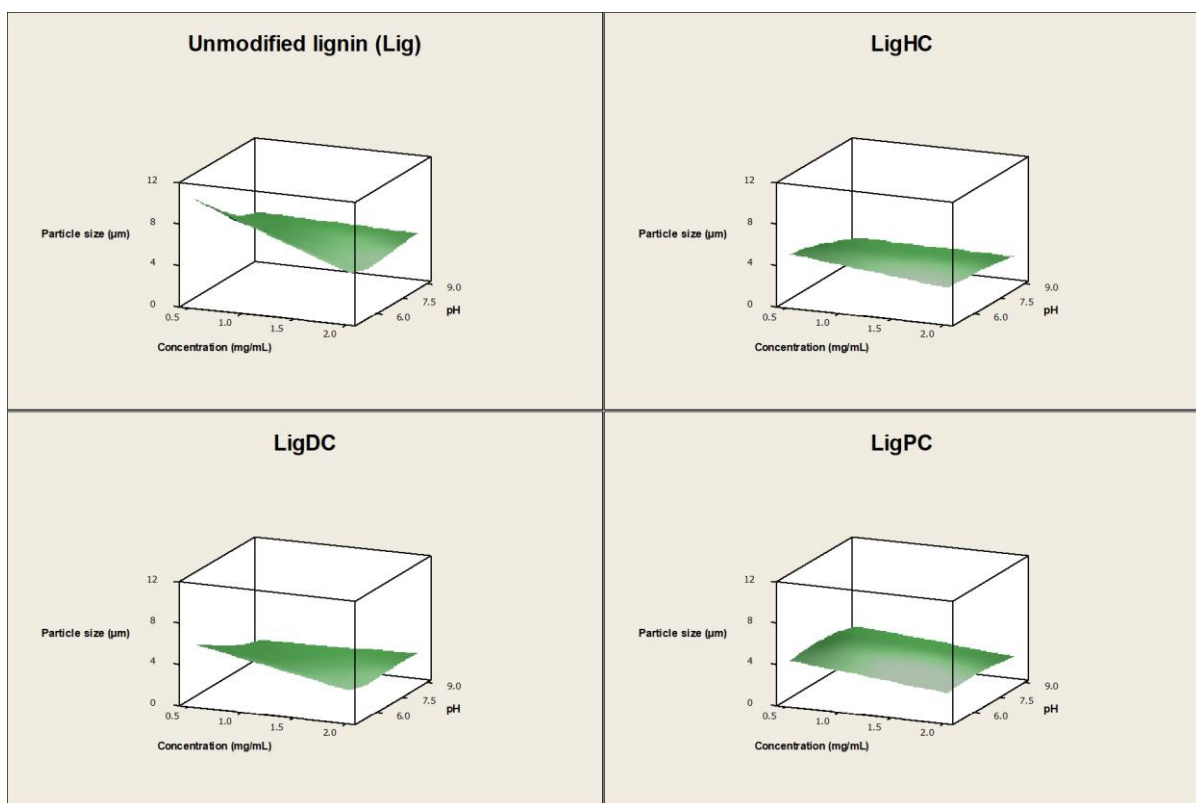


Figure E 3. Three-dimension surface plot for the prepared emulsions.