

# **Kraft Lignin as a Sustainable Flame Retardant Additive for Polymer Composites**

by

Periklis Dimitrios Alikiotis

A thesis

presented to the University of Waterloo

in fulfillment of the

thesis requirement for the degree of

Master of Applied Science

in

Chemical Engineering

Waterloo, Ontario, Canada, 2025

© Periklis Dimitrios Alikiotis 2025

## **Author's Declaration**

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the 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.

## Statement of Contributions

Chapter 3 of this thesis is adapted from a published manuscript “**Lignin as a sustainable filler of polyvinyl chloride composites: Effects of ash content and loading levels on thermomechanical and combustion properties**”, **International Journal of Biological Macromolecules**, **146527, 2025** in which I am first author. Prof. Mekonnen contributed to the review, validation, conceptualization, and supervision of the project.

## **Abstract**

Plastic waste is a widespread and continuing issue, including the leaching of toxic additives from microplastics. Lignin is the second most abundant biopolymer, and although previously considered as waste and used as fuel, lignin's availability and unique properties have garnered popularity as a sustainable and functional additive in many material applications. In this thesis, the versatility of lignin is explored at varying levels of valorization.

The first part of this work explored three differing purities of lignin and their effect on the properties of polyvinyl chloride (PVC) composites. These were tested alongside composites with differing concentrations of lignin and were all subject to various thermomechanical and flammability testing. Additionally, the decomposition kinetics of PVC and a lignin-PVC composite were explored. The industrially purified lignin outperformed the other purities mainly in mechanical properties, but the laboratory purified lignin retained the most heat capacity compared to the control. Additionally, at a concentration of 18 wt.% lignin, combustion indices were improved by 50 to 80%, but the elongation at break of these composites were reduced by 38.7%.

The second part of this work focused on incorporating a hydrophilic FR (ammonium polyphosphate) into natural rubber (NR), a hydrophobic polymer, by utilizing nano-containers constructed via the crosslinking of lignin. The properties of the lignin nanocontainers (LNCs) were studied to best enhance the dispersion of this filler within the NR at varying concentrations. These composites were tested alongside bulk incorporated lignin & FR as well as foamed samples to best determine the value brought by the LNCs. At a concentration of just 10 wt.% LNC, various flammability parameters improved and outperformed the bulk incorporated sample. This work demonstrated the versatility of lignin to by adding value to

polymeric materials without additional modification or being modified to improve its incorporation as a nanomaterial.

## **Acknowledgments**

Firstly, I would like to express my sincerest gratitude to Professor Tizazu Mekonnen for being an excellent supervisor and overall role model. You are a compassionate leader whilst having an unmatched dedication to your duties, and I am truly thankful for your guidance throughout my master's. I would also like to thank the rest of the lab group for all the good memories, kindness, and assistance throughout my time here. Specifically, I would like to thank Dylan Jubinville for maintaining the operations of the lab in peak conditions – this would have been all the more difficult without your work.

## **Dedication**

I dedicate this work to my family and friends that supported me throughout my academic journey. To my mother, Stavroula Stathopoulos, thank you for the constant love and support throughout this all. To my late father, Nikolaos Alikiotis, I know you would be proud of my achievements and who I am today.

# Table of Contents

|                                                                   |      |
|-------------------------------------------------------------------|------|
| Author's Declaration .....                                        | ii   |
| Abstract.....                                                     | iv   |
| Acknowledgments .....                                             | vi   |
| Dedication.....                                                   | vii  |
| Table of Contents.....                                            | viii |
| List of Figures.....                                              | x    |
| List of Tables .....                                              | xii  |
| List of Schemes.....                                              | xiii |
| List of Abbreviations .....                                       | xiv  |
| Chapter 1: Introduction.....                                      | 1    |
| 1.1 Motivation.....                                               | 1    |
| 1.2 Research Objectives.....                                      | 2    |
| 1.3 Thesis Outline .....                                          | 3    |
| Chapter 2: Background Information.....                            | 4    |
| 2.1 Lignin 4                                                      |      |
| 2.2 Extraction Methods.....                                       | 4    |
| 2.2.1 Sulfur-Bearing Sources.....                                 | 4    |
| 2.2.2 Sulfur-Free Sources .....                                   | 5    |
| 2.3 Lignin as a Biofiller .....                                   | 6    |
| 2.3.1 Thermoplastic Composites.....                               | 7    |
| 2.3.2 Rubber Composites.....                                      | 8    |
| 2.3.3 Comparison and compatibility with starch biomaterials ..... | 9    |
| 2.4 Nano-lignin .....                                             | 10   |
| 2.5 Flame Propagation .....                                       | 11   |
| 2.5.1 Mechanism.....                                              | 11   |
| 2.5.2 Flame Characterization .....                                | 12   |
| 2.6 Flame Retardants .....                                        | 14   |
| 2.6.1 Halogenated Flame Retardants .....                          | 14   |
| 2.6.2 Mineral Flame Retardants.....                               | 15   |
| 2.6.3 Bio-based Flame Retardants .....                            | 16   |
| 2.7 Lignin-based FRs .....                                        | 17   |
| 2.8 Lignin FR Nanomaterials.....                                  | 20   |

|     |                                                                                                                                                                          |     |
|-----|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 2.9 | Summary of Chapter 2 .....                                                                                                                                               | 22  |
|     | Chapter 3: Lignin as a sustainable filler of polyvinyl chloride composites: Effects of ash content and loading levels on thermomechanical and combustion properties..... | 24  |
| 3.1 | Introduction.....                                                                                                                                                        | 24  |
| 3.2 | Experimental .....                                                                                                                                                       | 27  |
|     | 3.2.1 Materials .....                                                                                                                                                    | 27  |
|     | 3.2.2 Processing methods.....                                                                                                                                            | 29  |
|     | 3.2.3 Degradation Kinetics .....                                                                                                                                         | 33  |
| 3.3 | Results & Discussion .....                                                                                                                                               | 37  |
|     | 3.3.1 Characterization .....                                                                                                                                             | 37  |
|     | 3.3.2 Viscoelastic Behaviour .....                                                                                                                                       | 42  |
|     | 3.3.3 Morphology.....                                                                                                                                                    | 45  |
|     | 3.3.4 Tensile Properties.....                                                                                                                                            | 46  |
|     | 3.3.5 Degradation Characteristics .....                                                                                                                                  | 48  |
| 3.4 | Conclusions.....                                                                                                                                                         | 56  |
|     | Chapter 4: Kraft Lignin Nano-Containers to Deliver Flame Retardants in Natural Rubber Composites.....                                                                    | 58  |
| 4.1 | Introduction.....                                                                                                                                                        | 58  |
| 4.2 | Experimental .....                                                                                                                                                       | 60  |
|     | 4.2.1 Materials .....                                                                                                                                                    | 60  |
|     | 4.2.2 Methods.....                                                                                                                                                       | 60  |
|     | 4.2.3 Lignin nanocontainer (LNC) synthesis.....                                                                                                                          | 60  |
|     | 4.2.4 NR composites fabrication.....                                                                                                                                     | 62  |
| 4.3 | Results and discussion .....                                                                                                                                             | 67  |
|     | 4.3.1 LNC characterization .....                                                                                                                                         | 67  |
|     | 4.3.2 Material characterization .....                                                                                                                                    | 74  |
|     | 4.3.3 Flammability testing .....                                                                                                                                         | 78  |
| 4.4 | Conclusions.....                                                                                                                                                         | 82  |
|     | Chapter 5: Concluding Remarks.....                                                                                                                                       | 83  |
|     | References.....                                                                                                                                                          | 85  |
|     | Appendix A: Supporting Information for Chapter 3 .....                                                                                                                   | 95  |
|     | Appendix B: Supporting Information for Chapter 4.....                                                                                                                    | 101 |

## List of Figures

|                                                                                                                                                                                                                                                                       |    |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| <b>Figure 1:</b> Schematic of flame propagation in polymers.....                                                                                                                                                                                                      | 12 |
| <b>Figure 2:</b> ATR-FTIR spectra of HpH lignin (bottom), LpH lignin (middle), and Wash lignin (top).....                                                                                                                                                             | 38 |
| <b>Figure 3:</b> TGA (a and b) and DTG (c and d) curves comparing grade (a and c) and loading (b and d) – under nitrogen. ....                                                                                                                                        | 40 |
| <b>Figure 4:</b> TGA (a & b) and DTG (c & d) curves comparing grade (a & c) and loading (b & d) – under air. ....                                                                                                                                                     | 41 |
| <b>Figure 5:</b> Heat capacity curves comparing grade (a) and loading (b).....                                                                                                                                                                                        | 42 |
| <b>Figure 6:</b> Storage modulus ( $E'$ ) (a & b) and $\tan \delta$ (c & d) curves comparing grades (a & c) and loading (b & d).....                                                                                                                                  | 43 |
| <b>Figure 7:</b> Parallel plate rheology results of complex viscosity with varied grade (a), and varied loading (b), as well as oscillatory moduli with varied grade (c) and varied loading (d). ....                                                                 | 44 |
| <b>Figure 8:</b> E-SEM images of samples N (a), W18 (b), L18 (c) and H18 (d) with their respective magnifications. ....                                                                                                                                               | 46 |
| <b>Figure 9:</b> Tensile results for ultimate tensile strength (a, d), Young's modulus (b, e), and elongation at break (c, f), with varying grade of lignin (a - c) and varying loading of Wash lignin (d - f). Error bars indicate $\pm$ one standard deviation..... | 48 |
| <b>Figure 10:</b> Combustion indices, $S$ ( $\text{min}^{-2} \text{K}^{-3}$ ), $C$ ( $\text{min}^{-1} \text{K}^{-2}$ ), $D_i$ ( $\text{min}^{-3}$ ), & $D_b$ ( $\text{min}^{-4}$ ), (a) and indices for samples relative to the values of sample N (b). ....          | 51 |
| <b>Figure 11:</b> Oxidative decomposition of neat PVC at varying heating rates, with conversion (a) and derivative weight loss curves (b).....                                                                                                                        | 52 |
| <b>Figure 12:</b> Sample deconvolution of sample N. ....                                                                                                                                                                                                              | 52 |
| <b>Figure 13:</b> OFW plots and activation energies as functions of conversion of deconvoluted curves for sample N. ....                                                                                                                                              | 53 |
| <b>Figure 14:</b> Experimental (solid lines) and modeled (dashed lines) TGA (a) and DTG (b) curves at varying heating rates for sample N under nitrogen. ....                                                                                                         | 55 |
| <b>Figure 15:</b> Experimental (solid lines) and modeled (dashed lines) TGA (a) and DTG (b) curves at varying heating rates for sample W27 under nitrogen. ....                                                                                                       | 55 |
| <b>Figure 16:</b> Proposed crosslinking reaction scheme.....                                                                                                                                                                                                          | 69 |
| <b>Figure 17:</b> ATR-FTIR spectra of the crosslinking reaction over time (a), comparing reactants with the initial reaction spectrum (b), and comparing the evolution of new peaks from the crosslinking reaction (c & d).....                                       | 69 |
| <b>Figure 18:</b> DLS plots for the fresh emulsion (a), and the emulsion kept overnight either with or without crosslinking (b & c, respectively).....                                                                                                                | 70 |
| <b>Figure 19:</b> DLS plots for LNCs dispersed in water (a) and water + Tween 20 (b). ....                                                                                                                                                                            | 71 |
| <b>Figure 20:</b> EDS from area marked in red for sample 5-LNC. ....                                                                                                                                                                                                  | 72 |
| <b>Figure 21:</b> E-SEM image of sample 5-LNC (a), with elemental mapping on phosphorus of the image (b), and overlaying the previous images to indicate overlaps (c). ....                                                                                           | 73 |
| <b>Figure 22:</b> E-SEM images of 10-LNC (a), 10-L+A (b), and 5-LNC (c & d). ....                                                                                                                                                                                     | 73 |
| <b>Figure 23:</b> Mechanical data for ultimate tensile strength (a), Young's modulus (b), elongation at break (c), toughness (d), and type O hardness (e). Error bars indicate $\pm$ one standard deviation.....                                                      | 75 |
| <b>Figure 24:</b> TGA (a) and DTG (b) curves – under nitrogen.....                                                                                                                                                                                                    | 76 |

|                                                                                                                                                                                                                                                                          |    |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| <b>Figure 25:</b> Char values following inert TGA.....                                                                                                                                                                                                                   | 77 |
| <b>Figure 26:</b> TGA (a) and DTG (b) curves – under air.....                                                                                                                                                                                                            | 77 |
| <b>Figure 27:</b> Combustion indices, S ( $\text{min}^{-2} \text{K}^{-3}$ ), C ( $\text{min}^{-1} \text{K}^{-2}$ ), $D_i$ ( $\text{min}^{-3}$ ), & $D_b$ ( $\text{min}^{-4}$ ), (a) and percentage improvement for samples relative to the values of sample N (b). ..... | 79 |
| <b>Figure 28:</b> HRR curves for select samples measured via SDT.....                                                                                                                                                                                                    | 80 |
| <b>Figure 29:</b> Linear burn (purple) and LOI data (orange).....                                                                                                                                                                                                        | 81 |
| <b>Figure 30:</b> Images of sample 5-LNC after LOI showcasing the char formed during burning (left, middle), and the char’s porous structure (right).....                                                                                                                | 82 |

## List of Tables

|                                                                                                                                          |    |
|------------------------------------------------------------------------------------------------------------------------------------------|----|
| <b>Table 1:</b> Summary of lignin sources and their respective properties. ....                                                          | 6  |
| <b>Table 2:</b> UL-94 vertical flame test categorical classification. ....                                                               | 14 |
| <b>Table 3:</b> Cone calorimetry data (in percent change relative to control) for lignin-FR PP composites [76]. ....                     | 19 |
| <b>Table 4:</b> Formulations in phr their corresponding sample names. ....                                                               | 29 |
| <b>Table 5:</b> Differential and integral forms of various reaction mechanisms [108]–[111]. ....                                         | 34 |
| <b>Table 6:</b> Visco-elastic properties in the glassy & rubber states and glass transition temperature as measured by DMA and DSC. .... | 43 |
| <b>Table 7:</b> Parameters for power law model within testing region. ....                                                               | 45 |
| <b>Table 8:</b> LOI values of tested samples. ....                                                                                       | 49 |
| <b>Table 9:</b> Final kinetic model parameters for sample N. ....                                                                        | 55 |
| <b>Table 10:</b> Final kinetic model parameters for sample W27. ....                                                                     | 55 |
| <b>Table 11:</b> Recipe for sample in per hundred rubber (phr). ....                                                                     | 63 |
| <b>Table 12:</b> Heat release data for select samples obtained via SDT. ....                                                             | 80 |
| <b>Table 13:</b> UL-94 horizontal burn (HB) test ratings. ....                                                                           | 81 |

## List of Schemes

|                                                                                                                                                   |    |
|---------------------------------------------------------------------------------------------------------------------------------------------------|----|
| <b>Scheme 1:</b> Material process flowchart for (a) lignin washing, (b) compounding and sample preparation, (c) extrusion and pelletization. .... | 28 |
| <b>Scheme 2:</b> Synthesis of APP-filled LNCs via emulsification, crosslinking, and freeze drying. ....                                           | 62 |
| <b>Scheme 3:</b> Fabrication of NR-LNC composites.....                                                                                            | 64 |

## List of Abbreviations

|                               |                                                       |
|-------------------------------|-------------------------------------------------------|
| <b>A</b>                      | Pre-exponential factor                                |
| <b>ADC</b>                    | Azodicarbonamide                                      |
| <b>APP</b>                    | Ammonium polyphosphate                                |
| <b>ATR</b>                    | Attenuated total reflectance                          |
| <b>C</b>                      | Flammability index                                    |
| <b>CR</b>                     | Coats-Redfern                                         |
| <b>D<sub>b</sub></b>          | Burnout index                                         |
| <b>D<sub>i</sub></b>          | Ignition index                                        |
| <b>DCP</b>                    | Dicumyl peroxide                                      |
| <b>DI</b>                     | De-ionized                                            |
| <b>DLS</b>                    | Dynamic light scattering                              |
| <b>DMA</b>                    | Dynamic mechanical analysis                           |
| <b>DMSO</b>                   | Dimethyl sulfoxide                                    |
| <b>DSC</b>                    | Differential scanning calorimetry                     |
| <b>DTG</b>                    | Derivative thermogravimetric                          |
| <b>E</b>                      | Activation energy                                     |
| <b>E'</b>                     | Storage modulus (obtained via extensional experiment) |
| <b>E''</b>                    | Loss modulus (obtained via extensional experiment)    |
| <b>E-SEM</b>                  | Environmental-Scanning Electron Microscopy            |
| <b>f(<math>\alpha</math>)</b> | Reaction mechanism as a function of $\alpha$          |
| <b>FGC</b>                    | Flame growth capacity                                 |
| <b>FR</b>                     | Flame retardant                                       |
| <b>FTIR</b>                   | Fourier transform infrared spectroscopy               |
| <b>FWO</b>                    | Flynn-Wall-Ozawa                                      |
| <b>G'</b>                     | Storage modulus (obtained via shearing experiment)    |
| <b>G''</b>                    | Loss modulus (obtained via shearing experiment)       |
| <b>g(<math>\alpha</math>)</b> | Integral form of f( $\alpha$ )                        |
| <b>HCl</b>                    | Hydrogen chloride                                     |
| <b>HpH</b>                    | High pH                                               |
| <b>ID</b>                     | Inner diameter                                        |
| <b>IPDI</b>                   | Isophorone diisocyanate                               |
| <b>K</b>                      | Flow consistency index                                |
| <b>LNC</b>                    | Lignin nano-container                                 |
| <b>LOI</b>                    | Limiting Oxygen index                                 |
| <b>LpH</b>                    | Low pH                                                |
| <b>m<sub>0</sub></b>          | Initial mass                                          |
| <b>m<sub>f</sub></b>          | Final mass                                            |
| <b>mHRR</b>                   | Mean heat release rate                                |
| <b>M<sub>n</sub></b>          | Number average molecular weight                       |
| <b>m<sub>t</sub></b>          | Mass at time = t                                      |

|                                    |                                                           |
|------------------------------------|-----------------------------------------------------------|
| <b>Mt</b>                          | Million metric tons                                       |
| <b>n</b>                           | Flow behaviour index                                      |
| <b>NaOH</b>                        | Sodium hydroxide                                          |
| <b>NR</b>                          | Natural rubber                                            |
| <b>PDI</b>                         | Polydispersity index                                      |
| <b>phr</b>                         | Per hundred resin/rubber                                  |
| <b>pHRR</b>                        | Peak heat release rate                                    |
| <b>PLA</b>                         | Poly(lactic acid)                                         |
| <b>PP</b>                          | Poly(propylene)                                           |
| <b>PVC</b>                         | Poly(vinyl chloride)                                      |
| <b>R</b>                           | Universal gas constant                                    |
| <b>R<sup>2</sup></b>               | Coefficient of determination                              |
| <b>R<sub>avg</sub></b>             | Average rate of mass loss                                 |
| <b>r<sub>cf</sub></b>              | Relative centrifugal force                                |
| <b>R<sub>max</sub></b>             | Maximum rate of mass loss                                 |
| <b>rpm</b>                         | Rotations per minute                                      |
| <b>S</b>                           | Comprehensive combustion index                            |
| <b>T</b>                           | Reaction temperature                                      |
| <b>T<sub>5%</sub></b>              | Temperature at 5% conversion                              |
| <b>T<sub>95%</sub></b>             | Temperature at 95% conversion                             |
| <b>tan(<math>\delta</math>)</b>    | Loss factor                                               |
| <b>T<sub>b</sub></b>               | Burnout temperature                                       |
| <b>t<sub>b</sub></b>               | Time to burnout                                           |
| <b>T<sub>g</sub></b>               | Glass transition temperature                              |
| <b>TGA</b>                         | Thermogravimetric analysis                                |
| <b>THR</b>                         | Total heat release                                        |
| <b>T<sub>i</sub></b>               | Ignition temperature                                      |
| <b>t<sub>i</sub></b>               | Time to ignite                                            |
| <b>t<sub>max</sub></b>             | Time to reach R <sub>max</sub>                            |
| <b>T<sub>pHRR</sub></b>            | Temperature at pHRR                                       |
| <b>w</b>                           | Contribution coefficient                                  |
| <b>ZnO</b>                         | Zinc oxide                                                |
| <b><math>\alpha</math></b>         | Conversion                                                |
| <b><math>\dot{\gamma}</math></b>   | Shear rate                                                |
| <b><math>\Delta t_{1/2}</math></b> | time spent at or above half the value of R <sub>max</sub> |
| <b><math>\eta_{app}</math></b>     | Apparent viscosity                                        |

# Chapter 1: Introduction

## 1.1 Motivation

Polymers have become a pervasive part of society, but with efforts moving towards improved environmental friendliness and sustainability, research into alternative polymers and their additives have increased. Nearly 8000 million metric tons (Mt) of plastics were made from 1950 to 2015, with their primary disposal pathway being incineration, significantly contributing to carbon dioxide emissions [1]. Since 2015, 6300 Mt of plastic has been generated, with only 9% being recycled, and 79% ending up in landfills or the environment [2]. The combination of increasing complexity and reduced product lifetime increases the difficulty of recycling plastics, so investigating more environmentally friendly options is of major importance. Plastics left to the environment exist for decades to centuries, generating microplastics as they degrade [3]. While concerns on the toxicity of polymers and microplastics rise, the additives used to process synthetic polymers leach into the environment and is the true cause of the aquatic toxicity of microplastics [4]. As such, the development of biodegradable, sustainable, and non-toxic polymeric additives is gaining major interest [5].

While polymers have an abundance of beneficial properties, many are extremely flammable due to their organic compositions which restricts their usage in many practical applications [6]. Halogenated flame retardants (FRs) provided great flame retardant properties but causes catastrophic damage to the environment due to its their toxicity, persistence, and bioavailability [7]. These FRs have had their use restricted in Europe and North America, spurring much research in the field of non-halogenated FRs [8].

Lignin is the second most abundant biomaterial, after cellulose, and is a random polyaromatic biopolymer whose composition changes depending on wood source [9]. It

constitutes 17 - 30 wt.% of oak wood biomass [10], for example. It is generated as commercial waste from the production of paper and ethanol, and was largely burned as fuel for heat and power [11]. More than 50 Mt of lignin is generated as waste annually, but less than 2% is recovered to be utilized as a higher value chemical [11][12]. Lignin can be separated from other components of lignocellulosic biomass through various purification methods, such as the Kraft pulping process, sulfite pumping, soda pulping, and the organosolv process, each of which slightly altering the structure of the resulting lignin [13]. The complexity and variability of lignin's structure has acted as a barrier to its implementation as a functional additive in the materials industry [14]. But recently lignin has seen increasing use in biomedical engineering, wearable sensors, wastewater treatment, energy storage, and flame retardant materials [15].

## **1.2 Research Objectives**

This thesis aims to investigate the suitability of Kraft lignin as a functional filler in polymer composites. Two distinct polymer systems were studied, with lignin's utilization explored in different ways. In the first, lignin was added without additional valorization to determine its latent ability to enhance a polymer's properties. In the second, lignin was chemically modified to provide additional functionality with its incorporation. The aim is to provide a thorough review on the versatility of lignin and how it can be used in different stages of modification.

The first area of exploration regards differing purities of Kraft lignin, and how they may affect the performance when added directly to a hydrophobic polymer. The purities of Kraft lignin represent the amount of time and money spent purifying them in differing ways, which explores the value added by each method. Additionally, the effect of the concentration of lignin was explored and how it affected the resulting properties as well as its dispersion throughout the polymeric matrix.

The second objective is to add functionality to lignin via crosslinking to generate a nano-container for the use of delivering a hydrophilic FR to a hydrophobic polymer. The nano-contained FR was compared directly to a bulk incorporated composite. This case provides an overview on a valorization method, and the value added by it through the improvement of the composite's properties.

### **1.3 Thesis Outline**

The remaining sections of this thesis are organized as follows: Chapter 2 provides the background information on lignin and its sources, flame propagation, and focuses on the use of lignin-based flame retardants among polymeric systems. Chapter 3 presents experimental research on the effects of three different grades of Kraft lignin, and the concentration of one of them, on the thermomechanical properties of the resulting polyvinyl chloride (PVC) composites. Flammability characteristics and decomposition kinetics are also explored. Chapter 4 provides a more functional use of Kraft lignin, as it is used to develop a nano-container to deliver ammonium polyphosphate (APP) (a hydrophilic FR) to natural rubber (NR), (a hydrophobic polymer). The synthesis of the lignin nanocontainers (LNCs) is explored in detail, and the composites are tested through a variety of flammability tests alongside a composite using bulk incorporated FR instead. Finally, Chapter 5 details the overall conclusions of this thesis as well as recommendations for future works.

## **Chapter 2: Background Information**

### **2.1 Lignin**

Lignin is constituted of three monomeric units – p-coumaryl alcohol (H), coniferyl alcohol (G), and sinapyl alcohol (S) – that polymerize randomly to form a complex, three-dimensional structure [16]. It is the second major component to wood that serves as a binding agent between wood fibers and act as a barrier to biological and enzymatic degradation [17]. Due to its method of synthesis and resulting structure, its characteristics are highly species and extraction dependant, making it incredibly difficult to characterize.

Lignin extracted from hardwood and softwood yield differing structures. Hardwood lignin is largely constituted of guaiacyl units (G precursor) whereas softwood lignin consists mainly of guaiacyl-syringyl units (G & S precursor) with similar amounts of H units [18][19]. The diversity and differing concentration of the resulting functional groups of lignin is at the core of its complexity. The ratio of the G & S units in particular governs the structure and functionality of the lignin, and can affect the chemical concentration and processing techniques to isolate or modify the lignin [20]. Additionally, the extraction method of lignin can affect its structure and functionality, and these methods are generally separated into sulfur-bearing and sulfur-free operations.

### **2.2 Extraction Methods**

#### ***2.2.1 Sulfur-Bearing Sources***

The largest production of lignin is via the Kraft process, making up 75% of global production [21]. This process utilizes sodium hydroxide and sulfite ion solutions to extract lignin during the production of paper and pulp [15]. Typically, only 2% of lignin is used for value-added application, with the rest being spent as fuel [21]. Recent advancements in recovery boilers

have allowed for high efficiency extraction using technologies such as LignoBoost and LignoForce processes [15][22]. The Kraft process generates what is known as sulfonated lignin, due to the presence of thiol groups.

Sulfite pulping is a more costly process that generates lignosulfonates, which has sulfonic acid groups as opposed to the thiol groups that constitute sulfonated lignin [23]. While they carry many similarities, there are a few key differences between these lignins. Lignosulfonates tend to have a higher sulfur content and a similar or larger molecular weight, and due to the sulfonic acid, lignosulfonates are water soluble [24]. This allows lignosulfonates to have a much broader range of applications, but Kraft processing being more widespread makes sulfonated lignin more readily available [25].

### ***2.2.2 Sulfur-Free Sources***

Soda lignin is generated in a very similar fashion to Kraft lignin – sodium hydroxide is used to open up the lignocellulosic biomass, but depolymerization is used to solubilize the lignin [26]. This results in a sulfur-free lignin of relatively low molecular weight, but with the presence of vinyl ethers [27]. This lignin has found use in the generation of phenolic resins and dispersants, but is of relatively low supply due to the low pulping performance of this process [28].

Organosolv lignin, as the name implies, utilizes organic solvents to isolate lignin. Organic solvent (typically ethanol) and water mixtures break down the chains of lignin over time to produce a very high purity lignin of low molecular weight & polydispersity that is insoluble in water [28][29].

While not an exhaustive list, these two sulfur-free sources represent large portions of popularity among researchers. Less researched options include hydrolyzed lignin, and the

dilute acid + steam explosion method, both describing the pre-treatment of lignin, typically performed in the bioethanol industry [30]. Additionally, all forms of lignin may be fractionalized to extract varying groups of molecular weight lignin with very low polydispersity [31].

**Table 1:** Summary of lignin sources and their respective properties.

| Property                                    | Sulfur-bearing Lignins        |                           | Sulfur-free Lignins                       |                                           |
|---------------------------------------------|-------------------------------|---------------------------|-------------------------------------------|-------------------------------------------|
|                                             | Kraft                         | Sulfite                   | Soda                                      | Organosolv                                |
| Raw Material                                | Softwood, hardwood [32]       | Softwood, hardwood [32]   | Agricultural waste, perennial plants [32] | Softwood, hardwood, perennial plants [32] |
| Solubility                                  | Alkali, organic solvents [32] | Water [32]                | Alkali [32]                               | Wide range of organic solvents [32]       |
| Number average molar mass ( $M_n$ , g/mol)) | 1000 - 3000 [32][33]          | 15 000 - 50 000 [32] [33] | 800 - 3000 [32] [33]                      | 500 - 5000 [32] [33]                      |
| Polydispersity                              | 2.5 - 4.0 [30][34]            | 4.2 - 9.0 [30] [34]       | 2.5 - 3.5 [30] [34]                       | 1.5 - 2.4 [30] [34]                       |
| Ash content (wt.%)                          | 0.5 - 3.0 [30] [34]           | 4.5 - 8.0 [30] [34]       | 0.7 - 2.3 [30] [34]                       | 0 - 1.7 [30] [34]                         |
| $T_g$ (°C)                                  | 108 - 165 [30] [34]           | 127 - 154 [30] [34]       | 150 - 155 [30] [34]                       | 89 - 97 [30] [34]                         |

### 2.3 Lignin as a Biofiller

Dominant applications of lignin revolve around its intrinsic antioxidant, antimicrobial, and anti-UV properties [11]. This includes applications to biomedical engineering, agriculture, and wastewater [15]. In materials applications, the focus of lignin has been on its abundant functional groups and its polyaromatic structure leading it to be used as a stabilizer, filler, compatibilizer, and reinforcer [17]. For instance, Tanjung et al. [35] utilized ethylated

organosolv lignin as a compatibilizer between polypropylene (PP) and chitosan to improve dispersion and the resulting mechanical properties of the composites.

The compatibility of lignin with any polymeric matrix is highly dependant on the relative hydrophobicity and molecular weight [15], of which there are many options when considering the various lignin types and additional modifications that can be made. More recent studies now involve some sort of chemical or physical modification when utilizing lignin in polymer composites [32].

### ***2.3.1 Thermoplastic Composites***

In a study by Barzegari et al. [36], the mechanical and rheological properties of polystyrene/Kraft lignin composites at up to 80 wt.% lignin content were studied. While the flexural and shear moduli were improved with increasing lignin content, the tensile strength, modulus, and elongation at break suffered due to the poor compatibility between lignin and polystyrene. Through the addition of a compatibilizer, the dispersion and adhesion between lignin and the polystyrene matrix was improved, also improving the mechanical properties. It was also found that increasing concentrations of lignin increased the crossover frequency, indicating that the elasticity of the blends decreased, likely due to the rigid nature of lignins aromatic structure.

Esterification is a commonly employed modification of lignin, demonstrated by Zhao et al. [37], where various lignin esters were added to PVC to enhance the thermal properties of the composites. While the native lignin increased the thermal stability, the mechanical performance decreased substantially. The ester-modified lignins improved both the thermal stability and the mechanical properties of the composites, with an optimal blend of properties resulting at a degree of esterification of around 40%.

Dias et al. [38] fabricated Kraft lignin-PP composites via reactive extrusion using maleic anhydride as a compatibilizer. Composites with the compatibilizer had major performance increases than those without, which tended to have worse properties than the control samples. Certain composites had mechanical and thermal properties suitable for industrial use, such as within the automotive sector, which typically use mineral fillers to improve properties as opposed to biological ones which are biodegradable.

### **2.3.2 Rubber Composites**

Rubbers are polymers of note since they heavily rely on carbon black, a petroleum product, as a filler [39] and would benefit highly from sustainable alternatives. In a study by Yu et al. [40] the incorporation of lignin at varying concentrations in natural rubber-silica composites (with a fixed total filler loading) was investigated. The lignin was incorporated in the aqueous phase in the natural rubber latex to better disperse it and prevent agglomeration as compared to other studies. This masterbatch was dried to form a natural rubber-lignin composite, and the rest of the materials were added via two-roll milling. The partial replacement of silica at 20 phr of lignin showed the most optimal mechanical properties whilst possessing the highest wet grip and low rolling resistance – two properties vital in tire formulations. This composite would also possess better anti-aging resistance and anti-flex cracking compared to just natural rubber-silica composites.

On improving the dispersion of lignin within styrene-butadiene rubber composites, Jiang et al. [41] utilized both modified sulfite lignin or epoxidized natural rubber to improve the compatibility, and therefore, the interfacial adhesion between these two compounds. Compared to the base blends, all composites containing lignin showed improved mechanical properties, improving the tensile strength by up to 6 times and the tear strength by 3 times. The

dispersion of the lignin highly depended on its modification, with modification by propylene oxide with epoxidized natural rubber yielding the best wet skid resistance and low rolling resistance in conjunction with improving mechanical properties and viscoelastic properties.

With some more advanced modification, the hydrophobicity of lignin could be improved to better incorporate into natural rubber, which was explored by Shorey et al. [42]. Various degrees of silylation of Kraft lignin were achieved and incorporated into natural rubber via solvent casting. With just a 5 wt.% incorporation of the modified lignin, the tensile strength increased by 44.4% and maximum strain by 40% compared to the control. The water absorption and compatibility were also improved when compared to unmodified lignin, showing improved dispersion provided by the modification.

### ***2.3.3 Comparison and compatibility with starch biomaterials***

In a study by Liu et al. [43], the effects of wood flour, cellulose, or lignin on PP and poly(lactic acid) (PLA) were explored in 50 wt.% filled composites. The addition of cellulose held positive improvements to the mechanical properties of both PP and PLA but worsened the thermal properties by a large margin due to the sudden decomposition over 100 °C sooner in PP and 50 °C sooner in PLA. Cellulose is a rigid fiber, which tends to increase mechanical properties when incorporated properly, to ensure proper alignment of the fibers. The lignin showed the largest improvements to the water absorption and to the thermal stability of both polymers due to its hydrophobic nature and charring ability, with lignin having the lowest onset to decomposition and largest char residue among all composites. The wood flour generally performed the worst overall, leading to its large particle size and difficulties dispersing within both polymeric matrices properly, as validated by SEM imaging.

Tanjung et al. [44] explored the properties of chitosan in PP composites with and without chemical treatment of organosolv lignin. The chitosan itself acted as a decent general filler – as its loading increased, the thermal stability, impact strength and Young’s modulus increased while the ultimate tensile strength and elongation decreased. However, once treated with lignin, all properties were improved, but specifically the ultimate tensile strength started to improve rather than decline. The improved mechanical properties were attributed to the decreased hydrophilicity of the treated chitosan as the lignin was acting as a compatibilizer, as corroborated by SEM imaging. Additionally, the results of the lignin treated chitosan composites were comparable to chitosan modified by synthetic agents, making lignin a suitable replacement.

## **2.4 Nano-lignin**

Whilst employing solvent methods for lignin extraction, i.e. organosolv lignin, spherical sub-particles of 144 nm on average were observed that improved antioxidant activity and UV properties whilst maintaining its polyaromatic and amorphous structure [45]. Various methods are used to generate spherical lignin nanoparticles including self-assembly, anti-solvent, high-voltage electrospinning, ultrasound chemical, and inverse miniemulsions, the latter of which have potential for nanocontainment due to their hollow structure [45]. On the nano scale, the reactivity of lignin is enhanced while providing improved anti-UV and mechanical properties [46].

To investigate the optimal incorporation method and concentration of lignin nanoparticles, Ikeda et al. [47] explored nanolignins incorporated into natural rubber at 5, 10, 20, and 40 phr using either soft processing (mixing while natural rubber in latex form) or more traditional two-roll milling. The incorporation using soft processing was superior to two-roll milling; it

provided a much better distribution and much larger improvements to the mechanical properties. While the elongation suffered minutely, the ultimate tensile strength increased by 77.0% with a negligible change to the glass transition temperature.

In a study by Xiong et al. [48] poly(vinyl alcohol) films were created via solvent casting that incorporated lignin nanospheres at 1, 3, and 5 wt.% to improve the UV-resistance which was compared to lignin as received, i.e. macro-lignin, in some tests. The preparation method created films that dispersed the nanolignin properly and did not generate macroscopic phase separation. The incorporation of the lignin nanospheres improved the thermal properties overall, with both the glass transition temperature and maximum rate of degradation temperature increasing, by 12 and 10 °C respectively, but slightly lowered the onset degradation temperature by roughly 5 °C. In terms of UV absorption, neat poly(vinyl alcohol) provided essentially no absorption, but the composite with just 1 wt.% lignin nanospheres provided 50% absorbance up to wavelengths of 400 nm, increasing to over 95% absorbance with the 3 wt.% composite. The macro-lignin provided roughly 80% absorption at 3 wt.% loading but had detrimental effects to the mechanical properties of the composite.

## **2.5 Flame Propagation**

### **2.5.1 Mechanism**

The burning of a material and the propagation of the flame is a complex mechanism of interactions between the condensed phase (i.e. the fuel) and the gas phase. An ignition source must first begin the process, causing the onset of thermal degradation (pyrolysis) of the polymer, releasing volatile gases and forming a carbonaceous char. These gases mix with the oxygen in the air to combust, forming non-flammable gases (smoke), light, and heat – a flame [49]. The heat generated by combustion transfers back into polymer (often referred to as

thermal feedback), continuing the cycle of until the propagation of the flame is impeded, typically when the fuel is spent. This process is summarized visually in **Figure 1**.

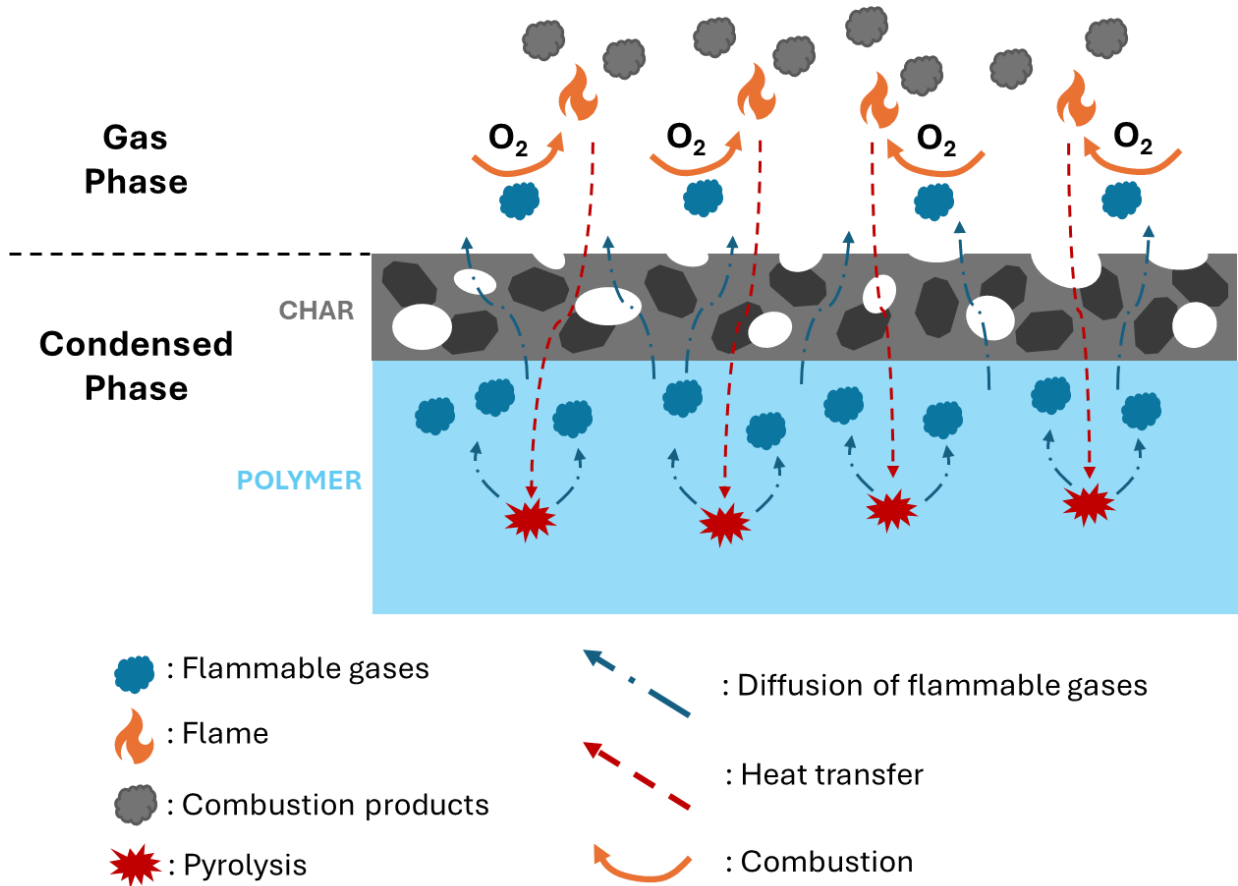


**Figure 1:** Schematic of flame propagation in polymers.

### 2.5.2 Flame Characterization

Due to the complex nature of flame propagation, a variety of characterization methods are employed to determine quantitative changes between flame retardant materials under specific circumstances.

Cone calorimetry (ASTM E1354 [50]) measures the response of a material plaque to controlled levels of radiant heat flux and can be done with or without an ignition source. Many

parameters are collected, with key ones including peak heat release rate (pHRR), total heat release (THR), time to ignition ( $t_i$ ), smoke density, and total smoke release.

Microscale combustion calorimetry (ASTM D7309 [51]) compares the pyrolysis and volatile combustion of a sample separately, with the sample's mass being roughly 5 mg. The sample is pyrolyzed to determine thermal stability and charring amount, with gases carried to a separate chamber. These gases are then combusted in pure oxygen, with the heat release calculated based on the change in oxygen concentration using Hugget's relation [52]. This method is an alternative way to measure the pHRR, THR,  $t_i$ , but also measures the heat release capacity, and flame growth capacity of the sample.

The limiting oxygen index (LOI) (ASTM D2863 [53]) is the minimum concentration of oxygen required to support flaming in a material. A controlled mixture of oxygen and nitrogen is supplied continuously through a glass chimney, and a small bar sample is ignited from its top face. To pass the test, the sample must extinguish prior to 3 mins of flaming, to prior to burning 5 cm of sample.

UL-94 V/H is a simple, categorical test that classify a material's in a vertical (equivalent to ASTM D3801 [54]) or horizontal (equivalent to ASTM D635 [55]) position, with the vertical test being the more 'aggressive' and stringent. For the horizontal test, samples are clamped horizontally and ignited at the far end. They must have a burning rate of less than 76 mm/min or must stop burning before 100 mm of material has burnt, at given dimensions. Materials that pass this test are given a rating of "HB". For the vertical test, samples are clamped vertically from the top and ignited two separate times from the bottom edge. The ratings V-2, V-1, and V-0 are achieved by surpassing the classifications listed below in **Table 2**.

**Table 2:** UL-94 vertical flame test categorical classification.

| Rating    | Flame duration after 1 <sup>st</sup> ignition | Flame duration after 2 <sup>nd</sup> ignition | Afterglow duration after 2 <sup>nd</sup> ignition | Flaming drips? | Sample burnt to holding clamp? |
|-----------|-----------------------------------------------|-----------------------------------------------|---------------------------------------------------|----------------|--------------------------------|
| UL-94 V-2 | $\leq 30$ s                                   | $\leq 250$ s                                  | $\leq 60$ s                                       | Yes            | No                             |
| UL-94 V-1 | $\leq 30$ s                                   | $\leq 250$ s                                  | $\leq 60$ s                                       | No             | No                             |
| UL-94 V-0 | $\leq 10$ s                                   | $\leq 50$ s                                   | $\leq 30$ s                                       | No             | No                             |

## 2.6 Flame Retardants

Flame retardants tend to affect the mechanism described previously by [56][57]:

- “Cooling” the flame via an endothermic reaction.
- Generating gases to dilute the concentration of oxygen.
- Disrupting radical propagation during combustion, typically via acid generation (often referred to as acid quenching).
- Generating stable, insulating (typically char) layer to limit gas diffusion and heat transfer.

When a flame retardant consists of a carbonizing source, an acid source, and a blowing agent, it is typically referred to as an intumescent flame retardant, since it can generate an intumescent char layer filled with radical quenching acid which causes major disruption to flame propagation. This typically manifests as large decreases to the transfer of heat and diffusion of flammable gases through the char layer [58][59].

### 2.6.1 Halogenated Flame Retardants

Halogenated flame retardants, as the name implies, are organic compounds that use the elements fluorine, chlorine, bromine, and iodine to inhibit the growth of fires in various materials. These compounds are generally very cheap and easy to produce industrially due to

the efficiency of the flame retardant effect of just a single halogen molecule [60]. But organohalogens, such as polybrominated diphenyl ethers, are being banned outright or voluntarily phased out due to rising environmental and safety concerns [61]. Their flame retardancy mechanisms mainly focus on acid quenching in the gas phase but often also rely on metal oxide synergists that, in conjunction with organohalogens, that lead to increasing charring but evolve volatile metal halides [60][49]. These compounds complicate the end-of-life disposal for these composites making them impossible to recycle and toxic if left to the environment [61]. Additionally, most fire-related deaths are caused by smoke inhalation, and the release of toxic halogenated compounds only worsens this effect [61].

### ***2.6.2 Mineral Flame Retardants***

In light of restrictions on halogenated flame retardants, mineral flame retardants were a natural replacement due to their sourcing from mineral deposits, making them fairly cheap, and generation of only water vapour and/or carbon dioxide in the gas phase [60]. These compounds rely on the low degradation point to absorb the heat generating by combustion whilst also generating water vapour to dilute the presence of oxygen in the gas phase [60][49]. The major drawback with these materials is that they require extremely large loadings to prove efficient at retarding flame propagation, typically in the range of 50 - 70 wt.%, which can lower the mechanical properties of the material and cause serious material defects [62][63].

Ramazani et al. [64] investigated the effects of mineral fillers, including aluminum hydroxide, in PP polyethylene copolymer composites. The addition of 30 wt.% aluminum hydroxide raised the LOI from 18.4% to 22.5%, an increase of 4.1%. Increasing amounts of this mineral filler progressively degraded the mechanical properties, with the tensile strength

decreasing by 38%, the elongation at break decreasing by 27%, and the impact strength decreasing by 50% at 30 wt.% aluminum hydroxide.

### ***2.6.3 Bio-based Flame Retardants***

Among all halogen-free, bio-based flame retardants, the focus is mainly on the incorporation of phosphorus by some means, as it one of the only naturally occurring, non-toxic acid sources that can act as an acid quencher during combustion [65]. While phosphorylation is a strong method of functionalizing organic compounds, its efficiency heavily depends on the relative reactivity of the functional groups and is limited by the degree of substitution for a given reaction [66]. This can make phosphorylation a complex and resource intensive option depending on the reactivity of the system. The blowing agent side of intumescency is typically achieved through nitrogen-containing compounds in bio-based FR, which typically decompose into molecular nitrogen, ammonia, hydrogen azide, carbon monoxide, or carbon dioxide gases [67][68]. However, these agents are not guaranteed to show identical reactivity and decomposition pathways in all conditions, so the use of them can vary from system to system [69].

Shumao et al. [70] studied the effects of ammonium polyphosphate (APP) on PLA composites processed via twin screw extrusion, of interest are two composites – one with and one without APP (loaded at 10.5 wt.%). The incorporation of APP at this concentration raised the LOI from 19.1% to 28.1% and yielded a UL-94 rating of V-0 where the control had received no rating. However, this composite saw a reduction in mechanical properties – its tensile strength fell by 13% and its impact strength fell by 27%. While this FR makes quite the impact on its own, its compatibility is extremely poor in many polymers which is apparent with the decrease in mechanical properties.

Chitosan's multi-hydroxyl structure is known to promote char formation during burning [71], and Hu et al. [72] investigated the intumescency of phosphorylated chitosan (via phosphorus pentoxide) in epoxy resin. Comparing to neat epoxy resin, the addition of 20 wt.% modified chitosan increased the LOI by 5% and lowered the PHR by 56%. Even just 5 wt.% lowered the PHR by 39%. The modified chitosan also lowered the evolution of smoke by over half and had very minor effects to the mechanical properties of the composites.

A novel flame retardant from Chang et al. [73] was synthesized from phosphorylated linseed oil and phosphorylated downstream corn oil and studied its effect on polybutylene terephthalate, incorporated via melt blending. The incorporation of 7.5 wt. % of the flame retardant was enough to raise the UL-94 rating of the polymer from a non-rating to V-0. Interestingly, the onset to degradation came roughly 20 °C sooner and the char value decreased by 3%, both indicating reduced thermal stability. Unsurprisingly, the addition of an oil-based additive caused the mechanical properties to suffer – the tensile strength was reduced by 13%, the modulus by 9%, and the elongation at break by a staggering 95.3% at 7.5 wt. % loading. While effective at improving the flame retardancy at a low concentration, the mechanical properties suffered extremely.

## **2.7 Lignin-based FRs**

The impact of lignin's flame retardancy alone was studied by Song et al. [74], where the flame retardancy of acrylonitrile-butadiene-styrene copolymer composites were at 5, 10, and 20 wt.% lignin. Increasing concentrations of lignin improved the thermal stability and char generation of the composites, as discussed previously in other composites. The heat release rates of the composites were slowed with the addition of lignin, with a 32% reduction in the peak heat release rate with the 20 wt.% composite attributed to the conjugated graphitic carbon layer

formed by the thermal degradation of lignin. They also confirmed that improved dispersion of lignin would aid the barrier effect of the char layer formed; in the composites with 10 wt.% lignin, the peak heat release rate was reduced by an additional 15% when a compatibilizer was added.

Laoutid et al. [75] studied the synergistic effects of magnesium hydroxide and lignin as flame retardants in poly(ethylene-co-vinyl acetate). The addition of just 20 wt.% lignin lowered the pHRR by 55%, but the THR was lowered by just 6% - at 60 wt.% these values are 78% and 3%, clearly indicating lignin's charring ability largely affects the rate at which heat is released, but doesn't prevent the composite from being nearly completely combusted. By adding 60 wt.% phosphorylated lignin, the THR is reduced by 33% with similar pHRR reduction. However, all these lignin composites had lowered  $t_i$ , indicating lowered thermal stability (roughly -40% on average). The composite with 60 wt.% magnesium hydroxide lowered the pHRR by 71%, the THR by 26%, but also managed to double the  $t_i$  (i.e. a percent change of +100%), which is quite the different fire performance compared to lignin considering its opposing mechanism. By forming composites using 40 wt.% magnesium hydroxide and 20 wt. % phosphorylated lignin, the resulting composite had a pHRR reduction of 83.5%, a THR reduction of 40%, and a  $t_i$  increase of 27%. These composites display a clear synergism of flame retardants when varying mechanisms are used in conjunction with one another but required very high loading to do so.

Chirico et al. [76] utilized blends of lignin and various FR fillers in PP composites, of note are aluminum hydroxide, APP, and melamine phosphate. Composites were formed using 14 wt.% lignin and 6 wt.% FR, and the following percent changes compared to the control were seen to the following cone calorimetry data:

**Table 3:** Cone calorimetry data (in percent change relative to control) for lignin-FR PP composites [76].

| FR                 | t <sub>i</sub> | pHRR | Mean HRR |
|--------------------|----------------|------|----------|
| Aluminum hydroxide | -43%           | -78% | -41%     |
| APP                | -27%           | -72% | -46%     |
| Melamine phosphate | -41%           | -74% | -44%     |

When used in conjunction with lignin, all the FRs generally perform the same in terms of heat release parameters, but interestingly the mineral FR performed very well at an incredibly low loading (6 wt.% itself, 20 wt.% FR total) in contrast to previously discussed studies that utilized mineral fillers at over 50 wt.% loadings. Even considering this, the APP outshines the other two in thermal stability, maintaining the largest time to ignition with only a 27% decrease.

The synthesis of a lignin-based flame retardant using polyethylenimine (blowing agent) and diethyl phosphite (acid source) was conducted by Liu et al. [77]. The polyethylenimine and diethyl phosphite were grafted directly onto the lignin to form functionalized lignin and was melt processed into wood-PP composites via batch mixing. With a loading of just 5 wt.% functionalized lignin, the peak heat release rate was decreased by 9%, the total heat release was reduced by 25%. But at a 15 wt.% loading, the functionalized lignin composites reduced the peak heat release by 19% and the total heat release by 18% when compared to the unmodified lignin composite at the same loading. It also achieved at V-1 rating where all other composites either failed or achieved a rating of V-2, showing clear signs of improvement to the flame retardancy of the composite.

In a study by Zhang et al. [78], APP was grafted directly onto lignin prior to batch mixing with PLA to form composites, which were tested alongside plain lignin composites. The

incorporation of just 3 wt. % of the modified lignin was enough for the composite to achieve a UL-94 rating of V-0, alongside an LOI of 27.6%, 0% UV transmittance, and improved thermal stability overall. The mechanical properties of the composites improved as well, with ultimate tensile strength, young's modulus, elongation at break, and impact strength all increasing at 3 wt.% loading compared to the control sample. However, cone calorimetry revealed that the modified lignin composites tended to release more carbon monoxide, roughly 31% more than the control at a 3 wt. % loading.

Song et al. [79] performed a thorough investigation on the incorporation of lignin, APP, and lignin grafted with APP in epoxy resins. Three samples of note were an APP sample, a physically blended lignin & APP sample, and a sample with the APP grafted directly onto the lignin. The sample with just APP had some improvement to all flame properties but did not achieve a UL-94 rating and reduced the tensile strength by 25% compared to the control. The physically blended sample managed to achieve a UL-94 rating of V-0 with additional improvements to the other flame characteristics (with the exception to the time to ignition, which was severely reduced), but its tensile strength was 43% worse than the control. The sample that utilized the APP-grafted lignin saw the best flame properties overall (with a 63% decrease to the pHRR), and its tensile strength was improved by 5% compared to the control. These results clearly show the impact of the intumescency brought by the synergy between APP and lignin, but also the importance of incorporation method to the mechanical properties of the composite.

## **2.8 Lignin FR Nanomaterials**

In a study by Meng et al. [80], lignin-based FR nanoparticles were synthesized for use in polyurethane composites. Lignin was functionalized with dichlorophenylphosphine oxide and

1, 4-dimethoxyacetylene (for compatibility), and was subsequently ultrasonicated then precipitated to collect the functionalized lignin nanoparticles. These were then melt blended with polyurethane via batch mixing. At 2 wt.% loading of the functionalized lignin, the composite achieved a UL-94 rating of V-2 and an LOI value of 22.4% where the control had no rating and an LOI of 18.5%. This composite also achieved a 50% reduction in the pHRR and a 52.8% reduction to the peak rate of smoke generation. A 2 wt.% composite of plain lignin tended to achieve values somewhere between the others, roughly halfway between them, in terms of flame properties. However, the mechanical properties of the functionalized lignin composite were improved, with a 39% increase to the ultimate tensile strength and a 3% increase to the elongation, where the plain lignin composite's ultimate tensile strength and elongation decreased by 24% and 30%, respectively.

Nano functionalized lignin particles for use in polyurethane elastomers was studied by He et al. [81]. Lignin was first functionalized with both nitrogen & phosphorus compounds (polyethyleneimine & 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, respectively) and ultrasonication & dialysation were used to form the lignin nanoparticles, isolated via centrifugation and freeze drying. This lignin was grafted directly to the polyurethane backbone and then dried to form the final films. At concentrations of 5 wt.%, plain lignin, functionalized lignin, and nano-functionalized lignin had LOI values of 21.4%, 27.9%, and 28.2%, respectively, with the latter two samples achieving a UL-94 rating of V-1 where the prior had no rating. The functionalization alone showed great benefit, with the nano size showing increased benefit, likely due to superior dispersion. Concentrations of 10 and 15 wt.% of the nano-functionalized lignin were also used, with LOI values of 29.8% and 30.8% respectively, with both achieving a rating of V-0. Cone calorimetry showed very similar results, with

increasing concentration reducing the pHRR and THR, but did also show increasing concentrations of carbon monoxide generation. In addition to the superior fire performance, the nano-lignin showed increased mechanical performance compared to the control, where the functionalized, but non-nano, sample had worsened properties overall.

Peil et al. [82] formulated hollow lignin nanocontainers to deliver APP to foamed PLA composites via carbon dioxide batch foaming. They utilized the inverse miniemulsion method and crosslinked the lignosulfonate to form stable nanocontainers, grafting PLA directly onto them. With the neat composites receiving no rating in the UL-94 test, at a loading of 9 wt.% FR did the composites achieve a V-0 rating. At this loading, the composite also had an LOI of 24%, a pHRR reduction of 96%, a THR reduction of 21% whilst improving the foaming properties likely due to the promotion of heterogenous nucleation of the pores.

## **2.9 Summary of Chapter 2**

Lignin is an extremely abundant and versatile biopolymer, with a wide range of availability and properties to choose from, differentiated based on source and extraction process. Its unique properties, such as its intrinsic antioxidant, antimicrobial, and anti-UV properties, and overall availability has made it an appealing material, where it is being applied to biomedical engineering, agriculture, wastewater, and construction industries.

Lignin is finding increased use in polymer systems, but its hydrophobicity lends it poor compatibility in both hydrophobic and hydrophilic polymers alike. This presents a use as a potential compatibilizer in composites, and its functionality due to its abundant reactive sites leave potential for various chemical modifications. This allows for flexibility in use, such as

to increase or decrease its hydrophobicity, and therefore, its compatibility within a choice polymer system.

Of its unique properties, is its poly-aromaticity which lends itself to flame retardancy due to the increased charring ability of aromatic structures. The formation of char is a key component of flame retardancy, as it reduces the diffusion of combustible gases to the surface of the polymer whilst reduces the heat transfer of the flame to the polymer, reducing the formation of these gases in the first place. Employing lignin in conjunction with other flame retarding materials (who operate under differing mechanisms), the potential for intumescency and synergistically improved flame retardancy increases drastically. Of note is APP which is a dense source of phosphorus – a critical acid quencher in halogen-free flame retardants. Due to its hydrophilicity, however, it can degrade the mechanical properties of polymers without appropriate compatibilization. Through the use of nano-fillers, improvements were seen to both the mechanical properties of fillers and the performance of flame retardants. This makes a nanolignin-based flame-retardant system incredibly appealing for the combination and synergies of all discussed effects.

## **Chapter 3: Lignin as a sustainable filler of polyvinyl chloride composites: Effects of ash content and loading levels on thermomechanical and combustion properties<sup>1</sup>**

### **3.1 Introduction**

Polymers have become an irreplaceable part of society due to their unique properties and application to various industries and global issues. Polyvinyl chloride (PVC) alone is a major part of the automotive, construction, and agricultural industries through the creation of PVC pipes, vinyl cladding, coatings, and overall reinforcement to existing materials [83][84]. The drive towards mass product fabrication and consumerism has increased plastic production immensely without major increases in recycling. The annual production of plastic hit 460 million tonnes in 2019, with some countries, such as the United States, Canada, and Australia, recycling only 9% of their plastic waste due to mainly the immense amounts of single-use packaging materials [85][84]. Growing concerns over the environmental impacts of plastic waste has called for a transition to more sustainable materials [85][86] that are more recyclable, reusable, and durable, keeping waste out of landfills. Biopolymers have gained regard as major additives or alternatives to current polymer production, the most abundant ones being cellulose and lignin, the latter produced as waste from the pulp and paper industry, largely from the Kraft process [87][88].

Reaching production rates of 50 million tons per year, PVC is the world's third-largest produced commodity plastic as it is inexpensive to produce, has high durability, good processability, and is lightweight [89][90]. More uniquely, it is inherently flame retardant due

---

<sup>1</sup> A version of this chapter has been published: Periklis D. Alikiotis, Tizazu H. Mekonnen, International Journal of Biological Macromolecules, 146527, 2025.

to the large chlorine content, in contrast to most other organic polymers, which are highly flammable [89][91]. A variety of additives, such as plasticizers and stabilizers are used to improve the processability and thermal stability of PVC, many of which are toxic and contain heavy metals [90][92], which along with hydrogen chloride (HCl), can be released during the combustion of PVC [93][94]. This poses environmental threats since, while virgin PVC is easily recyclable, these additives leach and complicate the recycling process [95].

Lignin is a complex macromolecule of high polydispersity composed of mainly guaiacyl, syringyl, and p-hydroxyphenyl units randomly connected to via ester or carbon-carbon bonds [20][96]. Its unique structure and potential as an additive have garnered popularity to adding value to current materials to improve strength and biodegradability whilst potentially reducing processing costs [97][17]. Lignin can be separated from other components in lignocellulosic biomass through a variety of the purification methods, such as the Kraft pulping process, sulfite pumping, soda pulping, and the organosolv process [26], each of which can slightly alter the chemical composition of the resultant lignin [13]. Lignin has been used to improve the thermal stability and flame retardancy of polypropylene (PP)-kenaf fiber composites, for example, but lignin can function as a filler, stabilizer, compatibilizer, or reinforcer in certain materials [98]. Among many polymers, such as PLA, PVA, and PP, the most common limitations for their incorporation of lignin is the need for a compatibilizer or the hydrophilicity of the polymer matrix [17]. For instance, Dias et al. [38] utilized maleic anhydride as a compatibilizer to form PP-lignin bio-composites, increasing the complexity and cost of producing said composites. Lignin is a major contender as a filler to PVC as they both share a hydrophobic nature [87][99] and may not require additional compatibilization.

In this work, the effects of lignin as a filler to PVC were explored throughout a variety of thermal, mechanical, and flame testing. The apparent solid-state kinetics were also investigated to provide insight as to how lignin may alter the degradation mechanisms of PVC. Kraft lignin was purified via acid precipitation and centrifugation to produce a low ash and neutral pH lignin. These, in addition to an industrially purified lignin, were used to determine the effect ash and pH on the composites. The concentration of the laboratory purified lignin was also explored to determine an optimal loading within these composites. It was hypothesized that Kraft lignin would perform poorly during mechanical testing due to the large ash content disrupting the polymeric matrix, resulting in a more brittle material. The presence of thiol groups in Kraft lignin [13] evolving into sulfur dioxide gas during combustion [100] was hypothesized to aid in flame retardancy by diluting the concentration of oxygen at the material's surface, expected to aid at much lower concentrations compared to mineral filler flame retardants, which are typically loaded above 50 wt.% [101]. Industrially purified lignin was expected to perform better as a filler by increasing the moduli of the material without sacrificing ductility. The laboratory purified lignin was generally expected to behave somewhere in between. Past studies have investigated the effects of lignin on certain properties of PVC, but the focus is only on torque rheology and choice mechanical properties [102], plasticized PVC [103], use additional compatibilizers [104]. In addition to the novelty provided by a more complete collection of tests, the authors are unaware of studies that use a variety of grades of lignin, or ones that characterize its flame & decomposition properties as in-depth.

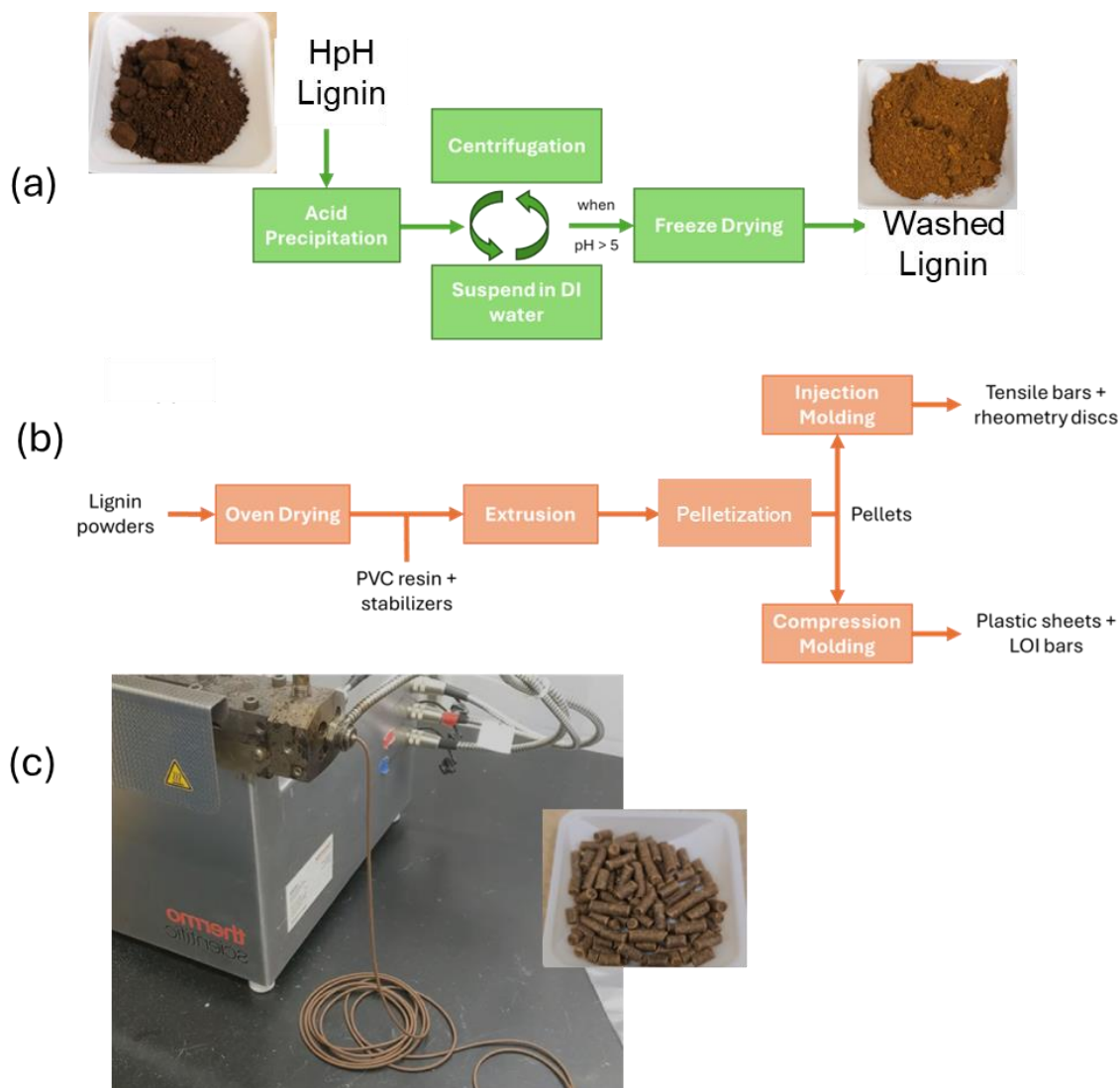
## 3.2 Experimental

### 3.2.1 Materials

Two grades of lignin were purchased from Alberta Pacific Forest Industries Inc. (Hinton, Alberta, Canada). The grades are HpH lignin ('High' pH  $\sim$  9, Kraft lignin) and LpH lignin ('Low' pH  $\sim$  2.6, purified Kraft lignin). PVC resin ( $M_n$  = 49 kDa, PDI = 2.2) was supplied by a premier exterior building materials company in Canada. Sulfuric acid ( $H_2SO_4$ , 98~99% solution) was purchased from Sigma-Aldrich (Oakville, Canada). A full material processing flowchart with sample images are shown in **Scheme 1** and in Appendix A (**Figure A1 - Figure A4**).

#### 3.2.1.1 Lignin Washing

Residual ash was removed from HpH lignin via acid precipitation, wherein a 1 M solution of sulfuric acid was slowly poured into a 10 wt.% aqueous solution of HpH lignin (pH  $\sim$  9) until the pH was reduced to  $\sim$  3. The acidic solution was centrifuged in a Heraeus Megafuge 1.0 at 4000 rcf for 5 mins. The supernatant was discarded, and the pellet was resuspended in DI water using a vortex mixer (15 sec, 3000 rpm). The previous steps (resuspension and centrifugation) were repeated until the supernatant had a pH  $>$  5, removing excess acid and water-soluble impurities in the process. The final lignin pellet was resuspended in a minimal amount of DI water and the suspension was freeze dried to generate a 'neutral' pH, low ash lignin powder, herein referred to as 'Wash lignin'.



**Scheme 1:** Material process flowchart for (a) lignin washing, (b) compounding and sample preparation, (c) extrusion and pelletization.

Prior to dry mixing, the lignin powders were dried at 105 °C for in a convectional oven to ensure a moisture level of under 5%, measured in a Sartorius Infrared Moisture Analyser MA35. The powders were ground and passed through a 250  $\mu\text{m}$  sieve (average particle size 123  $\mu\text{m}$ ) to ensure a consistent particle size. Finally, these powders were dry mixed with PVC resin and stabilizer compounds according to the formulations in **Table 4** prior to extrusion.

The formulations were created on a per hundred resin (phr) basis of PVC, where each number represents the weight ratio of the corresponding component. The numbers in the sample names indicate the corresponding weight percentage of each formulation (i.e. N represents neat PVC, L18 uses LpH lignin at 18 wt.%, W9 uses Wash lignin at 9 wt.%, etc.).

**Table 4:** Formulations in phr their corresponding sample names.

|                  | <b>N</b> | <b>H18</b> | <b>W18</b> | <b>L18</b> | <b>W9</b> | <b>W27</b> |
|------------------|----------|------------|------------|------------|-----------|------------|
| PVC Resin        | 100      | 100        | 100        | 100        | 100       | 100        |
| Stabilizer blend | 3.25     | 3.25       | 3.25       | 3.25       | 3.25      | 3.25       |
| LpH lignin       | –        | –          | –          | 23         | –         | –          |
| HpH lignin       | –        | 23         | –          | –          | –         | –          |
| Wash lignin      | –        | –          | 23         | –          | 10.2      | 38.2       |

### **3.2.2 Processing methods**

#### **3.2.2.1 Extrusion**

PVC blends were extruded in a Thermo-Scientific Process 11 twin-screw extruder at a maximum temperature of 190 °C and average screw speed of 50 rpm. The extruded blend was subsequently pelletized in preparation for injection molding.

#### **3.2.2.2 Injection molding**

Sample pellets were injection molded in a Thermo-Scientific HAAKE MiniJet Pro to generate five type V tensile dog bone samples for tensile testing and discs for parallel plate rheometry. Injection molding was performed at an internal temperature of 210 °C, mold temperature of 80 °C, and a pressure of 175 bar. Prior to testing, samples were left to condition at 23 °C and 50% humidity for a minimum of 40 hours in accordance with ASTM D618.

#### 3.2.2.3 *Compression Molding*

Sample pellets were compression molded in a Carver compression mold at 180 °C and 7.5 tonnes for 5 - 8 mins to produce samples for select tests.

#### 3.2.2.4 *Tensile Testing*

Tensile properties were evaluated by a Shimadzu AGS-X using a 10 kN load cell in accordance with ASTM D638. Five samples were tested for each formulation in a randomized order at 5 mm/min. Results for ultimate tensile strength, Young's modulus, and elongation at break were recorded.

#### 3.2.2.5 *Parallel Plate Rheometry*

Parallel plate rheometry was conducted using a Thermo-Scientific HAAKE MARS rheometer using rheometry discs of 20 mm in diameter. An oscillatory frequency sweep was conducted over 0.01 - 100 rad/s at a temperature of 200 °C and a plate gap of 1.3 mm. The power law model (Eq. 1) was fit to each data set to determine the flow consistency index (K) and flow behaviour index (n).

$$\eta_{app} = K\dot{\gamma}^{n-1} \quad (1)$$

where  $\eta_{app}$  is the apparent viscosity (Pa s) and  $\dot{\gamma}$  is the shear rate ( $s^{-1}$ ).

#### 3.2.2.6 *Fourier Transform Infrared (FTIR) Spectroscopy*

The chemical structure and functional groups of the lignin powders were evaluated using a Thermo-Scientific Nicolet 6700 FTIR equipped with attenuated total reflectance (ATR). Powders were loaded and held under slight pressure during an ATR test with 64 scans at a

resolution of 8 cm<sup>-1</sup>. The absorbance for each sample was collected over a spectral range of 500 - 4000 cm<sup>-1</sup>.

#### 3.2.2.7 *Differential Scanning Calorimetry (DSC)*

The melt properties of the PVC blends were evaluated using a TA Instruments Discovery DSC 2500. Compression molded sheets were cut into samples of 5 - 10 mg in mass, sealed in aluminum pans, and were subjected to the following method under a N<sub>2</sub> flow rate of 50 mL/min: 10 °C/min ramp to 200 °C, held isothermal for 5 mins, 10 °C/min ramp to 25 °C, held isothermal for 5 mins, 10 °C/min ramp to 200 °C. Analysis was performed on the second heating cycle.

#### 3.2.2.8 *Thermogravimetric Analysis (TGA)*

Ash determination of the lignin powders and decomposition behaviour of the PVC blends were evaluated using a TA Instruments Discovery TGA 55. The ISO 1762 method for ash determination was replicated using a TGA as reported in [105]. Lignin samples of 10 - 20 mg underwent the following method: 30 °C/min ramp from 20 °C to 105 °C, isothermal for 30 mins, 15 °C/min ramp to 525 °C, isothermal for 120 mins in an oxidative environment (60 mL/min air). Ash content was then calculated on a dry basis, after the isothermal hold at 105 °C to remove moisture from each sample. Decomposition behaviour of PVC blends was conducted using composite samples of 10 - 20 mg from compression molded sheets, and were subjected to a ramp of 20 °C/min from room temperature to 800 °C. This was performed under both inert (60 mL/min nitrogen) and oxidative (60 mL/min air) environments.

### 3.2.2.9 Dynamic Mechanical Analysis (DMA)

Visco-elastic properties were evaluated using a TA Instrument DMA (Q800 DMA). Samples were cut from compression molded sheets with width of ~ 6.5 mm, thickness of ~ 0.6 mm, and held between dual cantilever clamps at a length of 9.5 - 10 mm. Samples were subjected to a ramp of 5 °C/min from room temperature to 120 °C during a multi-frequency, constant strain testing procedure, with a strain of 0.1% and frequency of 1.0 Hz.

### 3.2.2.10 Limiting Oxygen Index (LOI)

The LOI for select samples was measured in accordance with ASTM D2863. Type IV specimens of dimensions 76 mm x 6.5 mm x 3 mm were fabricated via compression molding and were tested using top surface ignition. Samples were conditioned at room temperature for a minimum of 72 h prior to testing.

### 3.2.2.11 Combustion Indices

To assess the combustion performance of each blend, TGA and derivative thermogravimetric (DTG) curves in an oxidative environment were analyzed to produce various combustion indices [106][107]. The values of comprehensive combustion index (S), flammability index (C), ignition index (Di), and burnout index (Db), were calculated as follows:

$$S = \frac{R_{max} \times R_{avg}}{T_i^2 \times T_b} \quad (2)$$

$$C = \frac{R_{max}}{T_i^2} \quad (3)$$

$$D_i = \frac{R_{max}}{t_i \times t_{max}} \quad (4)$$

$$D_b = \frac{R_{max}}{\Delta t_{1/2} \times t_{max} \times t_b} \quad (5)$$

Where  $R_{max}$  and  $R_{avg}$  are the maximum and average mass loss rate (%/min),  $T_i$  and  $T_b$  are the ignition and burnout temperature (K),  $t_i$ ,  $t_{max}$  and  $t_b$  are the ignition, maximum, and burnout times (min), respectively, and  $\Delta t_{1/2}$  is the time spent at or over half the value of  $R_{max}$  (min).

S represents the comprehensive ability of the material to combust, whereas C represents the ability of the material to ignite.  $D_i$  and  $D_b$  reflect the material's ability to reach ignition and maintain combustion, respectively. With all these indices, larger values indicate that the material is more flammable, and lower values indicate the material is more flame retardant.

### 3.2.3 Degradation Kinetics

#### 3.2.3.1 Kinetic Theory

For a single decomposition reaction, the main variables required to describe its conversion with time would be the activation energy (E), pre-exponential factor (A), and the reaction mechanism,  $f(\alpha)$ , where  $\alpha$  is the conversion of the decomposition reaction [108]. These three variables are also referred to as the kinetic triplet. By assuming the Arrhenius equation can be used to describe the thermal dependence of the reaction rate constant, we can model the change in conversion using equations (6) and (7) as follows:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A \exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (6)$$

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f}$$

where  $m_0$ ,  $m_f$ , and  $m_t$  represent the initial mass, final mass, and mass at time =  $t$  of a material, respectively,  $R$  is the universal gas constant, and  $T$  is the reaction temperature.

Equation (6) can be represented in integral form,  $g(\alpha)$ , with expressions for  $f(\alpha)$  and  $g(\alpha)$  for various reaction models shown in **Table 5** [108][109].

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = A \int_0^t \exp\left(\frac{-E}{RT}\right) dt \quad (7)$$

**Table 5:** Differential and integral forms of various reaction mechanisms [108]–[111].

| Reaction Model                        | Differential Form – $f(\alpha)$                        | Integral Form – $g(\alpha)$              |
|---------------------------------------|--------------------------------------------------------|------------------------------------------|
| <b>Power law models</b>               |                                                        |                                          |
| Power law (P3/2)                      | $2/3\alpha^{-1/2}$                                     | $\alpha^{3/2}$                           |
| Power law (P2)                        | $2\alpha^{1/2}$                                        | $\alpha^{1/2}$                           |
| Power law (P3)                        | $3\alpha^{2/3}$                                        | $\alpha^{1/3}$                           |
| Power law (P4)                        | $4\alpha^{3/4}$                                        | $\alpha^{1/4}$                           |
| <b>Nucleation models</b>              |                                                        |                                          |
| Avrami-Erofeev (A2)                   | $2(1 - \alpha)[- \ln(1 - \alpha)]^{1/2}$               | $[- \ln(1 - \alpha)]^{1/2}$              |
| Avrami-Erofeev (A3)                   | $3(1 - \alpha)[- \ln(1 - \alpha)]^{2/3}$               | $[- \ln(1 - \alpha)]^{1/3}$              |
| Avrami-Erofeev (A4)                   | $4(1 - \alpha)[- \ln(1 - \alpha)]^{3/4}$               | $[- \ln(1 - \alpha)]^{1/4}$              |
| <b>Reaction-order models</b>          |                                                        |                                          |
| First order (F1)                      | $1 - \alpha$                                           | $- \ln(1 - \alpha)$                      |
| Second order (F2)                     | $(1 - \alpha)^2$                                       | $[1 - (1 - \alpha)^{-1}]/(-1)$           |
| Third order (F3)                      | $(1 - \alpha)^3$                                       | $[1 - (1 - \alpha)^{-2}]/(-2)$           |
| Fourth order (F4)                     | $(1 - \alpha)^4$                                       | $[1 - (1 - \alpha)^{-3}]/(-3)$           |
| <b>Diffusion models</b>               |                                                        |                                          |
| 1-D diffusion (D1)                    | $(1/2)\alpha^{-1}$                                     | $\alpha^2$                               |
| 2-D diffusion–Valensi (D2)            | $[- \ln(1 - \alpha)]^{-1}$                             | $(1 - \alpha)\ln(1 - \alpha) + \alpha$   |
| 3-D diffusion-Jander (D3)             | $(3/2)[1 - (1 - \alpha)^{1/3}]^{-1}(1 - \alpha)^{2/3}$ | $[1 - (1 - \alpha)^{1/3}]^2$             |
| 3-D diffusion-Ginstling (D4)          | $(3/2)[1 - (1 - \alpha)^{1/3}]^{-1}$                   | $[1 - (2/3)\alpha] - (1 - \alpha)^{2/3}$ |
| <b>Geometrical contraction models</b> |                                                        |                                          |
| Prout-Tompkins (R1)                   | $1$                                                    | $\alpha$                                 |
| Contracting cylinder (R2)             | $2(1 - \alpha)^{1/2}$                                  | $1 - (1 - \alpha)^{1/2}$                 |
| Contracting sphere (R3)               | $3(1 - \alpha)^{2/3}$                                  | $1 - (1 - \alpha)^{1/3}$                 |

### 3.2.3.2 Multi-step Kinetics

For multi-step reactions, each reaction will entail its own kinetic triplet with the addition of a contribution coefficient,  $w$ , which represents how much a single reaction contributes to the overall conversion of a reactant [112], i.e.,

$$\alpha = \sum w_i \alpha_i \quad (8)$$

$$\frac{d\alpha}{dt} = \sum w_i \frac{d\alpha_i}{dt} \quad (9)$$

In the context of DTG curves, a non-uniform curve will indicate a multi-step reaction as they must be the summation of other, smooth curves. Visual identification of DTG curves is not necessarily an accurate method of determining multi-step nature of a process; it is possible that a smooth curve encompasses more than one reaction step. For the purposes of this paper, this assumption will be considered sufficient.

### 3.2.3.3 Mathematical Deconvolution

With the knowledge of multi-step kinetics, we can perform mathematical deconvolutions on complex DTG curves to split apparent individual reaction steps, therefore splitting individual kinetic triplets. This method is not based in physicochemical theory but is purely model fitting. As such, any reference to the activation energy, pre-exponential factor, and reaction mechanism from this point onwards should be taken as apparent values.

The Weibull distribution (Eq. 10) was the mathematical model selected to deconvolute curves due to its ability to skew both left and right.

$$y = a_0 \left( \frac{a_3 - 1}{a_3} \right)^{\frac{1-a_3}{a_3}} \left( \frac{x - a_1}{a_2} + \left( \frac{a_3 - 1}{a_3} \right)^{\frac{1}{a_3}} \right)^{a_3-1} \exp \left[ - \left( \frac{x - a_1}{a_2} + \left( \frac{a_3 - 1}{a_3} \right)^{\frac{1}{a_3}} \right)^{a_3} + \frac{a_3 - 1}{a_3} \right] \quad (10)$$

#### 3.2.3.4 Flynn-Wall-Ozawa Method

The Flynn-Wall-Ozawa (FWO) method is what is known as a “model-free” method, as it can estimate the activation energy of a reaction without previously assuming a reaction mechanism. By incorporating Doyle’s approximation [113], the following expression is produced.

$$\ln \left( \frac{dT}{dt} \right) = \ln \left( \frac{AE}{Rg(\alpha)} \right) - 5.331 - 1.052 \left( \frac{E}{RT} \right) \quad (11)$$

Where  $dT/dt$  represents the heating rate of a DTG curve. The plot of  $\ln(dT/dt)$  vs.  $1/T$  should give a straight line whose slope can be used to determine the activation energy of a reaction. Once a reaction mechanism is selected, the pre-exponential factor can be determined from the intercept of this same plot.

#### 3.2.3.5 Coats-Redfern Method

The Coats-Redfern (CR) method is reliant on the reaction mechanism, and after some approximations [113] the following expression is obtained.

$$\ln \left( \frac{g(\alpha)}{T^2} \right) = \ln \left( \frac{AR}{\frac{dT}{dt} E} \right) - \frac{E}{RT} \quad (12)$$

The plot of  $\ln(g(\alpha)/T^2)$  vs.  $1/T$  can be used to determine the activation energy using the slope. A plot can be generated using each mechanism from **Table 5**, and their activation energies can be determined. The activation energies are then compared to the one previously

determined from the FWO method, the closest match indicating the closest representation of the reaction mechanism,  $f(\alpha)$ .

### **3.3 Results & Discussion**

#### **3.3.1 Characterization**

##### **3.3.1.1 FTIR Results**

ATR-FTIR spectra were collected for the various grades of lignin powder (**Figure 2**) to determine their characteristic differences, which will be carried to the blends. Absorption peaks at  $1580\text{ cm}^{-1}$  are observed between all samples and was attributed to C=C stretching within aromatic alkenes, which is present throughout the structure of lignin [88]. The largest relative concentration of these groups belongs to HpH lignin, as it represents the largest signal within its waveform. LpH lignin showed an absorption peak at  $1710\text{ cm}^{-1}$ , ascribed to C=O stretching within conjugated carboxylic acids generated via the acid precipitation of alkaline lignin [88][31]. The Wash sample (being HpH lignin that underwent acid precipitation and subsequent washing) showed a reduced signal to the peak at  $1580\text{ cm}^{-1}$  with the presence of a peak at  $1710\text{ cm}^{-1}$ , indicating the successful acid precipitation of HpH lignin to LpH lignin [31]. The vibrations attributed to syringyl and guaiacyl units at peaks  $1110$  and  $1023\text{ cm}^{-1}$  respectively was seen between all samples as they are defining features of lignin's structure [88].

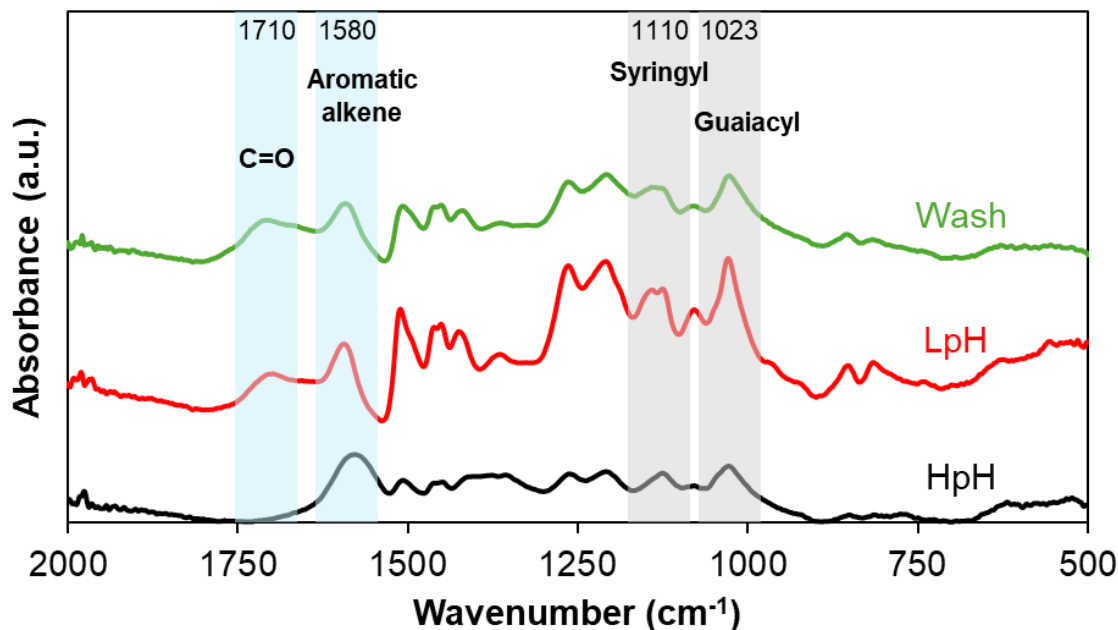


**Figure 2:** ATR-FTIR spectra of HpH lignin (bottom), LpH lignin (middle), and Wash lignin (top).

### 3.3.1.2 Ash content and pH

The presence of ash within each type of lignin sample will affect its performance as a filler within PVC. Any rigid filler will disrupt the polymeric matrix, increasing the tensile and Young's modulus, but will ideally not severely impact its elongation at break and overall toughness [114]. Ash present from the Kraft process is not necessarily well-suited for this as the particle size and distribution of these mineral impurities is not assured and could negatively impact the resulting composite.

The ash content of the lignin samples was measured, with Wash lignin having undergone washing via centrifugation to remove ash and residual acid from acid precipitation, resulting in an ash content of 3.49 w/w % and a pH of 5.2. The pH of all lignin samples was taken using a 10:1 DI water to lignin ratio. The Wash lignin had a significantly lower ash content compared to the HpH lignin (63.50 w/w % ash, pH = 8.9) by which it came from but had slightly more

ash than industrially purified LpH lignin (0.37% w/w % ash, pH = 4.5). The effects of the varying characteristics of the grade of lignin content will be discussed from here on out.

### *3.3.1.3 Thermal Properties*

The TGA of PVC in an inert atmosphere showed two distinct stages of decomposition, associated with dehydrochlorination of the PVC (250 - 350 °C) forming conjugated polyene compounds, followed by the release of hydrocarbons and generation of charred residue thereafter (400 - 500 °C) [115][116]. All lignin samples showed similar trends to that of sample N (no filler), but with varying levels of residues. Sample H18 showed larger residue due to its increased ash content compared to that of samples W18 and L18 (**Figure 3a**), due to a lower mass content that undergoes thermal degradation. Due to its complex polyaromatic structure, lignin loses very little carbon during charring and preferably undergoes dehydration at increasing temperatures, decomposing aliphatic units and forming aromatic ones [117][118][119]. As such, an increase in residue was seen with samples W9, W18, and W27 due to increasing amounts of charring material (**Figure 3b**). Slight changes in the decomposition process were seen, most notably with the samples H18, L18, and W27 (**Figure 3c**). These samples had lower degradation peaks that were also shifted to higher temperature by roughly 10 °C during the first stage of degradation, indicating a slight increase in the material's thermal stability due to the larger onset. The second stage of degradation remained largely unchanged.

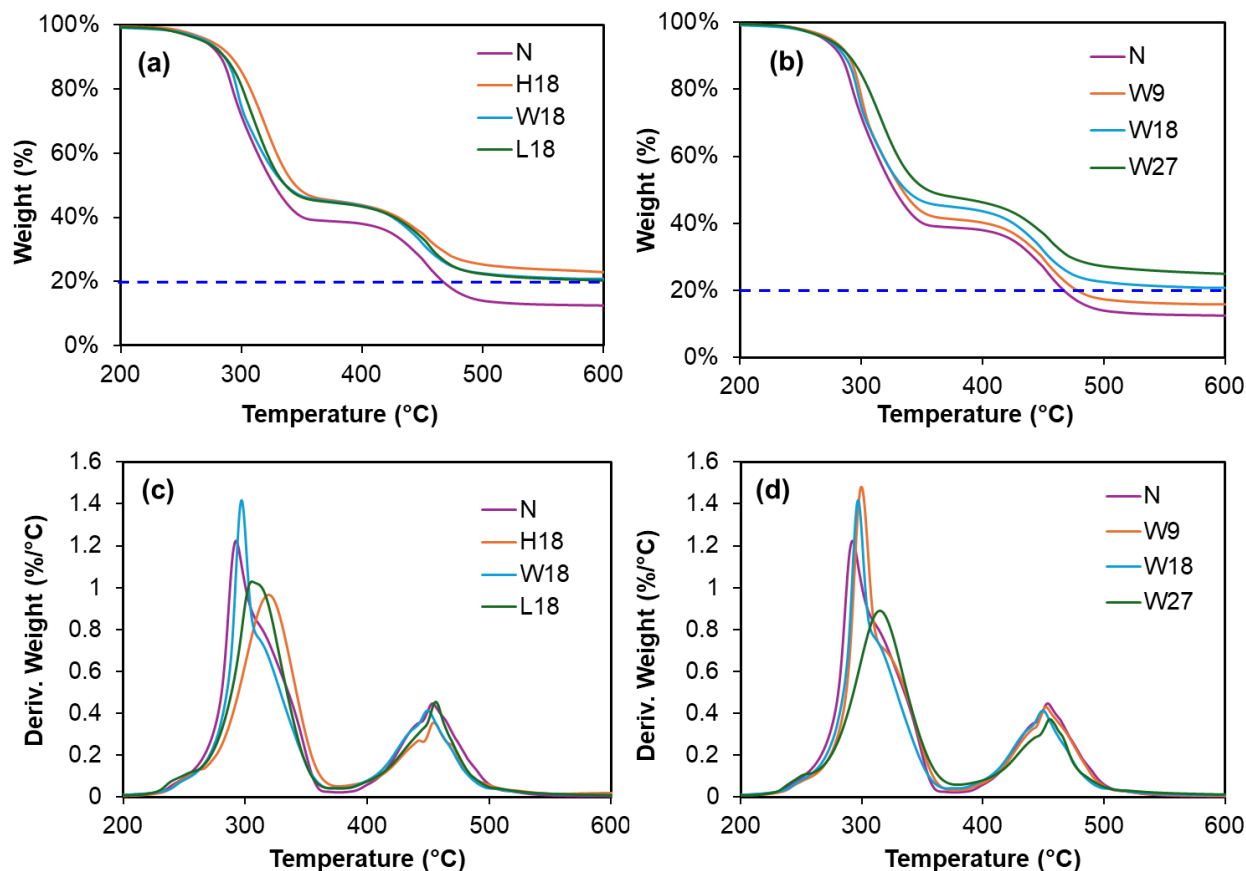


**Figure 3:** TGA (a and b) and DTG (c and d) curves comparing grade (a and c) and loading (b and d) – under nitrogen.

During decomposition under air, an additional stage of degradation was seen in the 500 - 600 °C range which involves the combustion of organic material [116]. The presence of oxygen also seemed to alter the mechanism of the first two stages, increasing the speed of the first stage (peak rate of 1.2 in **Figure 3c** rose to 2.5 in **Figure 4c**), and causing a sharp start to the second stage as seen with sample N (**Figure 4**). All samples had residues of < 1 wt.%, apart from sample H18 due to its mineral (i.e. incombustible) ash content. Additionally, samples followed relatively the same trends as in the inert atmosphere, except for sample W18, which had a much earlier combustion.

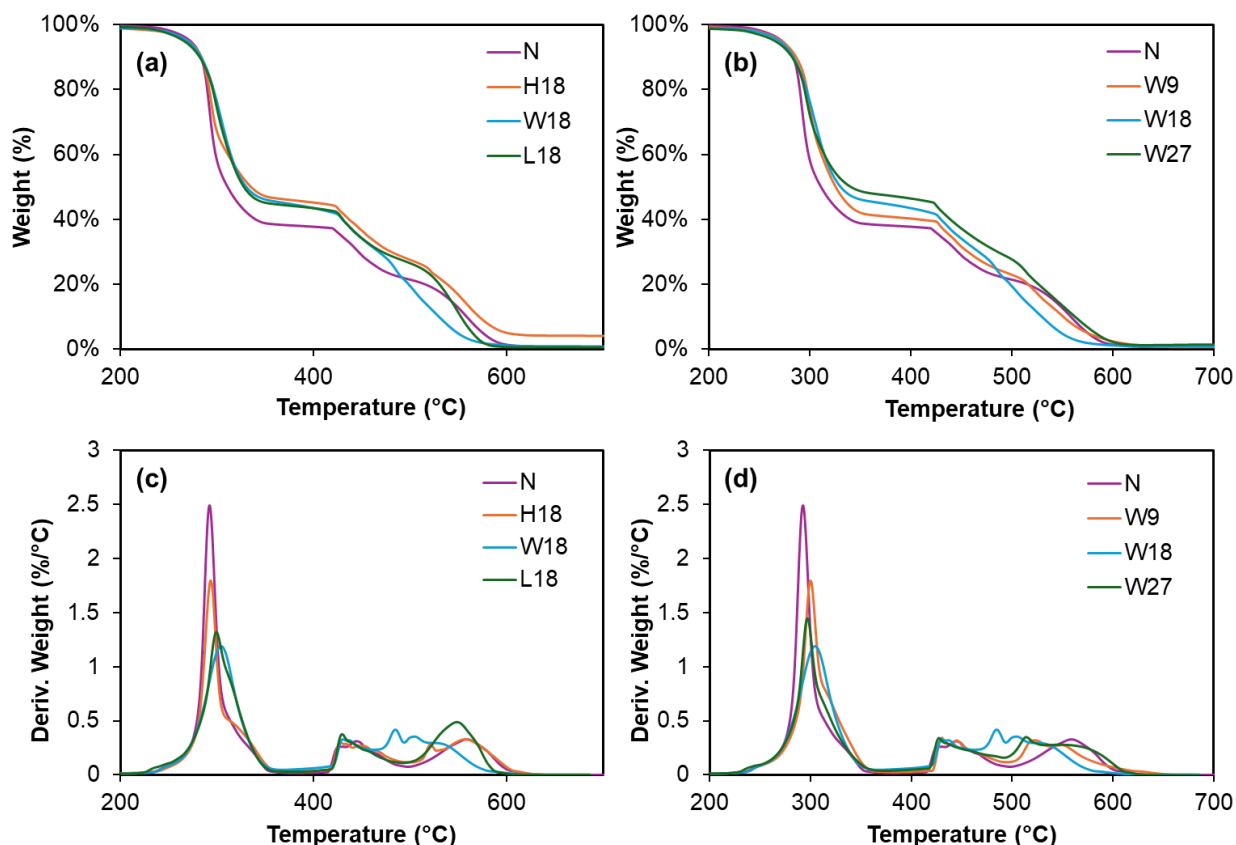


**Figure 4:** TGA (a & b) and DTG (c & d) curves comparing grade (a & c) and loading (b & d) – under air.

As seen in the heat capacity curves (**Figure 5**), the addition of lignin acts to lower the heat capacity of PVC across all samples, with the Wash lignin samples retaining the most heat capacity. The glass transition temperature ( $T_g$ ) from these curves (taken at the midpoint of the inflection) averages around 80 °C and was mostly unaffected by the addition of lignin. The largest change was that of L18, lowering the  $T_g$  by 3 °C from the average. Values and trends are fairly close to the literature  $T_g$  values for PVC collected via DSC [37], which also showed slight decreases in  $T_g$  when lignin compounds were introduced. Specific  $T_g$  values are presented in **Table 6**.

The L18 and W18 samples saw similar drops to heat capacity, lowering by roughly 25% of N's value, whereas W18 only saw a 5% drop (**Figure 5a**). The effect on concentration only saw a substantial change to sample W27 post glass transition; only then was its heat capacity significantly lowered (**Figure 5b**). Reduction to heat flow (and consequently the heat capacity) with the addition of lignin can be influenced by intermolecular interactions between lignin and the base material [120]. This suggests that the lignin grades display some variability in their compatibility with PVC.

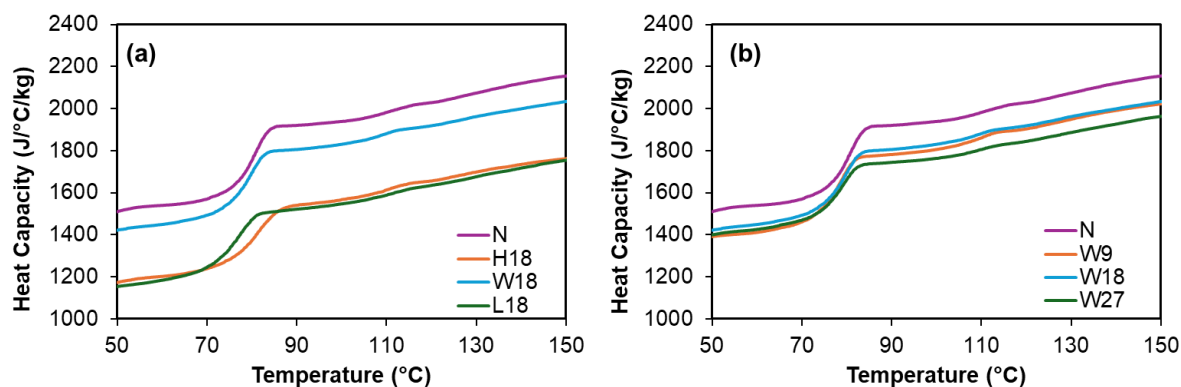


**Figure 5:** Heat capacity curves comparing grade (a) and loading (b).

### 3.3.2 Viscoelastic Behaviour

The addition of lignin works to raise both the storage modulus ( $E'$ ) and the  $T_g$  of PVC, observed from the shift of the tan delta peak curves (**Figure 6**), and is summarized in **Table 6**. This indicates improved thermomechanical properties at raised temperatures, in contrast to the worsened  $T_g$  as measured by DSC. The grade of lignin affected the  $T_g$  only slightly, with H18 and L18 increasing the  $T_g$  by  $\sim 2$  °C and the W18 associated increase was  $\sim 3.5$  °C. The lignin grade had a more significant effect on the moduli, with the Wash lignin having values below and over the sample N for both the storage and loss moduli. Both the H18 and L18 samples saw significant increases to their storage and loss moduli.

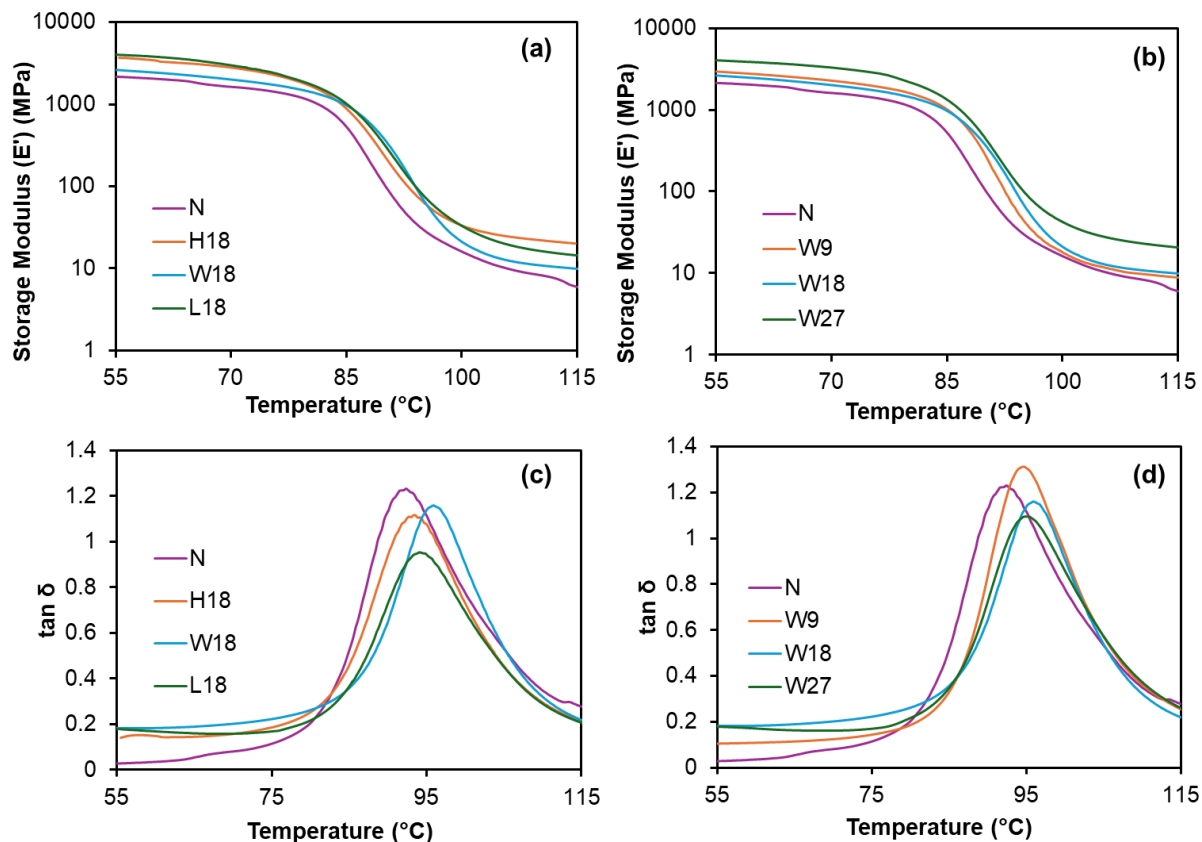


**Figure 6:** Storage modulus ( $E'$ ) (a & b) and  $\tan \delta$  (c & d) curves comparing grades (a & c) and loading (b & d).

**Table 6:** Visco-elastic properties in the glassy & rubbery states and glass transition temperature as measured by DMA and DSC.

| Sample | Glassy State ( $T_g - 10$ °C) |            |             |               | Rubbery State ( $T_g + 10$ °C) |             |               |                     | $T_g^*$ (°C)<br>* DSC Measurement |
|--------|-------------------------------|------------|-------------|---------------|--------------------------------|-------------|---------------|---------------------|-----------------------------------|
|        | $T_g$ (°C)                    | $E'$ (MPa) | $E''$ (MPa) | $\tan \delta$ | $E'$ (MPa)                     | $E''$ (MPa) | $\tan \delta$ | $E'$ (MPa) at 30 °C |                                   |
| N      | 92.39                         | 864.90     | 272.35      | 0.31          | 12.75                          | 8.27        | 0.65          | 2461.03             | 80.59                             |
| H18    | 93.57                         | 1126.32    | 426.28      | 0.38          | 26.75                          | 14.22       | 0.53          | 3668.62             | 81.20                             |
| W18    | 95.88                         | 857.80     | 337.94      | 0.39          | 12.59                          | 6.18        | 0.49          | 2845.65             | 80.04                             |
| L18    | 94.08                         | 1162.20    | 382.47      | 0.33          | 21.80                          | 10.66       | 0.49          | 4232.28             | 77.45                             |
| W9     | 94.65                         | 1052.55    | 334.92      | 0.32          | 12.11                          | 7.06        | 0.58          | 3341.10             | 79.39                             |
| W27    | 95.14                         | 1294.59    | 460.52      | 0.36          | 28.49                          | 16.24       | 0.57          | 4967.92             | 79.37                             |

All samples had similar slopes and slightly larger complex viscosities compared to the unfilled PVC (sample N), the largest increase belonging to sample W27 with negligible differences between the grades of lignin for both the complex viscosity and the moduli (see **Figure 7a** and **Figure 7b**). This indicates that these parameters are more affected by the

concentration of the lignin. Complex viscosity data from all samples were fit to the power law model, with results shown in **Table 7**, showcasing the jump in viscosity of sample W27 by the increase of its K value. The storage and loss moduli followed similar trends, where all samples increased compared to the unfilled PVC. This showcases the ability of lignin to incorporate into PVC, with the jump in viscosity in sample W27 due to reaching a critical value to the increase in friction between the filler and polymeric matrix. When comparing the moduli for the varied loading, the storage moduli of W9 and W18 were similar, with a large jump to W27, similar to the viscosity, but the loss moduli of these three samples were evenly distributed.

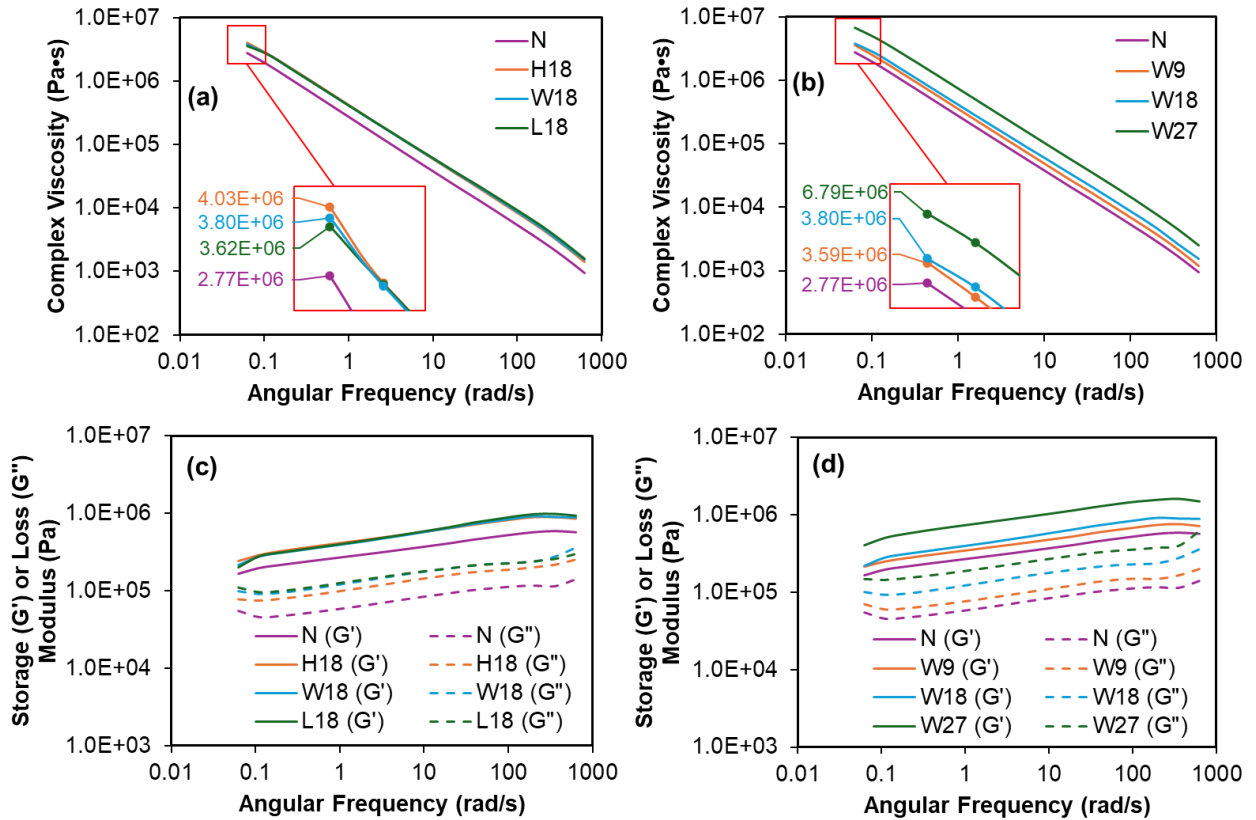


**Figure 7:** Parallel plate rheology results of complex viscosity with varied grade (a), and varied loading (b), as well as oscillatory moduli with varied grade (c) and varied loading (d).

**Table 7:** Parameters for power law model within testing region.

| <b>Sample</b> | <b>n</b> | <b>K (10<sup>6</sup>)</b> | <b>R<sup>2</sup></b> |
|---------------|----------|---------------------------|----------------------|
| N             | 0.1378   | 2.723                     | 0.9997               |
| H18           | 0.1426   | 3.849                     | 0.9995               |
| L18           | 0.1619   | 3.637                     | 0.9993               |
| W18           | 0.1527   | 3.679                     | 0.9995               |
| W9            | 0.1381   | 3.106                     | 0.9997               |
| W27           | 0.1448   | 6.343                     | 0.9994               |

### 3.3.3 Morphology

To observe the dispersion of lignin within PVC, Environmental Scanning Electron Microscopy (E-SEM) images were taken from the cross section of a pellet from all samples, a selection of them shown in **Figure 8** with the remaining images provided in Appendix A (**Figure A6 - Figure A10**). Sample N (**Figure 8a**) shows the matrix of fractured PVC with small gaps within the polymer matrix. In sample W18 (**Figure 8b**) it was apparent that some particles of lignin remained large and spherical, with some becoming smaller due to mechanical grinding during processing. These smaller particles can be seen filling in the small gaps within the polymeric matrix. Sample L18 (**Figure 8c**) has a much smaller particles that disrupt the polymer matrix less than seen with Sample W18. **Figure A9** shows a much lower magnification for sample L18, highlighting the lower particle size distribution and better dispersion of this lignin grade. Sample H18 (**Figure 8d**) has a similar distribution of lignin compared to sample W18, albeit with a much larger content of mineral ash. The mineral ash (**Figure 8d, i**) can be seen disrupting the polymer matrix where lignin particles of similar sizes (**Figure 8d, ii**) can be seen incorporating with the PVC quite well, reinforcing the hypothesis of PVC-lignin compatibility. The disruption of the polymer matrix is more evident at lower magnifications (**Figure A10**), where there are clear gaps surrounding the large mineral particles.

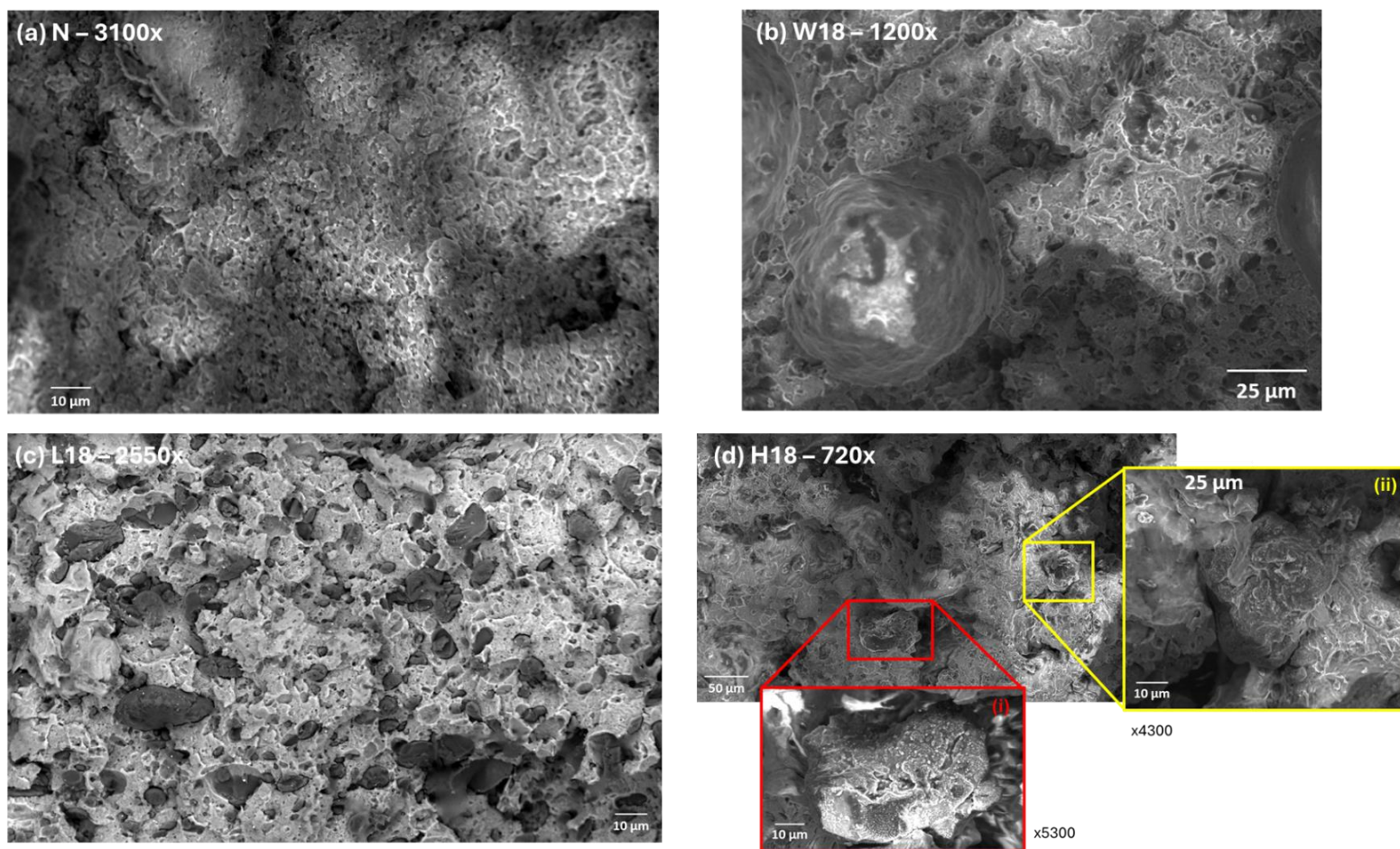


**Figure 8:** E-SEM images of samples N (a), W18 (b), L18 (c) and H18 (d) with their respective magnifications.

### 3.3.4 Tensile Properties

The grade of lignin shows significant effects on the tensile properties of PVC, with ash content directly affecting the tensile strength of the compounds. With decreasing ash content, there was an increase in the tensile strength of the resulting material (**Figure 9a**), but all samples significantly lowered the variability between tests compared to unfilled PVC. Young's modulus was more consistent among all samples, with H18 being the largest by only slightly, due to the ash/mineral residue behaving as a rigid filler (**Figure 9b**). The effect to the elongation of the samples was more dramatic, as the addition of lignin lowered the elongation, with high ash samples decreasing even more so (**Figure 9c**). Both H18 and W18 had very

similar values (roughly a 73% decrease), showing the sensitivity of the samples to ash, as sample L18 was able to prevent further loss to elongation having a very low ash content, with a decrease of only 38.7%. This loss of elongation can be seen with other PVC-biofiller composites; at similar concentrations starch, wood flour, and cellulose reduced elongation by 26.4%, ~49%, and ~77% respectively and all suffered decreases in tensile strength [121][122][123], whereas sample L18 was shown to have increased the tensile strength of the base polymer.

Additional samples were made with 4.5 and 13.5 wt.% loading for additional resolution for tensile testing. This shows the minimal loading of lignin required to improve the variability of the PVC in tensile strength, with the standard deviation decreasing significantly at 9 wt.% (**Figure 9d**). The tensile strength also peaks at 9 wt.%, decreasing steadily until 27 wt.% where the variability increases again. The increase of lignin steadily increases Young's modulus between all samples, without major changes to the variability (**Figure 9e**). Similarly, the increase of lignin steadily decreased the elongation without affecting the variability, until 18 wt.% (**Figure 9e**). At this point, the amount of filler consistently disrupts the PVC matrix such that none of the samples are able to elongate, resulting in a minimal elasticity and high stiffness.

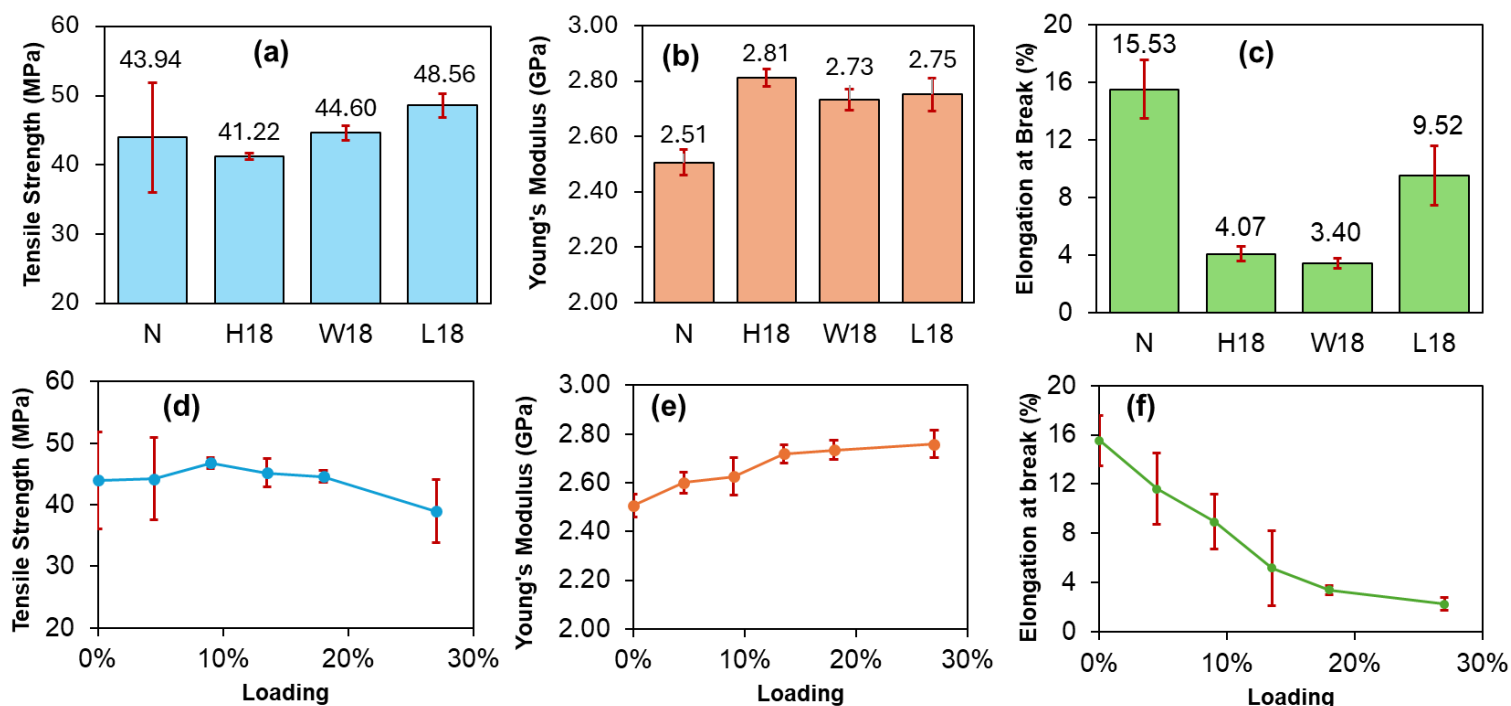


**Figure 9:** Tensile results for ultimate tensile strength (a, d), Young's modulus (b, e), and elongation at break (c, f), with varying grade of lignin (a - c) and varying loading of Wash lignin (d - f). Error bars indicate  $\pm$  one standard deviation.

### 3.3.5 Degradation Characteristics

#### 3.3.5.1 Limiting Oxygen Index (LOI)

Neat PVC provided the largest LOI across all tested samples (**Table 8**). While working with flame retardant samples, LOI test highlights materials which can dilute the concentration of oxygen to prevent fire propagation, which PVC can inherently do via the generation of HCl gas during combustion. As larger portions of the PVC are replaced with lignin (a primarily charring material) [117], this effect is less prominent and thus lowers the LOI value. This is observed with a near linear decrease in LOI between samples N, W9, and W18. This effect was also observed in [124] where the addition of 5 phr of cellulose to a PVC blend lowered the LOI from 46.7% to 44.4% (a 5% decrease). This is a much larger difference compared to lignin given that 10 phr of lignin (sample W9) lowered the LOI by roughly 6%.

Between samples of similar concentration but varying lignin grade, HpH lignin was able to retain the largest LOI value of 42.1%. HpH lignin contains thiol groups which can evolve into sulfur dioxide during combustion, diluting oxygen concentration at the sample's surface, raising the concentration of oxygen required to sustain combustion, i.e. raising the LOI value.

During combustion, neat PVC samples flaked and fell apart slowly as they were being burnt. All lignin samples behaved similarly to each other, all falling apart more rapidly with the drips still flaming. The lignin samples also sputtered during combustion and would form white ash when combustion had ceased. The neat PVC samples remained a dark black after combustion had ended.

**Table 8:** LOI values of tested samples.

|            |       |
|------------|-------|
| <b>N</b>   | 45.8% |
| <b>H18</b> | 42.1% |
| <b>L18</b> | 41.0% |
| <b>W18</b> | 41.4% |
| <b>W9</b>  | 43.0% |

### 3.3.5.2 *Combustion Indices*

Following the TGA runs at 20 °C/min under air, the combustion indices for all samples were calculated, with both absolute values and values relative to neat PVC (sample N) shown in **Figure 10**. The specific values are presented in Appendix A (**Table A1**). Larger combustion index values show a material's tendency to ignite sooner and combust faster, where lower values indicate a more flame-retardant material.

All lignin-based samples saw a decrease in every combustion index relative to sample N, the largest reduction was seen with samples W18 and L18 (**Figure 10b**). Sample H18 retained

the largest relative indices, showing the least flame-retardant effect between all samples, in stark contrast to it performing the best of all the lignin grades in LOI, as these values focus on the effects of charring rather than the concentration of air at the sample's surface. As mentioned previously, the charring of a lignin generates a complex polyaromatic structure. The complexity of this structure can reduce the capability of oxygen to diffuse within a material to propagate further combustion while also insulating the material against heat [125]. While all four relative combustion indices were roughly comparable, the W18 and L18 samples also displayed a significant decrease to the burnout index ( $D_b$ ) by roughly 80%. While their C remained unchanged, drops to  $D_b$  indicate that ignition temperatures were relatively unchanged, but it took much longer to burnout and/or the sample combusted at or above half the max rate for a longer period. This would lower the peak heat release of the flame, which is critical during flame propagation.

An optimal loading of Wash lignin was also observed, as there was a drop in all indices for samples W9 to W18, but from W18 to W27 there was a major increase to  $D_b$  and a slight increase to the rest. This suggests that, from the three loadings tested, the 18 wt.% of lignin provides optimal flame retardancy with worsening results thereafter.

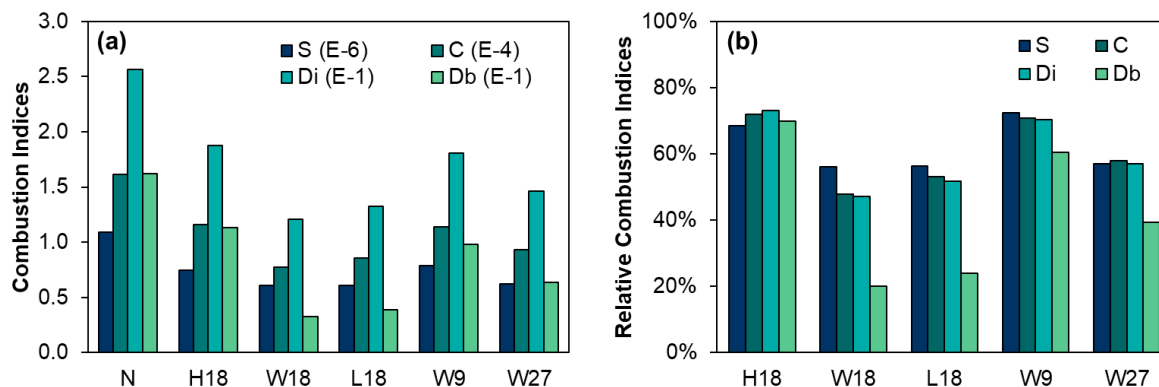


**Figure 10:** Combustion indices, S ( $\text{min}^{-2} \text{K}^{-3}$ ), C ( $\text{min}^{-1} \text{K}^{-2}$ ), Di ( $\text{min}^{-3}$ ), & Db ( $\text{min}^{-4}$ ), (a) and indices for samples relative to the values of sample N (b).

### 3.3.5.3 Decomposition kinetics

To deepen the understanding of the decomposition process, it would be important to understand how the kinetic triplet is affected by the addition of lignin into PVC. Following the guideline supplied by ICTAC [112], modelling of the kinetic triplet for samples N and W27 was explored using TGA data at varying heating rates.

Conversion and DTG curves were split where the derivative was near zero to aid in the deconvolution of the curves (see **Figure 11a** & **Figure 11b**). Deconvolution was performed with an incremental number of curves until the  $R^2$  value of the fit was at least 0.95. Any additional curves would likely be redundant and would reduce the accuracy of the modeled kinetics. A sample of the deconvolution can be seen in **Figure 12**. The deconvolution of sample N resulted in three curves, one in the first decomposition region, and two in the second.

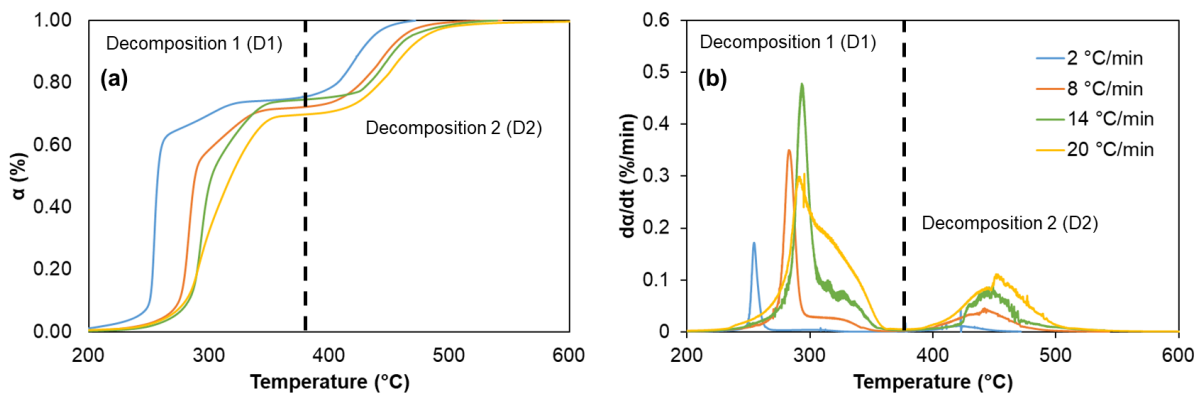


**Figure 11:** Oxidative decomposition of neat PVC at varying heating rates, with conversion (a) and derivative weight loss curves (b).

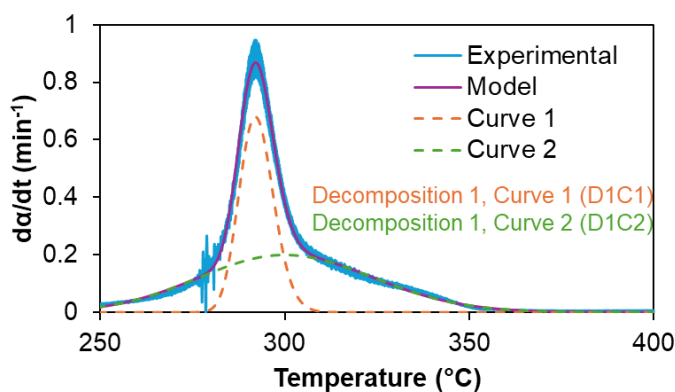


**Figure 12:** Sample deconvolution of sample N.

Each curve was then analysed using equation (11) at various conversions to produce the OFW plots presented in **Figure 13**. A curve and its corresponding activation energy can be considered accurate if it is constant across all conversion percents. Constant slopes, as seen in **Figure 13a**, represent the ideal constant activation energy, and can be more easily seen in **Figure 13d**. While D1C2 and D2C1 had changing activation energies, their fits were also changing (**Figure 13b** & **Figure 13c**), thus an average of the activation energies was taken over the portion with good fits to continue with modeling.

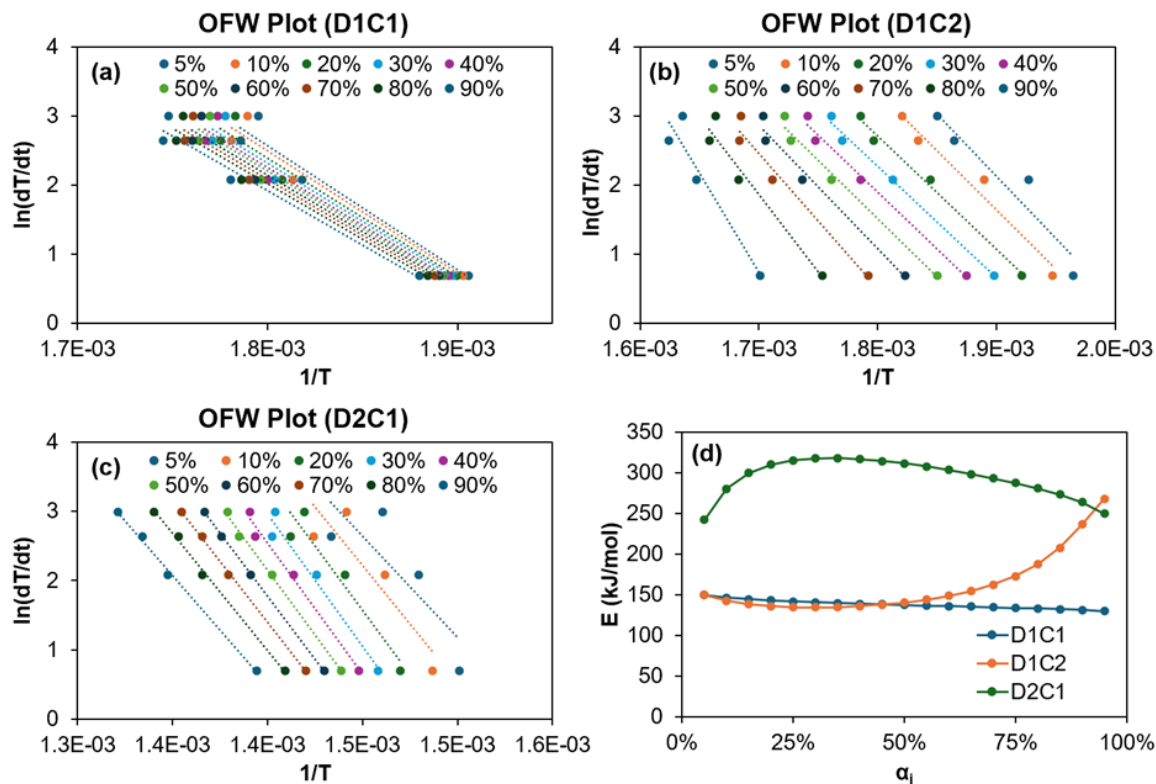


**Figure 13:** OFW plots and activation energies as functions of conversion of deconvoluted curves for sample N.

Using the activation energies determined via the OFW method, the CR method (Eq. 12) was used to determine the most appropriate mechanism for each individual curve. A sample for the results of the CR method on D1C1 is shown in **Table A2**, where the mechanism with the closest activation energy with a satisfactory  $R^2$  value was mechanism A4. This process was continued for all curves. By revisiting the OFW method using the determined mechanisms, the pre-exponential factor can be determined from the intercepts of the plots in **Figure 13**. With this and the contribution coefficients determined during deconvolution, all parameters needed to model the decomposition of sample N are known (**Table 9** and **Figure 14**). Identical analysis was performed on sample W27 to determine its kinetic parameters (**Table 10** and **Figure 15**).

Both models have adequate fits and have very similar E and A values for the first and second decompositions. The models did not quite incorporate the heating rate effect completely – the curves fit better at certain heating rates and diverge the larger or smaller they get. Neat PVC (sample N) had an extra curve for the first stage of decomposition, one following a nucleating mechanism (A4) and the other following a second order reaction mechanism (F2). This partly aligns with previous literature models, which found the best fit mechanisms were nucleating (A2) and diffusion controlled (~D3) [126]. At lower conversions, diffusion mechanisms have a much larger rate, but at larger conversions, higher order reaction mechanisms (such as F2) and D3 have very similar rates, so some fitting error could be responsible for this discrepancy. For sample W27 however, there was only one curve that was closest fit to a 3-D diffusion model (D3) with a slightly larger activation energy. This would suggest the addition of lignin increased the difficulty of the diffusion of HCl gas during the first stage of decomposition, impeding the material's decomposition.

**Table 9:** Final kinetic model parameters for sample N.

|                  | E (kJ/mol) | A (1/min) | w    |
|------------------|------------|-----------|------|
| <b>D1C1 (A4)</b> | 133.17     | 1.07E+12  | 0.53 |
| <b>D1C2 (F2)</b> | 138.38     | 9.48E+11  | 0.20 |
| <b>D2 (D3)</b>   | 291.65     | 5.66E+19  | 0.27 |

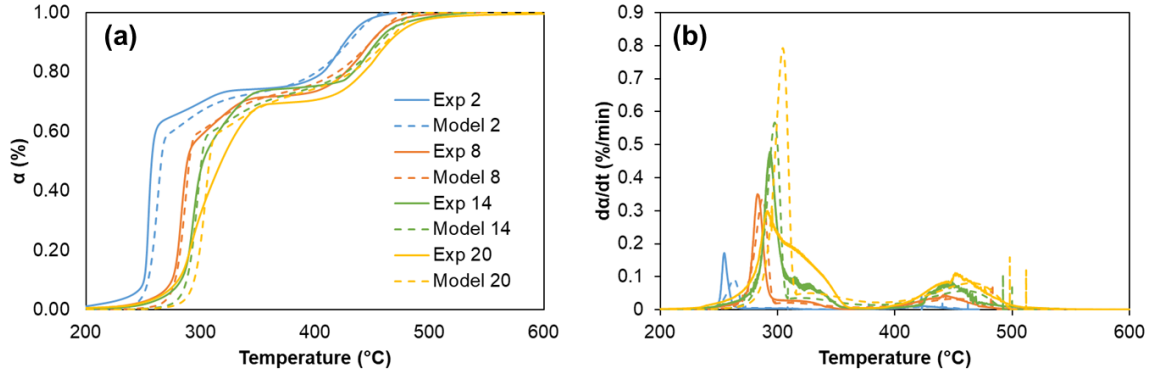


**Figure 14:** Experimental (solid lines) and modeled (dashed lines) TGA (a) and DTG (b) curves at varying heating rates for sample N under nitrogen.

**Table 10:** Final kinetic model parameters for sample W27.

|                | E (kJ/mol) | A (1/min) | w    |
|----------------|------------|-----------|------|
| <b>D1 (D4)</b> | 161.01     | 1.85E+13  | 0.72 |
| <b>D2 (F3)</b> | 300.82     | 6.01E+21  | 0.28 |

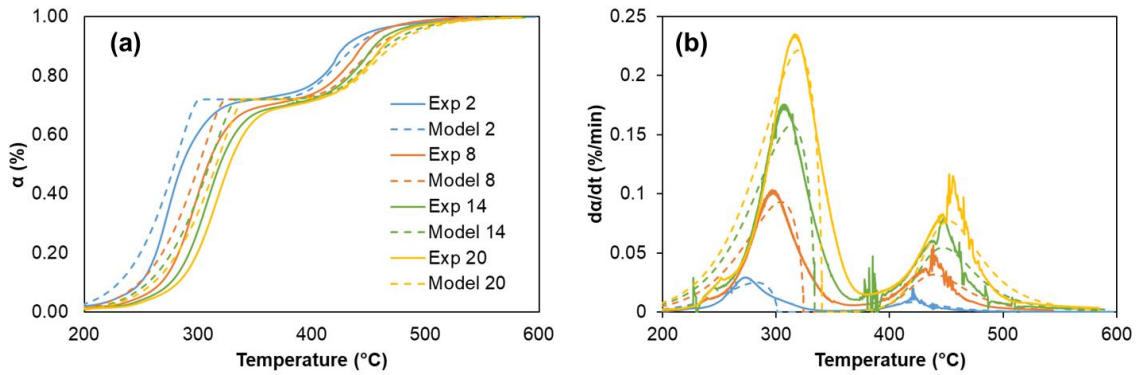


**Figure 15:** Experimental (solid lines) and modeled (dashed lines) TGA (a) and DTG (b) curves at varying heating rates for sample W27 under nitrogen.

For the second stage of decomposition, both models required only a single curve both with similar activation energies. Sample N's model best fit mechanism was D3 and had a pre-exponential factor two orders of magnitude smaller than that of sample W27, whose best fit mechanism was F3. As mentioned previously, diffusion mechanisms (such as D3) have much larger initial rates of conversion but can match rates seen in mechanisms of orders two or three (such as F3) at later points in time. This is evident when comparing the models, as sample N's onset is much faster than sample W27's, which reaches full conversion later than the two even though it has the larger A (which tends reactions to finish earlier in time). This is to highlight the effects of the mechanism overtaking the effects of the pre-exponential factor, making it the more decisive factor in the kinetics in this case.

### **3.4 Conclusions**

Kraft lignin (HpH, high pH) underwent acid precipitation and washing to successfully purify and lower the ash content of lignin, referred to in this paper as Wash lignin, which was also compared to industrially purified Kraft lignin (LpH, low pH) in a variety of tests. As the concentration of lignin was increased the most apparent changes were increases to complex viscosity (+37.2% for W18), Young's modulus (+8.76% for W18) and decreases to elongation at break (-78.1% for W18). The additional of lignin slightly lowered the LOI, but improved combustion indices by up to 80% through its charring behaviour. HpH lignin, with a relatively large ash content, performed worse in the elongation at break (-73.8%) with a slightly larger Young's modulus (+12.0%) when compared to LpH and W lignin, but retained the largest LOI due its thiol groups generating sulfur dioxide during combustion. LpH lignin saw the lowest losses to elongation (-38.7%) while improving both ultimate tensile strength (+10.5%) and Young's modulus (+9.56%). While all three grades lowered the heat capacity, HpH and LpH

lignin were lowered by similar amounts (-21.3%) and the Wash lignin managed to conserve the most heat capacity among them (-5.14%). Modeling the apparent kinetics of the decomposition of two samples showed the addition of lignin altered the apparent mechanism from nucleating to diffusion-controlled during the dehydrochlorination of PVC.

Due to its superior tensile performance, LpH lignin is recommended for further research at concentrations between 9 and 18 wt. % to balance improvements in combustion performance, ultimate tensile strength, & Young's modulus to loss of elongation. Further works could focus on analyzing additional flame characteristics of PVC-lignin composites, namely smoke generation and heat release rates.

## **Chapter 4: Kraft Lignin Nano-Containers to Deliver Flame Retardants in Natural Rubber Composites**

### **4.1 Introduction**

Currently, 79% of all plastic produced either reaches the environment or a landfill, degrading slowly and leeching microplastics and other toxic pollutants directly into the environment [127]. Given rising environmental concerns, the development of sustainable and renewable materials is of great importance. Natural rubber (NR) is among the few polymeric hydrocarbons that is generated directly through biological means [47], and is used widely where it may experience high-temperature or ignition sources, such as in automotives, electrical insulation, and construction [128][129]. With a limiting oxygen index (LOI) of just 18% [130], NR is already quite flammable, but it is also used as a foamed material which increases flammability due to the large surface area and hydrocarbon-based matrix [82]. Alternative polymeric foams are typically petroleum based and exert significant environmental stress throughout their life cycle [131].

The mechanism of flame propagation can be summarized as the thermal decomposition of the condensed phase (the polymer) that releases volatile gases that mix with oxygen in the gas phase which combust, releasing heat, auto-accelerating this process [6]. This bestows complexity at measuring a material's capability of burning. As such, a variety of flammability tests (most notably UL-94, LOI [53]) exist that must be passed in order for a material to become approved for use in various industries [132]. Given these difficult standards, polymers are typically filled with flame retardants (FRs) at very large percentages [128], which in some cases compromises the processability and physicomechanical properties [133].

Halogenated FRs, known to provide excellent fire inhibition [60], have come under scrutiny due to their impact on the environment and general safety concerns [61], which has spawned research into alternatives FR, namely bio-based ones [134]. Phosphorus-based FRs have been a popular point of research due to their multiple flame retarding pathways, versatility, and efficiency at low loadings [134]. Ammonium polyphosphate (APP) is a key contender as it includes both an acid source and a blowing agent, but when combusted in the presence of carbonaceous material, it can form a dense char layer [135][136], making it an intumescent FR [65]. The inclusion of lignin, the second most abundant biopolymer and a largely charring material, would only add to the charring ability of a FR [20][117]. Kraft lignin in particular is the most abundant source of lignin, as it is the most popular industrially-sourced lignin, generated as waste from the pulp and paper industry [88][137]. FR polymeric nanocomposites in particular can make tremendous improvements in a material's flame retardancy whilst improving its mechanical properties [6] in comparison to traditional mineral FR composites, which require large loadings and tend to deteriorate a polymer's mechanical properties [128]. A nano-lignin & APP FR would balance the need for a reduction in toxicity, the development of a bio-based filler, and the reduction in filled content.

This work focuses on expanding the work done by Peil et al. [82] by utilizing Kraft lignin to construct lignin nano-containers (LNCs) to deliver APP, a hydrophilic FR, to NR, a hydrophobic polymer. The composites are compared to a composite where lignin and APP are added in bulk form at the latex stage to compare the benefits and drawbacks of each method. Additionally, this work maintains the effort of using biological materials in biocompatible polymers, in contrast to similar works that utilize APP in epoxy resin composites [138] or lignin and APP in polyurethane [139].

## **4.2 Experimental**

### **4.2.1 Materials**

Sodium hydroxide (NaOH,  $\geq 97.0\%$ , Sigma-Aldrich - Oakville, ON), purified Kraft lignin (Alberta Pacific Forest Industries Inc. - Hinton, Alberta, ON), ammonium polyphosphate (APP, Aaron Chemicals LLC - San Diego, CA, USA), toluene (Sigma-Aldrich), sorbitan monooleate (Span 80, Sigma-Aldrich), oleic acid (90%, Sigma-Aldrich), polyoxyethylene sorbitan trioleate (Tween 85, Sigma-Aldrich), isophorone diisocyanate (IPDI, 98%, Sigma-Aldrich), polyethylene glycol sorbitan monolaurate (Tween 20, Sigma-Aldrich), natural rubber latex (61.52 wt.% NR, Chemionics Corp - OH, USA), azodicarbonamide (ADC, Sigma-Aldrich), dicumyl peroxide (DCP, Sigma-Aldrich), ZnO (Zinc oxide, Sigma-Aldrich), dimethyl sulfoxide (DMSO, Sigma-Aldrich).

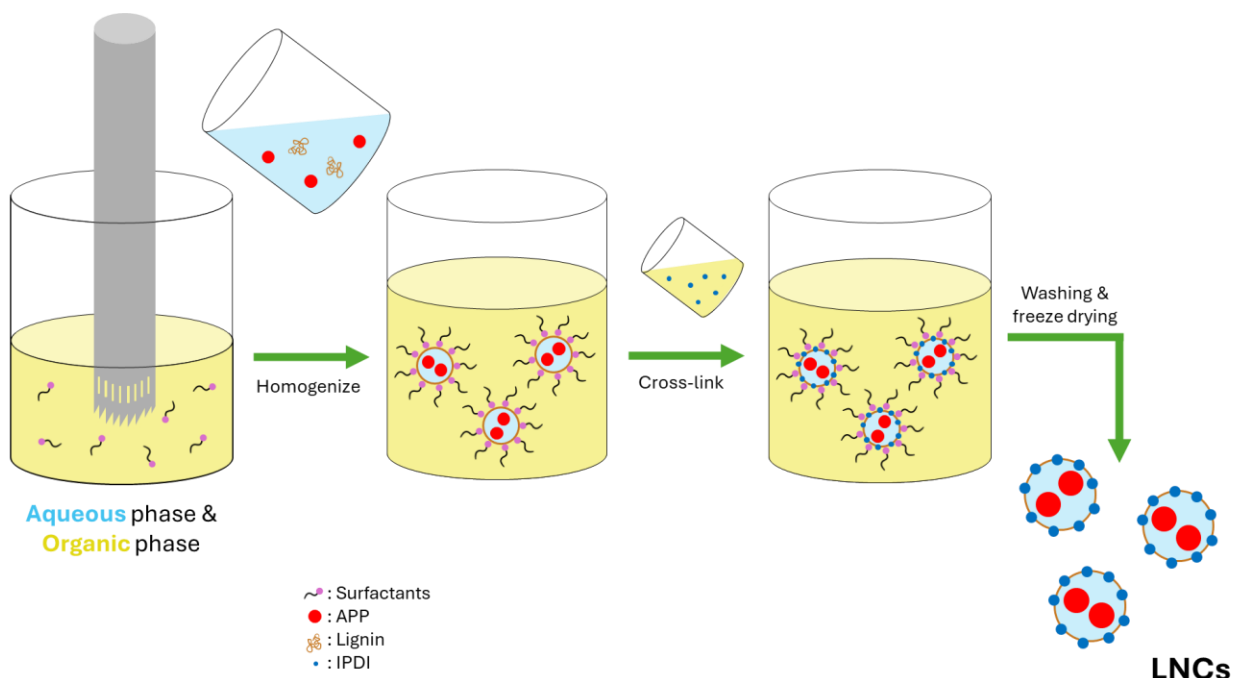
### **4.2.2 Methods**

#### **4.2.3 Lignin nanocontainer (LNC) synthesis**

The aqueous phase comprised of water (25 mL), NaOH (2 g), lignin (2 g), and APP (4.5 g) were added to a beaker and placed on a hotplate with magnetic stirring capability (400 rpm, 100 °C) until all components were completely dissolved. The evaporated water was replenished to maintain the composition. The organic phase comprised of toluene (95 mL), Span 80 (1 mL), oleic acid (0.75 mL), and Tween 85 (0.5 mL) were added to a large beaker and mixed thoroughly (400 rpm) at room temperature before proceeding. The crosslinking solution was comprised of toluene (23 mL), IPDI (0.43 mL), and Span 80 (0.5 mL).

Using a needle-tipped syringe (1 mm ID), the aqueous phase was added dropwise (~2 drops/sec) to the organic phase under aggressive homogenization (IKA homogenizer, 10,000 rpm) until the aqueous phase was completely incorporated. The resulting emulsion was transferred to a hotplate with aggressive stirring (700 rpm). While stirring, the crosslinking solution was added dropwise (~2 drops/sec) via burette to the emulsion, covered, and kept stirring overnight to generate the lignin nanocontainers (LNCs).

The emulsion was centrifuged (4200 rcf, 5 mins) to separate the LNC from the toluene but needed to be washed to remove the surfactants. The supernatant was discarded, and fresh toluene was added to each centrifuge tube. Then, each centrifuge tube was sonicated (1 min, 92% amplitude) to scrub each LNC of surfactant and was centrifuged again. This washing procedure was repeated until the supernatant was clear, typically 3 times total. The resulting pellet was laid out in a fume hood to allow for residual solvent to evaporate. The solvent-free pellets were freeze-dried to obtain a dried LNC powder. This procedure is summarized visually in **Scheme 2**.



**Scheme 2:** Synthesis of APP-filled LNCs via emulsification, crosslinking, and freeze drying.

#### 4.2.4 NR composites fabrication

The powdered LNCs were pre-dispersed in water at a ratio of 30 mL water, 2.5 g (dry weight) LNC, and 1 mL Tween 20, and were sonicated (2 mins, 92% amp). Multiple of these LNC dispersions were made to obtain larger filler contents. Calculated amounts of LNC dispersion (

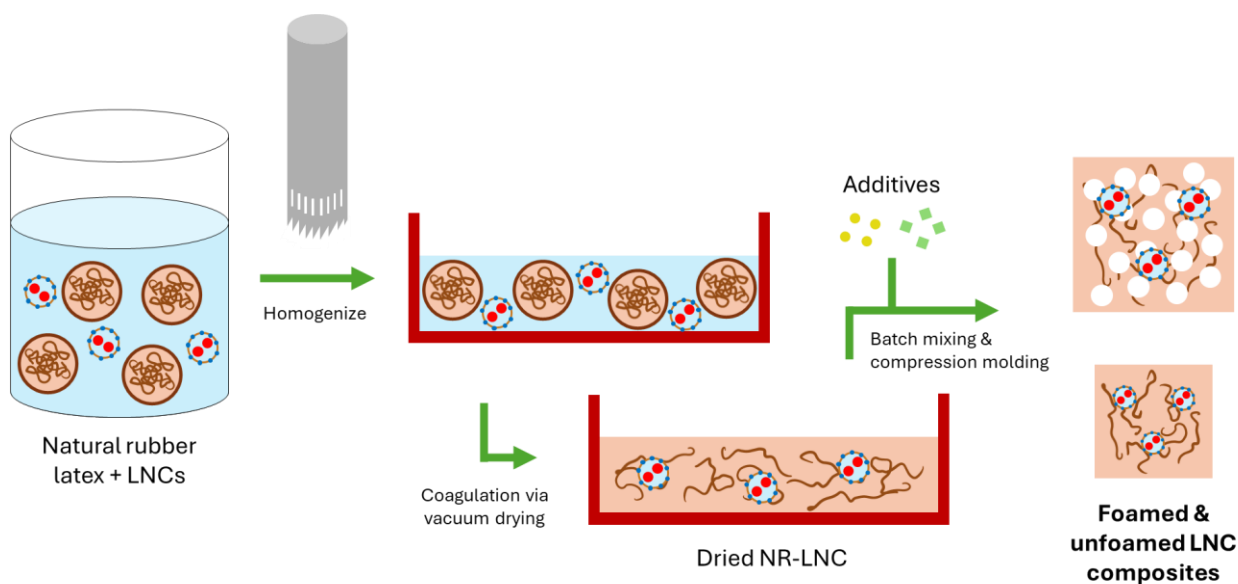
**Table 11)** was then added to NR latex under homogenization (IKA homogenizer, 10,000 rpm, 4 mins) to achieve proper dispersion. The latex/LNC mixture was transferred to a large silicon mold to form a thin layer and then dried in a vacuum oven at 500 mTorr and 50 °C to coagulate the rubber as quickly as possible to prevent agglomeration of the LNCs. The NR/LNC formulations were then mixed using a HAAKE Rheomix 3000 batch mixer (Thermo-Fisher Scientific Inc., Waltham, MA, USA) with foaming agents in proportions shown in

**Table 11.** The sample names in **Table 11** indicate the corresponding weight percentage of the FR added (i.e. 10-LNC is 10 wt. % LNC, 10-L+A is 10 wt. % of a lignin, APP, and NaOH blend that follows the same ratios as used during the LNC synthesis).

**Table 11:** Recipe for sample in per hundred rubber (phr).

|                                     | <b>Control (N)</b> | <b>2.5-LNC</b> | <b>5-LNC</b> | <b>10-LNC</b> | <b>10-L+A*</b> | <b>15-LNC</b> |
|-------------------------------------|--------------------|----------------|--------------|---------------|----------------|---------------|
| <b>Rubber</b>                       | 100                | 100            | 100          | 100           | 100            | 100           |
| <b>LNC</b> (*or lignin, NaOH & APP) | 0                  | 2.8            | 5.9          | 12.5          | 12.5           | 19.8          |
| <b>ADC</b>                          | 10                 | 10             | 10           | 10            | 10             | 10            |
| <b>DCP</b>                          | 1                  | 1              | 1            | 1             | 1              | 1             |
| <b>ZnO</b>                          | 1.5                | 1.5            | 1.5          | 1.5           | 1.5            | 1.5           |

After batch mixing, samples were formed into compression molded sheets in a Carver compression mold using an 80 mm x 80 mm x 5 mm mold at 140 °C and 1000 psi for 5 mins. The compression molded sheets were allowed to cool to room temperature before being placed in a 130 mm x 130 mm x 5 mm compression mold spacer at 180 °C and 3000 psi for 3 mins to degrade the ADC and foam the specimens. At these conditions, only the samples N and 10-LNC foamed, indicating the need for a case-by-case optimization relating to foaming agent and filler concentration. All samples were tested to explore the effects of foamed vs. non-foamed specimens on the performance of the flame retardant. Going forward, the N and 10-LNC samples that foamed will be referred to as N (f) and 10-LNC (f), respectively. The fabrication of the LNC composites is summarized in **Scheme 3**.



**Scheme 3:** Fabrication of NR-LNC composites.

#### 4.2.4.1 *Fourier transform infrared (FTIR) spectroscopy*

Thermo-Scientific Nicolet 6700 FTIR equipped with attenuated total reflectance (ATR) was used to investigate the change in functional groups throughout the crosslinking reaction to form the LNCs. Lignin and IPDI were mixed in DMSO, placed upon the ATR plate which was heated to 100 °C and held for 30 minutes. Spectral scans were taken every 10 minutes. The absorbance for each sample was collected over a spectral range of 500 - 4000  $\text{cm}^{-1}$  measured with 64 scans at a resolution of 8  $\text{cm}^{-1}$ .

#### 4.2.4.2 *Dynamic light scattering (DLS)*

The zeta potential and hydrodynamic radius of LNC emulsions and dispersions was measured using a Malvern Zetasizer Nano-ZS. Bulk solutions (0.5 mL) were diluted in their respective solvent (4 mL) in a glass cuvette, and three measurements were taken at 25 °C per sample.

#### 4.2.4.3 *Thermogravimetric analysis (TGA)*

The thermal stability of the rubber composites was evaluated using a TA Instruments Discovery TGA 55. The following method was used: 20 °C/min ramp to 105 °C, isothermal for 5 mins, 20 °C/min ramp to 650 °C. All samples were subjected to the test twice, once in an inert environment (60 mL/min nitrogen) and once in an oxidative environment (60 mL/min air), with analysis occurring on a dry basis, after the isothermal step at 105 °C.

#### 4.2.4.4 *Tensile test*

Tensile properties were evaluated by a Shimadzu AGS-X using a 500 N load cell. Four samples of 40 mm x 3 mm x 4 mm were tested for each formulation in a randomized order at 500 mm/min. Results for ultimate tensile strength, elastic modulus, elongation at break, and toughness were recorded.

#### 4.2.4.5 *Hardness*

Each rubber composite had their hardness tested in triplicate using a Type O Durometer in accordance with ASTM 2240. Compression molded specimens with thickness of 0.5 cm were used for the test, with all measurements occurring at least 12 mm from the edge and after 10 seconds of applying the durometer.

#### 4.2.4.6 *Combustion indices*

By analyzing the TGA and derivate thermogravimetric (DTG) curves in an oxidative environment, the combustion performance of each sample can be assessed using combustion indices [106][107]. The values of comprehensive combustion index (S), flammability index (C), ignition index ( $D_i$ ), and burnout index ( $D_b$ ), were calculated as follows:

$$S = \frac{R_{max} \times R_{avg}}{T_i^2 \times T_b} \quad (13)$$

$$C = \frac{R_{max}}{T_i^2} \quad (14)$$

$$D_i = \frac{R_{max}}{t_i \times t_{max}} \quad (15)$$

$$D_b = \frac{R_{max}}{\Delta t_{1/2} \times t_{max} \times t_b} \quad (16)$$

Where  $R_{max}$  and  $R_{avg}$  are the maximum and average mass loss rate (%/min),  $T_i$  and  $T_b$  are the ignition and burnout temperature (K),  $t_i$ ,  $t_{max}$  and  $t_b$  are the ignition, maximum, and burnout times (min), respectively, and  $\Delta t_{1/2}$  is the time spent at or over half the value of  $R_{max}$  (min).

The overall ability of the material to ignite and sustain combustion is represented by  $S$ , whereas  $C$  focuses on the ability of the material to ignite.  $D_i$  and  $D_b$  reflect the material's ability to reach the ignition point and maintain combustion, respectively. Larger values for all these indices indicate the increased flammability of a material, whereas lower values indicate increased flame retardancy.

#### 4.2.4.7 Simultaneous differential thermal (SDT) analyzer

The heat release of select samples during decomposition in an oxidative environment was evaluated using a TA Instruments Q600 SDT. Rubber samples of 10 - 20 mg underwent the following method: 20 °C/min ramp to 105 °C, isothermal for 5 mins, 20 °C/min ramp to 650 °C under 60 mL/min of air. Heat release data was analyzed on a dry basis, after the 105 °C isothermal step which removes excess moisture. Among other combustion calorimetry

parameters, including the peak heat release rate (pHRR), mean heat release rate (mHRR), temperature at the pHRR ( $T_{pHRR}$ ), and the total heat release (THR), the fire growth capacity (FGC) parameter [140] was calculated as follows:

$$FGC = \left( \frac{THR}{T_{95\%} - T_{5\%}} \right) \left( \frac{T_{95\%} - 298 K}{T_{5\%} - 298 K} \right) \quad (17)$$

Where  $T_{95\%}$  and  $T_{5\%}$  represent 95% and 5% conversion on the basis of heat release for each sample during the test.

#### 4.2.4.8 *UL-94 horizontal burn (HB) test*

The rating of HB of the UL-94 flame tests is the lowest rating in the standard, meant for samples that readily burn at atmospheric conditions. Samples were tested in accordance with ASTM D635 and were assigned the HB rating if they achieved a horizontal burn rate  $\leq 40$  mm/min or stopped burning prior to reaching the 100 mm reference line.

#### 4.2.4.9 *Limiting oxygen index (LOI)*

The LOI for all samples was measured in accordance with ASTM D2863. Type IV specimens of dimensions 76 mm x 6.5 mm x 3 mm were cut from compression molded sheets and were tested using top surface ignition. Samples were conditioned at room temperature for a minimum of 72 h prior to testing.

### 4.3 **Results and discussion**

#### 4.3.1 *LNC characterization*

##### 4.3.1.1 *FTIR analysis*

To demonstrate the crosslinking reaction between lignin and IPDI, both compounds were mixed and the evolution of their FTIR spectra evaluated over the course of 30 minutes (**Figure**

2a) alongside the spectra of the individual components and at the initial starting time (**Figure 2b**). Being a diisocyanate, IPDI carries two  $\text{N}=\text{C}=\text{O}$  groups with their spectrum reading at  $2255\text{ cm}^{-1}$  (**Figure 2b**), falling within the typical range of isocyanates of  $2280$  to  $2240$  [141][142]. As significant features to lignin chemical structure, vibrations ascribed to syringyl and guaiacyl at  $1305$  and  $1018\text{ cm}^{-1}$ , respectively were noted, between all spectra containing lignin (**Figure 2c**) [88]. Due to lignin's abundance of hydroxyl groups [88][30], the reaction between these groups and IPDI could generate urethane linkages, as has been done before with Kraft lignin [30], with the proposed reaction scheme shown in **Figure 16**.

Since lignin is a random biopolymer, its hydroxyl groups are both aromatic and aliphatic [30], so the resulting linkages are expected to be a mix of aromatic esters and aliphatic ethers, with these peaks visible at  $1260$  and  $1136\text{ cm}^{-1}$  (**Figure 2d**). Additionally, the formation of urethane linkages in this system form amide groups, which generate N-H ( $3340$  to  $3250$ ) and C=O ( $1680$  to  $1630$ ) stretching peaks [141] [142], and were found at  $3326\text{ cm}^{-1}$  (**Figure 2d**) and  $1670\text{ cm}^{-1}$  (**Figure 2d**) but only in the final reaction spectrum. The diisocyanate peak mentioned previously was visible throughout the entire reaction and indicates that some isocyanate functional groups remained unreacted or partially reacted within the lignin. Due to the generation of ester, ether, and amide groups over the course of the reaction, it was concluded that lignin was successfully crosslinked with the addition of IPDI.

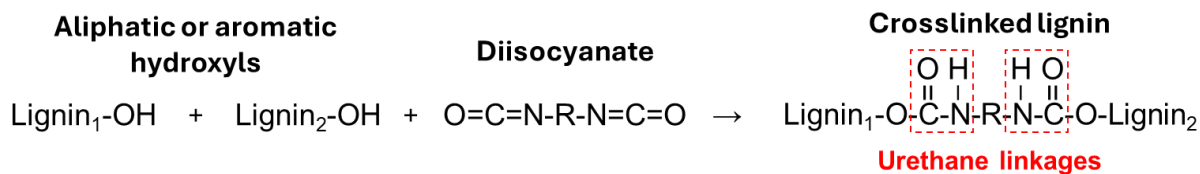


**Figure 16:** Proposed crosslinking reaction scheme.

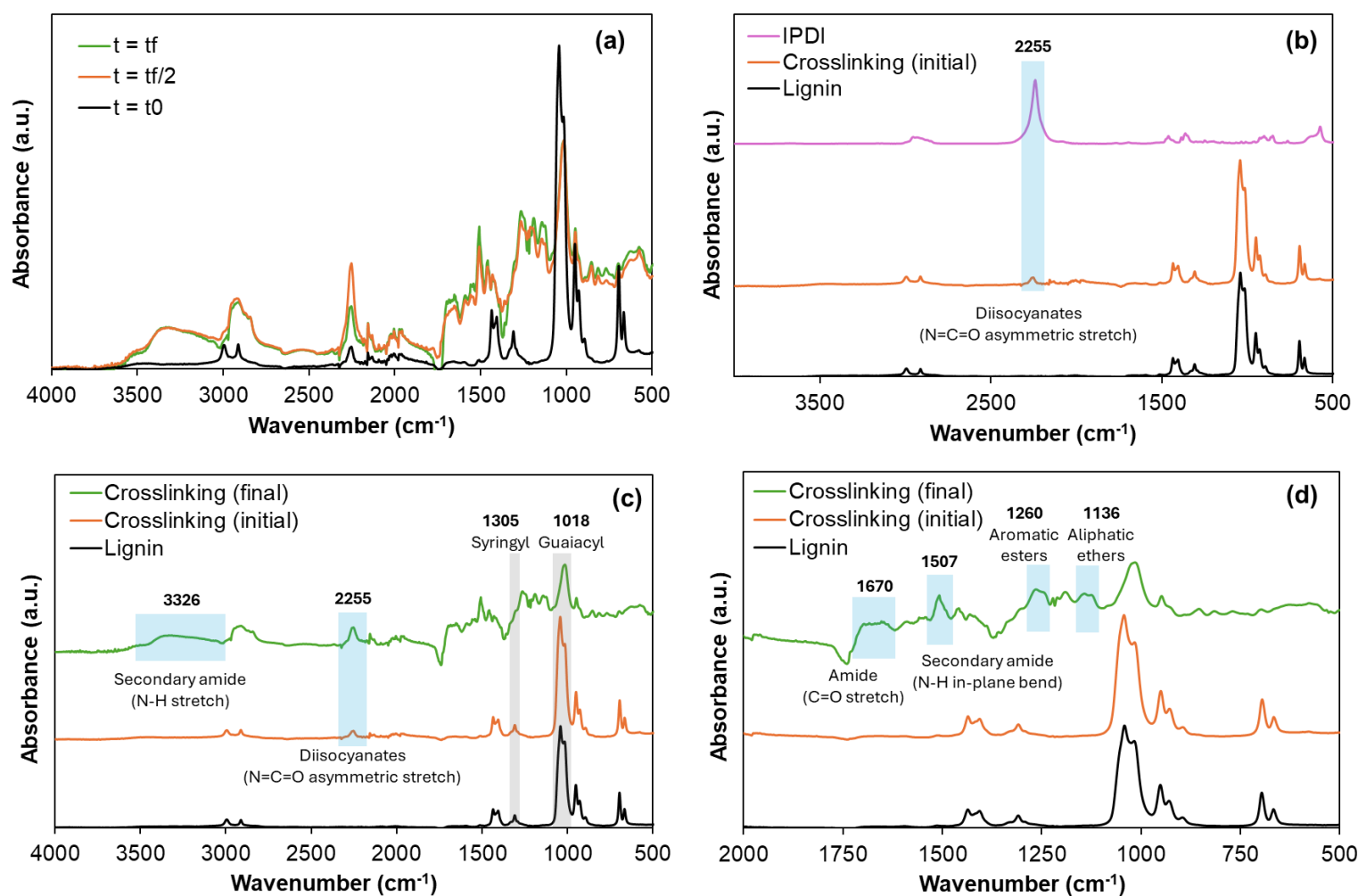


**Figure 17:** ATR-FTIR spectra of the crosslinking reaction over time (a), comparing reactants with the initial reaction spectrum (b), and comparing the evolution of new peaks from the crosslinking reaction (c & d).

#### 4.3.1.2 DLS Analysis

Prior to centrifugation, one batch of the LNC emulsion was stirred overnight without the addition of crosslinker added, while another batch contained the crosslinker. Afterwards, the particle size for each batch was measured to further explore the effect of the interfacial crosslinking between lignin and IPDI. The fresh emulsion exhibited a primary particle diameter of approximately 200 nm (**Figure 18a**). After overnight stirring, the batch with crosslinker retained a much smaller mean particle size of roughly 100 nm (**Figure 18b**), whereas the batch without crosslinker underwent significant coalescence, with its major particle size distribution shifting toward a mean of nearly 1  $\mu\text{m}$  (**Figure 18c**).

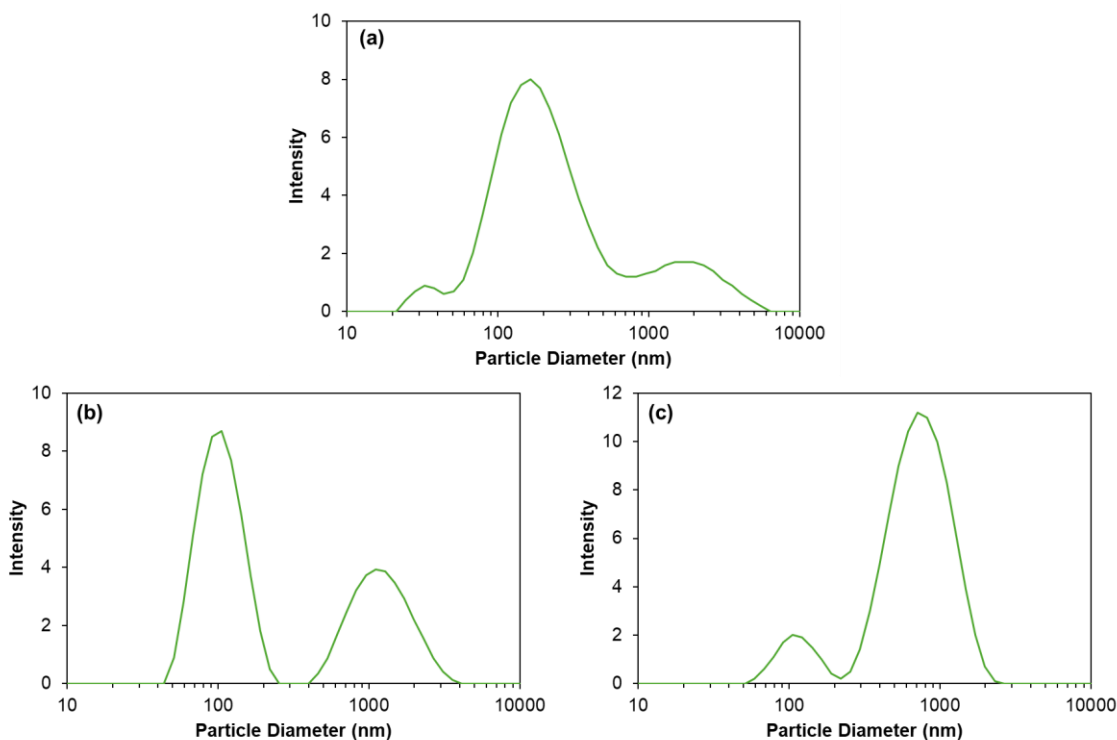


**Figure 18:** DLS plots for the fresh emulsion (a), and the emulsion kept overnight either with or without crosslinking (b & c, respectively).

To ensure the proper dispersion of the LNCs in NR latex, they were dispersed in both DI water and DI water with Tween 20, and their particle size distributions were measured, as

shown in **Figure 19**. The solution with no surfactant (**Figure 19a**) showed major agglomeration, with the bulk particle size well over 1  $\mu\text{m}$ , whereas the solution with surfactant (**Figure 19a**) retained the particle size to roughly 300 nm, reinforcing the importance of surfactant use when forming the NR-LNC composites. To further corroborate this conclusion, the zeta potential was measured for the Tween 20 sample. This resulted in a zeta potential of -42 mV, indicating a good stability of the particles within water, due to electrostatic repulsion when using Tween 20.

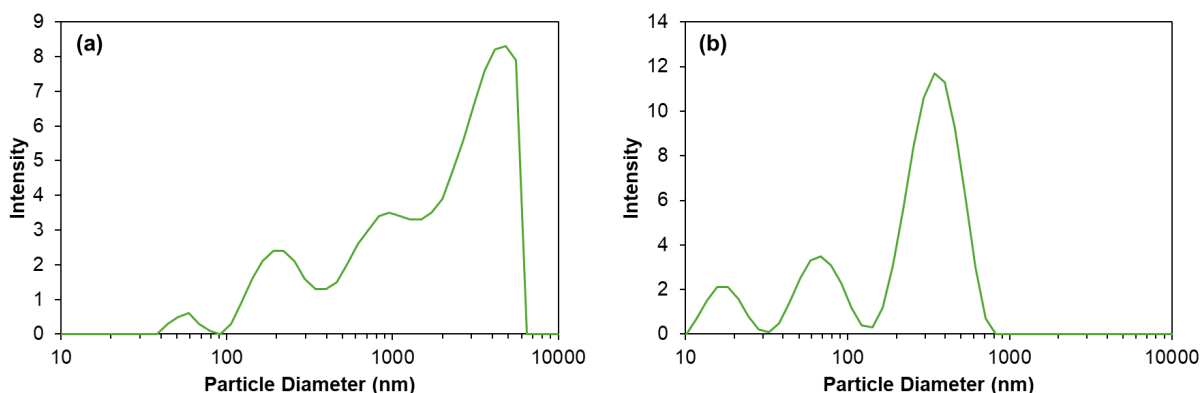


**Figure 19:** DLS plots for LNCs dispersed in water (a) and water + Tween 20 (b).

#### 4.3.1.3 SEM imaging

After fabrication of the composites, EDS was performed to verify the LNCs composition (**Figure 20**), while elemental mapping and SEM images were acquired to determine their dispersion (**Figure 21** & **Figure 22**, respectively). As shown in **Figure 20**, the area marked in red from the SEM image contained a white particle roughly 300 nm in diameter. EDS in this area determined 1.09 wt.% phosphorus and 0.75 wt.% sodium. Since phosphorus and sodium are major components of the LNC synthesis, originating from APP and sodium hydroxide, respectively, this confirms that the white particle is indeed an LNC. This was further supported when considering the N sample contained no white particles nor detectable phosphorus or

sodium (**Figure B1**). Elemental mapping (**Figure 21b**) further demonstrated that the distribution of phosphorus coincided with the white particulates (**Figure 21c**) observed in **Figure 21a**. The apparent noise was attributed to sample thickness, as some LNCs located outside the SEM focal plane (**Figure 21a**) were still detected during elemental mapping.

When comparing 10-LNC to 10-L+A, it can be observed that the LNC sample's white particulates overall remained spherically shaped and dispersed (**Figure 22a**), whereas the L+A sample had webs of white stretching between gaps in the rubber's matrix (**Figure 22b**), further indicating that the lignin is indeed acting as a container for the APP. There was a reduction in the dispersion efficiency of the LNCs between sample 10-LNC (**Figure 22a**) and 5-LNC (**Figure 22a**), as the 5-LNC sample manages to retain spherical LNCs in contrast to the clear aggregation in some area of the 10-LNC sample. **Figure 22d** provides an overview of the size distribution of the LNCs, as particles range in size from 100 nm to 1  $\mu\text{m}$  as discussed in the DLS analysis section (**Figure 19b**). All SEM images can be found in Appendix B (**Figure B2** to **Figure B6**).

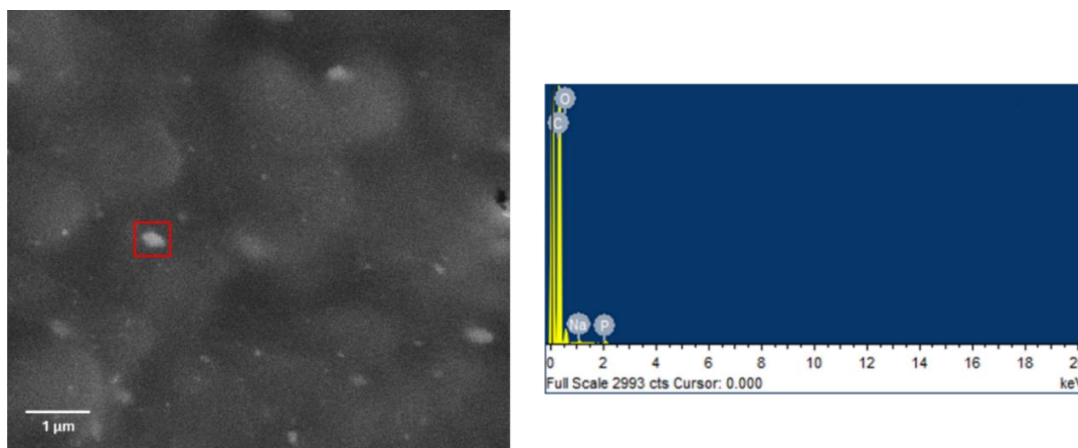


**Figure 20:** EDS from area marked in red for sample 5-LNC.

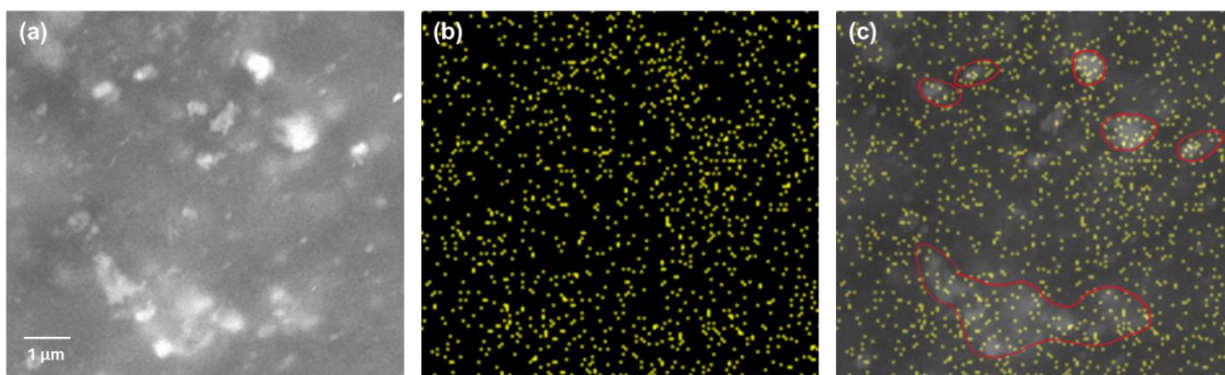


**Figure 21:** E-SEM image of sample 5-LNC (a), with elemental mapping on phosphorus of the image (b), and overlaying the previous images to indicate overlaps (c).

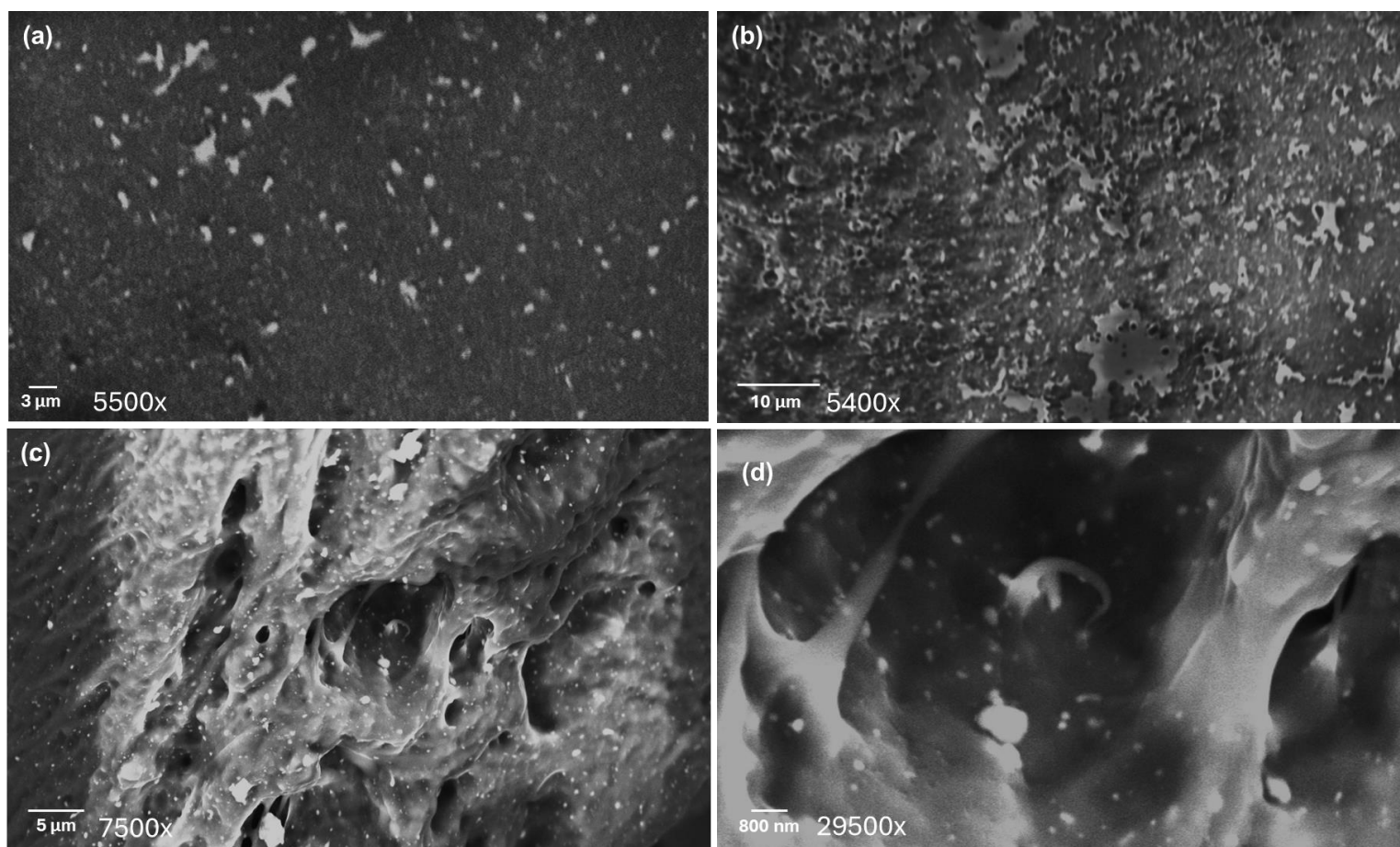


**Figure 22:** E-SEM images of 10-LNC (a), 10-L+A (b), and 5-LNC (c & d).

### **4.3.2 Material characterization**

#### **4.3.2.1 Mechanical properties**

The incorporation of LNCs to natural rubber generally improved all mechanical properties (**Figure 23**); the composites were stronger, stiffer, more ductile, and tougher than sample N which has been seen previously with other nano-lignin + natural rubber composites [143]. When comparing samples N and 2.5-LNC, the minor addition of LNCs cause spikes to the modulus and hardness, but all other properties remained the same as that of sample N. Sample 5-LNC is where increases were seen overall, with a maximum increase at 10-LNC with properties decreasing significantly with sample 15-LNC indicating an optimal loading at 10 wt. % in terms of mechanical properties. In terms of percent change, sample 10-LNC saw a 35% increase to the ultimate tensile strength, a 61% increase to the modulus, a 51% increase to the elongation at break, a 127% increase to the toughness, and a 65% increase to the hardness compared to sample N. Sample 10-L+A did outperform sample 10-LNC in some cases, but did have a lower elongation at break and toughenss with a larger hardness value, showcasing the ability of the nanomaterial to not disrupt the rubber matrix.

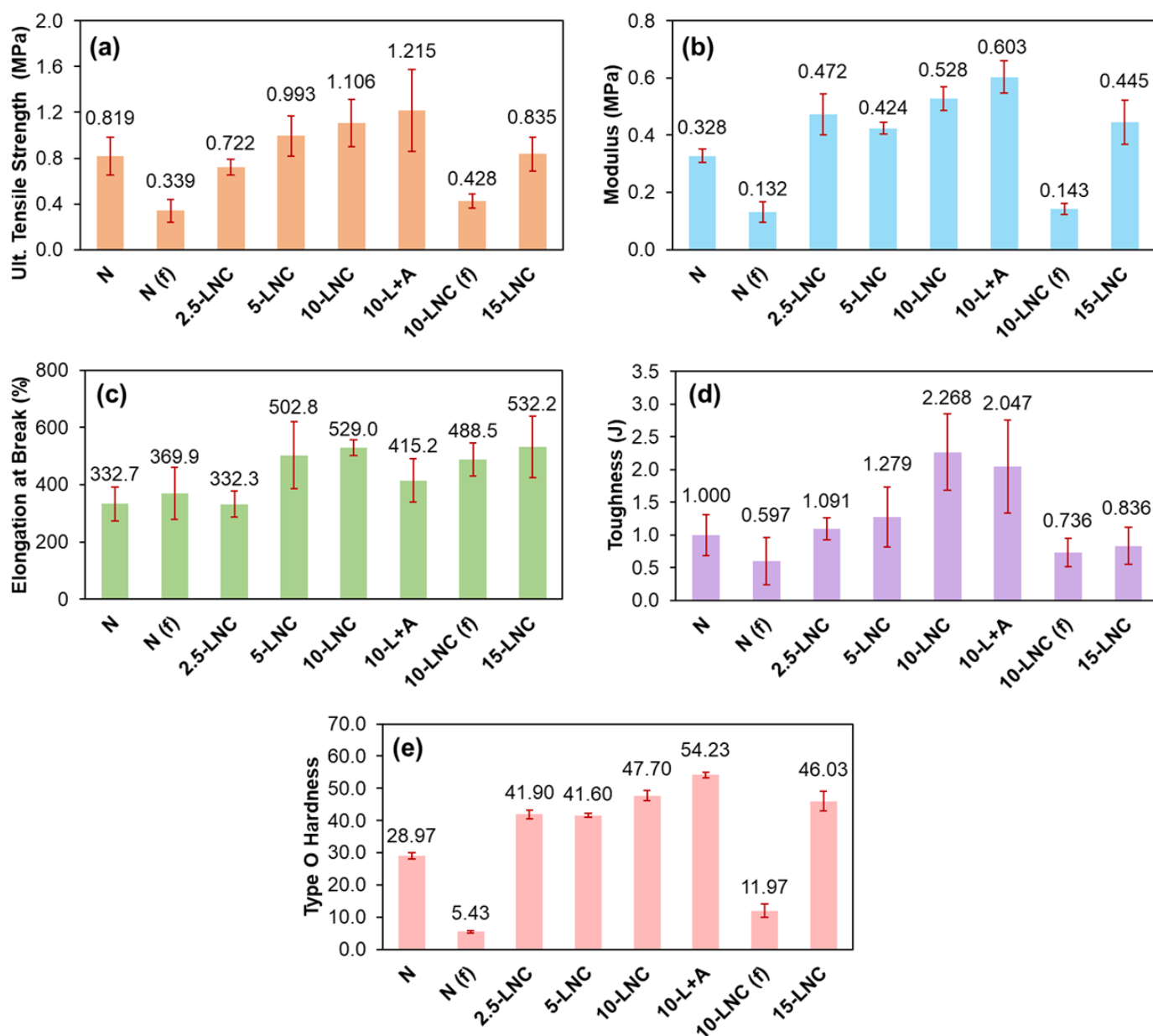


**Figure 23:** Mechanical data for ultimate tensile strength (a), Young's modulus (b), elongation at break (c), toughness (d), and type O hardness (e). Error bars indicate  $\pm$  one standard deviation.

#### 4.3.2.2 Thermogravimetric analysis (TGA)

From the TGA analysis, all rubber composites displayed one major decomposition stage with a minor onset stage (**Figure 24a**). The minor mass loss for NR compounds at the onset (150 - 300 °C) is typically associated with the volatilization of oils [39], and was attributed to the breakdown of short-chain polymers that generate the oils. The major decomposition (300 - 450

°C) is associated with the fragmentation of natural rubber, which generates various hydrocarbon gases [144]. With increasing FR content, the major decomposition yielded lower DTG peaks (**Figure 24a**) due to the increased charring. Interestingly, the 10 wt.% samples all yielded differing char amounts, with the foamed sample (10-LNC (f)) yielding the largest amount (at 6.73%), 1.72% more than the lowest sample at that same concentration (10-LNC) (**Figure 25**). This increase is largely due to lignin's charring characteristics [117], where it preferentially decomposes its aliphatic units through dehydration over its aromatic ones, forming a complex polyaromatic char [118][119]. APP also catalyzes the dehydration of materials to promote char formation, forming more stable and dense chars [135]. The 2.5-LNC sample had a practically identical char value to sample N, with a large jump of 2.43% char when compared to sample 5-LNC. Another major increase of 4.56% was seen between sample 10-LNC and 15-LNC, which are both of similar magnitude when considering the relative change in LNC content.

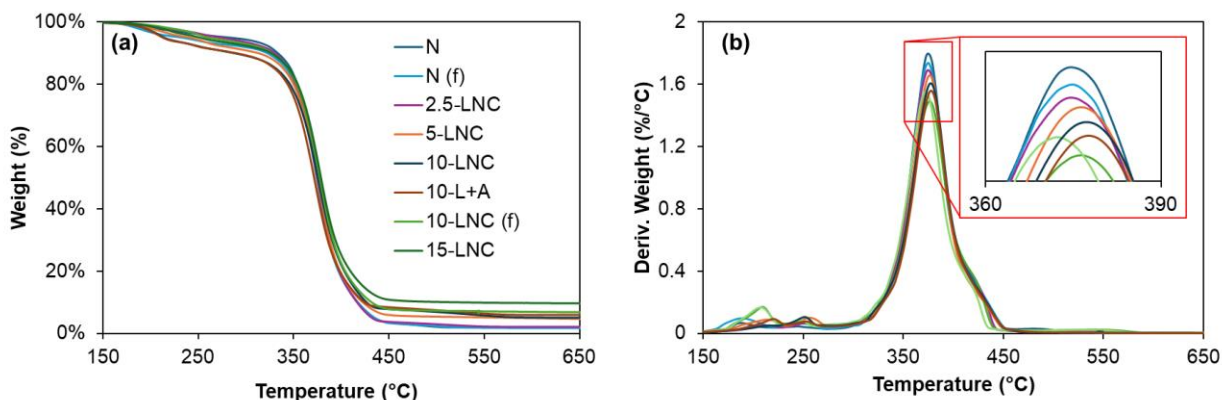


**Figure 24:** TGA (a) and DTG (b) curves – under nitrogen.

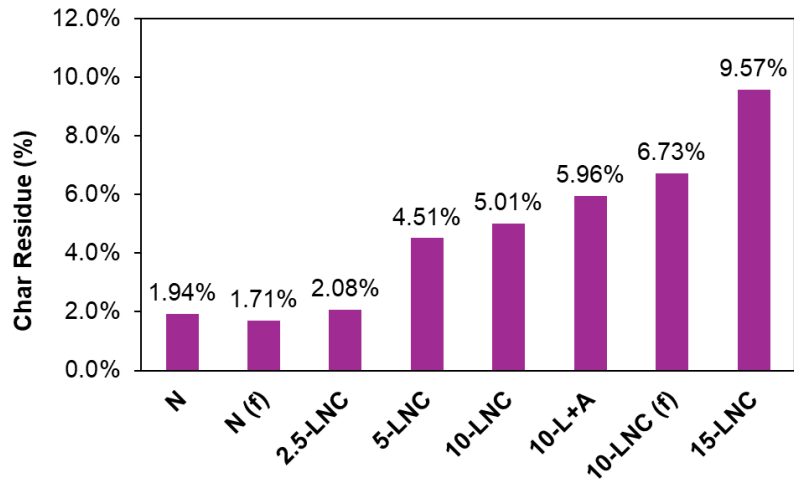


**Figure 25:** Char values following inert TGA.

The thermal decomposition under air (**Figure 26**) was very similar to that observed under nitrogen, except for an additional minor decomposition step between 450 - 550 °C, attributed to the combustion of organic materials [39]. Additionally, all samples tended to decompose slightly faster under air, for example, the peak rate for 5-LNC was 1.66 %/°C under nitrogen compared to 1.74 %/°C under air.

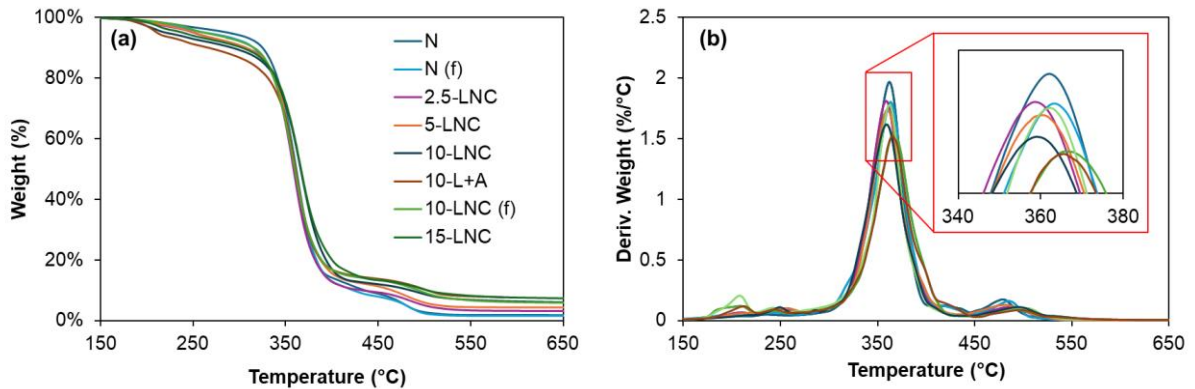


**Figure 26:** TGA (a) and DTG (b) curves – under air.

### 4.3.3 *Flammability testing*

#### 4.3.3.1 *Combustion indices*

Utilizing the TGA data under air, the combustion indices for all samples were calculated using equations (13) to (16) (**Figure 27a**). To better illustrate the trends, the percent “improvement” for each sample was calculated with respect to sample N (**Figure 27b**), where a decrease in any combustion index represents an improvement in flame retardancy. Across all samples, index C showed the least change, frequently showing a change of less than 10%, indicating that any rise/reduction in the max heating rate was offset by changes in the ignition temperature. As shown in **Figure 26a**, increasing the FR content tended to reduce the max heat rate, but also lowered the ignition temperature. The most notable improvements were observed in index S and  $D_b$ , which increased in a somewhat linear fashion with higher LNC content, plateauing at roughly 35% improvements between samples 10-LNC and 15-LNC. These improvements indicated that the LNC are generating dense chars during combustion that limit the rate of mass loss while maintaining the thermal stability of the material. In contrast, sample 10-L+A showed a pronounced decline in performance – index C and  $D_i$  worsening by 21% and 49%, respectively. While many other samples saw slight reductions, the decrease in improvement to  $D_i$  for 10-L+A indicate a worse thermal stability as it is affected by the max rate, ignition time, and time to reach the max rate. The 10-L+A sample also did not have the improvements to  $D_b$  as was seen with the other samples, but still retained some improvement to S. This indicates the inability of sample 10-L+A to retain its shape during combustion and would likely lose its mechanical properties quicker than an LNC sample.

Foaming also had a notable effect. The foamed sample N (sample N (f)) showed improvements in both S and  $D_b$ , likely because its pore structure promoted the formation of a

porous char, which can act as a greater barrier to heat transfer than a solid char under non-flaming conditions. Meanwhile, sample 10-LNC (f) had very similar performance to that of 10-LNC, albeit a much better  $D_i$ .

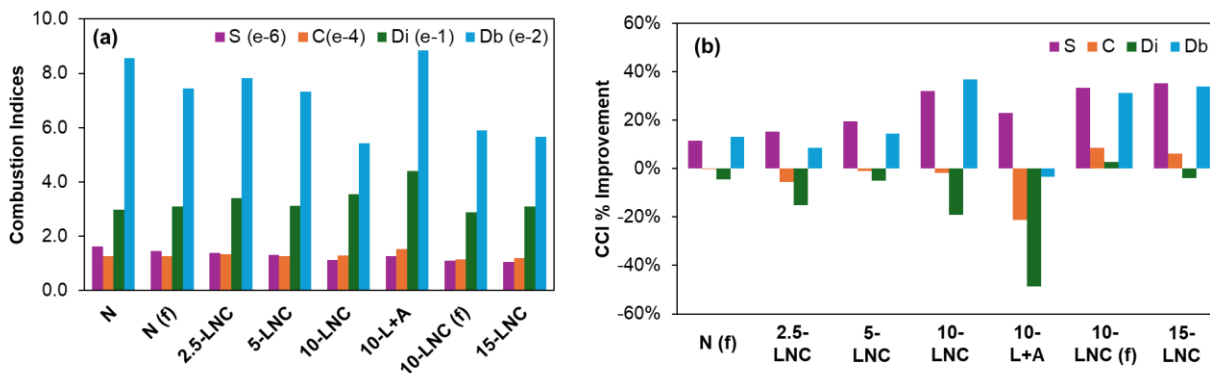


**Figure 27:** Combustion indices,  $S$  ( $\text{min}^{-2} \text{K}^{-3}$ ),  $C$  ( $\text{min}^{-1} \text{K}^{-2}$ ),  $D_i$  ( $\text{min}^{-3}$ ), &  $D_b$  ( $\text{min}^{-4}$ ), (a) and percentage improvement for samples relative to the values of sample N (b).

#### 4.3.3.2 SDT Analysis

The combustion indices are based on mass loss curves, but a more complete analysis requires investigating the actual heat released by the samples during combustion events [145]. **Figure 28** presents the HRR for select samples, all of which exhibit two major peaks, with the combustion calorimetry parameters shown in **Table 12**. The first peak ( $\sim 400^\circ \text{C}$ ) aligns with the major TGA peak (**Figure 26a**) and represents the generation of hydrocarbon gases from sample N, while the second peak ( $\sim 500^\circ \text{C}$ ) corresponds to the combustion peak. As shown below, the primary heat release occurs during combustion, whereas the combustion indices emphasized the first peak. Consistent with the combustion indices, sample N displayed the poorest fire performance, generating the highest heat release, though sample N (f) exhibited noticeable improvement. All other samples containing 10 wt.% FR showed very similar results, all lowering the combustion pHRR by approximately 40%. Between them, the 10-L+A sample outperformed the 10-LNC sample slightly, with lower parameters across the board. The best

performance was observed for the 10-LNC (f) sample, which achieved the lowest FGC (80.15), representing a 13.7% reduction compared to sample N. Overall, these results indicate that the processing method has little impact on the heat release during the combustion, whereas filler concentration exerts a stronger effect.

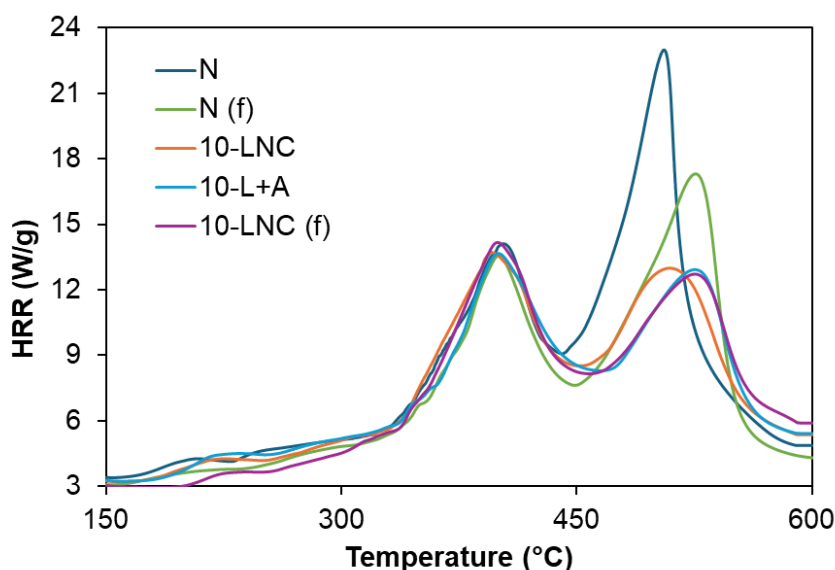


**Figure 28:** HRR curves for select samples measured via SDT.

**Table 12:** Heat release data for select samples obtained via SDT.

|            | pHRR (W/g) | mHRR (W/g) | T <sub>pHRR</sub> (°C) | THR (kJ/g) | T <sub>50%</sub> (°C) | T <sub>95%</sub> (°C) | FGC (J/g/K) |
|------------|------------|------------|------------------------|------------|-----------------------|-----------------------|-------------|
| N          | 22.99      | 9.16       | 505.58                 | 10.89      | 199.36                | 557.35                | 92.83       |
| N (f)      | 17.31      | 7.93       | 525.85                 | 10.46      | 202.16                | 598.43                | 85.36       |
| 10-LNC     | 13.72      | 8.20       | 395.62                 | 9.90       | 198.70                | 562.48                | 84.13       |
| 10-L+A     | 13.66      | 8.07       | 399.99                 | 9.76       | 198.27                | 562.80                | 83.05       |
| 10-LNC (f) | 14.17      | 7.96       | 399.67                 | 9.57       | 202.59                | 566.45                | 80.15       |

#### 4.3.3.3 Linear Burn & LOI

The linear burn rate and LOI results are presented in **Figure 29**, showing a strong inverse relationship between the two tests. As the linear burn rate decreases, the LOI increases – both indicating improved flame retardancy. However, all samples exhibited an LOI below 21%, suggesting that they will readily burn under atmospheric conditions. Unlike the earlier non-

flaming assessments, sample N (f) performed worse here, as its porous structure facilitated flame propagation. In contrast, the 10-LNC (f) sample showed the best performance, with a 78% reduction in burn rate compared to sample N (and an 84% reduction compared to sample N (f)), suggesting a possible synergistic effect between foamed structures and LNCs. As LNC concentration increased, more pronounced char formation was observed, unlike sample N, which primarily decomposed into a greasy, short-chain polymer residue. This greasy residue can be seen in **Figure 30a** & **Figure 30b**, just below the site of burning. **Figure 30c** showcases the char formed from sample 10-LNC after an LOI test. The char structure laid on top of the site of burning and formed a somewhat porous structure.

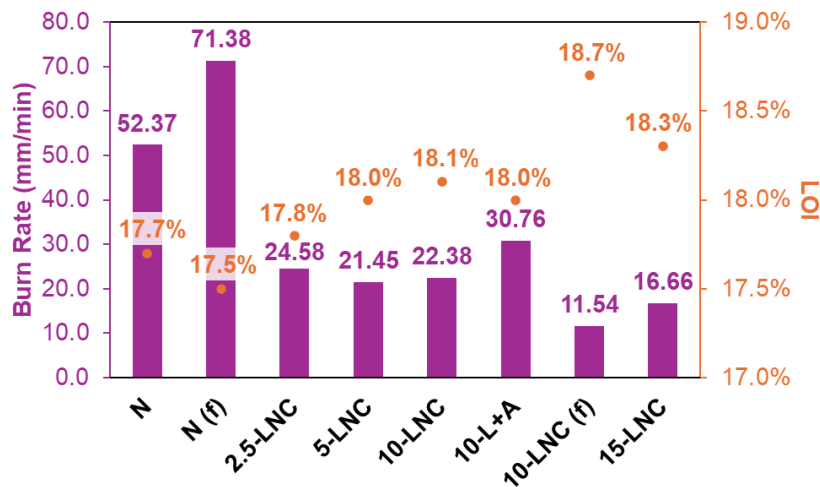


**Figure 29:** Linear burn (purple) and LOI data (orange).

**Table 13:** UL-94 horizontal burn (HB) test ratings.

|            | Rating |
|------------|--------|
| N          | Failed |
| N (f)      | Failed |
| 2.5-LNC    | HB     |
| 5-LNC      | HB     |
| 10-LNC     | HB     |
| 10-L+A     | HB     |
| 10-LNC (f) | HB     |
| 15-LNC     | HB     |

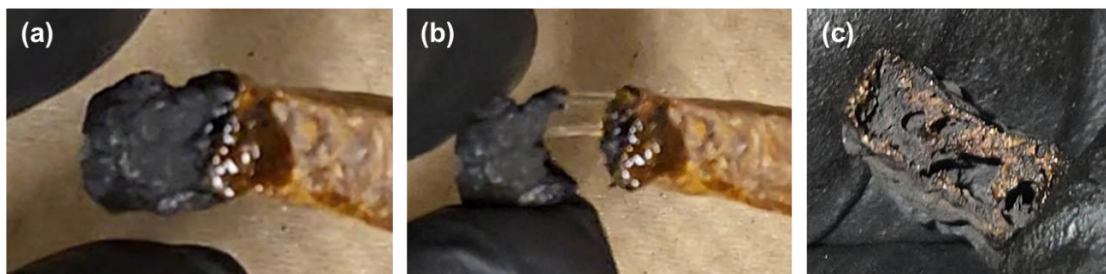


**Figure 30:** Images of sample 5-LNC after LOI showcasing the char formed during burning (left, middle), and the char's porous structure (right).

#### 4.4 Conclusions

Lignin nanocontainers (LNCs) were successfully synthesized using Kraft lignin and employed to deliver a hydrophilic flame retardant within a hydrophobic polymer matrix. The natural rubber (NR)/LNC composites demonstrated significant improvements to both flame properties and mechanical properties, particularly at 10 wt. % loading. Combustion indices improved by 35%, the peak heat release rate during combustion decreased by 43%, the linear burn rate dropped by 57%, toughness increased by 127%, and a UL-94 HB flammability rating was achieved where the control sample had previously failed. The LNCs appeared to be even more effective at providing flame retardancy in foams, with the foamed 10-LNC sample having the largest LOI and lowest linear burn rate. However, the melt-blended composite held very similar improvements to the flame retardancy, but was significantly worse in certain combustion indices, indicating potential poor retention of mechanical properties during burning as it tended to lose mass extremely quick Future work could include systematic comparisons with melt-blended materials and further optimization of the LNC synthesis process to improve scalability and practical applicability.

## Chapter 5: Concluding Remarks

The constant search for sustainable additives is an important yet never-ending task for research. New and old materials alike will constantly find applications in new niches and have an impact, no matter how small. This thesis focused on the versatility of Kraft lignin as a functional additive in hydrophobic polymers at various stages of valorization, from impure, sulfonated lignin, to purified lignin nano-containers. The conclusions for both studies are summarized below:

**Effects of ash content and loading in PVC:** The acid precipitation and washing of Kraft lignin (HpH) successfully purified and lowered the ash content (dubbed Wash lignin), but not as much as the industrially purified lignin (LpH) which had the most obvious effects on the mechanical properties, with the elongation at break reducing by 73.8% at 18 wt.% loading. LpH lignin at the same concentration only saw a reduction of 38.7% whilst improving both the tensile strength and the modulus by 10.5% and 9.56% respectively. This lignin also managed to reduce combustion indices by up to 80% while only slightly reducing the LOI. The Wash lignin typically performed in between these two lignins but behaved more as the LpH lignin. The exception being that the Wash lignin composite retained the most heat capacity (-5.14%) whilst both the HpH and LpH composites lowered it by similar amounts (-21.3%). Finally, through the modelling of the solid-state kinetics, it was shown that the incorporation of lignin altered the apparent mechanism from nucleating to diffusion-controlled during the dehydrochlorination of PVC.

**Synthesis of APP-filled lignin nano-containers:** Lignin was successfully crosslinked using IPDI to form APP-filled LNCs. The properties of the nanomaterial were thoroughly explored, and the dispersion was verified through E-SEM imaging. The LNC composites were

compared to a bulk-incorporated lignin & APP composite as well as foamed LNC composites in a variety of mechanical and flammability tests. The 10 wt.% loading of LNCs improved combustion indices by 35%, the peak heat release rate during combustion was reduced by 43%, the linear burn rate decreased by 57%, toughness increased by 127%, and a UL-94 HB flammability rating was achieved where the control sample had previously failed. Interestingly, the foamed sample at 10 wt. % had a larger LOI and nearly half the linear burn rate compared to its non-foamed counterpart, indicating some synergism between the LNC and foamed polymers in particular. The nano-encapsulation of flame retardants can be an appealing way of obtaining balanced flame retardant and physicomechanical properties as opposed to bulk incorporation of flame retardants.

Overall, the work here showcased lignin's ability to act as a flame retarding biomaterial while also having applications in advanced material applications through some additional modifications. While more work is required to see it used industrially, lignin has very unique properties and its potential should not be overlooked.

In terms of future research, it would be worth exploring the use of fractionated lignin in polymer composites, but while a slimmer PDI would improve consistency and mechanical properties, it's not obvious if the improvement would be worth the additional effort. Additionally, a production cost and life cycle analysis could shed additional light on the applicability of lignin as a sustainable filler for less restrictive applications. Lignin also has innate antimicrobial and UV resistant properties, so systems that would benefit from this should take priority. Lastly, as fire propagation is a complex subject, there are various other testing procedures to validate lignin's ability to improve flame behaviour of composites, namely cone calorimetry and smoke generation analysis.

## References

- [1] B. von Vacano *et al.*, “Sustainable Design of Structural and Functional Polymers for a Circular Economy,” *Angew. Chemie Int. Ed.*, vol. 62, no. 12, p. e202210823, Mar. 2023, doi: 10.1002/ANIE.202210823.
- [2] R. Geyer, J. R. Jambeck, and K. L. Law, “Production, use, and fate of all plastics ever made,” *Sci. Adv.*, vol. 3, no. 7, Jul. 2017, doi: 10.1126/SCIADV.1700782.
- [3] A. Chamas *et al.*, “Degradation Rates of Plastics in the Environment,” *ACS Sustain. Chem. Eng.*, vol. 8, no. 9, pp. 3494–3511, Mar. 2020, doi: 10.1021/ACSSUSCHEMENG.9B06635/ASSET/IMAGES/LARGE/SC9B06635\_0009.JPEG.
- [4] R. Beiras, E. Verdejo, P. Campoy-López, and L. Vidal-Liñán, “Aquatic toxicity of chemically defined microplastics can be explained by functional additives,” *J. Hazard. Mater.*, vol. 406, p. 124338, Mar. 2021, doi: 10.1016/J.JHAZMAT.2020.124338.
- [5] Muhammadi, Shabina, M. Afzal, and S. Hameed, “Bacterial polyhydroxyalkanoates-eco-friendly next generation plastic: Production, biocompatibility, biodegradation, physical properties and applications,” *Green Chem. Lett. Rev.*, vol. 8, no. 3–4, pp. 56–77, Oct. 2015, doi: 10.1080/17518253.2015.1109715.
- [6] W. He, P. Song, B. Yu, Z. Fang, and H. Wang, “Flame retardant polymeric nanocomposites through the combination of nanomaterials and conventional flame retardants,” *Prog. Mater. Sci.*, vol. 114, p. 100687, Oct. 2020, doi: 10.1016/j.pmatsci.2020.100687.
- [7] Q. Wu *et al.*, “Historical trends and ecological risks of polybrominated diphenyl ethers (PBDEs) and alternative halogenated flame retardants (AHFRs) in a mangrove in South China,” *Sci. Total Environ.*, vol. 599–600, pp. 181–187, Dec. 2017, doi: 10.1016/J.SCITOTENV.2017.05.002.
- [8] J. W. Mitchell, “The History and Future Trends of Non-Halogenated Flame Retarded Polymers,” *Non-Halogenated Flame Retard. Handb.*, pp. 1–16, Apr. 2014, doi: 10.1002/9781118939239.CH1.
- [9] R. B. Santos, E. A. Capanema, M. Y. Balakshin, H. M. Chang, and H. Jameel, “Lignin structural variation in hardwood species,” *J. Agric. Food Chem.*, vol. 60, no. 19, pp. 4923–4930, May 2012, doi: 10.1021/JF301276A/ASSET/IMAGES/LARGE/JF-2012-01276A\_0003.JPEG.
- [10] A. Le Floch, M. Jourdes, and P. L. Teissedre, “Polysaccharides and lignin from oak wood used in cooperage: Composition, interest, assays: A review,” *Carbohydr. Res.*, vol. 417, pp. 94–102, Nov. 2015, doi: 10.1016/J.CARRES.2015.07.003.
- [11] D. S. Bajwa, G. Pourhashem, A. H. Ullah, and S. G. Bajwa, “A concise review of current lignin production, applications, products and their environmental impact,” *Ind. Crops Prod.*, vol. 139, p. 111526, Nov. 2019, doi: 10.1016/J.INDCROP.2019.111526.
- [12] D. Stewart, “Lignin as a base material for materials applications: Chemistry, application and economics,” *Ind. Crops Prod.*, vol. 27, no. 2, pp. 202–207, Mar. 2008, doi: 10.1016/J.INDCROP.2007.07.008.
- [13] H. Chen, K. Wan, F. Zheng, Z. Zhang, Y. Zhang, and D. Long, “Mechanism insight into photocatalytic conversion of lignin for valuable chemicals and fuels production: A state-of-the-art review,” *Renew. Sustain. Energy Rev.*, vol. 147, no. May, p. 111217, 2021, doi: 10.1016/j.rser.2021.111217.

- [14] H. Luo and M. M. Abu-Omar, "Chemicals From Lignin," *Encycl. Sustain. Technol.*, pp. 573–585, Jul. 2017, doi: 10.1016/B978-0-12-409548-9.10235-0.
- [15] R. Gaspar and P. Fardim, "Lignin-based materials for emerging advanced applications," *Curr. Opin. Green Sustain. Chem.*, vol. 41, p. 100834, Jun. 2023, doi: 10.1016/J.COGSC.2023.100834.
- [16] N. N. Solihat *et al.*, "Lignin as an Active Biomaterial: A Review," *J. Sylva Lestari*, vol. 9, no. 1, pp. 1–22, Jan. 2021, doi: 10.23960/JSL191-22.
- [17] M. R. Ridho *et al.*, "Lignin as Green Filler in Polymer Composites: Development Methods, Characteristics, and Potential Applications," *Adv. Mater. Sci. Eng.*, vol. 2022, no. 1, p. 1363481, Jan. 2022, doi: 10.1155/2022/1363481.
- [18] E. Adler, "Lignin chemistry-past, present and future," *Wood Sci. Technol.*, vol. 11, no. 3, pp. 169–218, Sep. 1977, doi: 10.1007/BF00365615/METRICS.
- [19] A. Awal and M. Sain, "Spectroscopic studies and evaluation of thermorheological properties of softwood and hardwood lignin," *J. Appl. Polym. Sci.*, vol. 122, no. 2, pp. 956–963, Oct. 2011, doi: 10.1002/APP.34211.
- [20] B. Jiang *et al.*, "Lignin-Based Materials for Additive Manufacturing: Chemistry, Processing, Structures, Properties, and Applications," *Adv. Sci.*, vol. 10, no. 9, pp. 1–33, 2023, doi: 10.1002/advs.202206055.
- [21] D. D. S. Argyropoulos *et al.*, "Kraft Lignin: A Valuable, Sustainable Resource, Opportunities and Challenges," *ChemSusChem*, vol. 16, no. 23, Dec. 2023, doi: 10.1002/cssc.202300492.
- [22] L. Kouisni, A. Gagné, K. Maki, P. Holt-Hindle, and M. Paleologou, "LignoForce System for the Recovery of Lignin from Black Liquor: Feedstock Options, Odor Profile, and Product Characterization," *ACS Sustain. Chem. Eng.*, vol. 4, no. 10, pp. 5152–5159, Oct. 2016, doi: 10.1021/acssuschemeng.6b00907.
- [23] T. Aro and P. Fatehi, "Production and Application of Lignosulfonates and Sulfonated Lignin," *ChemSusChem*, vol. 10, no. 9, pp. 1861–1877, May 2017, doi: 10.1002/CSSC.201700082.
- [24] A. Vishtal and A. Kraslawski, "Challenges in industrial applications of technical lignins," *BioResources*, vol. 6, no. 3, pp. 3547–3568, 2011, doi: 10.15376/biores.6.3.vishtal.
- [25] M. K. R. Konduri and P. Fatehi, "Production of Water-Soluble Hardwood Kraft Lignin via Sulfomethylation Using Formaldehyde and Sodium Sulfite," *ACS Sustain. Chem. Eng.*, vol. 3, no. 6, pp. 1172–1182, Jun. 2015, doi: 10.1021/acssuschemeng.5b00098.
- [26] J. Ruwoldt, K. Syverud, and M. Tanase-Opedal, "Purification of soda lignin," *Sustain. Chem. Environ.*, vol. 6, no. February, p. 100102, 2024, doi: 10.1016/j.scenv.2024.100102.
- [27] J.-K. Xu and R.-C. Sun, "Recent Advances in Alkaline Pretreatment of Lignocellulosic Biomass," in *Biomass Fractionation Technologies for a Lignocellulosic Feedstock Based Biorefinery*, Elsevier, 2016, pp. 431–459.
- [28] F. José Borges Gomes, R. E. de Souza, E. O. Brito, and R. C. Costa Lelis, "A review on lignin sources and uses," *J. Appl. Biotechnol. Bioeng.*, vol. 7, no. C, pp. 100–105, 2020, doi: 10.15406/jabb.2020.07.00222.
- [29] M. Yáñez-S *et al.*, "Physicochemical characterization of ethanol organosolv lignin (EOL) from Eucalyptus globulus: Effect of extraction conditions on the molecular structure," *Polym. Degrad. Stab.*, vol. 110, pp. 184–194, Dec. 2014, doi:

- 10.1016/j.polymdegradstab.2014.08.026.
- [30] A. Eraghi Kazzaz and P. Fatehi, “Technical lignin and its potential modification routes: A mini-review,” *Ind. Crops Prod.*, vol. 154, no. May, 2020, doi: 10.1016/j.indcrop.2020.112732.
  - [31] T. V. Lourençon, F. A. Hansel, T. A. Da Silva, L. P. Ramos, G. I. B. De Muniz, and W. L. E. Magalhães, “Hardwood and softwood kraft lignins fractionation by simple sequential acid precipitation,” *Sep. Purif. Technol.*, vol. 154, pp. 82–88, 2015, doi: 10.1016/j.seppur.2015.09.015.
  - [32] K. Komisarz, T. M. Majka, and K. Pielichowski, “Chemical and Physical Modification of Lignin for Green Polymeric Composite Materials,” *Materials (Basel)*, vol. 16, no. 1, 2023, doi: 10.3390/ma16010016.
  - [33] L. -S. Ebers *et al.*, “<sc>3D</sc> printing of lignin: Challenges, opportunities and roads onward,” *Biopolymers*, vol. 112, no. 6, Jun. 2021, doi: 10.1002/bip.23431.
  - [34] J. Köhnke *et al.*, “Comparison of four technical lignins as a resource for electrically conductive carbon particles,” *BioResources*, vol. 14, no. 1, pp. 1091–1109, Dec. 2018, doi: 10.15376/biores.14.1.1091-1109.
  - [35] F. A. Tanjung, R. A. Kuswardani, C. I. Idumah, J. P. Siregar, and A. Karim, “Characterization of mechanical and thermal properties of esterified lignin modified polypropylene composites filled with chitosan fibers,” *Polym. Polym. Compos.*, vol. 30, Jan. 2022, doi: 10.1177/09673911221082482.
  - [36] M. Reza Barzegari, A. Alemdar, Y. Zhang, and D. Rodrigue, “Mechanical and rheological behavior of highly filled polystyrene with lignin,” *Polym. Compos.*, vol. 33, no. 3, pp. 353–361, Mar. 2012, doi: 10.1002/pc.22154.
  - [37] X. Zhao *et al.*, “Effect of lignin esters on improving the thermal properties of poly(vinyl chloride),” *J. Appl. Polym. Sci.*, vol. 136, no. 11, pp. 1–10, 2019, doi: 10.1002/app.47176.
  - [38] O. A. T. Dias, M. Sain, I. Cesarino, and A. L. Leão, “Development of high bio-content polypropylene composites with different industrial lignins,” *Polym. Adv. Technol.*, vol. 30, no. 1, pp. 70–78, 2019, doi: 10.1002/pat.4444.
  - [39] M. J. Fernández-Berridi, N. González, A. Mugica, and C. Bernicot, “Pyrolysis-FTIR and TGA techniques as tools in the characterization of blends of natural rubber and SBR,” *Thermochim. Acta*, vol. 444, no. 1, pp. 65–70, 2006, doi: 10.1016/j.tca.2006.02.027.
  - [40] P. Yu *et al.*, “A comprehensive study on lignin as a green alternative of silica in natural rubber composites,” *Polym. Test.*, vol. 54, pp. 176–185, Sep. 2016, doi: 10.1016/j.polymertesting.2016.07.014.
  - [41] C. Jiang, H. He, X. Yao, P. Yu, L. Zhou, and D. Jia, “The aggregation structure regulation of lignin by chemical modification and its effect on the property of lignin/styrene–butadiene rubber composites,” *J. Appl. Polym. Sci.*, vol. 135, no. 5, Feb. 2018, doi: 10.1002/app.45759.
  - [42] R. Shorey, A. Gupta, and T. H. Mekonnen, “Hydrophobic modification of lignin for rubber composites,” *Ind. Crops Prod.*, vol. 174, p. 114189, Dec. 2021, doi: 10.1016/j.indcrop.2021.114189.
  - [43] R. Liu, Y. Peng, J. Cao, and Y. Chen, “Comparison on properties of lignocellulosic flour/polymer composites by using wood, cellulose, and lignin flours as fillers,” *Compos. Sci. Technol.*, vol. 103, pp. 1–7, Oct. 2014, doi:

- 10.1016/j.compscitech.2014.08.005.
- [44] F. A. Tanjung, S. Husseinsyah, and K. Hussin, "Chitosan-filled polypropylene composites: The effect of filler loading and organosolv lignin on mechanical, morphological and thermal properties," *Fibers Polym.*, vol. 15, no. 4, pp. 800–808, 2014, doi: 10.1007/s12221-014-0800-0.
  - [45] J. Deng *et al.*, "Sub-micro and nano-lignin materials: Small size and rapid progress," *Ind. Crops Prod.*, vol. 164, p. 113412, Jun. 2021, doi: 10.1016/j.indcrop.2021.113412.
  - [46] F. Lu, Y. Wang, D. Sun, Y. Fu, F. Zhang, and R. Sun, "Research progress on the preparation of lignin micro/nano-particles and their biomedical applications," *Green Chem.*, vol. 27, no. 19, pp. 5400–5422, 2025, doi: 10.1039/D5GC00178A.
  - [47] Y. Ikeda *et al.*, "Reinforcing biofiller 'Lignin' for high performance green natural rubber nanocomposites," *RSC Adv.*, vol. 7, no. 9, pp. 5222–5231, 2017, doi: 10.1039/c6ra26359c.
  - [48] F. Xiong, Y. Wu, G. Li, Y. Han, and F. Chu, "Transparent Nanocomposite Films of Lignin Nanospheres and Poly(vinyl alcohol) for UV-Absorbing," *Ind. Eng. Chem. Res.*, vol. 57, no. 4, pp. 1207–1212, Jan. 2018, doi: 10.1021/acs.iecr.7b04108.
  - [49] G. Camino, L. Costa, and M. P. Luda di Cortemiglia, "Overview of fire retardant mechanisms," *Polym. Degrad. Stab.*, vol. 33, no. 2, pp. 131–154, 1991, doi: 10.1016/0141-3910(91)90014-I.
  - [50] ASTM, "Test Method for Heat and Visible Smoke Release Rates for Materials and Products Using an Oxygen Consumption Calorimeter," *ASTM Standards*. ASTM International, West Conshohocken, PA, Mar. 01, 2023, doi: 10.1520/E1354-23.
  - [51] ASTM, "Test Method for Determining Flammability Characteristics of Plastics and Other Solid Materials Using Microscale Combustion Calorimetry." ASTM International, West Conshohocken, PA, Oct. 01, 2021, doi: 10.1520/D7309-21B.
  - [52] R. Sonnier, H. Vahabi, L. Ferry, and J.-M. Lopez-Cuesta, "Pyrolysis-Combustion Flow Calorimetry: A Powerful Tool To Evaluate the Flame Retardancy of Polymers," 2012, pp. 361–390.
  - [53] ASTM, "Standard Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics ( Oxygen Index ) 1," *ASTM Stand.*, pp. 1–14, 2011, doi: 10.1520/D2863-23.
  - [54] [ASTM] American Society for Testing and Materials, "ASTM D3801: Test Method for Measuring the Comparative Burning Characteristics of Solid Plastics in a Vertical Position," *ASTM Int.*, pp. 1–9, 2019, doi: 10.1520/D3801-20A.
  - [55] ASTM International, "ASTM D635-22 Standard Test Method for Rate of Burning and/or Extent and Time of Burning of Plastics in a Horizontal Position," *ASTM Int.*, vol. i, p. 8, 2022, doi: 10.1520/D0635-22.2.
  - [56] M. Bar, R. Alagirusamy, and A. Das, "Flame retardant polymer composites," *Fibers Polym.*, vol. 16, no. 4, pp. 705–717, 2015, doi: 10.1007/s12221-015-0705-6.
  - [57] S. Boryniec and W. Przygocki, "Polymer Combustion Processes. 3. Flame Retardants for Polymeric Materials," *Prog. Rubber Plast. Technol.*, vol. 17, no. 2, pp. 127–148, May 2001, doi: 10.1177/147776060101700204.
  - [58] M. Dogan, S. D. Dogan, L. A. Savas, G. Ozelik, and U. Tayfun, "Flame retardant effect of boron compounds in polymeric materials," *Compos. Part B Eng.*, vol. 222, no. February, p. 109088, 2021, doi: 10.1016/j.compositesb.2021.109088.
  - [59] N. K. Kim, S. Dutta, and D. Bhattacharyya, "A review of flammability of natural fibre

- reinforced polymeric composites,” *Compos. Sci. Technol.*, vol. 162, pp. 64–78, Jul. 2018, doi: 10.1016/j.compscitech.2018.04.016.
- [60] A. B. Morgan and J. W. Gilman, “An overview of flame retardancy of polymeric materials: Application, technology, and future directions,” *Fire and Materials*, vol. 37, no. 4, pp. 259–279, Jun. 2013, doi: 10.1002/fam.2128.
- [61] S. Shaw, “Halogenated Flame Retardants: Do the Fire Safety Benefits Justify the Risks?,” *Rev. Environ. Health*, vol. 25, no. 4, Jan. 2010, doi: 10.1515/REVEH.2010.25.4.261.
- [62] D. Gheysari and A. Behjat, “The effect of high-energy electron beam irradiation and content of ATH upon mechanical and thermal properties of EVA copolymer,” *Eur. Polym. J.*, vol. 38, no. 6, pp. 1087–1093, Jun. 2002, doi: 10.1016/S0014-3057(01)00281-6.
- [63] F. Laoutid, P. Gaudon, J.-M. Taulemesse, J. M. Lopez Cuesta, J. I. Velasco, and A. Piechaczyk, “Study of hydromagnesite and magnesium hydroxide based fire retardant systems for ethylene–vinyl acetate containing organo-modified montmorillonite,” *Polym. Degrad. Stab.*, vol. 91, no. 12, pp. 3074–3082, Dec. 2006, doi: 10.1016/j.polymdegradstab.2006.08.011.
- [64] S. A. A. Ramazani, A. Rahimi, M. Frounchi, and S. Radman, “Investigation of flame retardancy and physical–mechanical properties of zinc borate and aluminum hydroxide propylene composites,” *Mater. Des.*, vol. 29, no. 5, pp. 1051–1056, Jan. 2008, doi: 10.1016/j.matdes.2007.04.003.
- [65] H. Nabipour and Y. Hu, “Introduction to flame retardants for polymeric materials,” *Bio-based Flame-Retardant Technol. Polym. Mater.*, pp. 1–27, Jan. 2022, doi: 10.1016/B978-0-323-90771-2.00018-3.
- [66] N. Illy, M. Fache, R. Ménard, C. Negrell, S. Caillol, and G. David, “Phosphorylation of bio-based compounds: the state of the art,” *Polym. Chem.*, vol. 6, no. 35, pp. 6257–6291, 2015, doi: 10.1039/C5PY00812C.
- [67] J.-B. Zhang, Z.-C. Tan, S.-H. Meng, S.-H. Li, and L.-M. Zhang, “Heat capacity and thermal decomposition of dicyandiamide,” *Thermochim. Acta*, vol. 307, no. 1, pp. 11–15, Nov. 1997, doi: 10.1016/S0040-6031(97)00323-7.
- [68] V. G. Kiselev and N. P. Gritsan, “Theoretical Study of the 5-Aminotetrazole Thermal Decomposition,” *J. Phys. Chem. A*, vol. 113, no. 15, pp. 3677–3684, Apr. 2009, doi: 10.1021/jp900285y.
- [69] E. Terrell and M. Garcia-Perez, “Application of nitrogen-based blowing agents as an additive in pyrolysis of cellulose,” *J. Anal. Appl. Pyrolysis*, vol. 137, pp. 203–211, Jan. 2019, doi: 10.1016/j.jaap.2018.11.027.
- [70] L. Shumao, R. Jie, Y. Hua, Y. Tao, and Y. Weizhong, “Influence of ammonium polyphosphate on the flame retardancy and mechanical properties of ramie fiber-reinforced poly(lactic acid) biocomposites,” *Polym. Int.*, vol. 59, no. 2, pp. 242–248, Feb. 2010, doi: 10.1002/pi.2715.
- [71] H. Salmah, F. Amri, and H. Kamarudin, “Properties of Chitosan-Filled Polypropylene (PP) Composites: The Effect of Acetic Acid,” *Polym. Plast. Technol. Eng.*, vol. 51, no. 1, pp. 86–91, Jan. 2012, doi: 10.1080/03602559.2011.618156.
- [72] S. Hu, L. Song, H. Pan, Y. Hu, and X. Gong, “Thermal properties and combustion behaviors of flame retarded epoxy acrylate with a chitosan based flame retardant containing phosphorus and acrylate structure,” *J. Anal. Appl. Pyrolysis*, vol. 97, pp.

- 109–115, Sep. 2012, doi: 10.1016/j.jaap.2012.06.003.
- [73] B. P. Chang, S. Thakur, A. K. Mohanty, and M. Misra, “Novel sustainable biobased flame retardant from functionalized vegetable oil for enhanced flame retardancy of engineering plastic,” *Sci. Rep.*, vol. 9, no. 1, p. 15971, Nov. 2019, doi: 10.1038/s41598-019-52039-2.
  - [74] P. Song, Z. Cao, S. Fu, Z. Fang, Q. Wu, and J. Ye, “Thermal degradation and flame retardancy properties of ABS/lignin: Effects of lignin content and reactive compatibilization,” *Thermochim. Acta*, vol. 518, no. 1–2, pp. 59–65, 2011, doi: 10.1016/j.tca.2011.02.007.
  - [75] F. Laoutid, V. Duriez, L. Brison, S. Aouadi, H. Vahabi, and P. Dubois, “Synergistic flame-retardant effect between lignin and magnesium hydroxide in poly(ethylene-co-vinyl acetate),” *Flame Retard. Therm. Stab. Mater.*, vol. 2, no. 1, pp. 9–18, Jan. 2019, doi: 10.1515/flret-2019-0002.
  - [76] A. De Chirico, M. Armanini, P. Chini, G. Cioccolo, F. Provasoli, and G. Audisio, “Flame retardants for polypropylene based on lignin,” *Polym. Degrad. Stab.*, vol. 79, no. 1, pp. 139–145, Jan. 2003, doi: 10.1016/S0141-3910(02)00266-5.
  - [77] L. Liu, M. Qian, P. Song, G. Huang, Y. Yu, and S. Fu, “Fabrication of Green Lignin-based Flame Retardants for Enhancing the Thermal and Fire Retardancy Properties of Polypropylene/Wood Composites,” *ACS Sustain. Chem. Eng.*, vol. 4, no. 4, pp. 2422–2431, Apr. 2016, doi: 10.1021/acssuschemeng.6b00112.
  - [78] Y. Zhang *et al.*, “Functionalizing lignin by in situ solid-phase grafting ammonium polyphosphate for enhancing thermal, flame-retardant, mechanical, and UV-resistant properties of polylactic acid,” *Chem. Eng. J.*, vol. 495, p. 153429, Sep. 2024, doi: 10.1016/j.cej.2024.153429.
  - [79] X. Song *et al.*, “Sustainable lignin-based high-efficiency flame-retardant epoxy resins with excellent mechanical properties,” *Int. J. Biol. Macromol.*, vol. 282, p. 136742, Dec. 2024, doi: 10.1016/j.ijbiomac.2024.136742.
  - [80] D. Meng *et al.*, “Constructing lignin based nanoparticles towards flame retardant thermoplastic polyurethane composites with improved mechanical and oxidation resistant properties,” *Int. J. Biol. Macromol.*, vol. 253, p. 126570, Dec. 2023, doi: 10.1016/j.ijbiomac.2023.126570.
  - [81] T. He, F. Chen, W. Zhu, and N. Yan, “Functionalized lignin nanoparticles for producing mechanically strong and tough flame-retardant polyurethane elastomers,” *Int. J. Biol. Macromol.*, vol. 209, pp. 1339–1351, Jun. 2022, doi: 10.1016/j.ijbiomac.2022.04.089.
  - [82] S. Peil *et al.*, “Encapsulation of Ammonium Polyphosphate in Lignin Nanocontainers Enhances Dispersion and Flame Retardancy in Polylactic Acid Foams,” *ACS Appl. Polym. Mater.*, vol. 6, no. 10, pp. 6096–6107, 2024, doi: 10.1021/acsapm.4c00787.
  - [83] K. J. Arun and M. Meena, “Application of PVC—A superior material in the fields of Science and Technology,” *Polym. Technol. Mater.*, vol. 63, no. 15, pp. 2089–2107, 2024, doi: 10.1080/25740881.2024.2365288.
  - [84] U. Lahl and B. Zeschmar-Lahl, “More than 30 Years of PVC Recycling in Europe—A Critical Inventory,” *Sustain.*, vol. 16, no. 9, 2024, doi: 10.3390/su16093854.
  - [85] Y. Peng, A. Prabhu, and C. Rinke, “Facing our plastic waste crisis: biorecycling as a promising solution,” *Microbiol. Aust.*, vol. 44, no. 1, pp. 52–56, 2023, doi: 10.1071/MA23013.
  - [86] J. Jambeck *et al.*, “the Ocean : the Ocean :,” *Mar. Pollut.*, vol. 347, no. 6223, pp. 768–,

- 2015, [Online]. Available: <https://science.sciencemag.org/CONTENT/347/6223/768.abstract>.
- [87] R. Saad and J. Hawari, "Grafting of lignin onto nanostructured silica SBA-15: Preparation and characterization," *J. Porous Mater.*, vol. 20, no. 1, pp. 227–233, 2013, doi: 10.1007/s10934-012-9592-z.
  - [88] S. B. Patrícia, X. Erdocia, D. A. Gatto, and J. Labidi, "Characterisation of Kraft lignin separated by gradient acid precipitation," *Ind. Crop. Prod.*, vol. 55, pp. 149–154, 2014, doi: 10.1016/j.indcrop.2014.01.023.
  - [89] X. Zhang, X. Feng, W. Guo, C. Zhang, and X. Zhang, "Chemically recyclable polyvinyl chloride-like plastics," *Nat. Commun.*, vol. 15, no. 1, p. 8536, 2024, doi: 10.1038/s41467-024-52852-y.
  - [90] Z. Ait-Touchente, M. Khellaf, G. Raffin, N. Lebaz, and A. Elaissari, "Recent advances in polyvinyl chloride (PVC) recycling," *Polym. Adv. Technol.*, vol. 35, no. 1, pp. 1–27, 2024, doi: 10.1002/pat.6228.
  - [91] H. Vahabi, F. Laoutid, M. Mehrpouya, M. R. Saeb, and P. Dubois, "Flame retardant polymer materials: An update and the future for 3D printing developments," *Mater. Sci. Eng. R Reports*, vol. 144, no. January, p. 100604, 2021, doi: 10.1016/j.mser.2020.100604.
  - [92] I. N. Unar, S. A. Soomro, and S. Aziz, "Effect of Various Additives on the Physical Properties of Polyvinylchloride Resin," *J. Anal. Environ. Chem*, vol. 11, no. 2, pp. 44–50, 2010.
  - [93] I. Mersiowsky, "Mersiowsky 2002- Long-term fate PVC in landfills," *Prog. Polym. Sci.*, vol. 27, pp. 2227–2277, 2002.
  - [94] A. A. Stec *et al.*, "Analysis of toxic effluents released from PVC carpet under different fire conditions," *Chemosphere*, vol. 90, no. 1, pp. 65–71, 2013, doi: 10.1016/j.chemosphere.2012.07.037.
  - [95] X. Jiang, B. Zhu, and M. Zhu, "An overview on the recycling of waste poly(vinyl chloride)," *Green Chem.*, vol. 25, no. 18, pp. 6971–7025, 2023, doi: 10.1039/d3gc02585c.
  - [96] Y. Tong, T. Yang, J. Wang, B. Li, Y. Zhai, and R. Li, "A review on the overall process of lignin to phenolic compounds for chemicals and fuels: From separation and extraction of lignin to transformation," *J. Anal. Appl. Pyrolysis*, vol. 181, no. July, p. 106663, 2024, doi: 10.1016/j.jaap.2024.106663.
  - [97] M. Mariana *et al.*, "A current advancement on the role of lignin as sustainable reinforcement material in biopolymeric blends," *J. Mater. Res. Technol.*, vol. 15, pp. 2287–2316, 2021, doi: 10.1016/j.jmrt.2021.08.139.
  - [98] H. A. Saffian *et al.*, "Mechanical Strength , Thermal Conductivity and Electrical Breakdown of Kenaf Core," *Polymers (Basel)*, vol. 12, p. 1833, 2020.
  - [99] C. Using *et al.*, "Enhancement of the Surface Hydrophilicity of Poly (Vinyl Chloride) Using Hyperbranched Polylysine with Polydopamine," *Coatings*, vol. 14, no. 103, pp. 1–16, 2024.
  - [100] L. Ferry, G. Dorez, A. Taguet, B. Otazaghine, and J. M. Lopez-Cuesta, "Chemical modification of lignin by phosphorus molecules to improve the fire behavior of polybutylene succinate," *Polym. Degrad. Stab.*, vol. 113, pp. 135–143, 2015, doi: 10.1016/j.polymdegradstab.2014.12.015.
  - [101] F. Hewitt and T. R. Hull, "Polymers and Polymeric Composites: A Reference Series,"

- Polym. Polym. Compos. A Ref. Ser.*, 2016, doi: 10.1007/978-3-642-37179-0.
- [102] F. Liu, K. Xu, M. Chen, and D. Cao, "The Rheological and Mechanical Properties of PVC-Lignin Blends," *Int. Polym. Process.*, vol. 27, no. 1, pp. 121–127, 2012.
  - [103] D. Banu, A. El-Aghoury, and D. Feldman, "Contributions to characterization of poly(vinyl chloride)-lignin blends," *J. Appl. Polym. Sci.*, vol. 101, no. 5, pp. 2732–2748, 2006, doi: 10.1002/app.23026.
  - [104] F. Liu, K. Xu, M. Chen, and D. Cao, "The Roles of Polyacrylate in Poly(vinyl chloride)-Lignin Composites," *Polym. Compos.*, vol. 32, no. 9, pp. 1315–1481, 2011, doi: 10.1002/pc.21163.
  - [105] F. Aldaeus, A. M. Olsson, and J. S. Stevanic, "Miniaturized determination of ash content in kraft lignin samples using oxidative thermogravimetric analysis," *Nord. Pulp Pap. Res. J.*, vol. 32, no. 2, pp. 280–282, 2017, doi: 10.3183/npprj-2017-32-02-p280-282.
  - [106] Q. Yang *et al.*, "Combustion, emission and slagging characteristics for typical agricultural crop straw usage in heating plants," *Thermochim. Acta*, vol. 702, no. July 2020, p. 178979, 2021, doi: 10.1016/j.tca.2021.178979.
  - [107] J. Huang *et al.*, "Combustion behaviors of spent mushroom substrate using TG-MS and TG-FTIR: Thermal conversion, kinetic, thermodynamic and emission analyses," *Bioresour. Technol.*, vol. 266, no. June, pp. 389–397, 2018, doi: 10.1016/j.biortech.2018.06.106.
  - [108] S. Vyazovkin, A. K. Burnham, J. M. Criado, L. A. Pérez-Maqueda, C. Popescu, and N. Sbirrazzuoli, "ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data," *Thermochim. Acta*, vol. 520, no. 1–2, pp. 1–19, 2011, doi: 10.1016/j.tca.2011.03.034.
  - [109] R. Zhou, B. Huang, Y. Ding, W. Li, and J. Mu, "Thermal decomposition mechanism and kinetic study of plasticwaste chlorinated polyvinyl chloride," *Polymers (Basel)*, vol. 11, no. 12, 2019, doi: 10.3390/polym11122080.
  - [110] S. R. Naqvi *et al.*, "Pyrolysis of high ash sewage sludge: Kinetics and thermodynamic analysis using Coats-Redfern method," *Renew. Energy*, vol. 131, pp. 854–860, 2019, doi: 10.1016/j.renene.2018.07.094.
  - [111] G. W. Ehrenstein, G. Riedel, and P. Trawiel, *Thermogravimetry (TG)*. 2004.
  - [112] S. Vyazovkin *et al.*, "ICTAC Kinetics Committee recommendations for analysis of multi-step kinetics," *Thermochim. Acta*, vol. 689, no. March, p. 178597, 2020, doi: 10.1016/j.tca.2020.178597.
  - [113] Coats and Redfern, "Kinetic parameter\_Coats and Redfern," *Nature*, vol. 201, pp. 68–69, 1964.
  - [114] E. L. Rodriguez, "Particulate filled polyester composites," *J. Mater. Sci. Lett.*, vol. 6, no. 11, pp. 1280–1282, 1987, doi: 10.1007/BF01794589.
  - [115] J. Zhou *et al.*, "Understanding the pyrolysis mechanism of polyvinylchloride (PVC) by characterizing the chars produced in a wire-mesh reactor," *Fuel*, vol. 166, pp. 526–532, 2016, doi: 10.1016/j.fuel.2015.11.034.
  - [116] M. Zhang, A. Buekens, X. Jiang, and X. Li, "Dioxins and polyvinylchloride in combustion and fires," *Waste Manag. Res.*, vol. 33, no. 7, pp. 630–643, 2015, doi: 10.1177/0734242X15590651.
  - [117] D. W. Rutherford, R. L. Wershaw, C. E. Rostad, and C. N. Kelly, "Effect of formation conditions on biochars: Compositional and structural properties of cellulose, lignin, and pine biochars," *Biomass and Bioenergy*, vol. 46, pp. 693–701, 2012, doi:

- 10.1016/j.biombioe.2012.06.026.
- [118] J. Ruwoldt, F. H. Blindheim, and G. Chinga-Carrasco, "Functional surfaces, films, and coatings with lignin - a critical review," *RSC Adv.*, vol. 13, no. 18, pp. 12529–12553, 2023, doi: 10.1039/d2ra08179b.
  - [119] R. K. Sharma, J. B. Wooten, V. L. Baliga, X. Lin, W. G. Chan, and M. R. Hajaligol, "Characterization of chars from pyrolysis of lignin," *Fuel*, vol. 83, no. 11–12, pp. 1469–1482, 2004, doi: 10.1016/j.fuel.2003.11.015.
  - [120] S. Kubo and J. F. Kadla, "Kraft lignin/poly(ethylene oxide) blends: Effect of lignin structure on miscibility and hydrogen bonding," *J. Appl. Polym. Sci.*, vol. 98, no. 3, pp. 1437–1444, 2005, doi: 10.1002/app.22245.
  - [121] D. S. Rosa, A. R. Rios, H. M. Viana, and M. I. B. Tavares, "Characterization of poly(vinyl chloride) compounds containing different levels of starch," *J. Vinyl Addit. Technol.*, vol. 22, no. 4, pp. 396–404, 2016, doi: 10.1002/vnl.21460.
  - [122] H. Djidjelli, J. J. Martinez-Vega, J. Farenc, and D. Benachour, "Effect of wood flour content on the thermal, mechanical and dielectric properties of poly(vinyl chloride)," *Macromol. Mater. Eng.*, vol. 287, no. 9, pp. 611–618, 2002, doi: 10.1002/1439-2054(20020901)287:9<611::AID-MAME611>3.0.CO;2-L.
  - [123] A. Boukerrou, M. Beztout, H. Djidjelli, S. Krim, and D. Hammiche, "The effect of chemical treatment of cellulose with epoxidized soybean oil (ESO) on the properties PVC/cellulose composites," *Mol. Cryst. Liq. Cryst.*, vol. 556, pp. 223–232, 2012, doi: 10.1080/15421406.2012.635966.
  - [124] N. Dutta and T. K. Maji, "Synergic effect of montmorillonite and microcrystalline cellulose on the physicochemical properties of rice husk/PVC composite," *SN Appl. Sci.*, vol. 2, no. 3, pp. 1–10, 2020, doi: 10.1007/s42452-020-2255-9.
  - [125] W. Liu, D. Q. Chen, Y. Z. Wang, D. Y. Wang, and M. H. Qu, "Char-forming mechanism of a novel polymeric flame retardant with char agent," *Polym. Degrad. Stab.*, vol. 92, no. 6, pp. 1046–1052, 2007, doi: 10.1016/j.polymdegradstab.2007.02.009.
  - [126] P. E. Sánchez-Jiménez, A. Perejón, J. M. Criado, M. J. Diáñez, and L. A. Pérez-Maqueda, "Kinetic model for thermal dehydrochlorination of poly(vinyl chloride)," *Polymer (Guildf.)*, vol. 51, no. 17, pp. 3998–4007, 2010, doi: 10.1016/j.polymer.2010.06.020.
  - [127] J. G. Rosenboom, R. Langer, and G. Traverso, "Bioplastics for a circular economy," *Nat. Rev. Mater.*, vol. 7, no. 2, pp. 117–137, 2022, doi: 10.1038/s41578-021-00407-8.
  - [128] S. Araby, B. Philips, Q. Meng, J. Ma, T. Laoui, and C. H. Wang, "Recent advances in carbon-based nanomaterials for flame retardant polymers and composites," *Compos. Part B Eng.*, vol. 212, p. 108675, May 2021, doi: 10.1016/J.COMPOSITESB.2021.108675.
  - [129] S. Junian, M. Z. H. Makmud, and J. Sahari, "Natural Rubber as Electrical Insulator : A Review," vol. 1, no. 1, pp. 1–12, 2019.
  - [130] L. Wan, C. Deng, Z. Y. Zhao, H. Chen, and Y. Z. Wang, "Flame Retardation of Natural Rubber: Strategy and Recent Progress," *Polym. 2020, Vol. 12, Page 429*, vol. 12, no. 2, p. 429, Feb. 2020, doi: 10.3390/POLYM12020429.
  - [131] R. Silva, A. Barros-Timmons, and P. Quinteiro, "Life cycle assessment of fossil- and bio-based polyurethane foams:a review," *J. Clean. Prod.*, vol. 430, p. 139697, Dec. 2023, doi: 10.1016/j.jclepro.2023.139697.
  - [132] X. Zhao *et al.*, "Lignin-derived flame retardant for improving fire safety and mechanical

- properties of polypropylene,” *J. Appl. Polym. Sci.*, vol. 140, no. 48, pp. 1–10, 2023, doi: 10.1002/app.54739.
- [133] R. Sauerwein, “Mineral Filler Flame Retardants,” in *Non-Halogenated Flame Retardant Handbook 2<sup>nd</sup> Edition*, Wiley, 2021, pp. 101–168.
- [134] M. M. Velencoso, A. Battig, J. C. Markwart, B. Scharrel, and F. R. Wurm, “Molecular Firefighting—How Modern Phosphorus Chemistry Can Help Solve the Challenge of Flame Retardancy,” *Angew. Chemie - Int. Ed.*, vol. 57, no. 33, pp. 10450–10467, 2018, doi: 10.1002/anie.201711735.
- [135] X. C. Jiang, P. Li, Y. Liu, and J. S. Wang, “Flame-retardant ramie fabrics with APP: flame retardancy, flame-retardant mechanism and mechanical properties,” *Cellulose*, vol. 30, no. 2, pp. 1321–1334, Jan. 2023, doi: 10.1007/S10570-022-04962-3/FIGURES/7.
- [136] H. Lavrenyuk, B. Mykhalichko, P. Garanyuk, and O. Mykhalichko, “New copper(II)-coordinated epoxy-amine polymers with flame-self-extinguishment properties: Elaboration, combustibility testing, and flame propagation rate measuring,” *Fire Mater.*, vol. 44, no. 6, pp. 825–834, Oct. 2020, doi: 10.1002/fam.2879.
- [137] R.-C. Sun, “Lignin Source and Structural Characterization,” *ChemSusChem*, vol. 13, pp. 4385–4393, 2020, doi: 10.1002/cssc.202001324.
- [138] X. C. Jiang, P. Li, Y. Liu, Y. W. Yan, and P. Zhu, “Preparation and properties of APP flame-retardant ramie fabric reinforced epoxy resin composites,” *Ind. Crops Prod.*, vol. 197, p. 116611, Jul. 2023, doi: 10.1016/J.INDCROP.2023.116611.
- [139] W. Lu *et al.*, “Lignosulfonate/APP IFR and its flame retardancy in lignosulfonate-based rigid polyurethane foams,” *J. Wood Sci.*, vol. 64, no. 3, pp. 287–293, Jun. 2018, doi: 10.1007/S10086-018-1701-4/TABLES/4.
- [140] R. E. Lyon, N. Safronava, S. Crowley, and R. N. Walters, “A molecular-level fire growth parameter,” *Polym. Degrad. Stab.*, vol. 186, p. 109478, Apr. 2021, doi: 10.1016/j.polymdegradstab.2020.109478.
- [141] E. Burzo, “Infrared spectroscopy of Polymers XIII: Polyurethanes,” *Spectroscopy*, vol. 38, no. 7, pp. 14–16, 2023, doi: 10.56530/spectroscopy.fn3378a3.
- [142] C. A. Cateto, M. F. Barreiro, and A. E. Rodrigues, “Monitoring of lignin-based polyurethane synthesis by FTIR-ATR,” *Ind. Crops Prod.*, vol. 27, no. 2, pp. 168–174, Mar. 2008, doi: 10.1016/j.indcrop.2007.07.018.
- [143] C. Jiang, H. He, H. Jiang, L. Ma, and D. M. Jia, “Nano-lignin filled natural rubber composites: Preparation and characterization,” *Express Polym. Lett.*, vol. 7, no. 5, pp. 480–493, 2013, doi: 10.3144/expresspolymlett.2013.44.
- [144] T. Kan, V. Strezov, and T. Evans, “Fuel production from pyrolysis of natural and synthetic rubbers,” *Fuel*, vol. 191, pp. 403–410, Mar. 2017, doi: 10.1016/J.FUEL.2016.11.100.
- [145] A. B. Morgan, “The Future of Flame Retardant Polymers – Unmet Needs and Likely New Approaches,” *Polym. Rev.*, vol. 59, no. 1, pp. 25–54, Jan. 2019, doi: 10.1080/15583724.2018.1454948.

## Appendix A: Supporting Information for Chapter 3

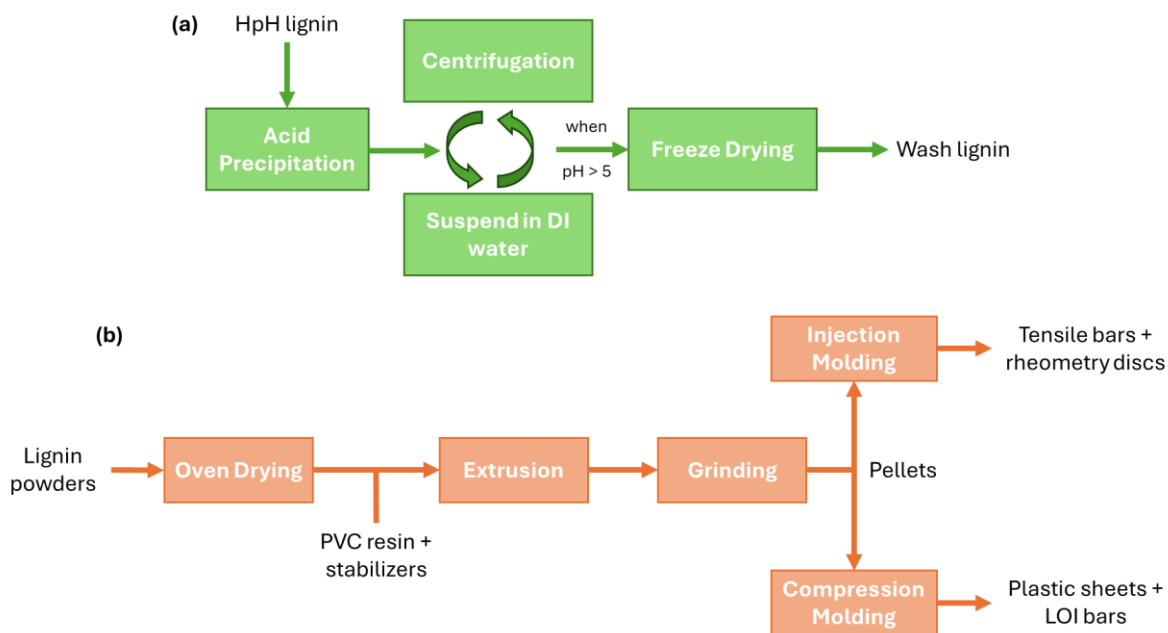


**Figure A1:** Material process flowchart for lignin washing (a) and sample creation (b).



**Figure A2:** HpH (a), LpH (b), and Wash (c) lignin powders.

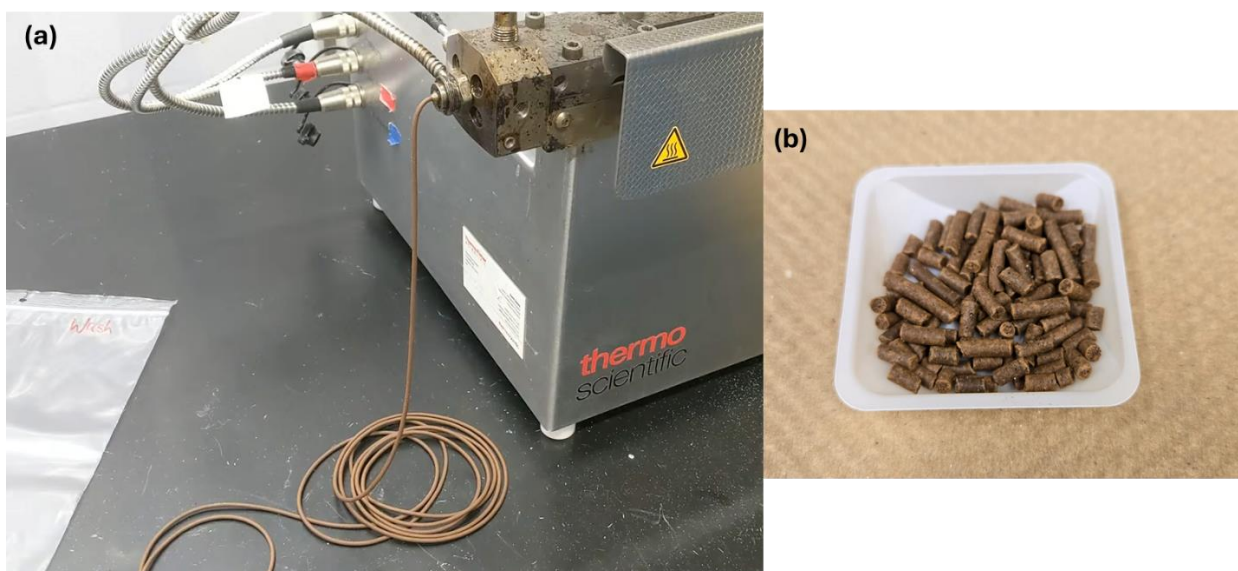


**Figure A3:** Extrusion processing (a) and pelletized sample (b).



**Figure A4:** Sample specimens (from left to right): tensile bar, rheometry disc, LOI bar, compression molded sheet.

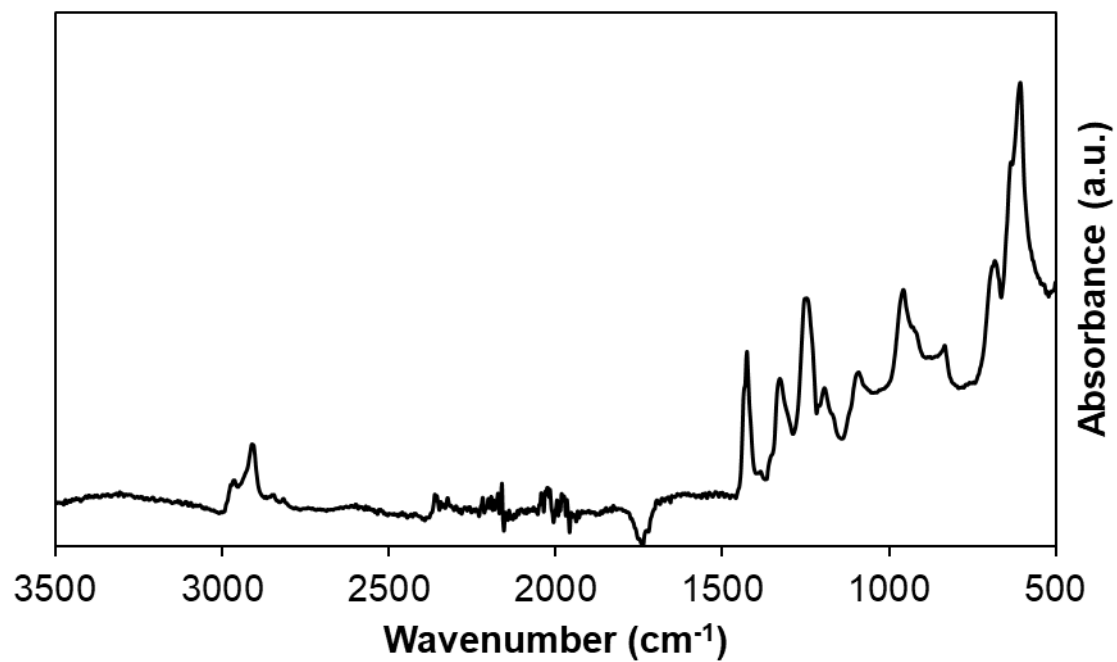


**Figure A5:** FTIR Spectrum of PVC resin.

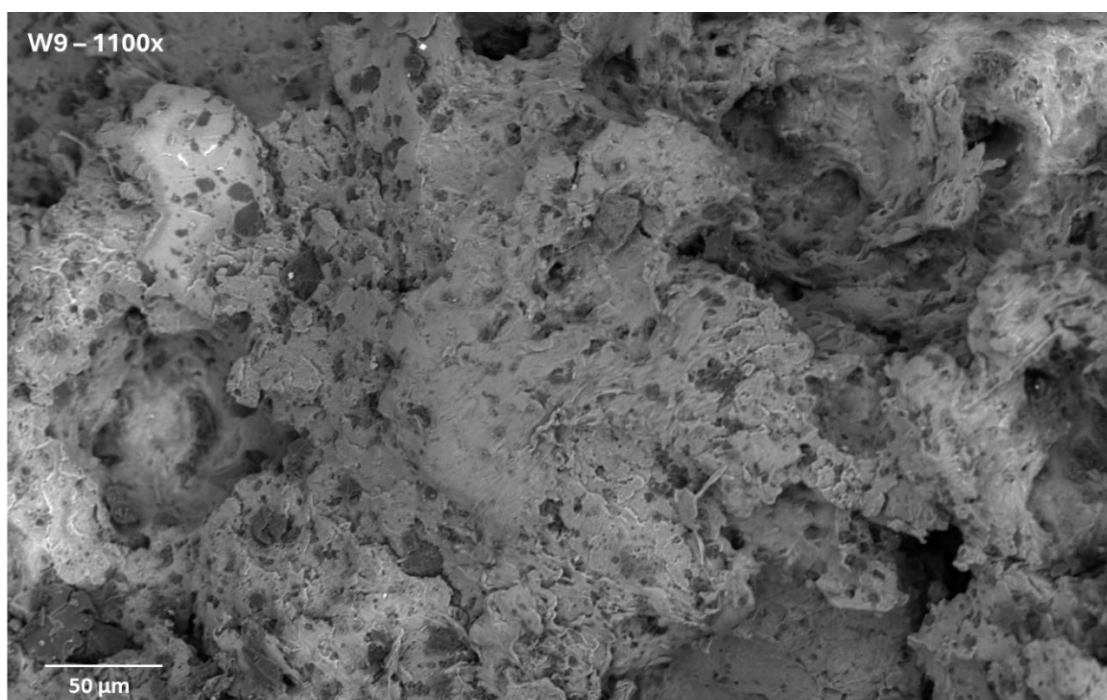


**Figure A6:** E-SEM image of sample W9 at 1100x magnification.

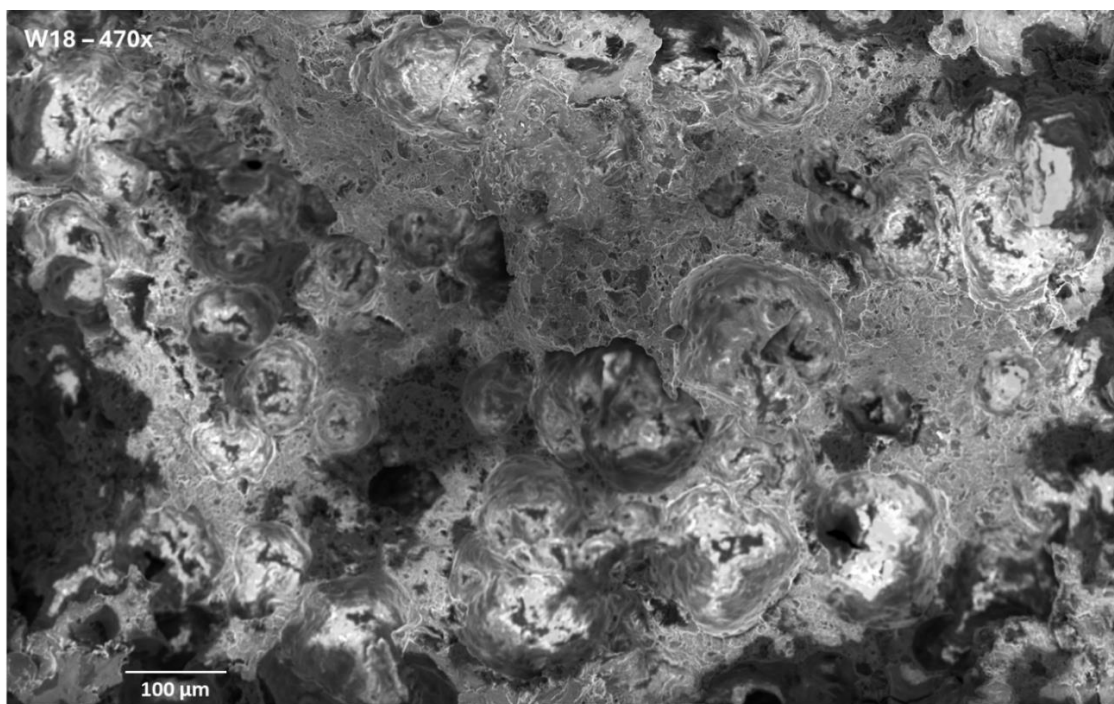


**Figure A7:** E-SEM image of sample W18 at 4700x magnification.

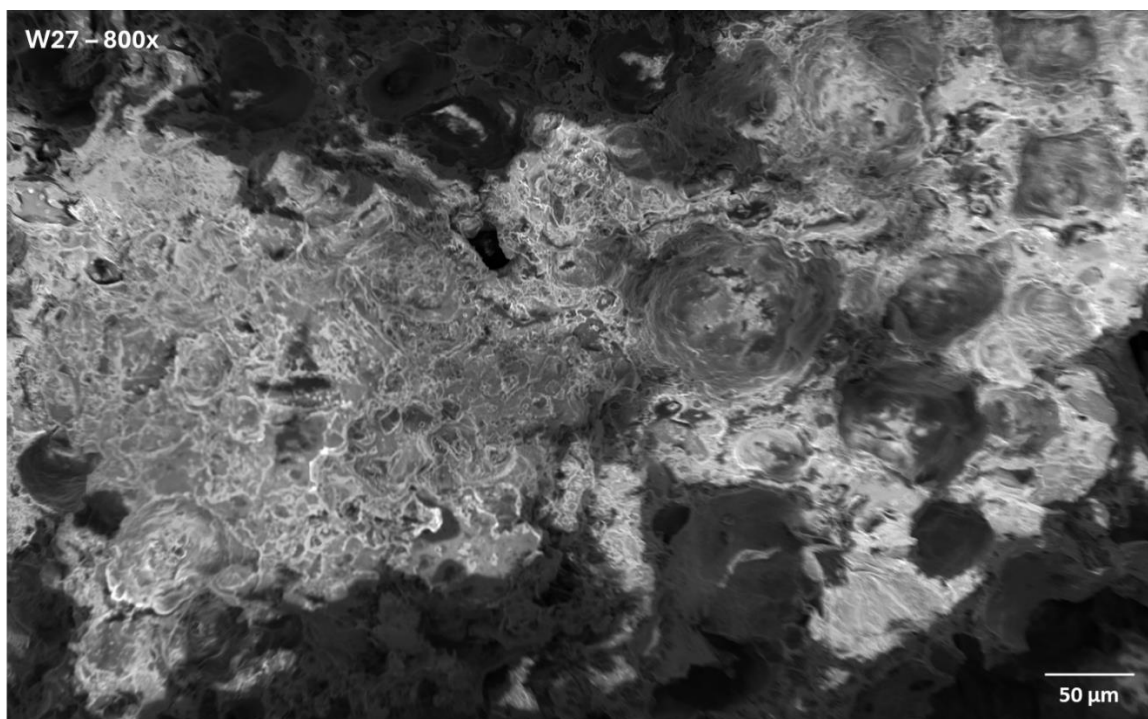


**Figure A8:** E-SEM image of sample W27 at 800x magnification.

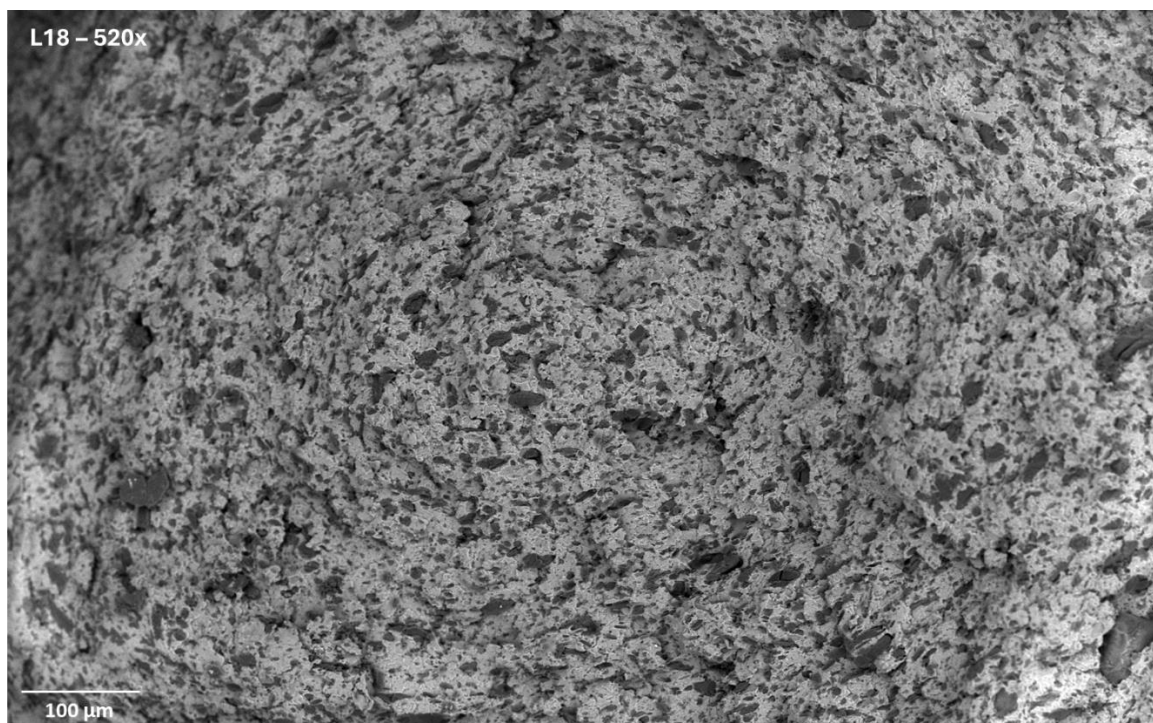


**Figure A9:** E-SEM image of sample L18 at 520x magnification.

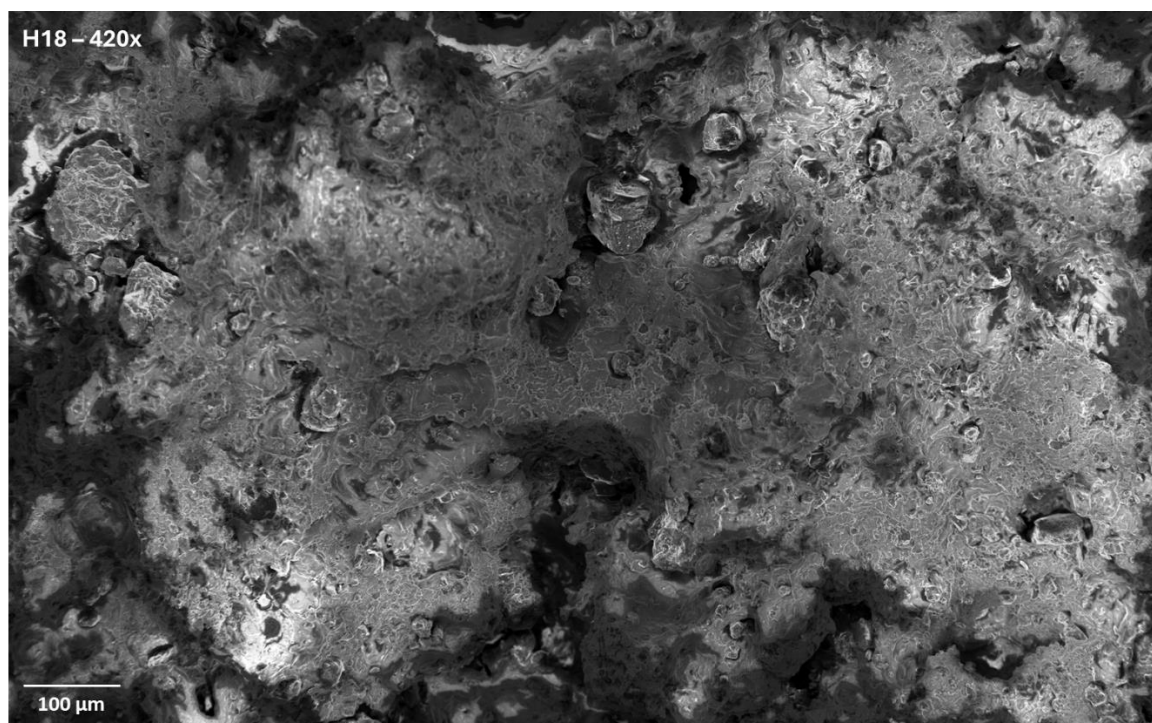


**Figure A10:** E-SEM image of sample H18 at 520x magnification.

**Table A1:** Calculated combustion indices.

|     | S<br>( $10^{-6} \text{ min}^{-2} \text{ K}^{-3}$ ) | C<br>( $10^{-4} \text{ min}^{-1} \text{ K}^{-2}$ ) | D <sub>i</sub><br>( $10^{-1} \text{ min}^{-3}$ ) | D <sub>b</sub><br>( $10^{-1} \text{ min}^{-4}$ ) | Relative S | Relative C | Relative D <sub>i</sub> | Relative D <sub>b</sub> |
|-----|----------------------------------------------------|----------------------------------------------------|--------------------------------------------------|--------------------------------------------------|------------|------------|-------------------------|-------------------------|
| N   | 1.09                                               | 1.61                                               | 2.56                                             | 1.62                                             | 1.00       | 1.00       | 1.00                    | 1.00                    |
| H18 | 0.75                                               | 1.16                                               | 1.87                                             | 1.13                                             | 0.69       | 0.72       | 0.73                    | 0.70                    |
| W18 | 0.61                                               | 0.77                                               | 1.21                                             | 0.33                                             | 0.56       | 0.48       | 0.47                    | 0.20                    |
| L18 | 0.61                                               | 0.86                                               | 1.32                                             | 0.39                                             | 0.56       | 0.53       | 0.52                    | 0.24                    |
| W9  | 0.79                                               | 1.14                                               | 1.80                                             | 0.98                                             | 0.72       | 0.71       | 0.70                    | 0.61                    |
| W27 | 0.62                                               | 0.94                                               | 1.46                                             | 0.64                                             | 0.57       | 0.58       | 0.57                    | 0.39                    |

**Table A2:** Results for the CR method for sample N D1C1.

|      | DECOMPOSITION 1 CURVE 1 |                |            |                |            |                |            |                |            |                |
|------|-------------------------|----------------|------------|----------------|------------|----------------|------------|----------------|------------|----------------|
|      | 2 C/min                 |                | 8 C/min    |                | 14 C/min   |                | 20 C/min   |                | Average    |                |
|      | E (kJ/mol)              | R <sup>2</sup> | E (kJ/mol) | R <sup>2</sup> | E (kJ/mol) | R <sup>2</sup> | E (kJ/mol) | R <sup>2</sup> | E (kJ/mol) | R <sup>2</sup> |
| P3/2 | 1022.86                 | 0.7549         | 877.00     | 0.8642         | 763.11     | 0.8298         | 647.51     | 0.8236         | 827.62     | 0.818          |
| P2   | 335.08                  | 0.7484         | 286.17     | 0.8591         | 248.08     | 0.8225         | 209.56     | 0.8147         | 269.72     | 0.8112         |
| P3   | 220.45                  | 0.7433         | 187.69     | 0.8550         | 162.24     | 0.8168         | 136.57     | 0.8077         | 176.74     | 0.8057         |
| P4   | 163.14                  | 0.7382         | 138.46     | 0.8508         | 119.32     | 0.8108         | 100.07     | 0.8003         | 130.25     | 0.8000         |
| A2   | 497.93                  | 0.8982         | 395.41     | 0.9586         | 351.55     | 0.9405         | 299.14     | 0.9372         | 386.01     | 0.9336         |
| A3   | 329.02                  | 0.8965         | 260.52     | 0.9577         | 231.22     | 0.9389         | 196.29     | 0.9353         | 254.26     | 0.9321         |
| A4   | 146.60                  | 0.9653         | 150.98     | 0.9883         | 177.34     | 0.9938         | 199.36     | 0.9894         | 168.57     | 0.9842         |
| F1   | 1004.67                 | 0.8998         | 800.08     | 0.9595         | 712.54     | 0.9420         | 607.69     | 0.9390         | 781.25     | 0.9351         |
| F2   | 1585.66                 | 0.9877         | 1170.09    | 0.9972         | 1069.42    | 0.9964         | 917.65     | 0.9960         | 1185.71    | 0.9943         |
| F3   | 2331.41                 | 0.9953         | 1641.16    | 0.9758         | 1525.13    | 0.9846         | 1313.67    | 0.9855         | 1702.85    | 0.9853         |
| F4   | 3145.25                 | 0.9854         | 2157.30    | 0.9487         | 2023.76    | 0.9634         | 1746.90    | 0.9650         | 2268.30    | 0.9656         |
| D1   | 1366.75                 | 0.7557         | 1172.42    | 0.8648         | 1020.62    | 0.8306         | 866.48     | 0.8246         | 1106.57    | 0.8190         |
| D2   | 1517.47                 | 0.7955         | 1278.04    | 0.8931         | 1119.19    | 0.8630         | 951.57     | 0.8578         | 1216.57    | 0.8523         |
| D3   | 1746.93                 | 0.8513         | 1431.52    | 0.9298         | 1264.71    | 0.9061         | 1077.57    | 0.9022         | 1380.18    | 0.8974         |
| D4   | 1590.64                 | 0.8149         | 1327.31    | 0.9061         | 1165.80    | 0.8781         | 991.91     | 0.8734         | 1268.91    | 0.8681         |
| R1   | 678.97                  | 0.7533         | 581.58     | 0.8630         | 505.59     | 0.8280         | 428.53     | 0.8214         | 548.67     | 0.8164         |
| R2   | 812.34                  | 0.8244         | 673.22     | 0.9123         | 591.68     | 0.8851         | 502.95     | 0.8802         | 645.05     | 0.8755         |
| R3   | 869.06                  | 0.8500         | 711.13     | 0.9289         | 627.64     | 0.9048         | 534.08     | 0.9006         | 685.48     | 0.8961         |

## Appendix B: Supporting Information for Chapter 4

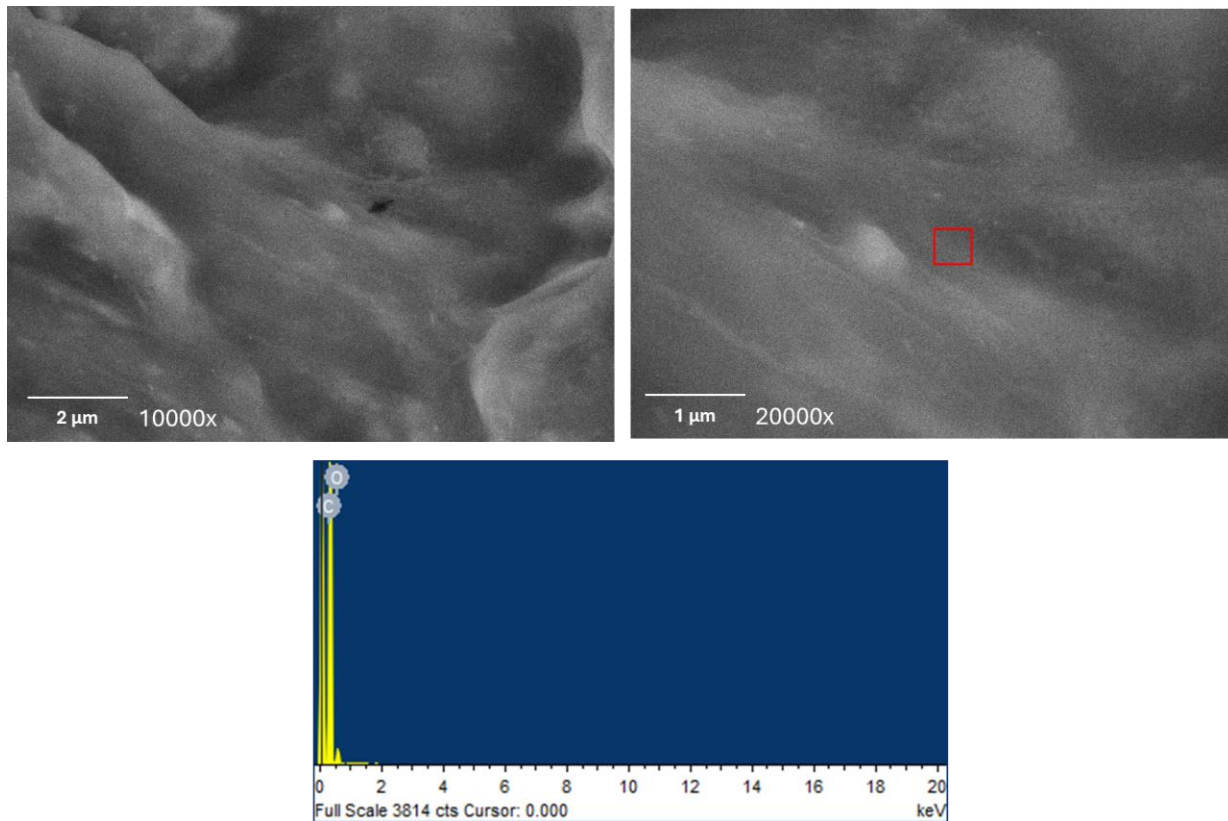


**Figure B1:** E-SEM images of sample N after drying with EDS on area marked in red.

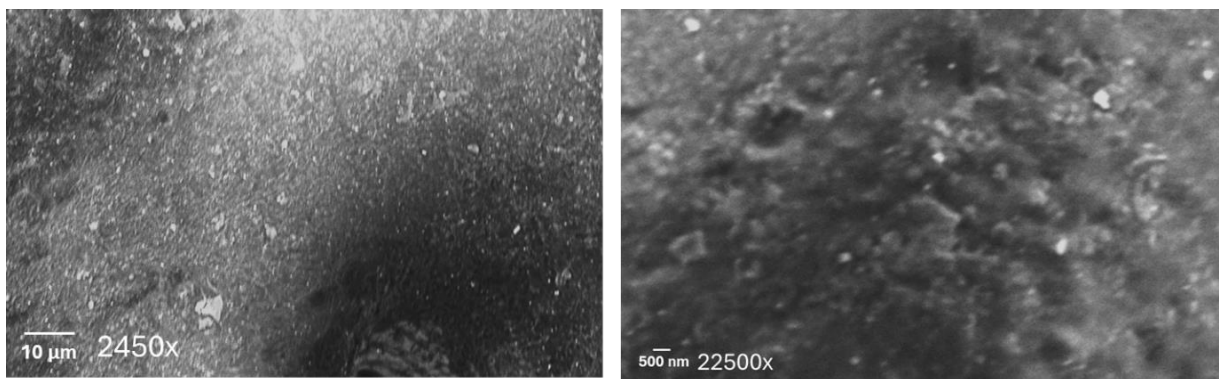


**Figure B2:** E-SEM images of sample 2.5-LNC after drying.

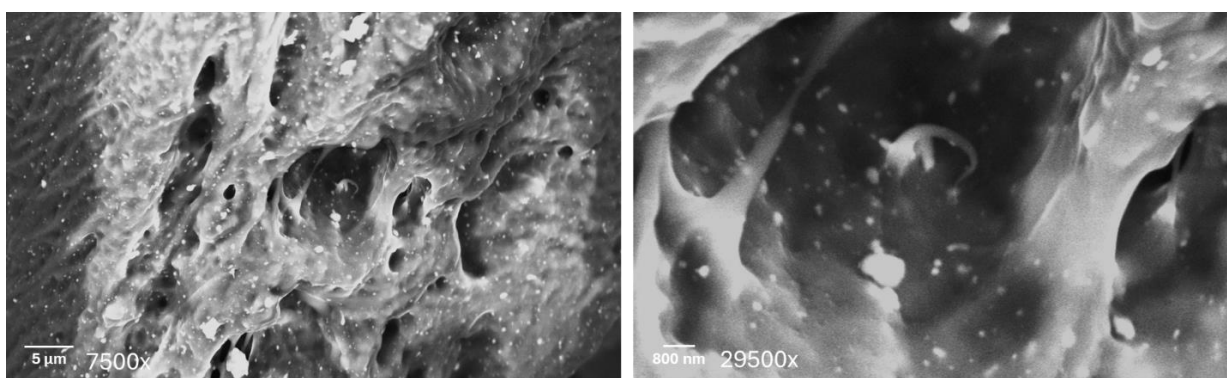


**Figure B3:** E-SEM images of sample 5-LNC after drying.

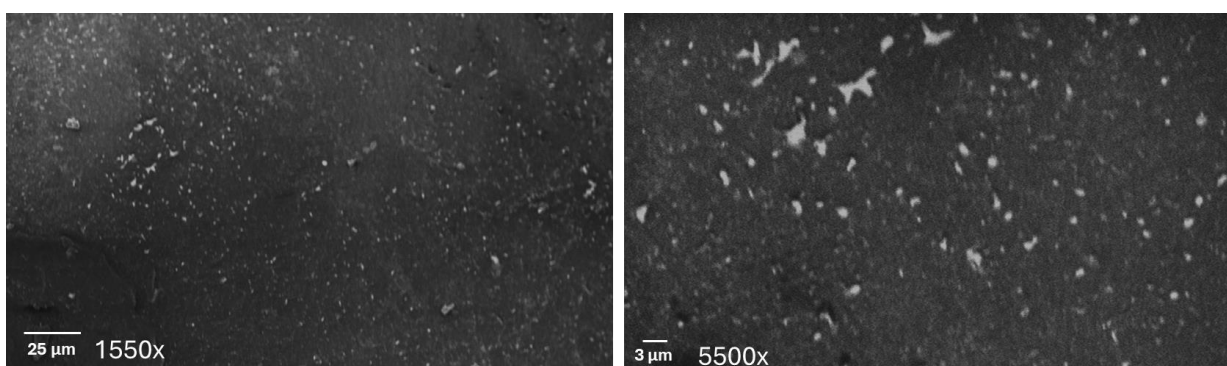


**Figure B4:** E-SEM images of sample 10-LNC after drying.

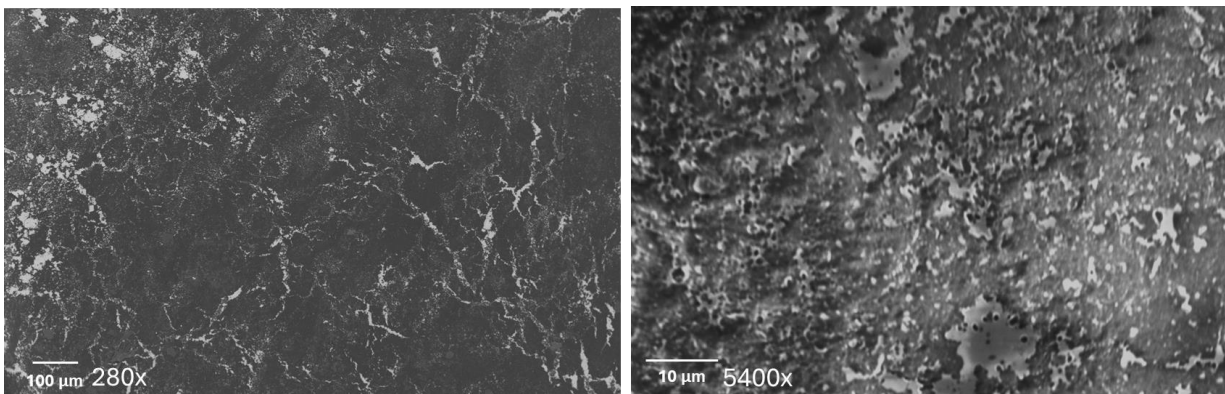


**Figure B5:** E-SEM images of sample 10-L+A after drying.

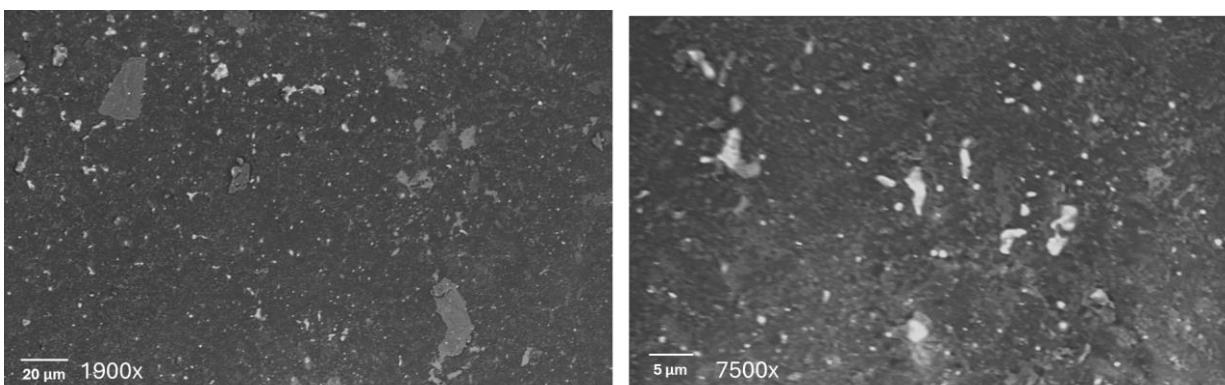


**Figure B6:** E-SEM images of sample 15-LNC after drying.