Bio flame retardant for Polylactic acid by combining phytic acid and lignin nanoparticles from lignosulphonate

M.T Chibika

orcid.org/0000-0002-3894-7991

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Supervisor:	Prof Andrew C. Eloka-Eboka
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DEDICATION

I dedicate this work to my son, Liam Thiago Chibika,my mother, Joyce Mubaiwa, my siblings Natasha,Lisa, Florence, Ronald, my late grandparents, Topinda and Vaidah Chadehumbe.

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ABSTRACT

Lignosulphonate nanoparticles/Phytic acid bio-flame retardant for PLA is a novel and environmentally friendly flame retardant that has the potential to revolutionize the fire safety industry. This research paper provides a comprehensive overview of the background, possible applications, process conditions, key results, and novelty of this innovative bio-flame retardant. The background of this dissertation stems from the growing concern over the use of traditional flame retardants, which often contain harmful chemicals that can pose serious health and environmental risks. In response to this, researchers have been exploring alternative, sustainable flame-retardant materials, and the combination of lignosulphonate nanoparticles and phytic acid has emerged as a promising candidate.

Polylactic acid (PLA) is a biodegradable polymer with applications in engineering, electronics, transportation, and aerospace due to its excellent properties; however, because it has an organic matrix, its thermal and fire retardancy needs improvement. Lignin has a high aromatic content and therefore offers a chance to use bio-based materials as nanoscale intumescent flame retardants. However, because of its structural heterogeneity, lignin requires modification with a material that has flame-retardant qualities. It has already been proven that combining lignin and PLA causes the matrix of a polymer to degrade during melt-processing. Phosphorous functionalized lignin nanoparticles, on the other hand, appear to reduce PLA degradation during melt-processing. Our goal was to create a high-functionality, bio-based phosphorus-containing flame-retardant that could be reactively incorporated into the PLA matrix to enhance flame retardant efficacy in a way that is sustainable. Through the combination of phytic acid and lignosulfonate, bio-based flame retardant was formulated. Functionalized lignin nanoparticles were synthesized by first combining lignosulfonate with phytic acid at 80ºC for 4hrs with magnetic stirring, followed by 1 hour of ultrasonication at a frequency of 20Hz with a cavitation probe of 3.175 mm, to give a nanoparticle dispersion, LNP-PA. The LNP-PA dispersion was spray-frozen on aluminium plate cooled with liquid nitrogen and kept frozen at -80ºC, followed by lyophilization.

Key results presented in this paper demonstrate the successful synthesis of functionalized lignosulphonate nanoparticles, superior flame-retardant properties of the lignosulfonate/Phytic acid bio-flame retardant compared to traditional flame retardants. The bio-flame retardant exhibits excellent fire resistance, low toxicity, and minimal environmental impact, making it a highly desirable alternative for various applications.X-ray powder diffraction (XRPD) spectrum showed that the pristine lignin and the functionalized NPs both have an amorphous structure, and the broadening of the spectra of the phosphorylated lignin after sonication shows the formation of nanoparticles, whose sizes were confirmed by dynamic light scattering (DLS). According to the

DLS measurements, the average particle diameter was 238 nm. However, scanning electron microscopy (SEM), revealed that there was agglomeration of particles after freeze drying but a significant particle size reduction of lignin was observed. Fourier transform infra-red spectroscopy (FTIR) spectrum showed a reduced intensity due to the loss of hydroxyl functional groups resulting from homolytic cleavage during ultrasonication, and phosphorylation. This was confirmed by ^{31}P-NMR, which shows the loss of hydroxyl functional groups, indicating that they reacted with the phosphate groups in PA. The appearance of peaks in LNP-PA's FTIR spectrum corresponding to P=O and P-O-R ester bonds proved that phytic acid had been chemically and successfully linked to lignosulfonate. The fire-retardant effect of the bio-flame retardant formulation was examined using a modified UL-94 tests. The control sample, pristine PLA burned more vigorously in the vertical method. Melting drips were observed in pristine PLA, PLA/LNP, and PLA/5LNP-PA, all of which were classified as V-2.PLA/10LNP-PA and PLA/15LNP-PA samples that had higher weight percentages of the bio-flame retardant additive demonstrated better fire behaviour and were classified as V-1 and V-0 respectively. All samples were classified as HB in the horizontal mode, and as the loading ratio of LNP-PA additives increased, the rate of burning decreased. The results are credited to the presence of lignosulfonate whose highly aromatic composition forms a carbon-based char layer which inhibits the diffusion of oxygen to the combustion site. Phytic acid also forms a char layer when it degrades due to the six phosphate groups within its structure, that produce phosphoric acid. This forms a protective layer which reduces the amount of fuel needed to sustain the combustion process and restricts heat flow in the material.

The novelty of this research lies in the development of a sustainable and effective bio-flame retardant that addresses the shortcomings of conventional flame retardants. Previously published research on this subject has reported on the use of pristine or phosphorous based macro-scale lignin to synthesize bio-flame retardants, and there has been few reports involving lignin nanoparticles or their combination with phytic acid. The combination of lignosulfonate and phytic acid offers a unique and innovative solution to fire safety concerns, paving the way for a more sustainable and eco-friendly approach to flame retardancy. Possible applications of lignosulfonate nanoparticle/Phytic acid bio-flame retardant include its use in various industries such as construction, textiles, and electronics, where fire safety is of utmost importance.

Key words: Bio-fire retardants, lignosulfonate, nanoparticles, phytic acid, polylactic acid, cone calorimetry.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF PUBLICATIONS OR CONFERENCE ARTICLES

1. **Marshall T. CHIBIKA** and Andrew C. ELOKA-EBOKA (2022). Phosphorylated lignin intumescent bio-flame retardants for bio-polymers https://nottingham-repository.worktribe.com/output/17381378. SET2022 conference proceedings (poster presentation), Istanbul, Turkey.

2. **Marshall T. Chibika** and Andrew C. Eloka-Eboka. A state-of-the-art review of biobased flame retardants from phosphorylated lignin for polymer composites and textile applications. Manuscript submitted and *under review in the Journal of Cleaner Production.*

ABBREVIATIONS

PLA	Polylactic acid
LNP	Lignosulfonate nanoparticles
LNP-PA	Lignosulfonate-Phytic acid nanoparticles
PA	Phytic acid
LS	Lignosulfonate
TGA	Thermal Gravimetric Analysis
FTIR	Fourier Transform Infra-Red Spectroscopy
DLS	Dynamic Light Scattering
XRPD	Xray Powder Diffraction Analysis
NMR	Nuclear Magnetic Resonance Spectroscopy
DSC	Differential Scanning Calorimetry
CC	Cone Calorimetry
LOI	Limiting Oxygen Index
UL-94	Underwriters Laboratory-94
HRR	Heat release rate
THRR	Total heat release rate
pHRR	Peak heat release rate

INTRODUCTION

The research outlined in this dissertation is introduced in this chapter. An overview of the focus and main points pertaining to the background and motivation of the project is given in Section 1.1. In Section 1.2, the problem statement is presented. The primary aim along with the specific objectives of this work will be addressed in Section 1.3, and the project's justification and limitations are covered in Sections 1.4 and 1.5, respectively. Finally, the outline of the dissertation is presented in Section 1.6.

1.1 Background and motivation

Polymeric materials possess remarkable chemical, mechanical, physical properties and that make them all-encompassing in all aspects of existence [1-3]. The high flammability inherent in the polymeric materials constitutes their primary drawback for use in applications in which resistance to fire is required [4]. A lot of fire-related accidents have been reported because of this polymer use [5]. Statistical data from the International Association of Fire and Rescue Services (CTIF) shows that, about two million fire accidents, which resulted in 20000-25000 deaths, were reported in Europe in 2018, and 60% of deaths were due to inhalation of smoke [6]. Furthermore, without environmental protection, there can be no sustainable economic development. Researchers from all around the world have demonstrated that the production of greenhouse gases and chlorofluorocarbons, CFCs from fossil fuels poses a major threat to the survival of people, plants, and animals. Therefore, the flammability of plastics is not the only issue faced globally, but the non-biodegradability of most synthetic plastics and their production from fossil fuels. According to studies, biodegradable biopolymers pose less of a hazard to the environment than fossil-based polymers, hence they should be used globally. Biodegradable plastics as well as the necessity for their use are being encouraged more and more for sustainable development due to the exponential awareness of environmental and waste management challenges around the world, in addition to the state underlying fossil fuel resources and their detrimental effects [7].

Polylactic acid (PLA), a plant-derived biodegradable polymer, has found many uses because it easily decomposes to lactic acid, which is considered environmentally friendly [8, 9].PLA is a renewable, and biodegradable plastic with good physicochemical, optical, and mechanical qualities [10]. PLA has been used in the development of textiles, engineering polymers, and food packaging materials [11].Even though PLA is sustainable, like other polymers, the major drawback is its high flammability [12].Therefore, the polymer flame retardancy of PLA needs improvement. The introduction of flame retardants (FRs) in polymeric materials is an attempt to minimize fire hazards posed by polymers [13]. Flame retardants are additives for plastic materials that make them resistant to combustion. These chemical compounds hinder the ignition phase of combustion, or slow down the spreading of flames during combustion [14]. The flame retardant (FR) compounds are categorized as follows: inorganic FRs, phosphorous-based FRs, nanofillers, halogenated FRs, and nitrogen-based. Nevertheless, most of the conventional FRs cannot be decomposed by microorganisms once they are disposed of in the landfill. In particular, halogen-based fire suppressants are not eco-friendly and pose health hazards for human beings and aquatic life, therefore there are legislative restrictions for their use [15].

Petroleum based organic compounds make up a large portion of commonly produced fire retardants (for example, organic-halogenated, organic-nitrogen, and organic-phosphorous compounds). They share the same challenges as other petroleum-based products: rising petroleum depletion, geopolitical issues, and climate change implications. Furthermore, halogen-based compounds have a poor reputation because they create specific environmental and health problems [16]. Bio-based flame-retardant compounds are gaining prominence in modern materials engineering applications. To ensure fire-safe polymer materials for a variety of industrial and engineering applications, halogen-free flame retardants are being developed. The challenges with conventional flame retardants are behind the growing awareness on the need to develop sustainable options for flame retardants in polymeric materials. In recent times, scientists have developed important polymer additives that are completely biodegradable and have been derived from renewable raw materials [17]. Bio-based flame retardants are substances that can be produced or synthesized from biomass [17, 18].

Bio-based polymer films with nanostructures have emerged as the future in the development of eco-friendly plastic material. Nanocomposite films are polymers that are composed mostly of plant-based (e.g., lignin, cellulose, starch, chitosan, protein) and synthetic (e.g., polylactic acid) polymers and nano fillers (e.g., clay, nanotubes, nanofibers, and nanoparticles). A combination of bio-polymers and nano fillers results in better properties in nanocomposite materials [19, 20]. Flame retardant (FR) nano-sized fillers can be blended with the polymer, or chemically complexed with the polymer, incorporated as an intumescent system to form a bio-composite system with diminished combustibility and flammability characteristics [20]. Research has shown that nanoparticles improve the mechanical, chemical and physical properties of bio-composites and are therefore effective as ingredients in flame retardant preparations but are rarely used alone [14]. Therefore, to make a totally biodegradable nano-bio composite, synthetic fillers like carbon or glass fibres should be replaced with bio-based nano fillers in the bio-based polymer matrix [2],[21]. According to, [22] ,“the use of sustainable bio-carbon fillers derived from waste biomass, industrial waste, and food waste demonstrates the enormous potential for lightweight sustainable composites in auto parts and other growing demands from the manufacturing sector”.

Non-biodegradable plastic waste is a major pollution problem. Significant research focusing on the manufacture of biodegradable materials has been reported in the literature. Bio-based polymers are excellent raw materials for making these materials [19].The European Bioplastics (EUBP) defines bioplastics material as those which are either derived from plant fibres, or are biodegradable or fit both characterizations [23]. Pollution from these fossil-fuel-derived polymers has drawn attention to the research and design of environmentally friendly, sustainable materials. The biodegradable polymers produced from renewable sources represent a viable solution to these negative effects [24].The non-biodegradability of traditional fossil fuel-derived polymer composites results in prolonging their existence in the environment. Waste materials cannot be recycled or reused easily, therefore they are either incinerated or discarded in landfills [22].

Biopolymers offer a substitute for the common organic and inorganic materials in various engineering applications. They have a lot of desirable properties which include biocompatibility, biodegradability, and cheaper costs in production. Lignocellulose has an immense amount of promise as an earthly resource that can replenish carbon. Lignin consists of between 20-35% of the lignocellulosic biomass [25]. Lignocellulosic materials are generated as waste by-products from agro-based industries, especially in the pulp & paper and ethanol industries based on lignocellulose. Lignocellulosic waste is cheap, renewable, and abundant. Unfortunately, most of the lignocellulosic waste is burnt as a way of disposal [26]. In recent years, this area has seen significant advances in research due to the renewable nature of the materials [27]. In accordance with this, industrial waste recycling presents a cost-effective and environmentally sustainable solution to obtaining sustainable, long-term renewable material supplies [28]. SAPPI Southern Africa runs five pulp and paper plants in South Africa, with a total yearly output of ninety-three cubic meters of sawn timber, tonnes of paper, six hundred and twenty-four thousand tonnes of paper pulp, and more than a million tonnes of dissolved pulp. SAPPI Tugela Millis generates 25,000 metric tonnes of lignosulphonate powder and thirty-five thousand tonnes of liquid material each year [29].

SAPPI Ngodwana Mill manufactures three hundred and eighty thousand tonnes of paper utilized in packaging, two hundred and fifty-five thousand tonnes of DP, and three hundred and twenty thousand tonnes of paper pulp per year. The mill generates 70% of its total output for exporting and 30% for consumption within its borders. The mill generates its own energy in the form of steam, as well as electricity, from both renewable and non-renewable resources. The mill undertakes meticulous measures to use the fewest natural resources as feasible, in order to minimize emissions, effluent release, and solid waste generation, and to improve the utilization of energy [30].

Scientific and engineering attention has been given to carbon nanostructures because they possess extraordinary physicochemical, electrical, mechanical, and thermal properties. Research focus is on the sintering of nanostructures from lignin because of the abundance of carbon in lignin. And with lignin being a waste by- product from the lignocellulosic ethanol, pulp and paper plants, synthesis of this nano lignin from these sources may reduce the carbon foot print [31].
Even as previous studies show that lignin, when used as a filler, encourages the degradation of PLA during melt processing, and that phosphorylated lignin nanoparticles (LNPs) reduce the degradability during processing [15],[32]. Therefore, Costes et. al [15],combined kraft/organosolv lignin and phytic acid, in the synthesis of a bio-based FR for PLA, in which phytic acid reduces the degradation due to lignin, by improving lignin particle dispersion in the polymer matrix of PLA. Flammability tests showed an improvement in fire retardancy, and, Chollet et.al [32] ,prepared and functionalized micro/nano lignin particles from Kraft lignin with diethyl chloro-phosphate to enhance their fire-behaviour in PLA.
Bio-based phytic acid, based on its non-toxicity and origin, from plant tissues, can be regarded as a green compound. It can be used as an environmentally friendly flame retardant in PLA [33]. Based on existing research on lignin and phytic acid flame retardant systems, a blend of lignin nanoparticles and phytic acid appears to have a greater future potential in bio-based flame-retardant solutions. This research will therefore focus on the development of a flame retardancy system for PLA using lignin nanoparticle fillers functionalized with phytic acid.
The system will be based on intumescence. Intumescence is the process of swelling up. Flame retardants whose mechanism is based on swelling up due to char formation are called intumescent systems [34], and those based on phosphorous function via this mechanism [35]. Phytic acid can form a char layer when it degrades because of the six phosphate groups in its structure, which produce phosphoric acid [36],[37] ,[38]. This forms a protective layer, as a result, less fuel is required to maintain the process of combustion and so the material's ability to transfer heat is restricted. [39].

1.2 Problem statement

Research and development in /of polymeric material has been witnessed for many years, with the materials becoming very important in daily life. Bio-composite polymers have gained prominence, but intensive research is needed to improve their properties. Apart from their mechanical properties, the fire safety of these materials requires more research because of their high flammability. The fire hazards due to their high flammability, especially from those with plant-based fillers may lead to loss of life and property. Given the current drive for the use of eco-friendly processes and materials, interest in bio-composites has grown, which however increases the risk of fire hazards [40].

PLA has evolved into a ubiquitous polymer with numerous applications. However, due to the strong flammability and propensity to spread fire, consideration as a good substitute for plastics developed via petrochemicals is less to be desired. Organo-halogen chemicals are conventional flame retardants that can be incorporated into PLA without substantial altering of its mechanical properties. These substances also tend to bioaccumulate and endanger both plants and animals which may limit their use and application [12].

The impact of flame retardants is to lessen burning ability, combustibility, fire hazards and toxic fume release. Unfortunately, many flame retardants—particularly the halogenated FRs—are not biodegradable and tend to persist in the environment. The persistence in the environment results in accumulation of toxic chemicals which find their way into wastewater streams and the food chain. This negative impact poses real danger to plants, animals and human beings [41].Hence, novel bio-based flame retardants (FRs) need to be introduced owing to their biodegradability and non-toxicity to the environment. Carbon based nanoparticles have great potential to become nano fillers in bio-composites owing to their excellent thermal properties.

Precursors used in the synthesis of carbon nanoparticles are important in the structure and properties of polymers. Currently, the precursors are obtained from the already depleting fossil fuels which also increase greenhouse emissions [31]. Lignocellulose is a sustainable, eco-friendly renewable source of carbon [42]. Recently, lignocellulose has gained attention as a potential substitute for petrochemical sources in the production of energy and environmentally friendly chemicals to reduce pressure on resources, cost of production and health issues related to the chemical industry [43],[44] ,[45]. Lignin is very abundant but underutilized in high value materials production. It is mostly used for energy generation. Only a few research articles have been produced, where proposals to utilize lignin as an additive to improve flame retardancy in bio-based polymers, in order to obtain fully biodegradable bio-composites [46].Consequently, there are growing interests to exploit lignin in other uses which include production of polymeric materials and carbon nanostructures.

1.3 Aim and objectives

1.3.1 Aim

The aim of this research is to develop a bio-flame retardant, to be used for improving the fire behaviour of polylactic acid (PLA) by using phytic acid-functionalized lignosulfonate nanoparticles.

1.3.2 Objectives

The chemical and physical properties of technical lignin depend on the botanical origin and the extraction methods used. For this research, commercially available Lignex (lignosulfonate) from SAPPI Paper and Pulp industry was used.

Objectives include to:

1. Synthesize phytic acid-functionalized lignosulfonate, nanoparticles (LNP-PA) and pristine lignin nanoparticles. The LNP-PA will be the bio-flame retardant additive to be incorporated in the PLA bio-polymer matrix.
2. Characterize the synthesized bio-flame retardant LNP-PA, pristine lignosulfonate nanoparticles (LNP) and unmodified lignosulfonate using Xray Powder Dispersive Spectroscopy (XRPD), Zeta Size Analysis, Nuclear Magnetic Resonance Spectroscopy, (NMR), Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) and Dynamic Light Scattering (DLS), TGA and DSC.
3. Prepare LNP/PLA and PLA/LNP-PA bio-composites with PLA as the polymer matrix, using varying loading concentrations for the LNP-PA bio-flame retardant additive via melt processing and solvent casting.
4. Carry out the UL-94 test to determine the flame retardance properties of each of the bio-composites.

1.4 Research Justification

Lives generally in the modern world are dependent on synthetic polymeric materials. However, their high levels of combustibility and flammability are a cause for concern in fire safety. In the interest of ensuring fire safety, flame retardant (FR) development has gained prominence in the science and engineering fields. Many of the available flame retardant (FR) additives have negatives impacts on the environment. Their synthesis is not eco-friendly and depends on fossil fuels. Various research entities are now focusing on the use of renewable resources to develop biodegradable flame retardants [47].

The long-term success of biodegradable flame retardants is contingent upon the environmental and economic viability of the materials derived from renewable resources. Therefore, this field requires non-fossil fuel-based resources to synthesize carbonaceous nanoparticles. Renewable sources such as plant biomass show a lot of potential for synthesizing nanostructures [48, 49].

The biomolecules from the forestry sector as well as other sources that are renewable appear to be the raw material of choice. These include cellulose, starch and lignin, all of which have excellent flame retardant potential. [50]. Lignin has unique qualities as a charring agent in flame-retardant chemicals as well as is an ideal source of carbon for the fabrication of nanostructures. Lignin production capacity is approximately 50 million tons but remains an underutilized by-product as it is seen as just a waste product. The research is justified in finding solutions for the prevention of fire hazard by using lignin nanoparticle fillers in biopolymer, which is not only cheap to produce, undervalued and renewable, but is also biodegradable. Nanoparticles possess unique properties, a fire retardancy system using nano lignin is a potential solution to the replacement of halogenated FR additives which are not environmentally friendly.

1.5 Limitations

The project aims to develop flame retardants for bio-based, in this case specifically for PLA. Therefore, the purpose is to reduce flammability and combustibility of PLA using lignin nanoparticles (LNP) and phytic acid. Technical lignin properties differ depending on the source and extraction method used, therefore for this research, lignosulfonate, extracted from the paper and pulp manufacturing processes, will be used. Introducing materials in a polymer matrix may enhance or reduce other properties like mechanical properties. Nanoparticles are known for improving mechanical, electrical, and thermal properties. However, this study will assume other properties are not affected by the approach used, but only focus on whether there is an improvement in flame retardancy. The properties that are not going to be part of this research represent a research gap that may need to be filled in the future.

1.6 Outline

This dissertation is presented in five chapters.

- **Chapter 1** focuses on the background and motivation for the research project. The problem statement, aim and objectives, justification and limitations of the project were presented in this chapter.
- **Chapter 2** provides an overview of the literature on the state-of-the-art in the development of bio-based flame retardants. The structure of lignin, the industrial extraction of lignin, lignin valorisation, functionalization techniques and the synthesis methods of lignin nanoparticles are discussed in this chapter. Lastly, the standard flame retardancy tests are described in this chapter.
- **Chapter 3** presents the methodology adopted for this research. The experimental work done on the synthesis of lignin nanoparticles, functionalization and the characterizations

are discussed in the chapter. The compounding, extrusion, compression moulding and the cone calorimetry of the PLA/LNPs/Phytic acid flame retardant bio-composites are presented in this chapter.

- **Chapter 4** gives a summary of the experimental work results obtained in this study.
- **Chapter 5** Based on the experimental findings, the conclusions to the stated objectives are presented in this chapter. There is a highlight of the information acquired in this study and its contributions to the body of currently available literature. This chapter identifies research gaps and presents recommendations for additional study.

LITERATURE REVIEW

2.1 Lignin

The most common biomass is lignin, which is followed by cellulose. This organic, aromatic in nature polymer is extremely complicated [51-55]. Approximately 15–35% of lignocellulosic biomass is made up of lignin, an aromatic, amorphous natural polymer. Industrial lignins are being produced in significant amounts each year as a by-product from bio-refineries based on lignocellulosic ethanol manufacturing and paper and pulping operations. Nevertheless, less than 2% of this enormous natural resource is valorized at present [56]. Long-term research has focused on the simple incorporation of lignin into polymer materials due to the concept's simplicity and the approach's potential for large atom economy. Due to its complex molecular structure, lignin typically undergoes rapid condensation upon isolation from biomass. As a result, lignin grows increasingly resistant to being upgraded and integrated into other materials [56]. The type and species of wood as well as—most importantly—the extraction techniques have a significant impact on the structure of lignin molecules [57-59]. Hardwoods have a significantly more varied lignin content than softwoods [60]. The functional groups, molecular masses, and the element composition of different types of lignin differ due to their origin and type of species. Because of this, the structure of lignin is very complicated as well as difficult to have a universal description of its structure [61].

2.1.1 Lignin Structure and Properties

It is generally agreed that lignin exists as a naturally occurring amorphous three-dimensional network polymer composed of phenylpropanoid units connected by carbon-carbon and C-O bonds [62, 63]. Lignin is composed of three distinct types of phenylpropane units: sinapyl, p-coumaryl and coniferyl alcohol [52, 64], which are distinguished by the extent of methoxylation in their aromatic ring distinguishing them from one another [15]. Through radical oxidation, monomers that make up monolignols, can form electrovalent bonds and undergo polymerization as part of the biomass growth cycle. Multicopper oxidases called laccases and peroxidases, also known as peroxide reductases, catalyze the polymerization of monolignols into syringil (S),p-hydroxyphenyl (H) and guaiacyl (G) residues. [66].The lignin precursors and their structures within lignin are shown in Figure 1.

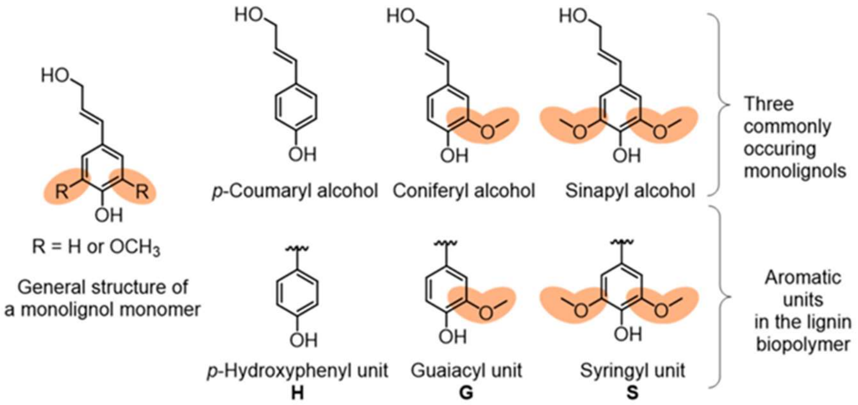


Figure 1.The monolignols and their structures in lignin [67]

The β-O-4 ether linkage is the most dominant electrovalent bond in lignin in a list that also includes the β-β, 5-5, β-5, dibenzodioxocin,4-O-5 and β-1 linkages as illustrated in Figure 2.

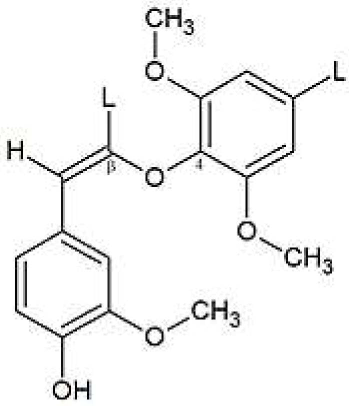


Figure 2: Lignin β-O-4 linkages [68]

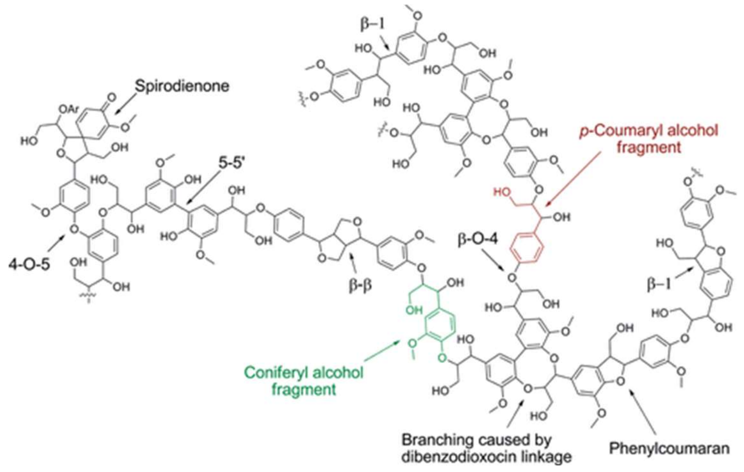


Figure 3: Softwood lignin structure [69]

The environment and the type of plant have an impact on the lignin's percentage and composition. There are differences in the proportions of p-coumaryl alcohol, coniferyl, and sinapyl alcohols in relation to the lignin levels in hardwood as well as softwood. Coniferyl alcohols account for almost 90% of softwood lignin, despite several recorded variations; in hardwood lignin, sinapyl and coniferyl alcohol are present in roughly equal amounts. Hardwood lignins primarily contain G and S units, with trace amounts of H units; softwood lignins primarily contain G units, with very small amounts of H units [70], as illustrated in Figure 3 and Figure 4.

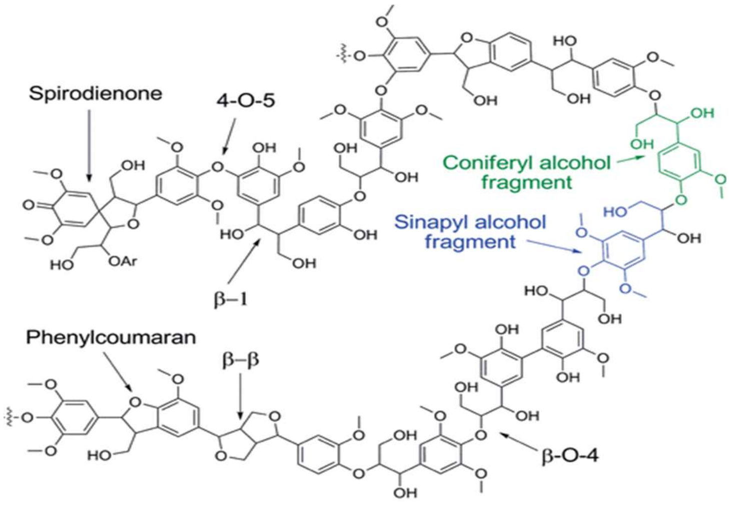


Figure 4:Schematic representation of lignin in hardwood [69]

2.1.2 Pre-Treatments of Lignocellulosic Biomass

The heterogeneity of wood structure results in the unavailability of a method for quantitatively isolating lignin without risking structural modification throughout the process. [57].As previously stated, the main source of technical lignin is the pulp and paper industry, which is obtained by hydrolytic, chemical, and mechanical processes. [71]. Lignin can be extracted from other lignocellulosic components using biological, chemical, and physical methods. One typical pulping method involves breaking the bonds between ether and ester. It's important to note that industrially yielded technical lignin is very different from the plant-derived native lignin. [60]. The five most popular pre-treatment methods used today to extract lignin are soda,sulfite,hydrolysis,soda,organosolv and kraft process [72] as shown in Figure 5.

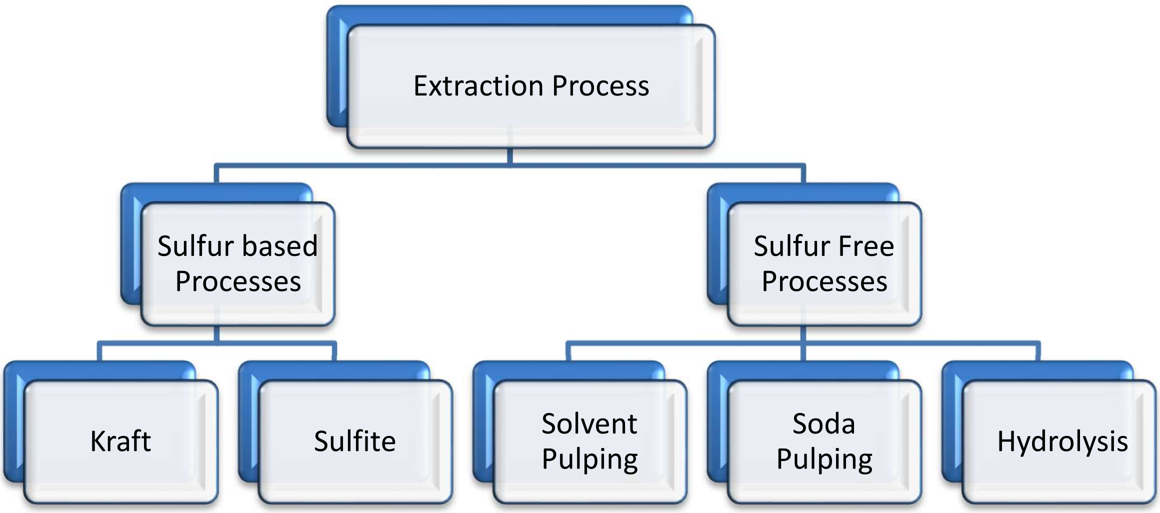


Figure 5: The different lignin extraction processes [73]

2.1.3 The Kraft Process

The sulfate (kraft) cooking method results in the formation of kraft lignin. It accounts for around 85% of total global lignin output [74]. The several lignin processes that take place throughout the kraft pulping process are divided into two categories: condensation and degradation reactions. Degradation reactions are favourable because they involve liberating the fragments of lignin which makes it easier to break them. Condensation reactions, on the other hand, result in the formation of alkali-stable links, and are therefore not preferred [75], as shown in Figure 6.The process involves the digestion of woody biomass at high temperatures and pressures in "white liquor," a sodium sulfide and sodium hydroxide water solution. The lignin that holds the fibrous material together is chemically dissolved by the white liquid. In the kraft process, approximately 90 weight percent of lignin in wood is dissolved in aqueous solutions of sodium sulfide and sodium hydroxide. Lignin is broken down into molecular mass fragments that are soluble in alkali solutions.

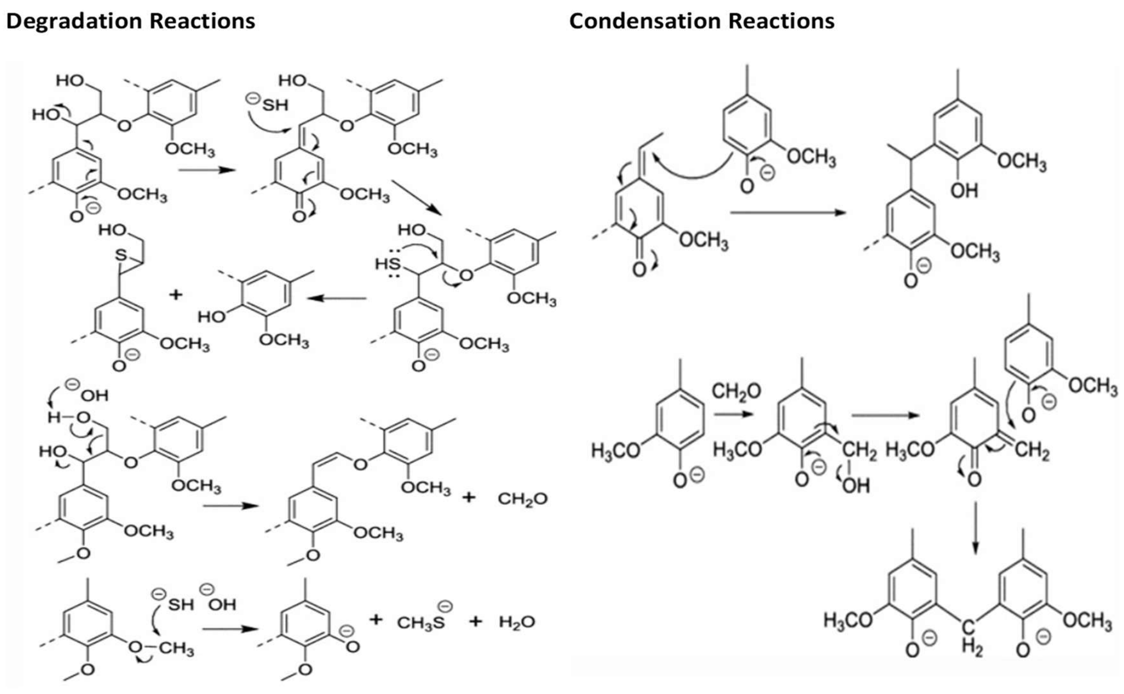

Degradation Reactions **Condensation Reactions**

Figure 6:The degradation and condensation reactions in the kraft pulping process [75-76]

Kraft lignin has several unique characteristics that set it apart from native lignin and other technical lignins. The substantial breaking of β-O-4 and α-O-4 bonds during cooking, results in it having a larger number of phenolic hydroxyl groups [74]. Furthermore, the intense cooking conditions result in the formation of certain biphenyl and other condensed structures. In general, the number of condensing units rises in the process [78].The model kraft lignin structure is shown in Figure 7.

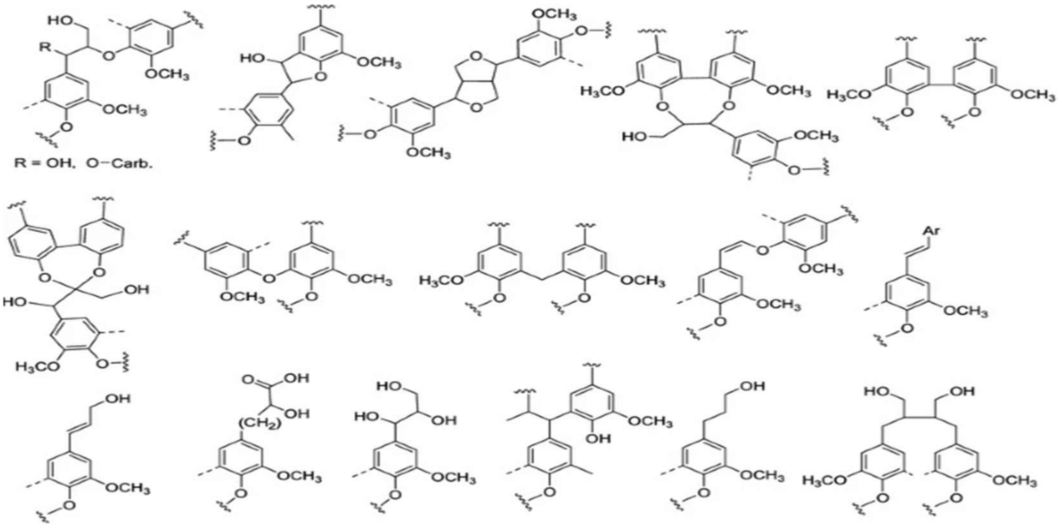


Figure 7: Model partial structure of Kraft Lignin [77]

2.1.4 Sulfite Process

Lignins derived from sulfite pulp procedures are known as lignosulfonates, with a delignification medium based on sulfurous acid and its sulphite salt containing Mg, Ca, Na, and ammonium, acting as buffers to the mixture [79]. Lignosulfonates have a high degree of sulfonation, which boosts their water solubility [80]. The sulfite pulping process is mainly characterised by hydrolysis and sulfonation. Acidic rupture of ether linkages, which connect several of the constituents of lignin, is responsible for most of the delignification in sulfite pulping forming electrophilic carbonium ions(hydrolysis) [62]. This is followed by sulfonation, in which sulfonates are formed when electrophilic carbonium ions generated during ether breakdown combine with bisulfite ions or sulfite ions (HSO_3^-/ SO_3) [77]. The α -carbon on the propyl side chain is the principal location for ether cleavage. Sulfite ions in solution combine with the intermediate benzylic cation at the α position to form units of benzyl sulfonic acid, and this enhances the lignosulfonates' solubility [80].Figure 8 gives a basic framework of how lignosulfonates are made under acidic conditions and under neutral conditions.

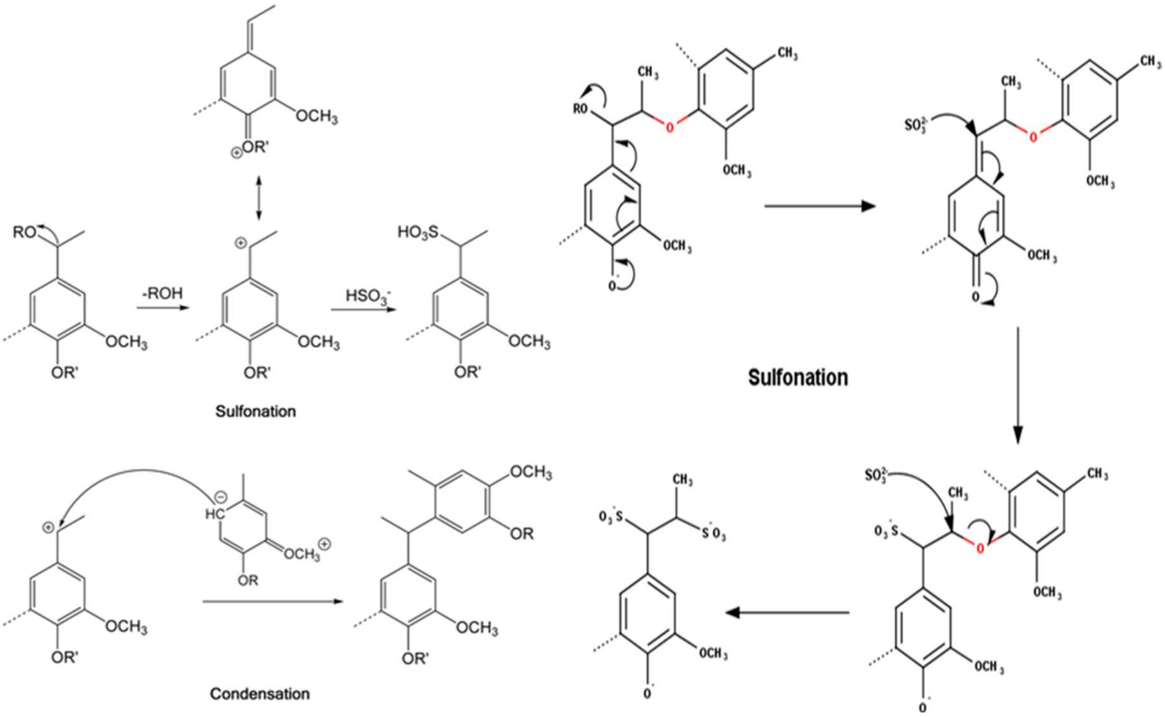


Figure 8.Reactions occurring production of lignosulfonates under acid and neutral conditions [77]

2.1.5 Organosolv Process

Organosolv lignin extraction uses organic solvents for the extraction of lignin from lignocellulosic biomass. The lignin is dissolved by an aqueous-organic solvents in a sulfur-free process, resulting in chemically active lignin with high purity. The organic solvents used include ethyl alcohol, propanone, methanol, acetic acid, or methanoic acid [81].The resulting lignin framework is comparable to that of native lignin in that it is virtually homogeneous, has a low molecular mass, and is polydisperse. A sufficiently severe process can cause lignin's molecular weight to decrease by 56%. Thus, the obtained lignin has a higher syringeal phenolic composition than that of aliphatic alcohol [82].The lignin is recovered through precipitation because of its hydrophicity [81] Nevertheless, has yet to be implemented effectively as a large-scale commercial process, owing to non-optimized extraction techniques for the utilized chemicals, which result in substantially greater operational expenses when weighed against alternative methods of isolation [83].

2.1.6 Soda Process

The soda pulping method, frequently used for processing herbaceous plants like wheat straw and kenaf [84],yields soda lignin [85]. A common soda method uses anthraquinone (catalyst) and aqueous sodium hydroxide (thirteen-sixteen % by mass) to break down lignocellulosic material at temperatures between 140–170 °C [86]. The soda lignin possesses a large carboxylic acid content due to the oxidation of aliphatic alcohol sites, which renders it challenging to recover using filtration or centrifugation techniques [87]. The soda lignin, nevertheless, has further benefits in high value-added uses, especially in polymer composites or biodegradable plastics [88].

2.1.7 Hydrolytic Process

Hydrolysis of wood, catalysed by enzymes or acids, has been explored to use carbohydrates to synthesize ethanol via breaking the lignin-carbohydrate bonds [89]. Because it contains the unhydrolyzed carbohydrates plus residual lignin, the resultant hydrolytic lignin has the highest amount of bonded carbohydrates. Hydrolysis lignin is structurally similar to natural lignin in comparison to other technical lignins [89].Due to the poor hydrolytic efficacy and multiple condensed structures caused by dehydration processes, hydrolysis lignin has a relatively high molecular weight [91].Enzymatic hydrolysis lignin is produced through an enzymatic hydrolytic technique that uses cellulases and hemicellulases to break down cellulose and hemicellulose in lignocellulosic biomass, precipitating lignin in the process [57]. The process is both economical and environmentally friendly [63]. The hydrolytic lignins are sulfur-free and generally insoluble in water and several organic solvents. They do, however, have a structure comparable with native lignin compared to other industrial lignin with between sixty to eighty wt% lignin [84].

2.1.8 Functionalization of lignin

Lignin provides an opportunity to synthesize a wide range of products, and it will have an impact on the future circular economy through its valorization. The techno-economic importance of lignin depends on its extraction process and the technical needs of its intended engineering application. One area in which lignin can play a very big role in advanced material processing, sustainability and the green economy is the production of biobased flame retardants whose existence can reduce the use of conventional, toxic halogenated flame retardants. Because of their sustainability, distinctive aromatic structure, and high charring potential, lignin-based flame retardants are very promising next-generation flame retardant. The polymeric uses of lignin in modern materials are limited due to their difficulty in synthesis, chemical inertness, fragility, and inherent structural variability. As a result, to obtain value-added advanced applications, the structural features of lignin, as well as approaches to improving its attributes, must be widely researched. The combination of commercially accessible polymers with lignin can yield lignin-based polymeric materials with desirable characteristics can be created [67].

In addition to its large molecular structure, lignin's depth of complexity is demonstrated by the presence of multiple functional groups. Although lignin contains a variety of reactive sites, such as carboxyl, hydroxyl, carbonyl and methoxyl, its relatively low reactivity makes it difficult to use for certain applications. This is because lignin typically has at least one methoxyl functional group within its backbone. To get around this restriction, lignin's physiochemical qualities have been improved through functionalization, which is basically a structural modification. Functionalization can include modifying the structure of chemically reactive sites or increasing the reactivity of hydroxyl groups [68].

In general, there are three main types of lignin chemical-based modification techniques that have been studied: modification of hydroxyl group, formation of new chemically functional sites, and fragmentation/depolymerization [81]. The distribution of functional groups within the phenylpropanoid structure forms the basis that promotes the functionalization reactions [92],as summarised in Figure 9.

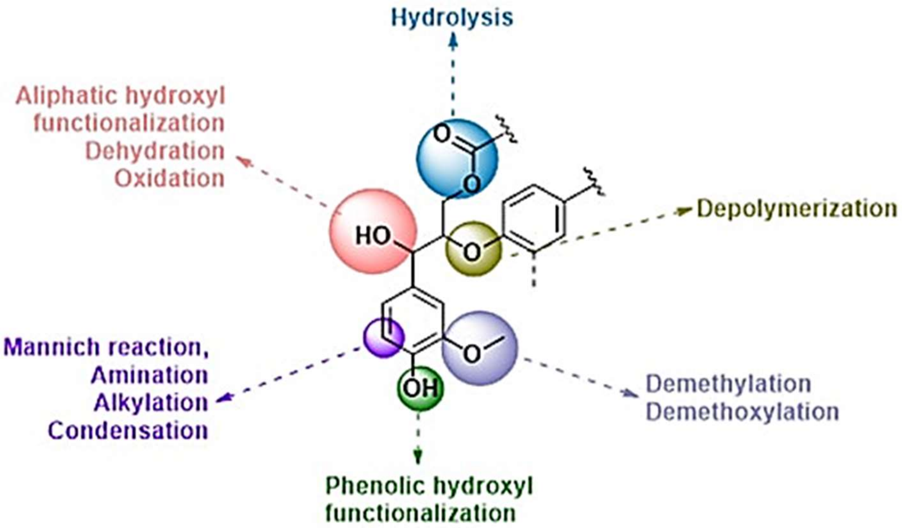


Figure 9:Lignin functional groups with potential for chemical modification [92]

Among the possible reactions are sulfomethylation, phosphorylation, epoxidation, hydroalkylation, acylation, methylation, phenolation, and esterification. Several of the functionalized lignin compounds show exceptional thermal stability [67, 68].Figure 10 summarizes the different pathways for lignin chemical modification [92].

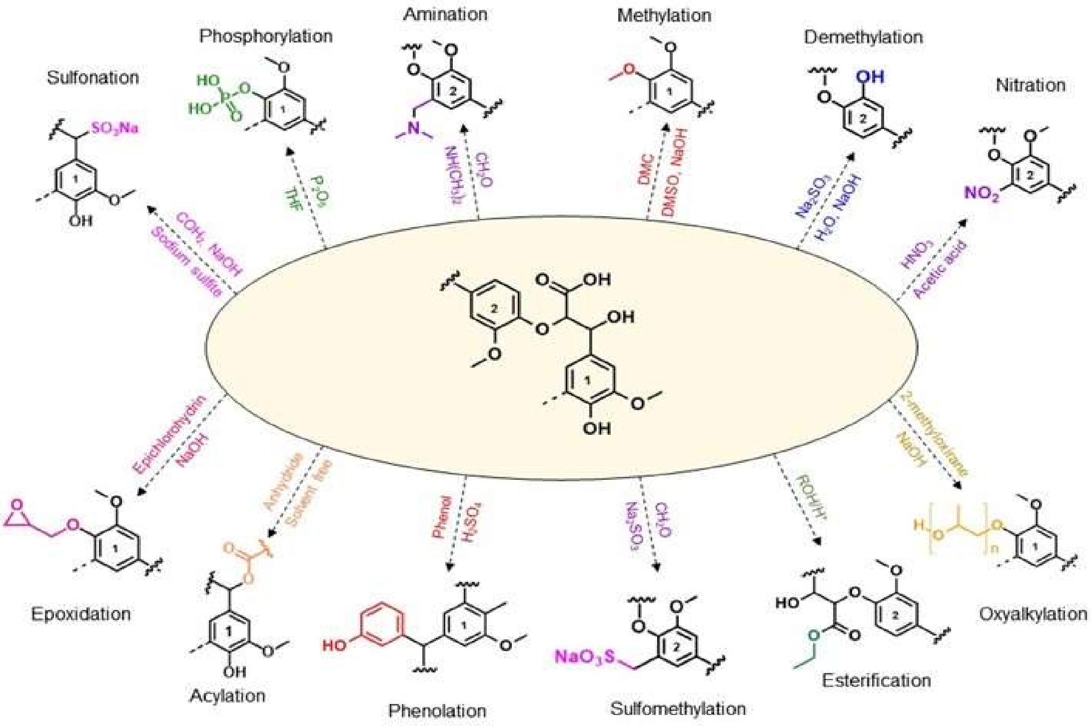


Figure 10:Functionalization routes for lignin [92]

In the last ten years, phosphorylating lignin to give polymers enhanced flame retardancy has drawn a lot of attention. Phosphorylated substances have long been incorporated as flame retardants in flammable plastics due to their exceptional thermal stability. By phosphorylating hydroxyl and phenolic reactive groups in lignin, sustainable flame retardants can be produced, offering lignin's valorisation a genuine commercial opportunity [92].

2.2 Synthesis methods for lignin nanoparticles

A nanomaterial is a material that has at least one of its dimensions on the nanometre scale, which is from 1nm to 100 nm. These materials have unique biological, thermal, mechanical, and electronic properties that cannot be found in traditional materials. Combining these distinctive properties with their exceptional abilities has culminated in structures with greatly enhanced efficiency and novel applications [31]. Nanoparticle research has experienced growth in recent times, as the fabrication of novel materials for engineering is vital for maintaining technological innovation. A lot of research has been undertaken regarding the nanoscale utilization of similar bio-based polymers, like cellulose. Lignin presents an opportunity for growth in this area, therefore nano lignin research has seen rapid growth with various methods having been developed over the past few years. The section below reviews some of the techniques that have been used to synthesize lignin nanoparticles.

2.2.1 Self-assembly

In the technique of self-assembly, a sequential or arranged framework is produced as consequence of several intermolecular non-covalent interactions like permanent dipoles, hydrophobic, electrovalent, hydrogen-bonding, and London dispersion forces. This is a common technique for making nanoparticles [63].

2.2.2 Anti-solvent precipitation

This process entails dissolving lignin in organic solvents like DMSO and THF where the lignin is generally soluble, followed by re-precipitating it in anti-solvents like water, acid solutions and supercritical carbon dioxide [93, 94].These chemical processes are well documented in research with particle sizes ranging from 40-600 nm [73, 95-105].

2.2.3 Physicochemical techniques

The major goal of the procedure is to create lignin nanoparticles using mechanical shear forces or ultrasound, such as homogenizing, ultrasonication, and a mix of numerous mechanical techniques, that can successfully prevent needing to undergo laborious further processes [106, 107]. When compared to the original lignin, there are no noticeable differences between the molecular structure and functional groups of the LNPs produced by the mechanical approach.

Higher reactivity is attained while maintaining the original lignin's fundamental physicochemical properties. The benefits of the physicochemical method's straightforward application and robust process control are also more obvious.

2.2.3.1 Ultrasonic assisted synthesis

The ultrasonic assisted synthesis method involves the breaking of lignin covalent bonds using ultrasound waves [108].In this technique, the fast production, expansion and collapse of microbubbles caused by cavitation resulting from ultrasonic waves. The cavitation results in areas of very high temperatures, pressure, and shear forces [109]. The lignin polymer cleaves into smaller lignin molecules which results in the overall reduction of the size of the particles [110].

2.2.3.2 Homogenization

It was previously reported by [111, 112] that lignin nanoparticles can be produced mechanically using homogenizers. The lignin molecules in a suspended or emulsified solution are dispersed and homogenized using the high-frequency shear homogenization technique. In contrast to the ultrasonic approach, considerable shear force is used to break bonds in lignin [93].

2.2.4 Summary of lignin nanoparticle synthesis techniques

Table 1:Summary of lignin nanoparticle synthesis techniques

Technique	**Range of particle size**	**References**
Self-Assembly	100-200 nm	[95, 101, 113-117]
Ultra-sonic assisted synthesis	80-1100 nm	[116, 118-121]
Homogenization	25-170 nm	[111, 112]
Anti-solvent precipitation	40-600 nm	[73, 95-105]

2.3 Phytic acid

Phytic acid, scientifically known as inositol hexakisphosphate acid, is made up of 28 percent phosphorus. It is abundant and is plant-derived from oil seeds, legumes, beans, and grains [122]. There have already been some fascinating studies on the use of phytic acid-based fire retardants in various types of textile fabrics in scientific literature. This organic polyphosphoric acid, specifically, has been extensively used as a flame retardant since it is environmentally safe [123], biocompatible [125], and nontoxic [126].

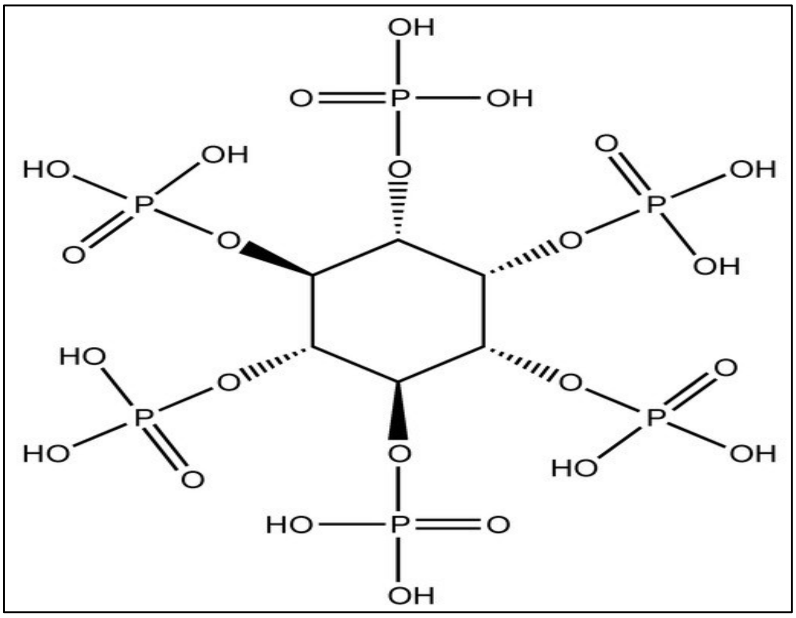


Figure 11:Structure of phytic acid [127]

Phosphate flame retardant works by absorbing heat during the decomposition process and creating a crystalline barrier between oxygen and fire. Oxyphosphoric acid compounds, which are generated during the breakdown of phosphorus-based FR compounds, promote the dehydrogenation of polymeric materials to carbon, allowing char to be formed. Phosphorus is also a far more potent free radical scavenger than chlorine or bromine [128].There has been growing interest over the years in using functionalized bio-based flame retardants. Phosphorylation is the most common approach for making bio-based products fire-resistant.

2.4 Polylactic Acid

In recent times, there has been a significant surge in interest in the production of biopolymers owing to growing worries about resource depletion and increased pollution. Polylactic acid (PLA) is a biopolymer that is widely produced worldwide, making it a viable option for product commercialization among other biopolymers[129].Polylactic acid (PLA), shown in Figure 12, is a bio-based, biodegradable polyester made from renewable resources. PLA can be decomposed by soil microbes under specified temperature and humidity conditions [130, 131]. PLA is an aliphatic polyester produced from lactic acid building blocks [132], produced by converting corn starch into lactic acid (which is a natural and sustainable material) as a feedstock through microbial fermentation or via a petroleum-based process [133].

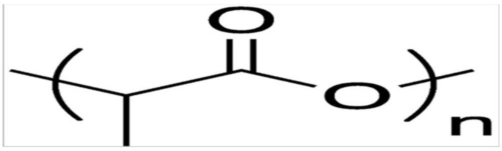


Figure 12:Structure of Polylactic acid (PLA) [47]

Lactic acid can be converted directly to polyesters via the poly-condensation process of lactic acid owing to the existence of alcohol and carboxyl groups or by first converting lactic acid to the dimerized form followed by ring-opening polymerization [131]. Figure 13 shows the ring-opening polymerization method used to make polylactic acid [48].

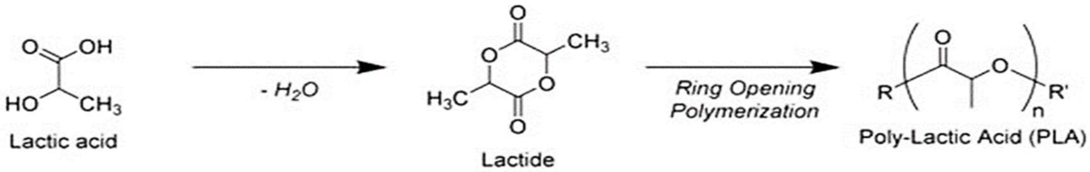


Figure 13:Ring open polymerization method for PLA. Reproduced from [48]

Polylactic acid has an extensive variety of uses, from manufacturing to the private sector and possesses excellent economic potential and extremely promising market prospects [129]. Polylactic acid, for instance, has superior mechanical characteristics and may be utilized to produce multiple plastic products for packaging, electronics, and textiles for industrial and domestic purposes. This is why its superior performance has sparked demand for its bulk production [134].PLA, like other polymers, is highly flammable and this limits its applications, and a lot of research is ongoing to improve its flame retardancy properties.

2.5 Polymer Combustion

Heat, fuel, and oxygen are the three main components needed for the combustion cycle to begin and continue. Heating a substance to the pyrolysis temperature produces flammable gases, liquid condensates, and char. At higher temperatures, like combustion temperatures, those flammables continue to burn [135].Polymers break down gradually in the presence of enough heat, producing flammable gases that combine with oxygen in the surrounding air to create an ignitable source. Ignition happens spontaneously or around the flash point whenever the temperature is sufficiently high for autoignition. A portion of the heat that is released during combustion flows to the substrate, encouraging additional breakdown. A self-sustaining combustion cycle occurs if there is sufficient heat to keep the polymer degradation rate high enough to keep the volatile amount within the combustibility limits [136]. Polymers are combustible due to their primarily carbon and hydrogen chemical composition. Carbon is the main component of all organic polymers [6].

Although bonds between carbons are the basic structural components of all polymer compounds, some polymers also contain carbon-nitrogen and carbon-oxygen bonds depending on the availability of heteroatoms in their primary chains [6].If organic polymers are heated to a sufficient degree, they can all undergo thermal degradation. When these bonds break, highly volatile gases are released, which helps the fire spread, having previously absorbed part of the heat supplied. [137]. Figure 14 summarizes the cycle of combustion. Thermal degradation of plastics is dependent on several factors, including the polymer's structure, the conditions under which its degradation occurs, and the existence of polymer fillers/additives in the material [138]. While each polymer's degradation and stability are affected by the factors listed above, nearly all polymers degrade within a temperature range from 250 to 450 °C [139]. Whenever organic and inorganic substances are subjected to heat, they deteriorate thermally. The process is termed a fire if the thermal destruction of flammable materials is an oxidation process and typified by the formation and emission of heat and light. In this endothermic pre-ignition phase, the material undergoes dehydration, pyrolysis, and evaporation of volatiles. In the next phase, the volatiles are ignited and oxidized to produce a flame. The flame is a visible marker and an indicator of the heat produced, which is the light released by the fire [128]. Combustion is almost always a gaseous process. Inside this gaseous phase, volatile flammable species undergo an exothermic oxidation process.

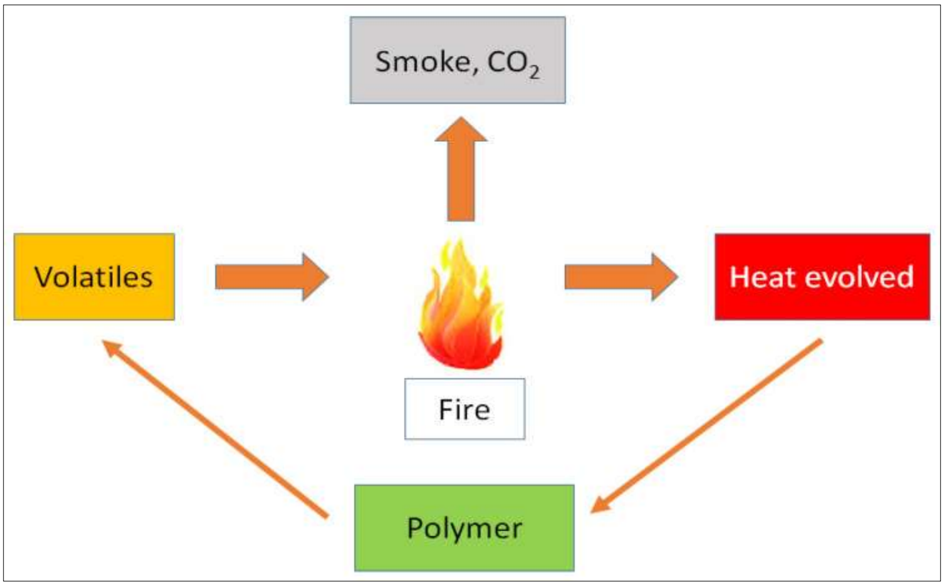


Figure 14:Combustion Cycle of polymers [6]

The combustion process releases a lot of heat energy, smoke, and solid particles in the form of ash and soot. The smoke is mainly composed of highly toxic fumes. In a bio-composite, which is a combination of a bio-based polymer matrix and a reinforcement agent of plant origin, the properties of the polymer control the fire behaviour and thermal stability of the bio-composite. In practice, polymers chosen for the polymer matrix should have a high thermal degradation resistance, which can prolong up to temperatures ranging from 150-250°C, low combustibility, and should be able to maintain their shape up to around 400°C. Over the years, various strategies for reducing flammability in fossil-based fuels have been explored, and implemented, and are constantly being improved [140]. Those same strategies are being used for bio-composites [141].

2.6 Characterization of Polymer Combustion Behaviour

Numerous methodologies are employed to examine the burning characteristics of polymers.

2.6.1 Cone Calorimetry

Cone calorimetry,Figure 1, is one method that has drawn a lot of attention due to its excellent performance for combustion behaviours time to ignition (TTI), time of combustion (TOC), total heat released (THR), heat release capacity (HRC), heat release rate (HRR) and peak heat release rate (pHRR), are all measured by the device during the combustion of polymers [142]. During the combustion test phase, the mass loss of released carbon monoxide and carbon dioxide content as well as total smoke release are also detected [143].

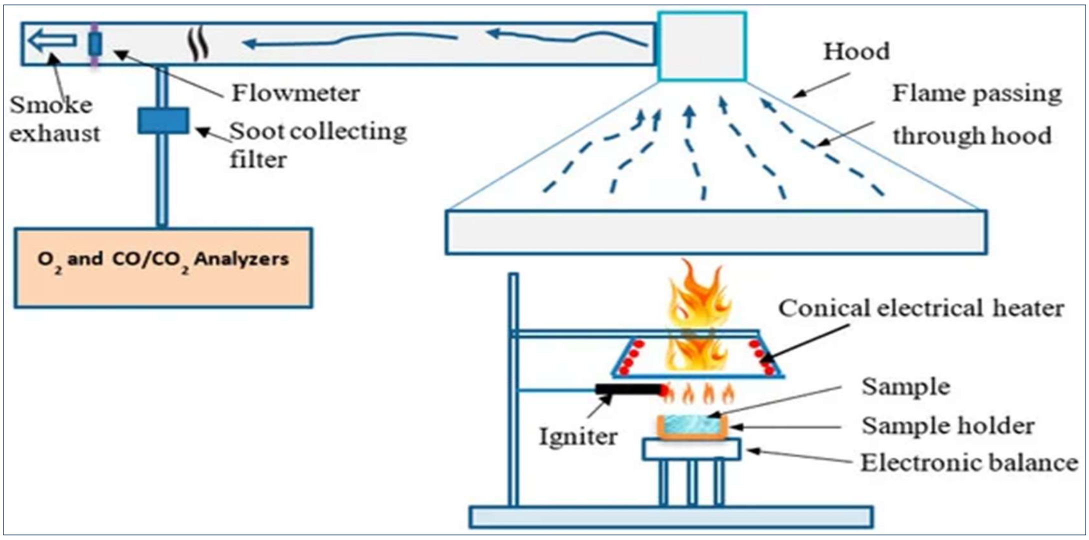


Figure 15:Cone calorimeter schematic [144]

2.6.2 Limiting Oxygen Index

An additional evaluation involves calculating the limiting oxygen index (LOI), a measurement that indicates the lowest amount of oxygen utilized in the system with a mixture between oxygen and nitrogen during polymer combustion [145]. The LOI test simulates combustion, which is not the real world. It is limited to the classification of materials that are self-extinguishing or combustible [146].Figure 16 shows the setup for the LOI experiment.

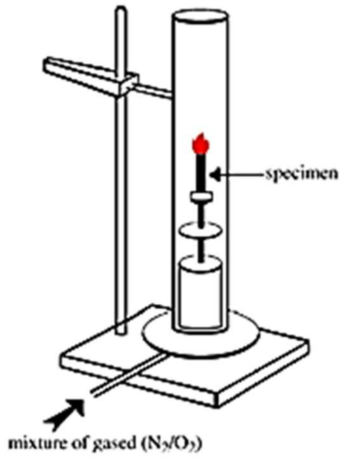


Figure 16:LOI schematic [145]

2.6.3 Underwriters Laboratories (UL-94)

The Underwriters Laboratories (UL-94) standard serves to categorize materials according to their flammability. This standard's flammability test measures and records the materials' reaction to the applied heat and flame to perform a preliminary screening of their fire performance. By following the ASTM D635 and ASTM D3801 standards, the general burning test can be performed in both horizontal and vertical orientations respectively [147].The procedure will be further described in Chapter 3.

2.6.4 Thermal gravimetric analysis

Temperature-dependent changes in a substance's physical and chemical characteristics are measured by TGA (ASTM E-1131). The percentage of weight of raw materials left after heating relative to weight loss at the starting temperature is used to compute the thermal properties of the polymer at the end of the cycle of heating [136]. Char residues are regarded as parameters obtained by TGA to analyse the thermal characteristics of polymeric materials [142] .

2.7 Current Fire Retardancy Strategies

1. **Use of highly flame-retardant polymers (Inherently flame-retardant polymers)**

To reduce polymer flammability, it's vital to synthesize a high thermal stability polymer that has less propensity to release flammable gases upon thermal decomposition. Thermally stable polymers, on the other hand, may have performance restrictions and are frequently too expensive and complex to produce. As a result, to confer flame retardancy to a polymer, manufacturers use various fire retardants [148]. These polymers have extraordinary flame suppressant properties. Unfortunately, they are very expensive and have aging challenges, therefore they are only suited for a few applications (for example in aerospace and military industries) [149]. These include polyphenylene-benzobisthaizole (PBZT) and polyphenylene-bezobisoxazole (PBO) [6, 150].Figure 17 shows the structures of the two polymers.

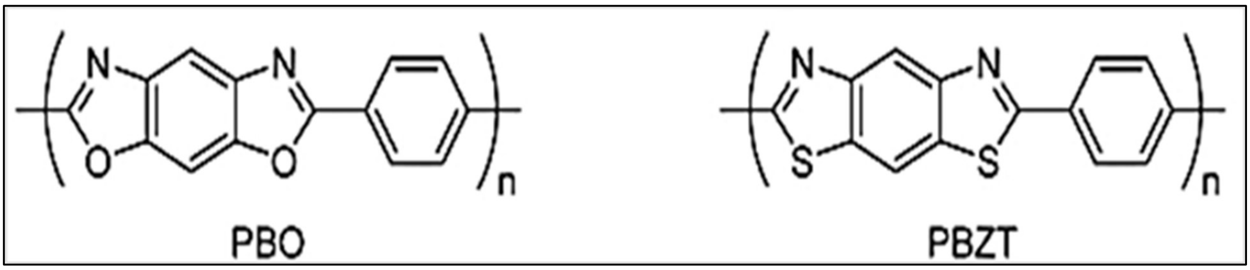


Figure 17:The structures of PBO and PBZT [6]

Novel inherently flame-retardant polymers have been reported by several researchers. Zhang et. al synthesized inherently flame-retardant calcium alginate fibre. The thermal degradation mechanism AND pyrolysis products of calcium alginate fibre were investigated. The Calcium alginate fibre showed intrinsically flame-resistant properties, with an LOI value of 48.0, compared to approximately 20.0 for viscose fibre. The heat release rate (HRR) and total heat release values (THRR) of viscose fibre were much higher with respect to those of inherently flame-retardant fibre, according to cone calorimetry. It was also discovered that the burning of inherently flame-retardant fibres created more residues than the combustion of viscose fibres [151].

Wang et.al [152] formulated polypropene(PP) copolymer an inherently flame-retardant embedded with self-extinguishing properties, generated by integrating a phosphorus-based molecule into the polypropene molecules. This was achieved through a two-step polymerization based on propylene coordination polymerization,and then diethyl-(4-vinyl benzyl) phosphonate (DEVBP) atom transfers free radical polymerization (FRP). Different formulations of polyphosphonate-containing PPs with DEVBP contents were prepared and the thermal degradation behavior was analyzed. The results demonstrated that the phosphonate-containing PP had a different mechanism of decomposition than pure PP, resulting in more char residue. The phosphonate-containing PP had better flame-retardant qualities than PP in the cone calorimeter, limited oxygen index, and UL-94 tests.

Xu et. al,[153], developed a new inherently flame-retardant composite material using and nano-cuprous oxide and zinc alginate. The composite materials were characterized, and their ignitability and combustion characteristics were evaluated. The composites showed a high thermostability and a limiting oxygen index (LOI) of 55, making them nearly non-flammable. When compared to ZnAlg, the ZnAlg/ Cu_2O composites demonstrated a significant improvement in flame retardancy.

2. Use of Flame retardants

To prevent polymeric materials from burning, chemical additives known as flame retardants (FR) are introduced to the material. Among the flame retardants employed with polymers are melamine, metal hydroxides, organophosphorus and halogenated compounds. Flame retardants are generally divided into two distinct groups: additive or non-reactive and reactive, as shown in Table 2 below. Additive approaches entail the physical addition of flame-retardant materials to polymers. The physical integration of flame-retardant additives to polymers is known as an additive treatment. In contrast with flame retardants based on polymer treatment, non-reactive type fire retardants usually function by way of a deformation process at high temperatures, within the range where combustion takes place. Polymeric materials, mineral fillers, and hybrid organic materials are increasingly prevalent as flame-suppressants [154]. The two sub-divisions of the additive type are the inorganic and organic [55]. Reactive-type methods, as opposed to additive-type ones, depend on chemically modifying polymers to include fire retardant elements [56-57]. The reactive type is chemically introduced within the matrix of the polymer during the process of polymerization, in some cases after the completion of the polymerisation process [47].

Table 2:Summary differences between additive and reactive types [148]

Reactive type	**Additive type**
Chemical reactions are used to incorporate them into the polymer.	Physical blending is used to incorporate them into the polymer.
Bond chemically with the polymer, becoming part of the polymeric structure.	No chemical bonding with the polymer, will therefore not be part of the polymer structure.
Addition can only be done in the beginning stages of the manufacturing process.	Addition to the polymer structure can be done at any point throughout the manufacturing process.

This strategy is divided into two categories, (a) Incorporation of Flame retardants which utilize the additive type of flame retardants, and (b) Chemical modification of polymer surface which uses the reactive type of flame retardants.

a) Incorporating Flame Retardants in Polymers (additive type approach)

In this technique, additives that possess good flame-retardant properties are added to the polymer via melting [6]. It is a cheap process that results in the addition of the correct amounts to impart flame retardancy [155]. These polymers have extraordinary flame suppressant properties. During the production process, additive fire retardants are physically combined with polymeric materials, where in each case the fire retardants do not react chemically with the plastics. Inorganic additives are often used as fillers and can be produced with halogenated chemicals [156]. In the polymer industry, halogenated chemicals comprising bromine, chlorine, and other elements are the most common addition flame retardant materials due to their low cost and excellent performance [157]. Brominated flame retardants (BRFs) are the most prevalent flame-retardant chemicals in plastic Organo-halogen based flame retardants are mostly those that are brominated. Thermal decomposition of chlorinated and brominated substances produces HCl and HBr, respectively. Chlorine and bromine radicals are created when these react with H and OH radicals in the flame. The redox reactions of the flame are slowed by halogen radicals, which are less reactive than H or OH radicals [136]. Low-cost brominated flame retardants work on a wide range of polymers. It's worth noting that halogenated flame retardants are harmful to humans and animals, and many have been outlawed. Notwithstanding all environmental and toxicological concerns, halogenated chemicals are nonetheless widely used due to their low cost and great performance. Halogenated acids (HX) are flame retardants that inhibit combustion chain reactions by scavenging active radicals (H• and OH•) and bigger organic fragments (R) [158]. Figure 18 below shows examples of halogenated FRs.

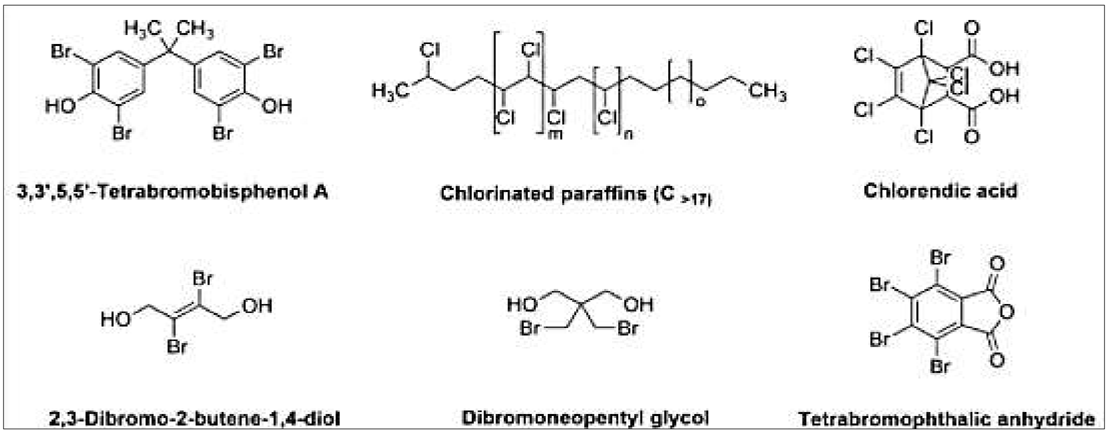


Figure 18:Examples of halogenated FRs [128]

Another well-known effective strategy involves the addition of non-flammable fillers into the structure of the polymer. The choice of fillers is centred on compounds with the ability to absorb heat from the combustion process and degrade endothermically through decarboxylation or dehydration. Metal Hydroxides and carbonates are good choices for this strategy [159]. The release of molecules of water also slows down the polymer's burning process and lowers its temperature. A good example of this kind of chemical is hydrated aluminium hydroxide, which breaks down into aluminium oxide when exposed to heat, providing a layer of protection on the polymer material surface, that strongly retards flame propagation [128]. Magnesium hydroxide, on the other hand, has better thermal stability than aluminium hydroxide because it decomposes in the range of 320–350 °C compared to 200–230 °C, aluminium hydroxide, making it much easier to synthesize polymeric materials with this filler. The filler decomposes due to heat, inducing a charring effect, which prevents both heat and air from reaching the material [160]. Borates, silicates, and organosilanes form similar physical barriers in the form of boron and silicate glass whilst other types of fillers impart fire retardancy by releasing gases that act by removing radicals [161]. The discharge of significant amounts of non-combustible gases (e.g., Nitrogen, Ammonia, Sulphur dioxide, and Carbon dioxide) lessens the combustion rate and temperature by diluting flammable and poisonous combustion gases, as well as oxygen. Furthermore, fillers that boost a material's thermal resistance (such as iron oxides antimony or zinc) perform well as thermal retardant fillers. The low cost of fillers makes them preferable in imparting flame-retardancy in polymers. It should be emphasized, however, that a small weight percent of filler can be introduced into the polymer without impairing its mechanical strength [127].

b) Chemical modification of polymer surface (reactive type approach)

In this approach, there is the chemical modification of the monomer before polymerization resulting in a flame-retardant polymer. An example of a chemically modified polymer is Trevira CS, a PET fibre with excellent fire retardant due to the chemical modification of its monomer [137].Inherently flame retardant exists but not all polymers possess this special property. Nylons, polyesters, polypropylenes, and other useful, cost-effective polymeric materials are not fire-resistant. They should always be treated with flame retardant chemicals to reach the necessary level of fire resistance. As previously stated, reactive-type fire retardants confer improved fire resistance to a polymer, either through the manufacture of a fire-suppressant polymer or through the incorporation of a reactive component to a polymer, which is accomplished by adding a flame retardant component on the side chain or terminal end via a chemical reaction [162].

Several synthetic routes can be used to synthesize or modify polymeric substrates to create polymers containing polar or reactive groups. The two main techniques used for chemical modification are polymer functionalization and polymer grafting. Functionalization refers to a process that begins with a previously non - functional polymer and adds functional groups to the base polymer chain. The two methods are closely related. In most cases where polymer grafting is desired, the first step is the creation of a functionalized or reactive polymer substrate, followed by functional group reactions along the base polymer chain (polymer backbone) with other monomers or polymers [163]. The following are the procedures used to create a functionalized polymer: Direct copolymerization, which is a type of copolymerization that occurs when monomers, one with a functional group, react to form a copolymer. For example, poly(St-alt-MA) is a functionalized copolymer produced from the reaction between maleic anhydride(MA) and styrene(St) [164]. End-functionalization-several possible routes have been suggested for this technique, (i)The first one involves modification of the ends of a polymer chain, (ii) breaking the growth of a polymer chain, or (iii) breaking the chain growth before functionalization of the ends of the polymer chain. The three suggested routes all involve species with the required functional groups [163]. Graft polymerization is a technique wherein monomers are linked by covalent bonds and polymerized to the polymer backbone. The grafting method is for adding of reactive groups to a polymer. Since they comprise at least two distinct monomer units, which are not the same as the main polymer chain, these polymers can also be described as graft copolymers [165]. It is made up of one or more of the following techniques: (i) grafts of homopolymers or copolymers containing functional groups are synthesized in situ, commencing with monomers along pre-existing polymeric chains (ii) usage of existing polymeric materials with reactive species and chain ends with affinity to the polymeric backbone; (iii) reaction or exchange of changeable atoms of the polymer base chain by functional monomers [166, 167].

3. Surface treatment of polymer

Another technique to prevent polymers from burning is coating the material surfaces with flame-retardant coatings which naturally act as barriers to oxygen, foaming or melting when exposed to high temperatures. An insulating layer is formed which delays heat and mass transfer between phases [127]. This strategy is simple to apply and has numerous advantages. The most significant advantage of the technique is the impartation of fire retardancy properties on the material with no mechanical property changes. This approach works with a variety of materials, including plastics, metals, wood, and fabrics. Cold plasma is one of several technologies used to change the polymer surface. The polymer surface is treated to reach optimal functional properties while preserving the material's physicochemical characteristics. Cold plasma technology or small coatings of organic material are used to initiate surface functionalization processes on a material's surface [168]. Most retardant coatings are built on 'traditional' intumescent systems; nevertheless, there are significant research ongoing on this subject, and many variables in the formulation can be changed. Intumescent formulations may be produced to satisfy specific fire protection needs, depending on the substrate employed [141].A thorough understanding of intumescence necessitates an examination of physicochemical processes [169]. Various mechanisms have been suggested, including flame suppression, heat loss owing to melt flow and pouring, surface barriers with char development, acid-catalysed dehydration, and char promotion. The creation of a burnt layer affects the efficacy of intumescent flame suppressants significantly [170]. Acid source, for example ammonium polyphosphate (APP),melamine phosphate, boric acid, phosphoric acid, sulfuric acid including their derivatives], carbonization source, for example pentaerythritol, mannitol, starch, dextrins, and blowing agent, usually nitrogen-based compounds that release ammonia, carbon dioxide and water vapor are the three components of IFRs [171]. The acid source is responsible for dehydrating the carbonizing agent to form a carbonaceous layer. The acid source should decompose at a temperature lower than the degradation temperature of the carbonizing agent [137]. The carbonizing agent is usually a carbohydrate, which dehydrates near the polymeric material temperature of decomposition, forming a protective char in the process [143]. The quantity of char created is dependent on the number of carbon atoms and the reactive hydroxyl groups in the carbohydrate [170]. The most prevalent intumescent flame-retardant formulation is the APP–PER–MEL system, which includes ammonium polyphosphate (APP), pentaerythritol (PER), and melamine (MEL), usually found in epoxy, acrylic, and urethane composites. The APP–PER–MEL system's char generation and flame retardancy processes have been extensively explored [171, 172].

In the case of a fire, the coating intumesces when exposed to heat, creating a thermally shielding char that prevents heat from spreading to the materials [5]. Around 250℃, the intumescence process for this formulation begins, with APP degrading to polyphosphoric acid and an amine. Dehydration of PER by polyphosphoric acid via esterification occurs about 320-400℃, followed by char formation. Ammonia and water are removed in this procedure, resulting in a cyclic phosphate ester, which is then converted into pentaerythritol diphosphate by a series of repeated reactions as above. Melamine, the blowing agent, breaks down at the same temperature as the char-forming processes. The vapours produced condense into tiny bubbles, foaming and swelling the char. The coating hardens into a dense, multicellular substance, slowing the heat transfer rate from the fire to the polymer. As a result, the NH_3 and CO_2 produced, cause the char to expand [173]. The nature of the intumescent char determines the qualities of fire-suppressant coatings [77-79]. Xu et .al,[80], investigated the effectiveness of adding eggshells to the APP-PER-MEL system and subsequently reported that the introduction of chicken eggshells to the standard APP–PER–MEL system can increase fire suppression and smoke reduction by forming more thermally stable, intumescent char. Wang et.al [81], reported that the fire resistance of nano coatings made of acrylic nanocomposite was superior to flame retardant coatings made of traditional acrylic resins. The char structure's anti-oxidation and char output may change at high temperatures due to the presence of nano-SiO2 particles in acrylic nanocomposite. Polyacrylate and melamine-formaldehyde resins in commercialized intumescent coatings have all been thoroughly studied [174]. Melamine-formaldehyde resins, in addition to the polymeric matrix resin, serve as a blowing agent in this formulation, with a high foaming factor [175]. Another type of amino-based resin is urea-formaldehyde resin (UF), which is frequently utilized in textiles, wood, and paper. Melamine may be integrated into UF whilst on condensation to increase the strength of bonds and resistance to water while decreasing the amount of free formaldehyde [66].

2.7.1 Action-mechanism of flame retardants

Systems that are meant to be flame-retardant either function in physical or chemical action. They might interfere with the various combustion cycle processes that take place [143]. Ignition, heating, thermal decomposition, and flame spreading throughout the polymer are the stages of the combustion cycle [176]. The mechanisms are explained in the following section:

2.7.1.1 Chemical action

A gaseous phase mechanism: this is whereby flame retardants working in the gaseous state combine with Hydrogen and Hydroxyl radicals in the gas phase to generate unreactive molecules, resulting in a considerable reduction in heat balance and fire propagation. The flame retardant disrupts the radical chain reaction in the combustion process, which occurs in the gaseous phase. As a result, the exothermic reaction is halted, and the system starts to cool, causing a reduction in the supply of combustible until its eliminated. When polymers are pyrolyzed, they can react with oxygen, causing chain branching processes that speed up the burning process. Most of these systems rely on phosphorus-based or halogenated chemicals [177]. When polymers are pyrolyzed, they can react with oxygen, causing chain branching processes that speed up the burning process. By inhibiting hydroxyl and hydrogen-free radicals from interacting with air and CO, halogenated or phosphorous flame retardants disrupt the free radical chain mechanism. As a result of the quenching of radicals, the exothermic oxidation flame chemical reactions are disrupted, leading to the impediment to combustion This mechanism is also called flame poisoning [178].

Condensed phase mechanisms: unique silicon or phosphorus-containing compounds may trigger cross-linking interactions throughout the material at high temperatures, resulting in a glassy or ceramic surface with efficient barrier properties both against volatile and transfer of heat transfer. By changing the pyrolysis process route, fire retardant compounds in the condensed phase reduce the volume of gaseous flammable materials generated. Char, H2O, and CO2 are frequently formed as a result [177]. The gases are reduced by the passive protective material. The char blocks heat and mass transfer, protecting the fibre. Carbon is stabilized and inhibited from forming flammable gases. The two key reactions in flame retardants involved in the condensed phase system are cross-linking and dehydration. Most of these reactions occur in phosphorus-based FR compounds [178]. Fire retardants can also work physically, using the following mechanism:

2.7.1.2 Physical Action

Cooling effect/Thermal quenching: Hydrated compounds and metal hydroxides can be used as FR fillers. They absorb energy and break down during the combustion process, cooling the fire environment in the process [177]. Heat sink effect is another term given to this process. Fuel dilution: occurs when inert gases (H2O, CO2, NH3) are released during the combustion process, whilst some flame retardants cause the combustible gas mixture's oxygen concentration to drop. This effectively slows down the reaction pathway by limiting the concentrations of reactants [178].

Protective layer effect: Some FR additives form a gaseous or protective barrier which separates the condensed and the combustion phase medium. This reduces the rate of movement of combustible gases and thermal degradation of the polymer [177]. Heat is generated by the burning of volatile chemicals in the polymer, and if enough heat returns to the polymer, its thermal degradation continues because the self-sustenance nature of the burning cycle. The additives must have the ability to restrict heat transmission from the source of heat while also preventing oxygen from reaching the combustible material [6]. In addition to that, they impede pyrolysis gases from reaching the material's surface. This mechanism is common in phosphorous, silicon, and boron compounds [178].

Dilution effect/inert gas dilution: These additives, during their thermal decomposition, produce inert and non-combustible decomposition gases. These induce the dilution of the fuel in both the solid and gas phases, lowering the amount of oxygen and flammable gases below the ignition limit, and preventing it from igniting. In the combustion cycle, the more critical chemical processes that fire retardants impact occurs in the solid and gaseous phases [170].

2.7.2 Flame retardancy mechanism for bio-based compounds

Depending on whether the mechanism is physical or chemical, as well as the phase in which it occurs (that is, the condensed or gas phase), the mechanisms of action of flame retardants are divided into different categories [179,180] . All bio-based flame suppressant systems work by physically restraining the flame, primarily through the charring effect [181]. A heat sink is aided by the char that is produced at the sample's surface [182]. This heat sink stops heat from spreading to the main body of the material [183].

2.7.3 Intumescent Flame-Retardant Systems

The Latin term "intumesce," which means "to swell up," is where the word "intumescence" originates [184]. When heated, intumescent flame-retardant additives go through a process of thermal degradation that results in "intumescent char," a foamy, multifaceted residue that is thermally stable. When these materials are added to a polymeric material that is subsequently involved in a fire, they create an intumescent char that builds up on the surface as the polymer is consumed, protecting the underneath materials from the flames and offering insulation to them [185]. This charred layer shields the underneath polymer material from heat and fire and stops oxygen from entering the combustion site. Non-halogenated flame retardants, that do not break down into dioxins, are used in present-day intumescent flame-retardant systems. These flame retardants are less harmful for humans and the environment compared to their halogen-containing equivalents. Conversely, dioxins and compounds similar to them can be produced by the breakdown of halogenated benzene compounds. [186]. Figure 19 shows the IFR mechanism and Table 3:Components of IFR system summarizes the different components in an IFR system.

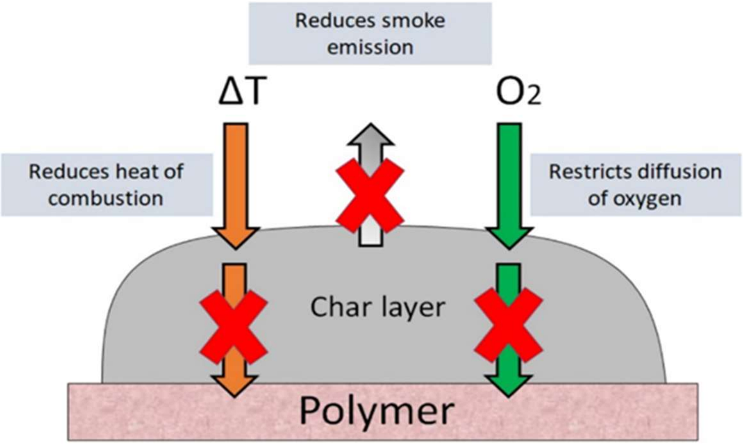


Figure 19:Intumescent flame-retardant system mechanism [6]

Table 3:Components of IFR system [148]

Component	Remarks
Charring/Carbonizing agent Polyhydric alcohols (erythritol and its oligomers-inositol,sorbitol, pentaerythritol, arabitol, pentaerythritol dimer and trimer) saccharides (maltose, arabinose,glucose) polysaccharides (dextrin,starch,cellulose) polyhydric phenols (resorcinol) Phenol-formaldehyde resins Methylol melamine	Should have a substantial number of carbon atoms, resulting in a carbonaceous material with a considerable quantity of hydroxyl groups that can undergo esterification with acids after its thermal decomposition. Its dehydration should occur near the polymeric material decomposition temperature.
Acid Source/dehydrating agent Tricresyl phosphate Amine salt, ammonium salt, esters of phosphoric acid (ammonium phosphate and polyphosphate, melamine and urea phosphate tributyl) Organophosphorus compounds Haloalkyl phosphates Phosphoric acid Alkyl phosphates boric acid and its derivatives (ammonium borate and borax) tricresyl phosphate	Usually, inorganic acids but some organic-based are being discovered. They should have the ability to give out acids during their thermal decomposition which are responsible for esterification of hydroxyl groups in the charring agent/acid source. Decomposition of the acid source should be at temperatures below the degradation range of the carbonizing agent.
Blowing agents Nitrogen compounds (Amines and amides) Polyamides Urea-formaldehyde resins Dicyandiamide Melamine Urea	Decomposition of the blowing agent through an endothermic reaction,produces a large amount of non-flammable gases which include CO_2 and NH_3 during its thermal decomposition, causing melting and subsequent swelling of the char. The breakdown of the blowing agent occurs at approximately the same temperature as that of the char-forming processes.

2.8 Phosphorus-based flame retardants

Phosphorus-based fire retardants are a popular solution to halogen-based fire retardants, and they can work in two distinct approaches to prevent fire in polymer materials [8]. The first approach converts the polymer into carbonaceous char by means of the thermal breakdown of phosphorus-based fire retardants into phosphoric acid [187]. The second mechanism involves quenching the free radicals through migration into the gaseous phase; in certain instances, both mechanisms are used simultaneously [188]. Phosphorus-based fire retardants burn relatively extensively, particularly when the production of gaseous phase breakdown products is reduced by converting both the polymeric material and the flame suppressor into char. Because these volatile compounds could be detrimental to health, it's best to convert them to carbon-containing char [36]. Depending on the phosphorous compound structure, different fire retardant mechanism approaches can be applied for different polymers [189]. Phosphorus-containing flame retardants comprise among [190] others, those stated in the previous section, APP, red phosphorus [148], phosphonate, phosphate ester (pyrophosphate and polyphosphate) [187], and phosphonate, phosphate ester (pyrophosphate and polyphosphate) [191], and novel FRs based on phytic acid. The structures of some of these chemicals are shown in Figure 20.

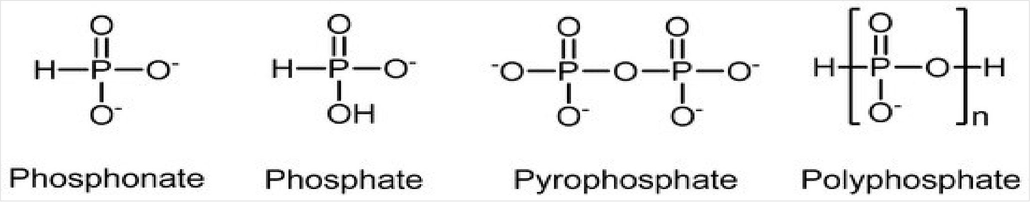


Figure 20:Structures of phosphate moites [187]

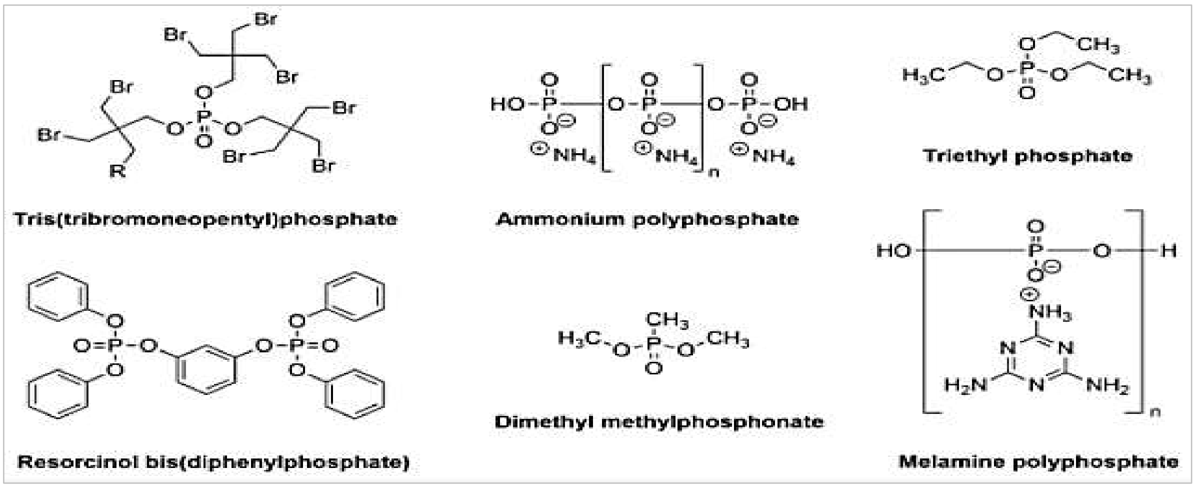


Figure 21:Examples of phosphorous based flame retardants [128]

2.8.1 Phosphorylated Bio-based FR additives for biopolymers

Various biobased materials do not have adequate flame-retardant properties on their own, however, phosphorylation can result in a viable flame-retardant agent. The several phosphorous-based modification methods for the manufacture of phosphorus-containing flame retardants in biopolymers, reported in the literature are discussed in this chapter. The section excludes lignin-based flame retardants as they will be discussed later. Several researchers have reported their work in different biopolymers in the past decade. A group of researchers, Reti et al. [107], reported one of the novel strategies of a bio-based, phosphorylated system for imparting flame retardancy in PLA. They modified the conventional PLA/PER/APP flame retardant system by replacing PER with the bio-based FR additives, in the form of lignin and starch. Cone calorimetry, LOI and UL-94 tests were applied to evaluate the fire resistance characteristics. The composites comprising lignin and starch had a lower LOI value than the PLA/APP/PER composite and UL-94 V0 classification in contrast to V2 for the PLA/APP/PER. Cone calorimetry tests show a decrease in pHRR and conclude an intumescence-based FR mechanism. To ensure maximization of the amount of bio-based additives in the composite, optimization of the loading ratios was used to create new composites, which were tested again for flame retardant characteristics. A composite with a loading ratio of 60wt percent PLA,12wt percent APP, and 28wt percent starch recorded a LOI value of 32%.

Suardana et. al [99], studied the effect of different diammonium phosphates (DAP) on the FR characteristics of PLA /PP and natural fiber bio-composites. DAP was added to the bio composites to enhance flame retardancy. Flammability tests were conducted on the composites and the results showed that a high percentage of DAP in the bio composites improved the flame retardancy but affected other mechanical properties like tensile strength. In the same period, Feng et al. [108], explored the effect of β-cyclodextrin (CD) as a bio-based source of carbon, combined with APP and MA to form APP/MA/CD, as a flame-suppression formulation for PLA. Flammability tests indicated that a 20% loading ratio of APP/MA/CD indicated double char residue formation, LOI value of 34.2, and UL-94 V0 rating. Another research to improve the fire properties of PLA was reported by Wang et .al [113], who synthesized IFR PLA/starch/Microencapsulated ammonium polyphosphate (MCAPP) bio-composite via melt blending. The MCAPP was added to enhance the FR characteristics of the composite and to hinder the reaction between APP and starch. The flame-suppression characteristics were evaluated using MCC, UL-94 test, and LOI test. The bio-composite had a much lower pHRR and THRR than neat PLA.

Mauldin et .al [101] investigated a bio-based FR for PLA.In their work, a novel polyphosphate based on isosorbide was created and used as a flame retardant for polylactic acid (PLA). The flame-retardant PLA contained 97% by mass bio-based content. Based on UL-94 flammability testing, isosorbide-based polyphosphates were reported to be excellent PLA fire retardants, capable of self-extinguishing flames in at most 2 seconds, and in the UL-94 tests, they attained V2 and V0 ratings at polyphosphonate weight percentages of 5% and 15%, respectively. Fox et .al [112] reported their work to improve the FR properties of PLA, intumescence-based systems were generated based on APP. For the carbon source in the system, three different compounds namely, nanofibrillated cellulose (NFC), PER, and POSS-modified NFC. Flammability tests showed that the cross-linked system produced by PLA, POSS, and cellulose produces composites with better fire resistance and physico-mechanical properties when compared to alternative intumescing formulations.

2.8.2 Phosphorylated Lignin based FRs for Polylactic acid (PLA)

Réti et al. [192] examined PLA's flammability using various FRs. Initially, the ammonium polyphosphate (APP)/pentaerythritol (PER) system was employed, as prior research had demonstrated its favourable behaviour in polyethylenic matrix structures. The PER was then substituted with bio-resources like starch and lignin. According to their findings, materials containing starch and lignin had lesser LOI values than the composite made of PLA and APP, but they are still commercially viable. Blends that included lignin had a significantly lower LOI value (32 vol. percent) than blends that contained starch (40 vol. percent). Conversely, these formulations (V0 against V2 rating) had a greater UL-94 rating compared to those involving PER. Cone calorimetry was used to analyse lignin-based blends afterward, and the results showed that these formulations had the best FR due to the charring effect of lignin, which causes a less rapid heat release rate (HRR).

In 2012, Zhang et al. [183] enhanced the charring effect of urea-modified lignin in polylactic acid.Ammonium polyphosphate (APP) and lignin chemically modified by urea have been combined to create an innovative intumescent flame-retardant (IFR) framework that increased the flammability of PLA. LOI, TGA, UL-94 vertical cone calorimeter test,were used to evaluate the thermal stability fire behaviour of IFR–PLA composites. The findings demonstrated that urea-functionalized lignin combined with APP exhibited significantly higher thermal stability and fire-resistance than did pristine lignin and APP combined.

Zhang et al. [193] conducted a study in the same year wherein they synthesized lignin–silica hybrids (LSHs) as well as examined their flame-retarding effect in PLA. LSH and Ammonium polyphosphate were added to PLA as a new intumescent flame-retardant (IFR) structure to increase PLA's resistance to flames. The flame-retardant effect of LSH and APP and in PLA was examined LOI, CC, and vertical burning (UL-94) tests. The morphology of the char residue has changed since with the addition of APP/LSH to the PLA system. In PLA composites, a continuous and dense intumescent charring layer is generated, which demonstrates greater flame retardancy than PLA/APP and PLA/APP/lignin composites. All the data demonstrate that combining APP and LSH can improve flame-retardant properties while also increasing the strength of PLA [193].

Costes et al.[194] put forward a method to use lignin as an additive to increase PLA's flame retardancy. They investigated the impact of the type of lignin, and the functionalization of lignin with phosphorus and nitrogen. For their investigation, they used lignin from Kraft and Organosolv. Cone calorimeter Thermogravimetric analysis and UL-94 were utilized to examine the fire properties and thermal performance of PLA composites with 20% modified and unmodified lignin. When untreated lignins were integrated, char was produced, which decreased the THR and the pHRR. However, this also led to a reduction in the Time To Ignition as well as a significant loss of PLA's thermal properties throughout melt processing. The solution devised by the researchers involved functionalizing lignin through the grafting of phosphorous and nitrogen. By substantially enhancing the fire-retardant qualities and limiting PLA degradation, the functionalized lignins enabled the PLA/lignin composite materials to achieve UL-94 classification V-0. Costes et al.[122, 194] went on to develop A simple approach that combines phytic acid and lignin to increase PLA's flame resistance. Phytic acid and lignin combined were used as a straightforward method to create a bio-based flame-retardant system in PLA. The outcomes show that blending these two substances is an innovative way to maximize their positive effects while reducing their drawbacks. PLA fire behaviour is improved by either 20-weight percent lignin or 20-weight percent phytic acid alone because they both produce a char barrier that insulates PLA during burning. According to the researchers, adding phytic acid to lignin reduces peak heat release rate (pHRR) by 44% in cone calorimeter testing and results in a V-2 classification in the UL-94 test [122].

Cayla et al. [195] developed a PLA intumescent system for a flame retardant textile using lignin and Ammonium Polyphosphate (APP). Melt extrusion was used to make various formulations of and/or ammonium polyphosphate (APP), which were then hot-pressed into sheets. PLA with 5% AP; PLA with 5%, 10%, and 20% kraft lignin (LK); and the ternary blend PLA 90%-LK5%-AP5%. The addition of ammonium polyphosphate improves the thermal stability of the composites marginally, and the residual at 500 °C increases with lignin due to its charring capability. According to the UL-94 test outcomes, PLA-APP composites are less flammable than PLA. Although PLA-LK-APP does not decrease TTI, it does lower HRR because of char formation. Therefore, 5 weight percent of LK and 5 weight percent of APP are sufficient to produce an effective FR effect.

2.9 Phosphorylated Nanoparticles intumescent systems

Nanoparticles improve the mechanical strength of polymers as well as their flame retardance. Titanium, nanoclays, silica, carbon nanotubes, silsesquioxane, nano metal oxides and sepiolites and others are examples of these materials [135]. A lot of scientific and engineering attention has been given to carbon nanostructures because they possess extraordinary physicochemical, mechanical, electrical, and thermal properties. A lot of research is focusing on the sintering of nanostructures from lignin because of the abundance of carbon in lignin.With lignin being a waste by-product from the lignocellulosic ,pulp and paper plants, the synthesis of these lignin nanoparticles from these renewable sources may reduce the carbon footprint [31].To explore the potential of lignin nanoparticles as FRs, Chollet, et al.[196], investigated and published a study report on the interest in employing lignin nanoparticles as a fire-resistance agent in polymers, which was the first report on this approach at that time. Kraft lignin was used to make lignin nanoparticles from lignin microparticles. Diethyl chlorophosphate and diethyl (2-(triethoxysilyl) ethyl) phosphonate were used to functionalize micro and nano lignins. Their results demonstrated that grafting a large amount of P onto the surface of lignin nanoparticles allows them to be applied as effective flame-retardant additives. They reported that untreated lignin micro and nanoparticles reduce PLA thermal stability dramatically during TGA measurement, phosphorylated lignin particles reduce the thermal degradation during melt processing, increase the TTI and gives significant reduction in pHRR.

2.10 Summary

This chapter focused on the review of literature related to the aim of the research. The major highlights are presented below:

- PLA is a biodegradable polymer with immense potential to replace petroleum-based polymers in many engineering applications. However, its potential use is restricted due to its flammability and propensity to spread fire. Therefore, researchers are working on strategies to improve its fire behaviour.
- Lignin is a highly aromatic component of lignocellulosic biomass. Industrially, it a is by-product of the pulp and paper industry where different extraction processes are used to extract it into different technical lignins, namely, lignosulphonate (sulfite process), kraft lignin (kraft process), organosolv lignin (organosolv process), soda lignin (soda process) and hydrolytic lignin (hydrolytic processes). Lignin is an excellent charring agent in intumescent flame-retardant systems for polymer.
- Due to the structural heterogeneity of lignin, considering the unique molecule structure of lignin and the plethora of diverse functional groups on its structure, numerous researchers

have investigated chemical processes for altering such groups. The chemically modification techniques of lignin can be grouped into three major categories: fragmentation/depolymerization, creation of novel chemically active sites, and hydroxyl group modification. Aliphatic alcohol and aromatic units are responsible for hydroxypropylation, esterification, etherification, phosphorylation, and alkylation-based modification with epoxides and urethanization.

- Carbon-based nanomaterials are being considered for several applications in engineering due to their unique physical, chemical and mechanical properties. Lignin, being a carbonaceous material is a good raw material for sustainable synthesis of carbon-based nanomaterials. Researchers are focusing on devising different methods to synthesize nanomaterials from lignin.
- To the best of our knowledge, the use of lignin nanomaterials as flame-retardant additives in PLA has not been reported significantly in the literature.
- Phosphorus-based compounds have been researched extensively as flame-retardant systems, alone or in combination with other compounds. The different formulations have been seen to be successful, but their drawback is that some of the solutions are not bio-based and do not the support the green synthesis principles.
- Phytic acid is a bio-based compound that has excellent flame-retardant properties owing to the presence of its six phosphate groups. Phytic acid can form a char layer when it degrades because of the presence of six phosphate groups in its structure, which produce phosphoric acid. This forms a protective layer that reduces the amount of fuel needed to sustain the combustion process and restricts heat flow in the material.
- A combination of phytic acid and macro-scale Kraft lignin and Organosolv lignin.
- To the best of our knowledge, a combination of phytic acid and lignosulphonate nanoparticles to impart flame-retardant properties in PLA has not been reported in the literature.
- Flame-retardant systems work chemically or physically depending on their design. They have the potential to disrupt the different processes occurring in the combustion cycle. The stages of combustion include heating, decomposition, ignition, and the spreading of the flame in the polymer.
- When intumescent material is heated above a specific temperature, it starts to swell and expand, which causes a charred layer to form on the outside of the material. This charred layer shields the underlying material from heat and flames and stops oxygen from diffusing to the combustion site. Current intumescent flame-retardant systems do not use halogen-based compounds which are toxic. Therefore, more research is biased towards using non-toxic compounds which include phosphate-based compounds.

The system we designed for flame-retardant PLA is based on intumescence, which in this case harnesses the flame-retardant properties of both lignosulphonate and phytic acid. Having considered all the literature and the aim of this research, we came up with our experimental design which is described in Chapter 3.

RESEARCH METHODOLOGY

This chapter will focus on the experimental methods to be used in the research. The methods to be used for characterisation of lignin, synthesis, and characterisation of phytic acid-functionalized lignin nanoparticles LNP-PA which is the flame bio-flame retardant formulation, synthesis of PLA/LNP-PA bio-composites and the flammability tests for the polymer composite will be discussed in this section.

3.1 Materials

Lignosulfonate used was obtained from SAPPI. Phytic acid (PA) 50% (w/w) solution, DMSO, was purchased from Sigma Aldrich. PLA pellets HT101, with a density of approximately 1.24g/cm^3, melting point 175 °C, glass transition temperature 60 °C, moulding temperature 180-190 °C and melt flow rate was purchased from Orinko Advance Plastics Co., Ltd (Hefei, China). Liquid nitrogen was obtained from the Unit for Environmental Science and Management, North-West University.

3.2 Experimental methods

The synthetic route of the bio-flame retardant PLA is summarised in the following flow chart, as shown in Figure 22.

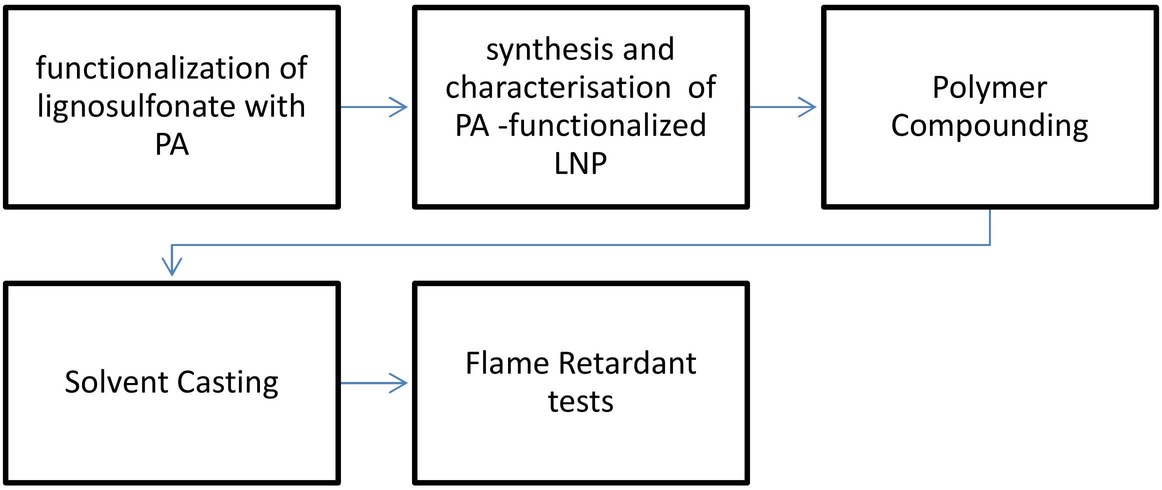


Figure 22:Summary of the synthetic route of bio-flame retardant PLA composites.

3.2.1 Functionalization of the lignosulfonate with Phytic Acid (PA)

Excess lignosulfonate (approximately 50 g) was dissolved in 250 ml Phytic acid solution (0.1 %). The solution was heated under reflux at 80°C with stirring using a magnetic stirrer for 4h. The phosphorylated lignosulfonate/PA solution was filtered to remove undissolved lignin. The functionalization process is summarised below in Figure 23.The method was modified from the lignin functionalization protocol reported by [197].

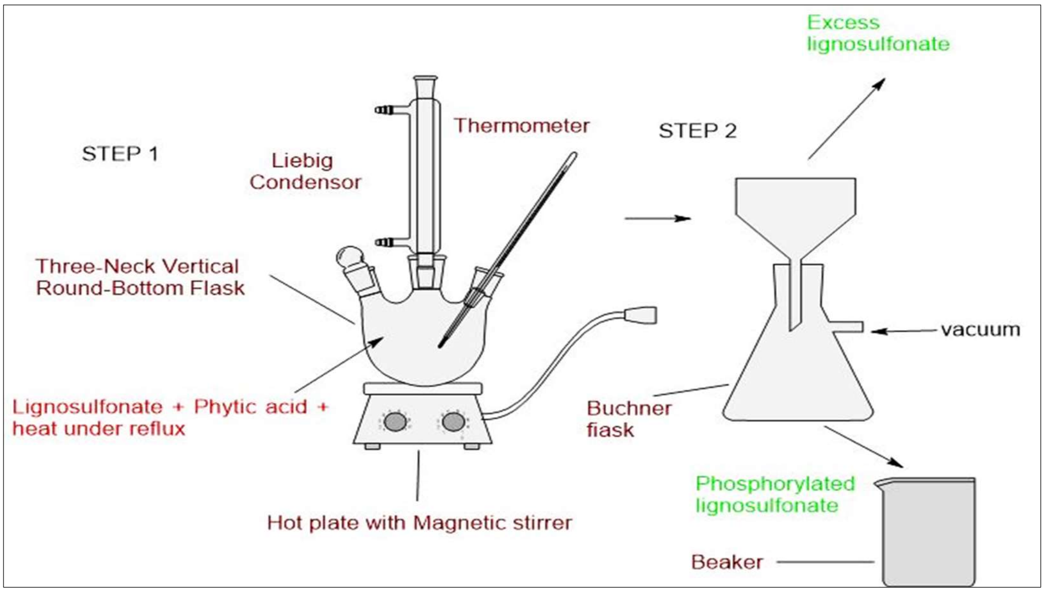


Figure 23:Functionalization of lignosulfonate with Phytic Acid

3.2.2 Ultrasonic-Aerosol assisted synthesis of PA functionalized lignin nanoparticles (LNP-PA)

The resulting solution was sonicated for 1hr with particle size monitored every 30 minutes in a similar method to [121].Ultrasonication was done at 40% amplitude with a 600W,20kHz,15amp sonic horn with a micro cavitation probe diameter of 3.175 mm (Sonic and Materials VC600/CV17) as shown in Figure 24 (a).The procedure was repeated with pristine lignosulfonate for comparison.

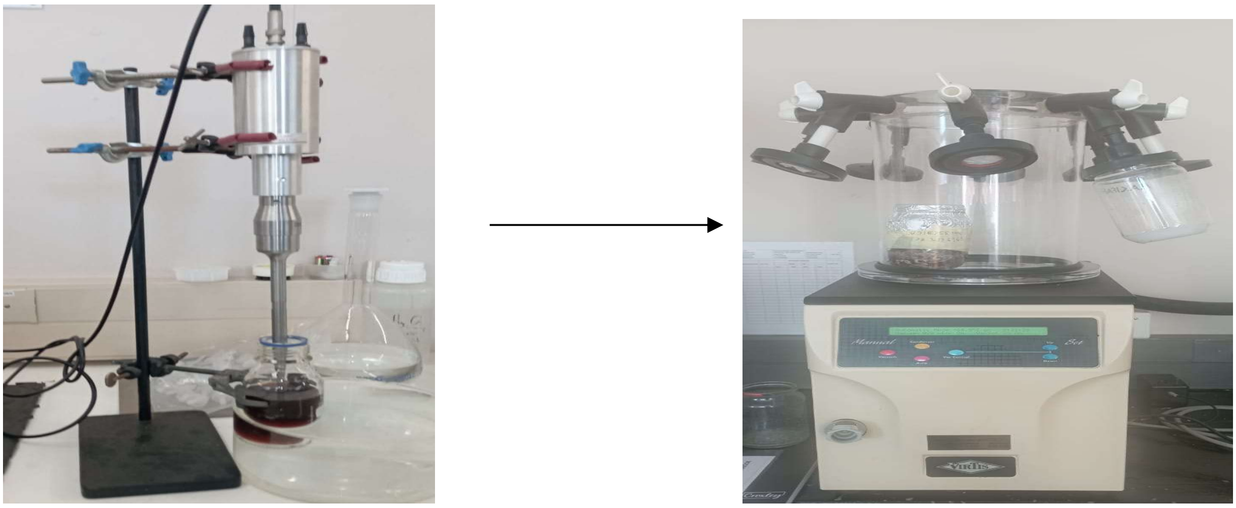


Figure 24:a) Ultra sonification of lignosulfonate-PA solution and b) freeze drying/lyophilization

The solution was kept overnight at approximately 0°C for 24hours.The solution was then filtered using a 0.45μm syringe filter, and sonicated again for 5 minutes. The solution was transferred to a hand sanitizer spray bottle and was sprayed onto a an aluminium plated cooled with liquid nitrogen in a similar protocol by [118, 198].The lignin nanoparticle entrapped droplets were then lyophilized to obtain a dry powder, in a freeze dryer (VIRTIS, United Scientific) Figure 24(b) .The powder was kept oven dried for further analysis.

3.3 Characterisations of the LNP-PA

3.3.1 X-Ray Powder Diffraction Analysis (XRPD)

X-ray powder diffraction patterns were obtained using a PANalytical Empyrean diffractometer (PANalytical, Almelo, Netherlands). This was done to investigate the modifications in crystallinity and ordering. The measurement conditions used were target, Cu; voltage,40kV; 30mA current; divergent slit ,2mm; anti-scatter slit,0.6 mm; detector slit, 0.2mm; monochromator; scanning speed,2°/min (step size, 0. 025°; step time,1.0sec).

3.3.2 Particle Size Determination

The functionalized lignosulfonate powder and the unfunctionalized lignosulfonate nanoparticles were suspended in 10% methanol/de-ionized water diluent and sonicated for 5 minutes. Diluted samples of the formulations (0.4mg/ml) were used to determine their droplet size (polydispersity index and mean diameter). Dilution was necessary to reduce the effects of multiple scattering [212]. The process to determine these parameters was done by dynamic light scattering (DLS) using Malvern® Zetasizer Nano ZS (Malvern Instruments, Worcestershire, UK) with each data sample averaged over three repeated readings.

3.3.3 Scanning Electron Microscopy (SEM)

Morphological analysis was carried out using scanning electron microscopy (SEM).FEI Quanta FEG 250 electron microscope operated at 20kV The powdered samples were spread on the sample holder. To prevent potential charging effects on electron beam scanning, the samples were dried in an oven for 24 hours and coated with gold sputtering.

3.3.4 FTIR Spectroscopy

Fourier Transform Infra-Red Spectroscopy is an analytical technique for the identification of functional groups in a compound [198]. FTIR was carried out to identify the functional groups and any structural changes in lignosulfonate, lignosulfonate nanoparticles and in the functionalized lignosulfonate nanoparticles .The FTIR measurements were carried out using a IRTracer-100 FTIR Spectrophotometer (SHIMADZU Corporation, Kyoto, Japan) at 64 scans at a resolution of 4 cm^{-1} with an ATR range of 750-4000cm^{-1}.The peaks were then compared with those found in the literature to positively identify the functional groups.

3.3.5 Nuclear Magnetic Resonance Spectroscopy (NMR)

^{13}P NMR was carried out to investigate the success of the phosphorylation reaction with phytic acid by observing the change in the hydroxyl group content using the Bruker Advance II 400MHz spectrometer. The samples were dissolved in DMSO-d6, filtered, and added to the NMR tubes [73]. ^{13}P-NMR was achieved by 16 scans and a pulse delay of 4s. The chemical shift data was referenced to DMSO-d6.

3.3.6 TGA

Thermogravimetry is a procedure to decide the change in mass of a substance as a function of temperature. These measurements are used to investigate the thermal and structural characteristics of the materials. These TGA evaluations can be utilized to choose materials for specific uses, predict their performance, and enhance product quality [31]. A Mettler DTG 3+ (Mettler Toledo, Greifensee, Switzerland) was used to record TGA thermograms. Powder samples, weighing 5-8 mg were placed in open aluminium cells, (100 µl) and heated to an end temperature dependent on the melting point of the sample, at a heating rate of 10°C/min, with a nitrogen gas flow of 35 ml/min. The procedure was done on the PLA polymer blends to study their thermal behaviour.

3.3.7 DSC

Differential Scanning Calorimetry (DSC) was conducted on the LNP and LNP-PA to investigate their thermal behaviour when subjected to a temperature gradient [31]. The main parameters we were interested in in were the glass transition temperature and the melting point, as this give an idea of the thermal stability of the nanoparticles.A Mettler DSC 3+instrument (Mettler Toledo, Greifensee, Switzerland) was used to record the DSC thermograms. Samples, weighing approximately 3 - 5 mg were placed in aluminium crimp cells (40 µl) and heated to 230°C with a heating rate of 10°C/min, with a nitrogen gas flow of 35 ml/min.

3.4 Synthesis of PLA/LNP-PA bio-composites

3.4.1 Compounding

PLA bio-composites containing LNP-PA were melt compounded using an SHJ-20 laboratory 28mm co-rotating twin screw extruder with five temperature zones, hopper to die, set at 140°C/160°C/170°C/180°C/185°C respectively [122].

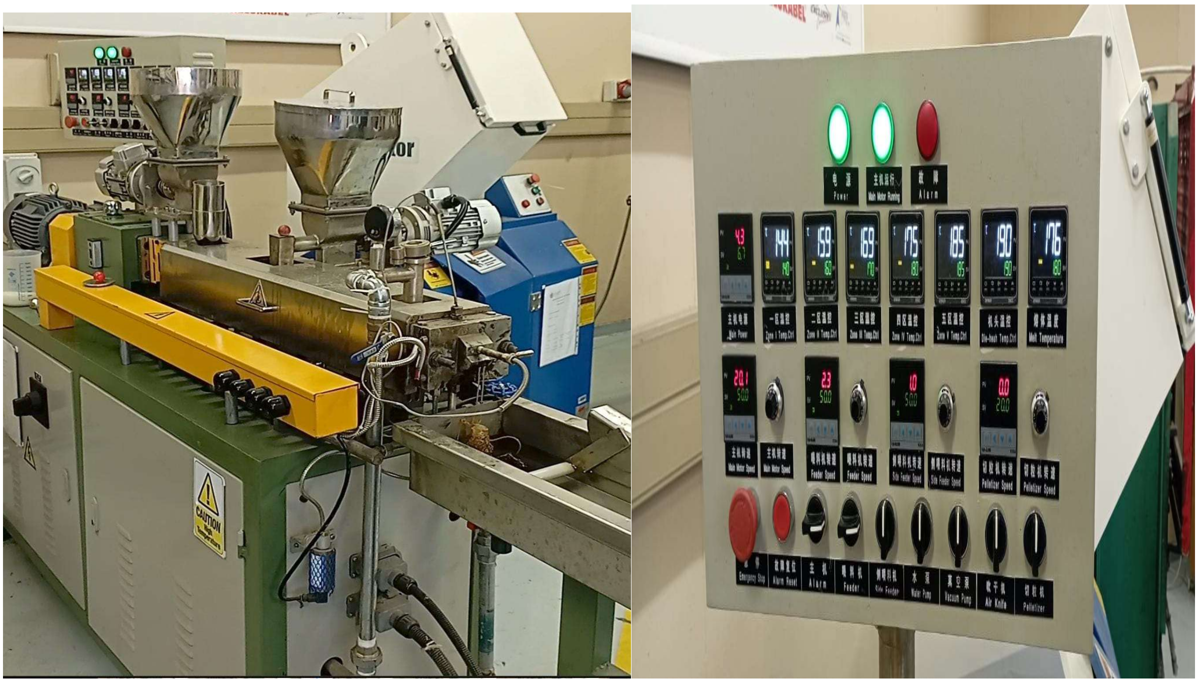


Figure 25: Twin screw extruder and temperature zones used for compounding.

The bio-composite blends, with the difference in colour intensity as the wt % of the bio-flame retardant additive LNP-PA increases are shown in Figure 26.

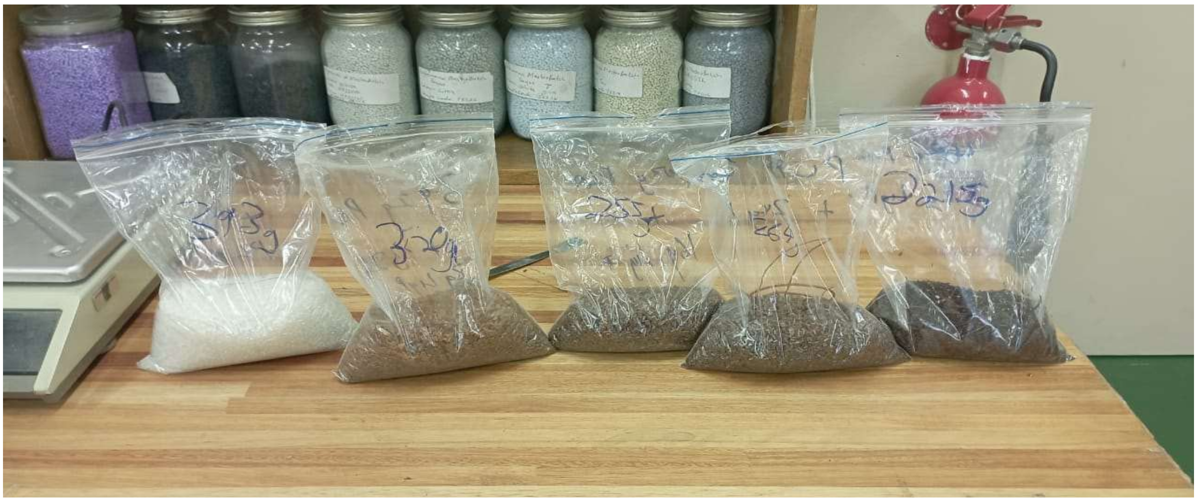


Figure 26: PLA/LNP-PA Bio-composite blends.

3.4.2 Solvent Casting

The specimens for flammability tests could not be prepared successfully by both compression moulding and injection moulding due to the brittleness of PLA and the malfunctioning of the injection moulding machine. Solvent casting was used to prepare filaments for use in a modified UL-94 flammability test. The solvent casting method was adopted from [199, 200].Magnetic stirring was used to dissolve the compounded polymer pellets (PLA/LNP-PA) in chloroform for 72 hours at room temperature. The solution was then stirred for 30 minutes with an ultrasonic homogenizer. The polymer solution was cast into petri dishes covered with a sheet made from Teflon and left to stand for three days to enable the solvent to evaporate steadily at room temperature before removing the bio-composite films from the mould. The PLA/LNP-PA films were washed with distilled water and dried at room temperature in the air before being stored in a moisture-free environment. Following the same procedure, the pristine PLA and PLA-LNP samples were used as a reference. The solvent casting process schematic is shown in Figure 27.

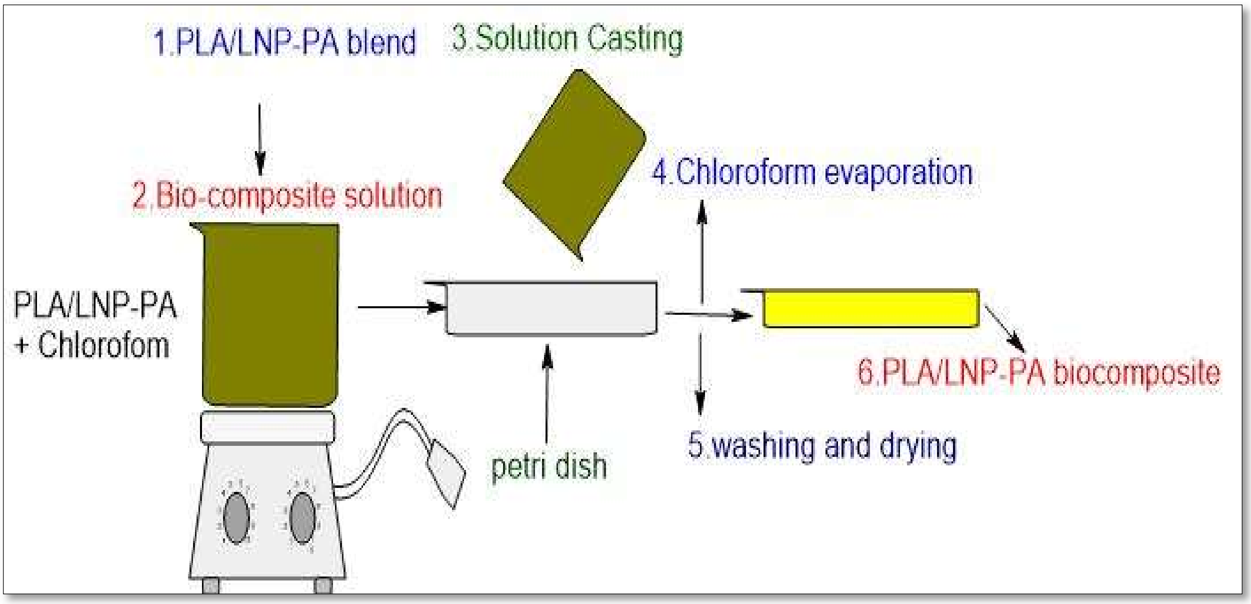


Figure 27:Solvent casting schematic. Adopted from [199, 200]

3.5 Flammability tests for the PLA/LNP-PA bio-composite

The flame retardance of the PLA/LNP-PA bio-composite formulations was done using the most popular test for determining a sample's ignitability and flame spread when it is exposed to a tiny flame, the UL-94 test, developed by Underwriters Laboratory. This test protocol was established for polymeric substances that are used as gadget and device components. The purpose of the results is to provide an initial assessment of their flammability acceptance for a given application. The material's ultimate acceptance is contingent upon its integration into fully compliant equipment that satisfies the applicable standard [201, 202].The test can be done in the horizontal or vertical direction. The standards followed in this research are : **ASTM D 635-03,** “Standard Test Method for Rate of Burning and/or Extent and Time of Burning of Plastics in a Horizontal Position”[201] and **ASTM D 3801-10**,” Standard Test Method for Measuring of the Comparative Burning Characteristics of Solid Plastics in Vertical Position”[202].Five different formulations with varying loading ratios of the LNP-PA bio-flame retardant were evaluated. The table below shows the different formulations.

Table 4:Different formulations of PLA bio-composites

Name	Composition
PLA	PLA 100%
PLA/LNP	PLA 90%: Lignin nanoparticles 10%
PLA/5LNP-PA	PLA 95%: LNP-PA 5%
PLA/10LNP-PA	PLA 90%: LNP-PA 10%
PLA/15LNP-PA	PLA 85%: LNP-PA 15%

3.5.1 UL-94 Vertical test (ASTM D 3801-10)

A polymer sample (125 mm x 13 mm, with variable thicknesses up to 13 mm) suspended vertically above a cotton patch is used for the standard UL-94 test. The sample is exposed to two 10-second flame exposures using a calibrated flame in an environment free from outside air currents. The flame is extinguished after the initial 10-second exposure, and the sample's self-extinguishing time is noted. The self-extinguishing time is also termed the after-flame time, t_{flame} [202]. If polymer dripping occurs, cotton ignition is noted, and if cotton does not ignite, dripping is acceptable. Subsequently ,the identical sample is ignited again, and the self-extinguishing time and dripping characteristics are noted [203].The material is classified from No vertical rating (NR),V-0,V-1 and V-2.The material is classified as V-0 (the best rating) if it self-extinguishes without dripping in less than 10 seconds following each ignition. It is classified as a V-1 if it self-extinguishes in less than 30 seconds after each ignition without dripping, and as a V-2 if the cotton ignites. The specimen will be classified as NR if it fails to self-extinguish prior to burning entirely, which is t_{flame} greater than 30 seconds. Figure 28 shows the schematic of the UL-94 vertical and horizontal tests [204].

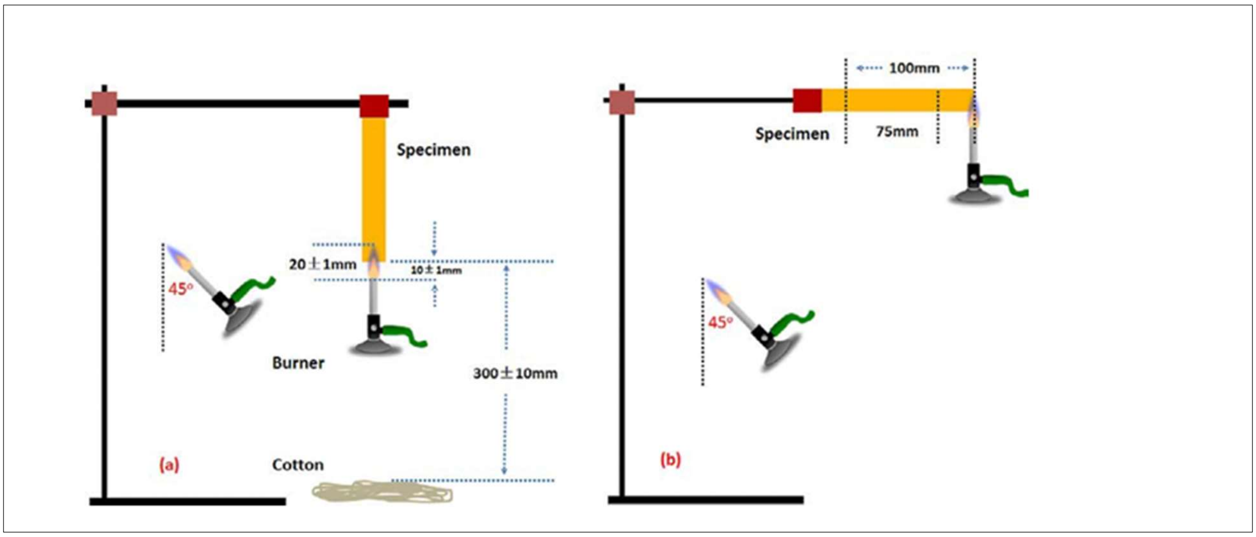


Figure 28:Schematic of UL-94 (a)Vertical and (b) Horizontal Tests [205]

A modified UL-94 procedure for testing was applied in this investigation. The specimens utilised are filaments 125 ± 0.5mm length x 10 ± 0.5 mm in width x ~5 mm. In each instance, the bottom of the sample is exposed to flame, and the burner's top is positioned 10 mm from the test specimen's bottom edge. After 10 seconds, the flame is applied and removed. The after-flame time, or t_1 is measured. The flame stays active for an additional 10 seconds after extinction, at which point the subsequent flame time t_2 is determined.

3.5.1 UL-94 Horizontal Burning Test (ASTM D 635-03)

A specimen is tilted 45 degrees and supported horizontally in the horizontal version of UL-94. This research used a modified test with respect to specimen size. Filaments of size 125 mm x 10 mm x ~ 5 mm were used. Two lines, spaced 25 and 100 mm apart from one end of the specimen, are used for marking each test specimen. The test specimen is held up horizontally at one side, and for thirty seconds, the end that is unattached is held up against a flame. The duration and intensity of the burning are noted after the flame is extinguished [201]. The burner was positioned so that the flame contacts the test specimen's end. This was done for 30 seconds, up to when the flame front reached to the 25 mm point. The burning time, t_1 was recorded. As soon as the flame front reached the 100 mm mark, the time noted in seconds was recorded as burning time (t_2). When the length of burning was still below 100 mm, it was measured as Y. The length of the burning extent is calculated by subtracting the unburned length from 100 mm [206]. The classifications used in the UL-94 tests are summarised in the table below:

Table 5: UL-94 V and HB test classifications [205, 207]

Criteria Condition	**V-0**	**V-1**	**V-2**
After flame time (t_1 or t_2) for each individual test specimen.	≤ 10 s	≤ 30 s	≤ 30 s
After flame and after glowing time ($t_2 + t_3$) for each individual test specimen, after second flaming.	≤ 30s	≤ 60 s	≤ 60 s
Total flame time ($t_1 + t_2$) for the 5 test specimens	≤ 50s	≤ 250s	≤ 250s
Flaming dripping allowed	No	No	Yes
Cotton indicator ignited by ignited by faming drops dripping from individual test specimen	No	No	Yes
After flame of after glowing to the clamp	No	No	No
If t_{flame} >30s, the classification is No vertical rating, NR. In this case the burning is sustained, or the test specimen burns 125 mm till it reaches the top clamp.125 mm up to the top clamp.			
For UL-94 H test, the classification is as follows- HB Rating: If a material doesn't burn more than 40 mm per minute and has a thickness of between 3 and 13 mm, it will be categorized as an HB material. The burning rate for material thinner than 3 mm shouldn't be more than 75 mm per minute. Regardless of thickness, the material will also be rated as HB if it burns out before the 100mm mark.			

3.6 Summary

The phytic acid-functionalized lignosulfonate nanoparticles (LNP-PA) were synthesized and incorporated into the structure of PLA. The LNP-PA were characterized using DLS, XRPD, NMR, FTIR and SEM, while the bio-composite, PLA/LNP-PA was evaluated for thermal stability and fire-behaviour using TGA and a modified UL-94 test respectively. The results are presented and discussed in Chapter 4.

RESULTS AND DISCUSSION

The results and analysis of the experimental work and characterisations conducted in this research are discussed in this chapter. The first section will focus on the synthesis and characterisation of the bio-flame retardant formulation, **LNP-PA**. Three lignosulfonates are discussed, and these are: Lignosulfonate, lignosulfonate nanoparticles (LNP-PA) and the phytic acid-functionalized lignosulfonate nanoparticles (LNP-PA). The last section will present the results of the fire behaviour of the PLA after combining it with the bio-flame retardant formulation.

4.1 Characterisations of the bio-flame retardant formulation (LNP-PA)

The bio-flame retardant formulation was analysed using XRPD, FTIR, Dynamic light scattering (DLS), Scanning electron microscopy (SEM), Thermal gravimetric analysis (TGA), Nuclear magnetic resonance spectroscopy (NMR) and Differential scanning calorimetry (DSC). The results are presented in this section.

4.1.1 X-ray powder diffraction spectroscopy (XRPD)

The XRPD results shown in

show that all the 3 samples have an amorphous structure, due to the observation of a typical halo pattern at 2θ= 21°.This is attributed to the less organized, heterogeneous stacked arrangement of aromatic layers [207].The peak is more broad compared to synthetic polymers like PS which implies a wider distribution range of intermolecular distance between chains [207, 208].

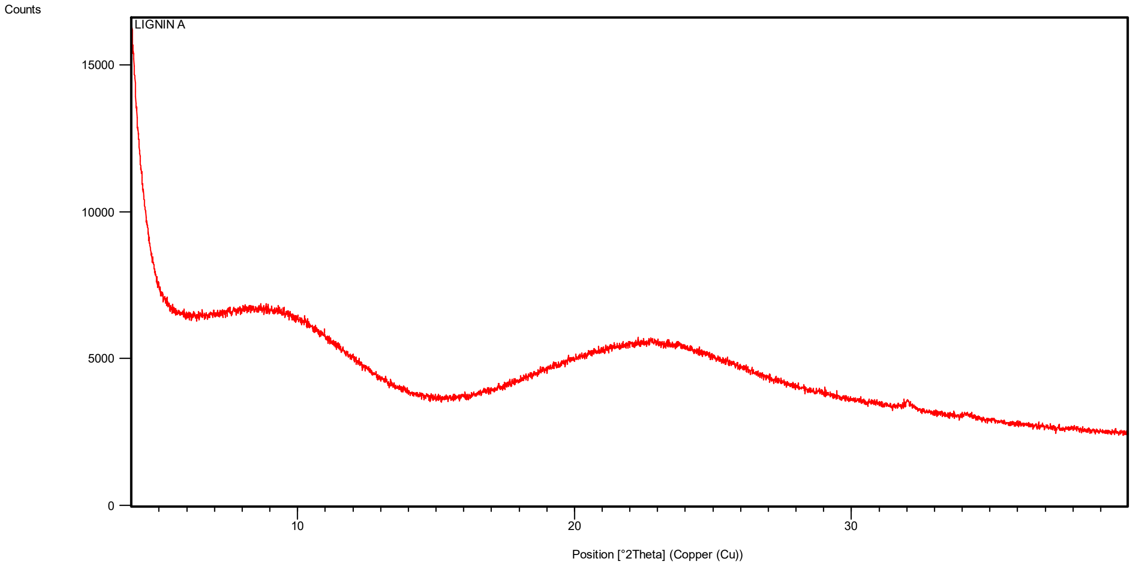


Figure 29 (a): XRPD pattern for pristine lignoslufonate

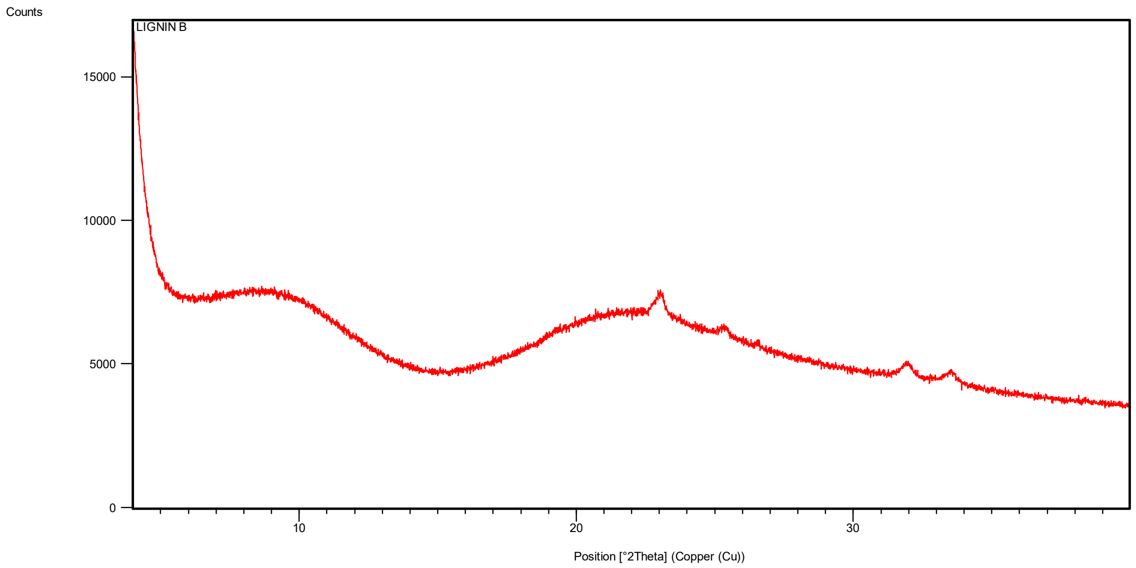


Figure 29 (b): XRPD pattern for LNP

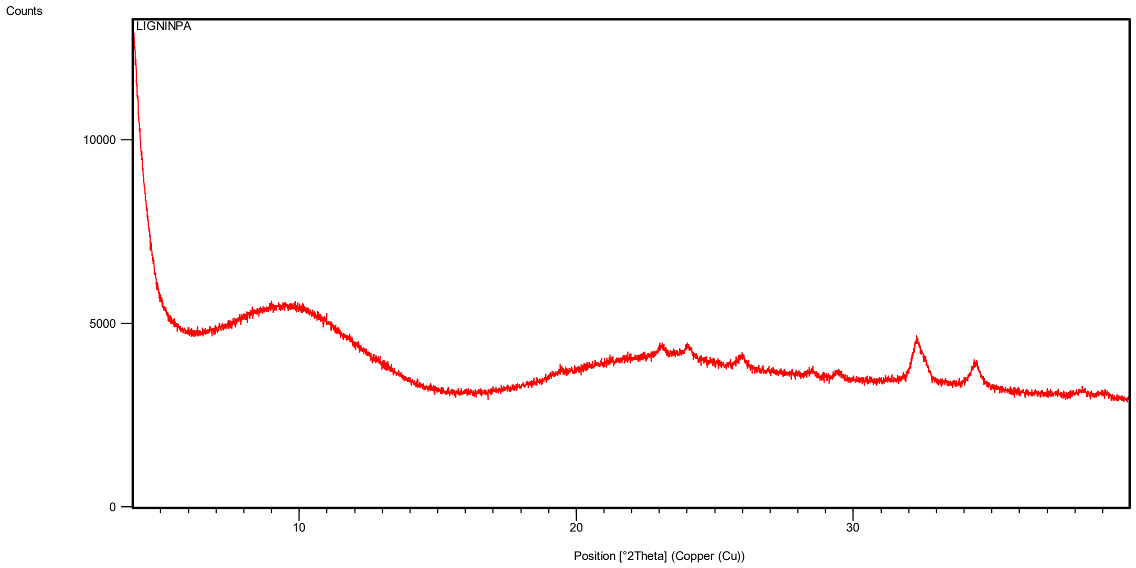


Figure 29 (c): XRPD pattern for LNP-PA

Peaks are observed at approximately 32° and 35°.According to [209], they are due to residual cellulose which is still part of lignosulfonate structure [207].The peaks disappear in LNP-PA which suggests their reaction during the functionalization reaction. There is a small reduction in crystallinity and broadening of peaks after sonication-spray freezing-lyophilization in lignosulfonate which suggests the formation of lignin nanoparticles. However, there are no changes in the amorphous structure of lignin and the peaks resemble spectra of other lignins and nanoscale lignin reported in literature [210].

4.1.2 Dynamic light scattering (DLS) – Particle size determination

The size of particles and the uniformity of the size distribution are crucial factors to consider during synthesis of polymer additives. Particles with a uniform size distribution will be distributed uniformly in a polymer matrix. Non-uniformly distributed sized particles can result in weak areas in the matrix caused by large particles that will have a small surface area or small particles which may not be adequately sized to reinforce the matrix, resulting in weak hydrogen bonding. It was therefore imperative to control particle size during synthesis [211]. Multi-modal distributions were utilized for particle size characterisations due to the poly-dispersibility and large particle size of lignosulfonate. From the DLS measurements, a large variation was observed in the particle size with two peaks at 941.5 nm and 2690 nm, and a polydispersity index of 0. 409.The average particle size was a diameter of 4036 nm as shown in Figure 29.

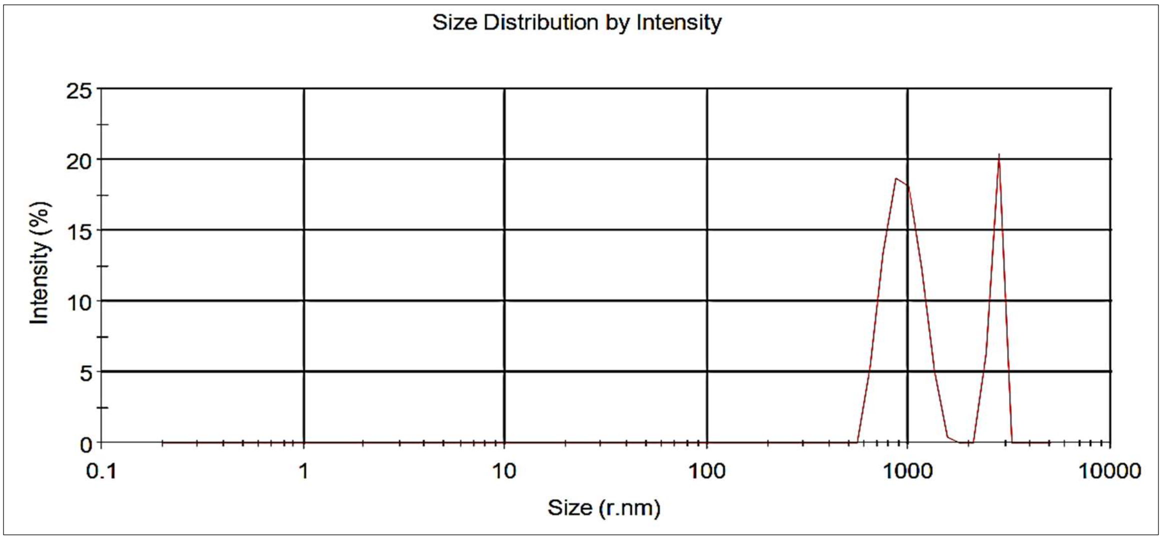


Figure 29: Lignosulfonate particle size before sonication

The β-O-4 linkages are weaker in comparison to other C-O-C bonds in lignosulfonate. Sonication can cleave these bonds causing depolymerization [211]. This results in significant particles size reduction as shown in Figure 30 and Figure 31 after 1 hour of sonication. The pristine lignin shifted from multi-modal peak to monomodal peak in the unmodified LNPs which had an average size of 232nm and a pdi of 0.261 as shown in Figure 30.The value for the pdi indicates a good polydispersity in the LNPs due to sonication induced cleavage of bonds in lignosulfonate [212].

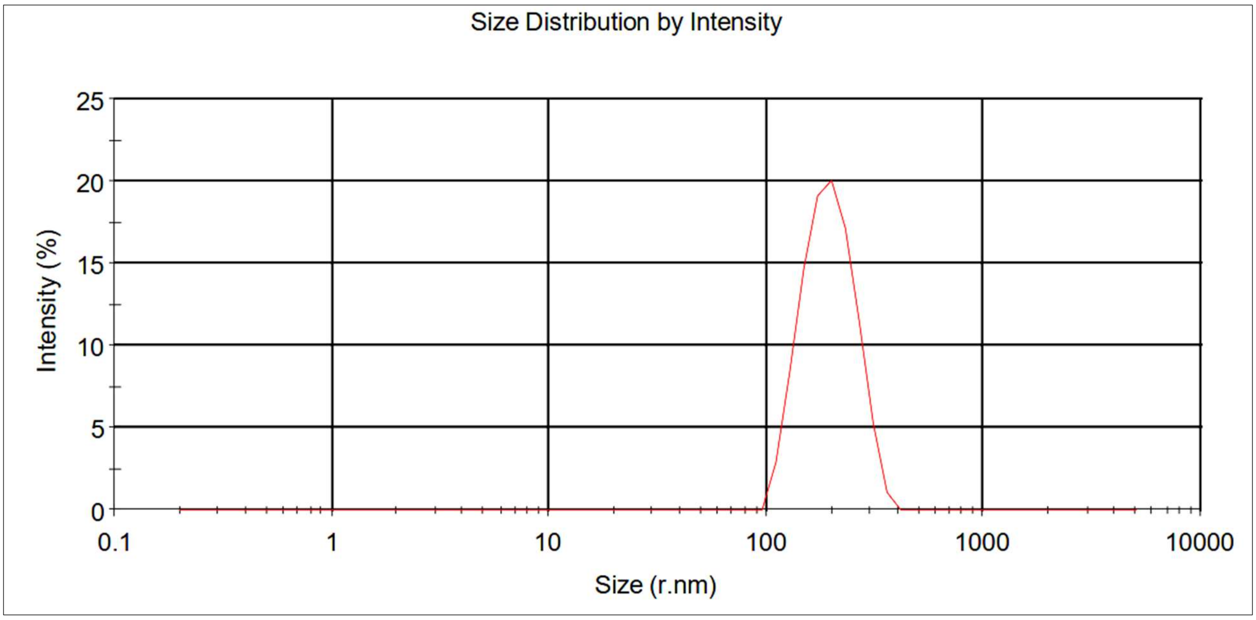


Figure 30:unmodified LNPs after 1 hour of sonication

The best size reduction in the functionalized LS-PA NPs was obtained after 1 hour of sonication with three peaks at 136.8 nm,2475 nm and 20.17 nm, pdi of 0.418 with an average particle size radius 119 nm in functionalized LS-PA NPs as shown in Figure 31.The presence of three peaks is attributed to cleavage of the lignosulfonate particles, deprotonation of hydroxyl groups due to phosphorylation and the heterogeneity of the particle size distribution before sonication [211].

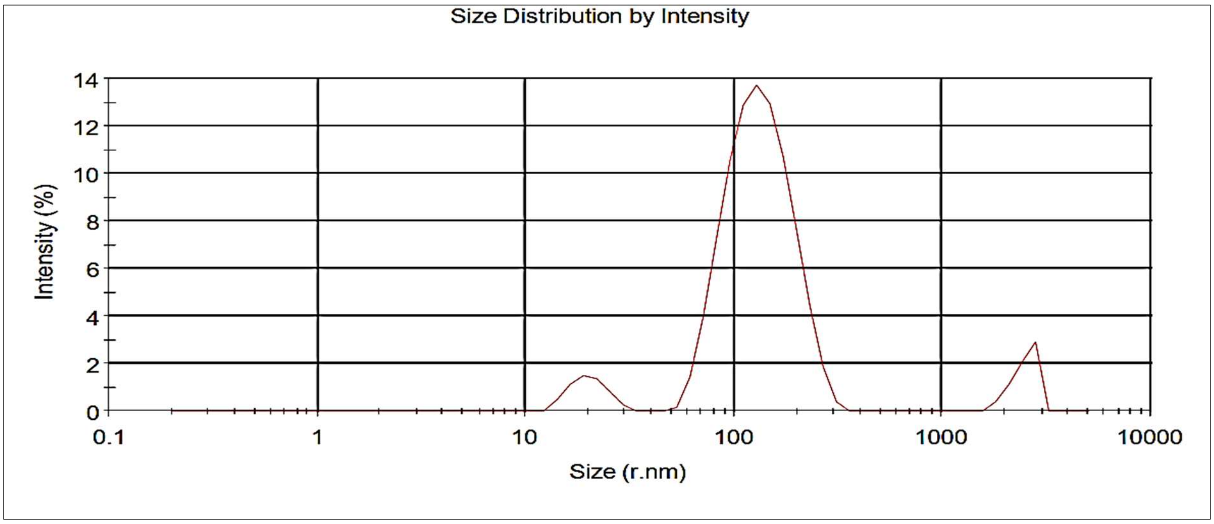


Figure 31: functionalized LS-PA after sonication

4.1.3 Scanning electron microscopy (SEM)

The morphology of the lignosulfonate and the LNP-PA was compared using SEM. presents the SEM micrographs of the lignosulfonate and LNPs.The micrographs show that the particles have irregular shapes, with size was in the range of between smaller nanosized of around 500nm to larger particles with sizes in hundreds of microns. DLS measurements showed an average diameter of about 238 nm showing that after freeze drying, most of the nanoparticles agglomerated as shown in the SEM images in Figure 32.The observations showed a similar pattern to that reported by [211].

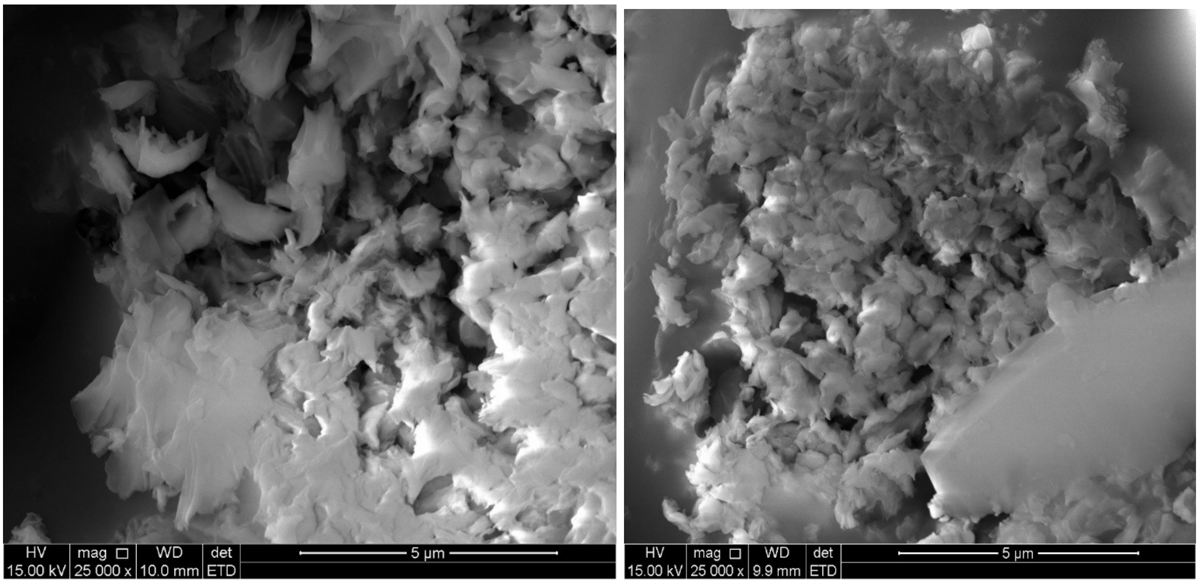


Figure 32:SEM images of lignosulfonate and LNPs

4.1.4 Fourier transform infra-red spectroscopy (FTIR)

The lignosulfonate (LS), the sonicated lignosulfonate (lignosulfonate nanoparticles, LS-NP) and the functionalized lignosulfonate-PA nanoparticles (LS-PA NPs) follow the same pattern as found in the literature but some changes in intensity due to ultrasonication and functionalization. Lignin FTIR spectroscopy always gives complicated bands which may vary in different sources and extraction techniques for the lignin [121].The primary bands identified in this research are consistent with those described in previous studies for different technical lignins including lignosulfonate.Figure 33 shows the FTIR spectra for lignosulfonate used in this study.

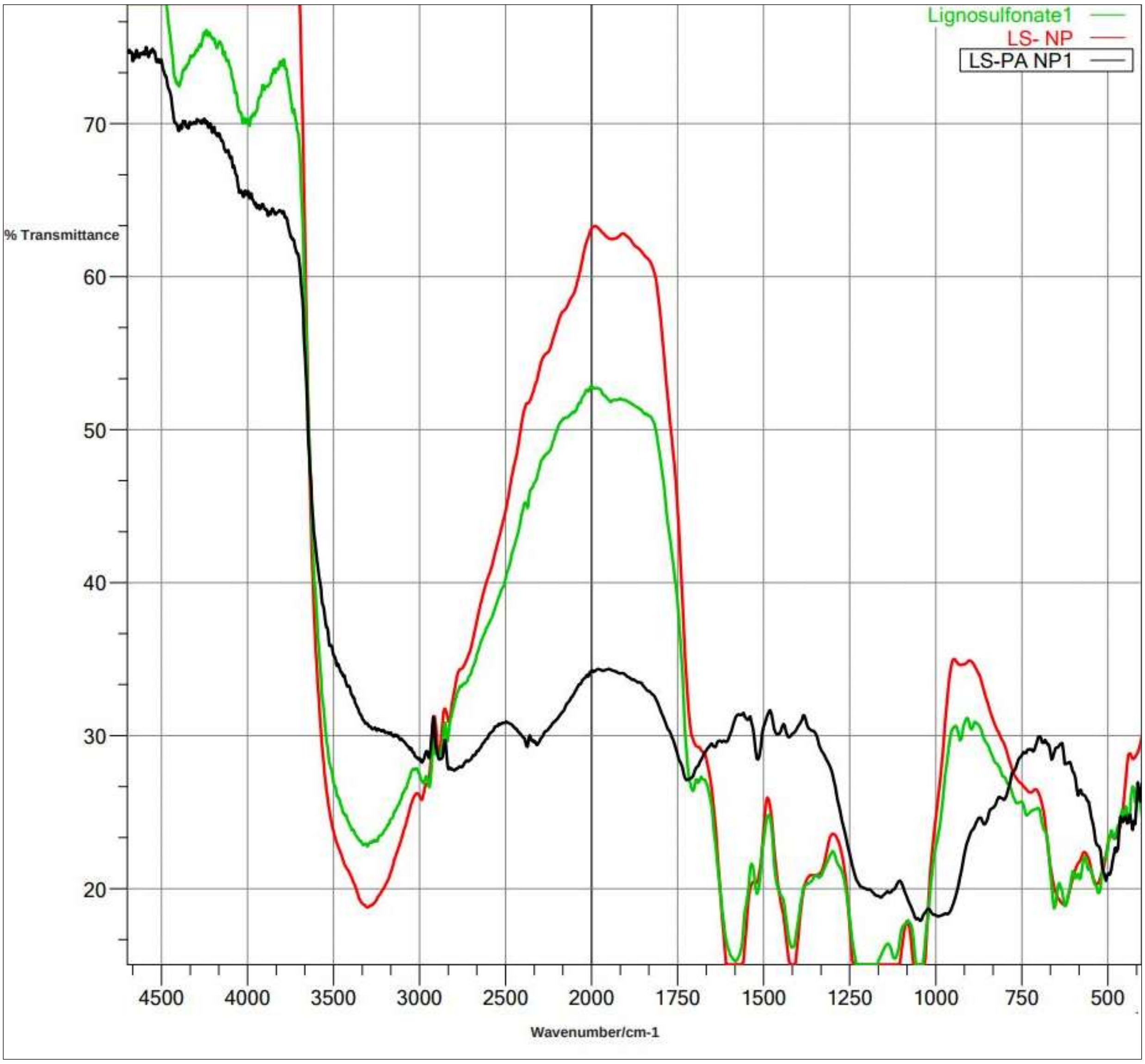


Figure 33:FTIR Spectra for lignosulfonate, LNP and LNPA NP

The characteristic peaks are broad, strong peaks in the range, of 3650-3200 cm $^{-1}$ due to the hydrogen bonded OH in aliphatic, phenolic alcohols and carboxylic acids. A band is seen around 1600 cm $^{-1}$ due to conjugated C=O stretching and bands around 1510 cm $^{-1}$ due to aromatic stretching. Other bands are observed between 1100-1200 cm $^{-1}$ due to C-O in primary alcohols, C-H and C-C deformation vibrations in aromatic rings,1150 cm $^{-1}$ due to deformation vibrations C-H of guaicyl rings, 1450 cm $^{-1}$ due to C-H deformation in combination with benzene ring vibrations [212]. The peak observed around 625cm $^{-1}$ is due to the sulfonic groups formed during the sulfite pulping process when the secondary aliphatic alcohol groups in lignin react with sodium sulfite.

4.1.5 Functionalization of lignosulfonate

Functionalization of lignosulfonate with phytic acid is a phosphorylation reaction which, according to the FTIR spectra did not result in degradation of the lignin structure, but brought a few changes in lignosulfonate-PA.

In comparison to the lignosulfonate structure, the LS-PA NP spectra have a strong, broad and intense peak at 1030 cm $^{-1}$ due to P-O-R ester bonds due to the phosphate groups [213], with R representing lignosulfonate. Another characteristic absorption peak is observed at 1400 cm $^{-1}$ attributed to the P=O bond [213],suggesting the phosphorylation of lignosulfonate with PA via ester linkages . There is a significantly reduced intensity of the 3200-3500 cm $^{-1}$ band which can be attributed to the reaction of hydroxyl groups in lignosulfonate with the phosphate groups in phytic acid. There is a small shift of bands to lower values due to hydrogen bonding between lignosulfonate and phosphate groups. However, it should be noted a small peak is observed at 3000 cm $^{-1}$ which can be credited to the hydroxyl groups within the phosphate groups. The band observed around 1600 cm -1 due to conjugated C=O stretching in lignosulfonate has reduced intensity in LS-PA NP. However, it is worth noting that there is reduced intensity of some bands due to homolytic cleavage of some bonds due to sonication, as discussed in the next section.

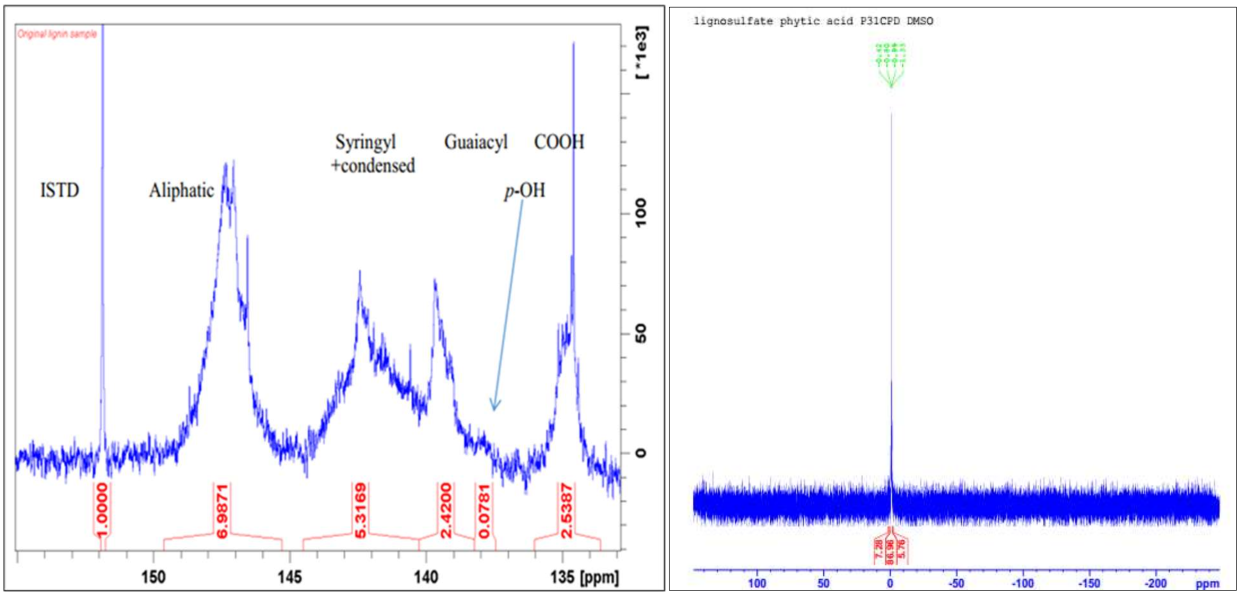
4.1.6 Ultrasonication of lignosulfonate and lignosulfonate-PA

The strong peak, with a transmittance of 36% at 1050 cm $^{-1}$ is due to the β-O-4 linkages in lignosulfonate [214].A reduced intensity of this peak, characterised by a transmittance of 82% in ultrasonicated lignosulfonate (LS-NP) indicates a cleavage of the β-O-4 linkages, as previously suggested by [211].The peaks in the range 1100-1200 cm $^{-1}$ represent aryl ether linkages [211, 214] in the lignosulfonate. They have significant reduced intensity with a transmittance of about 85% in LS-NP whilst in lignosulfonate-PA NPs the transmittance is about 52%.The reduced intensity can be attributed to homolytic cleavage reactions preceded by condensation reactions, which result in 4-O-5 and 5-5 lignin linkages, similar to the suggested mechanisms by [121, 215]. The 1262 cm-1 signal was most likely generated by C=O and C-O stretching of guaicyl groups [211]. Although there was a decrease in intensity, the intensity relative to neighbouring peaks appeared to remain unchanged when comparing the LS and LS-NP samples, indicating little to no alteration to the guiacyl groups[211],but a significant change was observed in LS-PA NP.

4.1.7 ^{31}P NMR

^{31}P NMR was used to determine if phosphorylation was successful by looking for changes in the hydroxyl (OH-) groups in the unmodified lignin and the modified lignosulfonate-phytic acid NPs.

Figure 34 (a) ^{31}P NMR of pristine lignosulfonate obtained by [216] using the Argyporolous method [217] and (b) phytic acid-functionalized lignosulphonate nanoparticles.



(a) (b)

Figure 34: ^{31}P NMR spectrum for (a) unmodified lignin and (b) phytic acid functionalized lignosulfonate

The spectrum for unmodified lignin reflects a band in the range of 145-150 ppm due to aliphatic hydroxyl functional groups. The syringyl together with condensed hydroxyl groups are present in the range 140-145 ppm while the band 138-140 ppm id for the guaiacyl hydroxyl groups. P-hydroxyphenyl hydroxyl groups are observed from 138-140 ppm whilst the carboxylic hydroxyl shows up in the band 133-136 ppm. The spectrum functionalized lignosulfonate-phytic acid NPs shows 4 peaks at –0.4 ppm, -0.8 ppm, - 0.99ppm and -1.33 ppm. The changes are similar to those detected by FTIR, which are the disappearance of the hydroxyl, guaicyl, p-hydroxyphenyl, syringyl + condensed and carboxylic hydroxyl groups caused by phosphorylation of these groups with phytic acid. The suggested changes to the structure of lignin is the formation of P-O-R ester bonds, where R is lignin as reported by [73, 216] from their analysis of phosphorylation of lignin using 2D ^{1}H-^{31}P HSQC NMR, which we could not do in our laboratory due to the malfunctioning of our HSQC equipment.

4.2 Suggested structure of phytic acid-functionalized lignosulfonate

The results allowed us to suggest a structure for the bio-based flame-retardant additive. A thorough examination allowed us to prove that phosphate groups form covalent bonds to the structure of lignin. This agrees with previously reported phosphorylation of lignin reports by [207, 218].

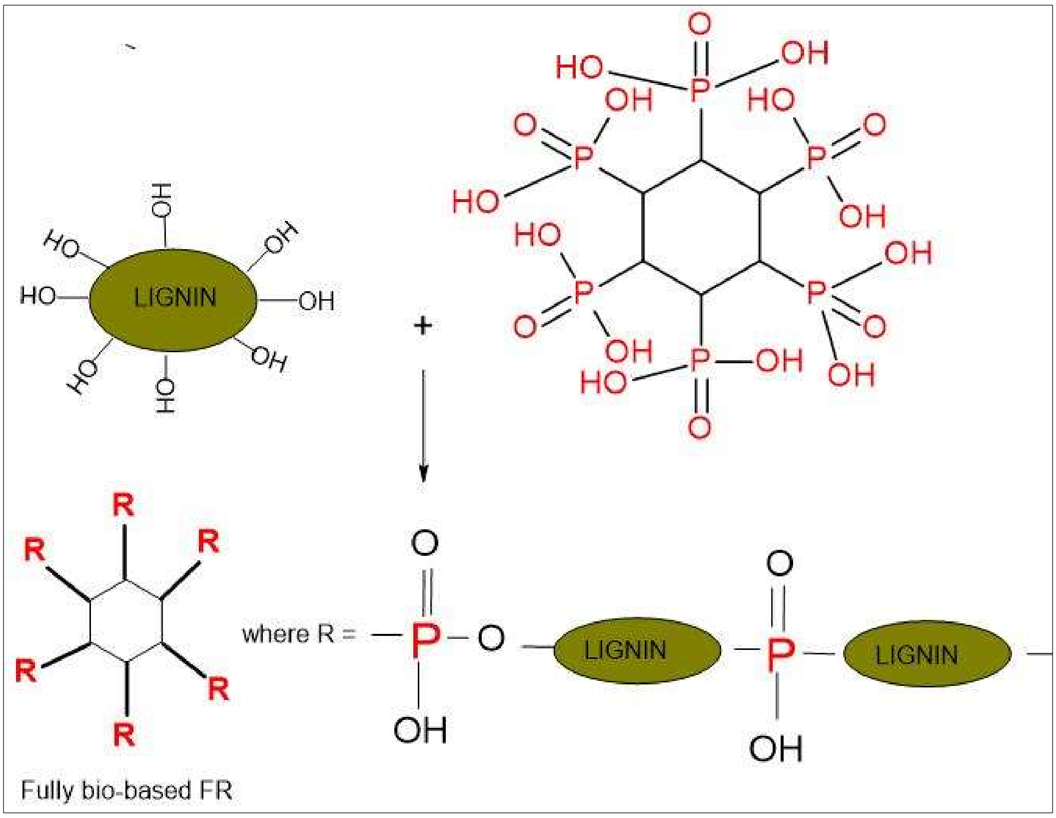


Figure 35:Synthetic route for bio-based FR (LNP-PA)

4.3 Thermal stability of the LNP and LNP-PA

4.3.1 DSC

The DSC thermal stability results obtained for the LNP and LNP-PA results are shown in the thermographs in Figure 36 and Figure 37 respectively, and in Table 6.

Table 6:DSC results summary

Sample	Glass Transition Temperature (Tg)/ ºC		Melting Point (Tm) /ºC
	T_{onset} / ºC	$T_{midpoint}$/ ºC	
LNP	54,39	62,19	92.10
LNP-PA	53,61	67,18	106.41

The glass transition temperature (T_g) is a crucial factor in deciding whether lignin and LNPs can be used as bio-flame retardant composite fillers. T_g provides an accurate measure of the macromolecule chain's mobility, which is dependent on a number of factors including molecular mass, chemical and physical crosslinking, and the existence of strong intermolecular bonds (such as hydrogen bonding) [194].The glass transition temperature values of pristine lignin typically range from 90 -180 °C [219].These values are lower than previously reported values of 160-190J/g for unmodified lignin and could be due to the size reduction resulting from ultra-sonication. However, the values for LNP-PA are slightly higher than LNP, which shows a better thermal stability for LNP-PA. This which makes it a better flame-retardant additive compared to LNP.

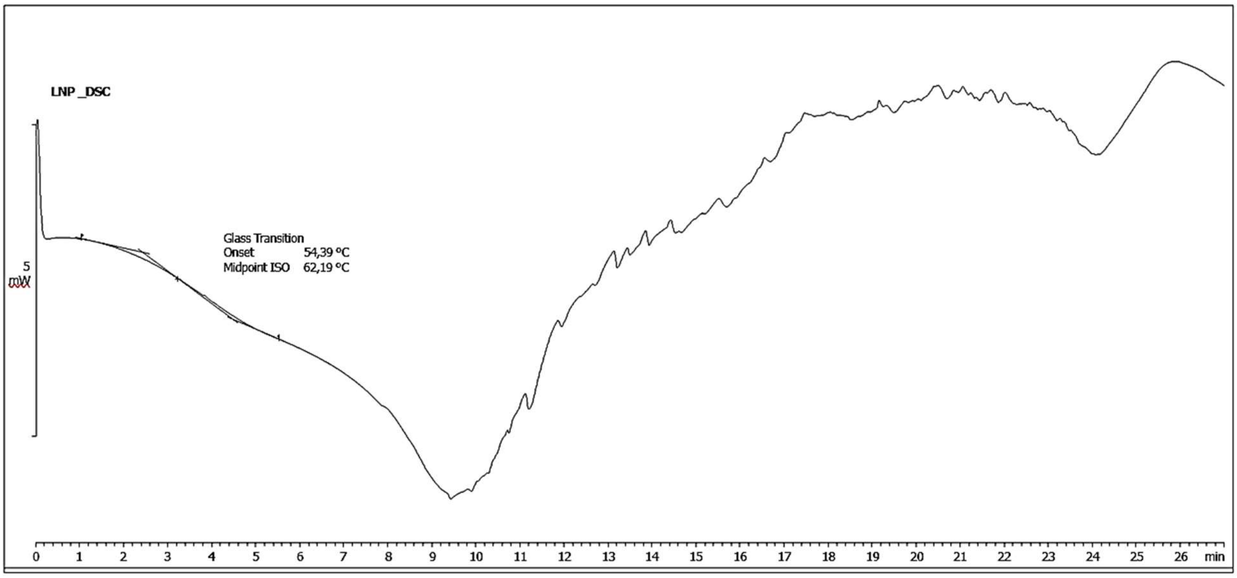


Figure 36:DSC thermograph for LNP under Nitrogen at 10ºC/min

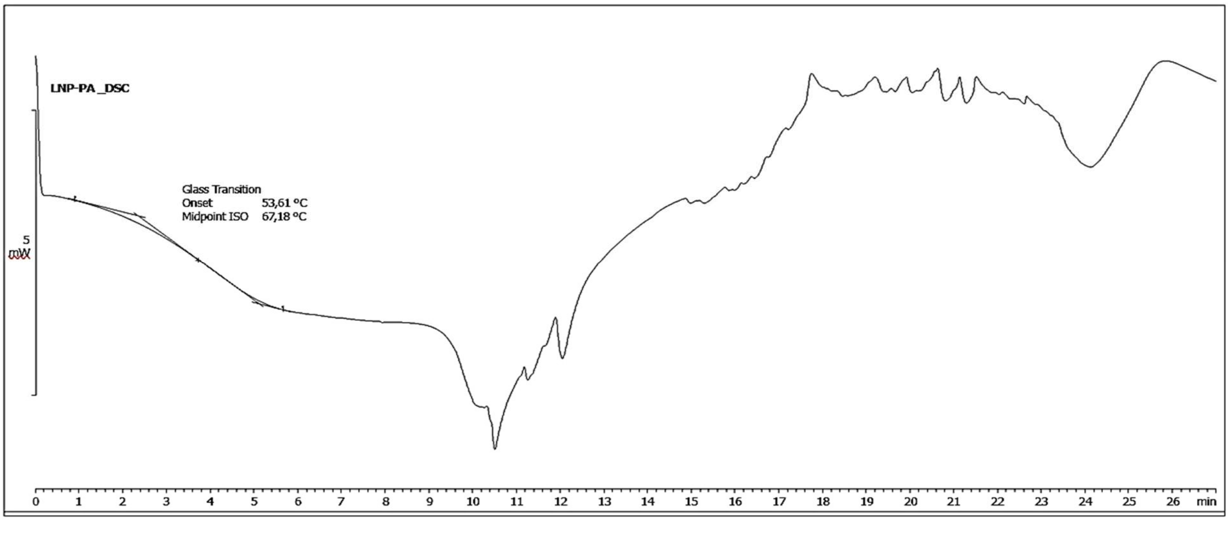


Figure 37:DSC thermograph for LNP-PA under Nitrogen at 10ºC/min

4.4 Flammability and thermal stability tests for the LNP/PA/PLA bio-composite

4.4.1 TGA

The TGA results for the pristine PLA,PLA/LNP-PA and PLA/LNP-PA blends as shown in Figure 38,indicate that the thermal degradation process takes place in the temperatures range of approximately 350 °C to 450 °C. Numerous descriptions of lignin's thermal degradation can be found in the literature [183]. Water is released at the beginning of its breakdown, which is followed by the first step of decomposition (230–260 °C), which causes propanoid side chain cleavage to produce low molecular weight products. A significant amount of methane is produced during the main decomposition step, which takes place at higher temperatures (250–450 °C). This is caused by the lignin main chain breaking, and it is followed (above 500 °C) by a number of rearrangements and condensation reactions of the aromatic structure, which result in the formation of char structures, which break down above 650 °C. This char only remains thermally stable in anaerobic environments and completely disintegrates in oxygenated environments [32]. The increased concentration of the bio-flame retardant additive LNP-PA causes a shift to higher values of degradation temperatures.

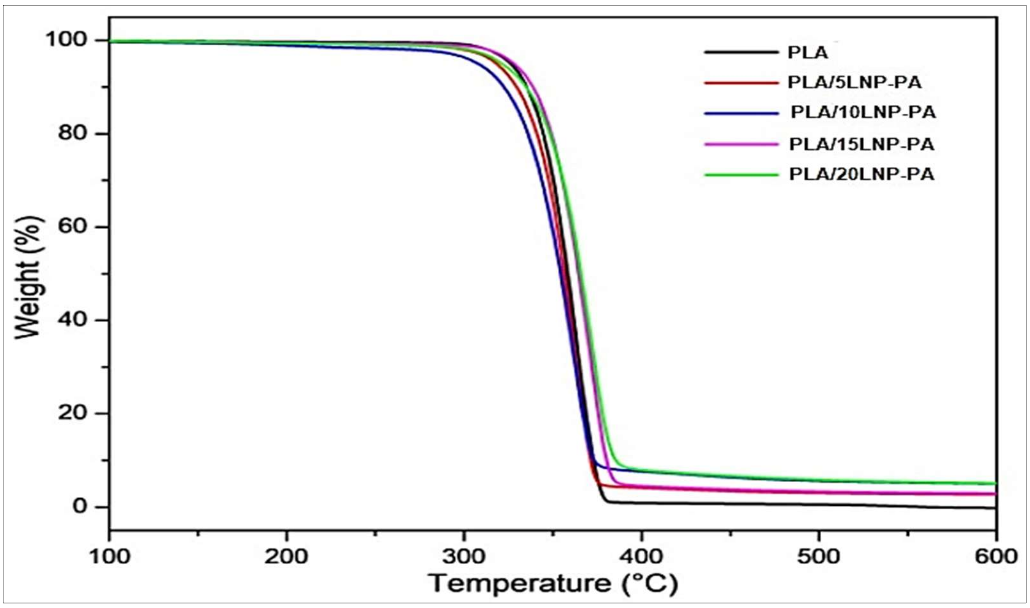


Figure 38:TGA results for PLA/LNP-PA bio-composites

However, there are some important observations to note. Regarding PLA/LNP and PLA/5LNP-PA composites, they had T$_{(5\%)}$ of 319 and 310°C and T$_{(20\%)}$ values of 340 and 335°C, respectively. It can be inferred that PLA/LNP and PLA/5LNP-PA composites had less thermal stability than PLA alone. This means that the first decomposition step of bio-flame retardant consisting of LNP alone. The thermal stability of PLA is significantly reduced when lignin is used an additive within its structure, as observed during TGA analysis conducted in nitrogen atmosphere. Similar observations have been reported by [122], and this has been credited to the effect of the degradant lignosulphonate phenolic hydroxyl and carboxylic acid groups, observed during TGA analysis conducted in nitrogen atmosphere. Similar observations have been reported by [194, 196].In the case of the higher loading concentrations of LNP-PA, the PLA/10LNP-PA and PLA/15LNP-PA had $T_{(5\%)}$ of 328 and 321°C and $T_{(20\%)}$ values of 340 and 347°C, respectively .This implied that PLA decomposed later than LNP-PA. Due to the rapid weight loss caused by the first step of LNP-PA's breakdown, the higher the LNP-PA concentration at a lower temperature, the faster the PLA sample lost weight. We have previously stated in previous chapters that PA, like other phosphate-based compounds, reduce the thermal degradation of PLA. Consequently, when the flame-retardant additive concentration was increased, more PA segments were released at higher temperatures, and the PLA's thermal degradation was reduced. The bio-composites mass loss % percent reduced as the LNP-PA concentration increased. This trend is similar to what was observed by [122] in a similar study.

T (5%)/ºC	T (20%)/ºC	T (50%)/ºC	T (80%)/ºC	Mass loss/%
325	343	363	370	100
319	340	362	370	97.4
310	335	355	370	95.4
328	351	370	390	97.2
321	347	381	395	95.2

Table 7:TGA results of PLA/LNP-PA summary

4.4.2 Modified UL-94 Vertical test

As previously mentioned, UL 94 is frequently used to assess the phenomenon of relative flammability and melt dripping in polymeric materials [46]. The modified UL-94 V test showed the self-extinguishing properties of PLA/15LNP-PA which achieved a V-0 rating. PLA/LNP attained a V-2 rating and this was only improved as the loading ratio of the bio-flame retardant additive was increased. The results are summarised in

Table 8.

Table 8:UL-94 V test results

Sample	flame time (s)		Cotton Dripping	Ignition	Rating
	t_1 (s)	t_2 (s)			
PLA	31	16	Yes	Yes	V-2
PLA/LNP	24	20	Yes	Yes	V-2
PLA/5LNP-PA	21	18	No	Yes	V-2
PLA/10LNP-PA	15	12	No	No	V-1
PLA/15LNP-PA	10	8	No	No	V-0

When pristine LNP is added to PLA, the combustion time increases. This might be explained by the fact that the pristine lignin breaks down at a lower temperature than the polymer matrix; as a result, there is high flammability and the samples achieve a V-2 classification using the UL 94 test, similar to reports by [223]. On the other hand, LNP-PA reduces the overall combustion time, which limits the flammability of nanocomposite materials. Moreover, the flame-retardant qualities get stronger as the LNP-PA content rises. Specifically, the nanocomposites with 10–15 weight percent LNP-PA exhibit a noteworthy decrease in overall combustion time and are rated V-1 and V-0 respectively. It is noted that a layer of protective char forms during the test, functioning as a barrier to the transfer of mass and heat. It is anticipated that the presence of other impurities and phosphate functionality in PLA will cause a thermally stable compound to form in the condensed phase [223]. This compound will also help to form an effective char layer, which will cause the PLA to self-extinction and increase the rating.

4.4.3 Modified Horizontal Burning test

To investigate the burning rate and extent of burning of the bio-composite formulations, the following variables were calculated based on the ASTM 635-03 standard test [220].Three specimen samples were used for each formulation.

i) Average burning time, $Tb_{av} = \frac{60\Sigma(t_2 - t_1)}{n}$ ……equation 1

where n is the total number of specimens and t is time in **seconds**.

ii) Average extent of burning, $L = \frac{\Sigma(100-Y)}{n}$ …. equation 2

where n is the total number of specimens and L is length damaged in **mm**.
where Y is the length of sample that has not been burned.

iii) The Rate of burning, $R_b = \frac{L}{Tb_{av}}$ …. equation 3

iv) Self-extinguishing (SE)

v) No-burning (NB)

The results are shown in Table 9.

Table 9:Horizontal burning test results summary

Sample	Tb_{av} **(min)**	L **(mm)**	Rate of Burning **(mm/min)**	SE	NB	HB
PLA	4.30	100	23.25	-	-	HB
PLA/LNP	4.70	100	21.27	-	-	HB
PLA/5LNP-PA	6.60	100	15.15	-	-	HB
PLA/10LNP-PA	8.15	100	12.27	-	-	HB
PLA/15LNP-PA	1.70	20	11.74	Yes	-	HB

In reference to the HB test, pure PLA achieved a linear burning rate of 23.25 mm/min, which matches the standard and qualifies it for the HB rating [221, 222].The inclusion of pure, unfunctionalized lignosulfonate does not significantly decrease the PLA's burning temperature. As the bio-flame retardant additive LNP-PA was added, the average extent of burning and the rate of burning of PLA decreased. The bio-flame flame retardant additive LNP-PA 15 wt% ratio resulted in self-extinguishing in PLA after 1.70 minutes. Furthermore, it should be noted that PLA burns at a low rate of 23.25 mm/min, which is consistent with previous studies,[221, 222], on the polymer's flame retardancy. Like what is seen in the literature, combining phytic acid and lignin in PLA composites exhibit a lower burning rate relative to pristine lignin. Furthermore, compared to PLA, the flame extinction occurred more quickly for the composites with higher LNP-PA contents (10 and 15 wt.%), demonstrating the more significant effect of additive content on the additive material's flame extinction properties in PLA.This is indicates that the LNP has a better flame-retardant effect when combined with phytic acid. This is attributed to the presence of phytic acid in the bio-flame retardant formulation.

4.4.4 Summary of flammability test

The bio-flame retardant formulation's fire-retardant effect was investigated using a modified UL-94 evaluation. The test specimens were 125 mm x 10 mm x 5 mm filaments in both horizontal and vertical orientations. Three duplicates of each sample were burned, and the results were averaged. In the vertical method, the control sample, pristine PLA, burned more vigorously. Melting drips were found in pristine PLA, PLA/LNP, and PLA/5LNP-PA, which were all classified as V-2.PLA/10LNP-PA and PLA/15LNP-PA samples with higher bio-flame retardant additive weight percentages demonstrated better fire behaviour and were classified as V-1 and V-0, respectively. All samples were classified as HB in the horizontal mode, and the rate of burning decreased as the loading ratio of the bio-flame retardant additive increased. The presence of lignosulfonate, whose highly aromatic composition forms a carbonaceous char layer that inhibits oxygen diffusion to the combustion site, is credited with the results. Because of the presence of six phosphate groups in its structure, which produce phosphoric acid, phytic acid can degrade and form a char layer [36],[37] ,[38]. This creates a protective layer that reduces the amount of fuel required to sustain the combustion process while also limiting heat flow in the material [39].In this intumescent-based system, phytic acid also serves as an acid source. It dehydrates the lignosulfonate nanoparticles that are acting as the charring agent, causing them to swell and protect the PLA from fire, heat, and oxygen. The results also show that functionalized lignosulfonate nanoparticles outperform pristine lignosulfonate nanoparticles in terms of flame retardancy.

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The goal of the study was to create an intumescent, bio-based flame retardant for PLA by combining lignosulfonate nanoparticles with phytic acid, in order to have a bio-based functional polymeric composite with low environmental impact that would meet the necessary mechanical requirements for conventional applications while also having good flame retardancy. PLA is regarded as a viable alternative to plastics made from crude oil and has garnered increasing attention in recent decades because of its superior mechanical qualities. However, PLA does have certain drawbacks, especially a high flammability. To address this deficiency, we successfully designed an intumescent-based flame-retardant system for PLA. This is a passive fire resistance system in which light char that is produced by the flaming polymer materials slows down heat transfer because they are poor heat conductors. The system requires a charring/carbonizing agent. Lignin, being bio-based and highly aromatic was chosen as a perfect candidate for the system. In addition to this, it is necessary to have an acid source or dehydrating agent for the intumescent flame-retardant system. Given that many phosphorous-based compounds had been either highly effective flame retardants or their intermediates, phytic acid was chosen as bio-based phosphorous containing raw ingredient for the formulation. As a result, lignosulfonate was effectively functionalized by phytic acid and transformed into nanoscale using ultrasonication and spray-freeze drying. By using FTIR and NMR, the chemical structure of LNP-PA was verified, and the size of the particles was measured as 238nm using DLS, while XRPD examined the crystallinity of the LNP-PA. However, there is a reduction in the intensity of hydroxyl groups caused by both sonication and phosphorylation. Compared to lignosulfonate the functionalized LNPs spectra have a strong band at 1030 cm^{-1} caused by to P-O-R ester bonds due to the phosphate group, with R representing lignin. In addition, a band is observed at approximately 1350 cm^{-1} due to the P=O bond, due to the phosphorylation of lignosulfonate with PA through ester bonds. The reduced absorbance in the range 3100-3450 cm^{-1} band is due to the reaction of hydroxyl and phosphate groups. The structure of lignosulfonate was also altered by sonication. For example, in lignosulfonate, the band with an intense absorbance of 64% at 1040 cm^{-1} emanating from the β-O-4 linkages is reduced to 18% in unmodified LNPs, indicating homolytic cleavage of the β-O-4 linkages. NMR analysis confirms some of these assumptions. This was further verified by ^{31}P -NMR, which revealed the loss of hydroxyl functional groups, suggesting that they reacted with the phosphate groups in phytic acid, indicating that chemical modification with phytic acid was successful. This may be attributed to homolytic cleavage during sonication and the reaction of the lignosulfonate hydroxyl groups with the phosphate groups in phytic acid. The suggested changes to the structure of lignin are the formation of P-O-R ester bonds, where R is lignin, based on their analysis of phosphorylation of lignin using 2D ^{1}H-^{31} P HSQC NMR, which we were unable to do in our laboratory due to HSQC equipment malfunction.The next goal was to enhance PLA's fire behaviour by using the bio-flame retardant LNP-PA that had been synthesized. Using melt extrusion, consistent five PLA/LNP-PA blends were synthesized with different loading ratios of the flame-retardant additive. To create samples for flammability tests such as Cone Calorimetry, LOI, UL-94 and mechanical test specimens, compression moulding and injection moulding were utilized. However, because PLA is brittle, we were unable to obtain samples for additional testing. As a result, we had to use the modified UL-94 to test for flammability after resorting to the solvent casting method. Modified UL-94 tests and TGA were then carried out on the samples to determine flammability and thermal stability. TGA results showed an increased thermal stability as the loading ratio of LNP-PA increased. The modified UL-94 V test showed the self-extinguishing properties of PLA/15LNP-PA which achieved a V-0 rating. PLA/LNP attained a V-2 rating and this was only improved as the loading ratio of the bio-flame retardant additive was increased. In the horizontal burning test, pure PLA attained a linear burning rate of 23.25 mm/min, which is in accordance with the standard and qualifies it for the HB rating. The incorporation of pure, unfunctionalized lignosulfonate has no significant effect on the PLA's flame-retardant behaviour. The average extent of burning and rate of burning of PLA decreased as the bio-flame retardant additive was loaded After 1.70 minutes, the bio-flame flame retardant additive LNP-PA 15 wt% ratio self-extinguished in PLA.

The suitability, major findings and contributions of this study based on the obtained on the key values of this study are summarised below:

Suitability of the Method:

The method employed in this study is suitable for addressing the high flammability of PLA by developing a bio-based flame-retardant system. The use of lignosulfonate nanoparticles and phytic acid, along with techniques such as ultrasonication, spray-freeze drying, and melt extrusion, demonstrates a comprehensive approach to enhancing the flame retardancy of PLA. The incorporation of various testing methods, including modified UL-94, TGA, and mechanical tests, further validates the suitability of the method for evaluating the performance of PLA/LNP-PA blends.

Major Findings:

1. Successful functionalization of lignosulfonate nanoparticles with phytic acid, leading to the formation of bio-based flame retardant LNP-PA with enhanced flame retardancy for PLA.

2. Increased thermal stability observed in PLA/LNP-PA blends as the loading ratio of the bio-flame retardant additive were increased.
3. Achievement of self-extinguishing properties in PLA/15LNP-PA blend, as indicated by the V-0 rating in the modified UL-94 test.
4. Improved flame-retardant behaviour of PLA with the incorporation of LNP-PA, as evidenced by reduced burning rate and extent of burning.
Contribution of this study:

The study contributes to the development of bio-based flame-retardant systems for PLA, addressing its high flammability and enhancing its flame retardancy. The successful synthesis and functionalization of lignosulfonate nanoparticles with phytic acid, along with the evaluation of PLA/LNP-PA blends using various testing methods, provide valuable insights into the potential applications of bio-based flame retardants in polymer composites. Additionally, the achievement of self-extinguishing properties in PLA/15LNP-PA blend demonstrates the practical significance of the study in improving the fire behaviour of PLA-based materials.

5.2 Recommendations for future work

The results of this dissertation's successful series of investigations meet the objectives and demonstrate that combining PLA with phytic acid-functionalized lignosulfonate nanoparticles can increase PLA's flame retardancy. The study raises several other questions and opportunities for more research. The recommendations include sections considered to be the next step, building on the current dissertation as a basis for additional research, as well as sections that were eliminated owing to time constraints. Below is an outline of these.

- Use injection moulding to make standard UL-94 test specimens.
- Conduct standard UL-94 tests instead of the modified UL-94 test we used in this research.
- Investigate the flammability of the various blends of PLA/LNP-PA using other standard tests which include cone calorimetry and limiting oxygen index.
- Vary the weight percent ratios of lignosulfonate and phytic acid during functionalization and use these to investigate their flame-retardant effect on PLA composites.
- Conduct mechanical tests which include flexural, tensile, impact, hardness, shear and compression tests on the PLA/LNP-PA blends to investigate the effect of the bio-flame retardant formulations on the mechanical properties of the PLA blends. This is because the polymer blends maybe flame-suppressant but their applications in areas in which mechanical strength is important maybe limited.
- Investigate biodegradability of the PLA/LNP-PA blends.
- Study the morphology and crystallinity of the PLA/LNP-PA blends.

- Examine the study's reliability further and validate the findings in this dissertation with additional DSC and TGA for the thermal behaviour, FTIR and NMR for the chemical structure analysis for both the LNP-PA and the PLA/LNP-PA polymer blends.
- Conduct gas phase and condensed phase analysis using methods like TGA-FTIR, Py-GC-MS and ^{13}C.
- Investigate the thermal behaviour of the bio-flame retardant and polymer blends using TGA under oxygen conditions.
- Investigate other solvents that can be used for solvent casting as chloroform is very toxic.

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