Eco Friendly Filler Modified Sustainable Polymer Composites for Improved Mechanical Performance

MS Thesis

By

RASHID KHAN

CIIT/SP24-R06-025/LHR

COMSATS University Islamabad

Pakistan

Fall 2025

Eco Friendly Filler Modified Sustainable Polymer Composites for Improved Mechanical Performance

A Thesis submitted to
COMSATS University Islamabad, Lahore Campus

In partial fulfillment
of the requirements for the degree of

Master of Science in
Chemistry

By

RASHID KHAN
CIIT/SP24-R06-025/LHR

Department of Chemistry
Faculty of Chemistry

COMSATS University Islamabad Pakistan

Fall 2025

Eco Friendly Filler Modified Sustainable Polymer Composites for Improved Mechanical Performance

This thesis is submitted to the Department of chemistry in partial fulfillment of the requirements for the award of the degree of Master of Science in chemistry

Name	Registration Number
RASHID KHAN	CIIT/SP24-R06-025/LHR

Supervisory Committee

Supervisor

Prof. Dr. Zulfiqar Ali

(Professor)

Department of Chemistry

COMSATS University Islamabad

Lahore Campus

Co-Supervisor

Dr. Sadaf ul Hassan

(Assistant Professor)

Department of Chemistry

COMSATS University Islamabad

Lahore Campus

Member

Dr. M. Shahid Nazir

(Assistant professor)

Department of Chemistry

COMSATS University Islamabad

Lahore Campus

Certificate of Approval

This thesis titled

Eco Friendly Filler Modified Sustainable Polymer Composites for Improved Mechanical Performance

By

RASHID KHAN

CIIT/SP24-R06-025/LHR

has been approved

for the Degree of MS chemistry

at COMSATS University Islamabad, Lahore Campus

External Examiner: _____

Dr.

Supervisor: _____

Prof. Dr. Zulfiqar Ali
Department of Chemistry CUI
Lahore Campus

Head of Department: _____

Dr. M. Shahid Nazir
Department of Chemistry CUI
Lahore Campus

Author's Declaration

I RASHID KHAN, CIIT/SP24-R06-025/LHR hereby declare that I have produced the work presented in this thesis, during the scheduled period of study. I also declare that I have not taken any material from any source except referred to wherever due that amount of plagiarism is within acceptable range. If a violation of HEC rules on research has occurred in this thesis, I shall be liable to punishable action under the plagiarism rules of the HEC.

Date: _____

Signature of the Student

_____

RASHID KHAN

CIIT/SP24-R06-025/LHR

Certificate

It is certified that RASHID KHAN, CIIT/SP24-R06-025/LHR has carried out all the work related to this thesis under my supervision at the Department of Chemistry, COMSATS University Islamabad, Lahore Campus, and the work fulfills the requirement for the award of MS degree.

Date: _____

Supervisor:

_____

Prof. Dr. Zulfiqar Ali

Department of Chemistry

COMSATS University Islamabad

Lahore Campus

Dedication

Dedicated to My Late Mother, Whose Memory Continues to Inspire Me, and to My Loving Father, Sisters, and Brothers, Whose Unwavering Support, Encouragement, and Sacrifices Made This Work Possible.

It is also respectfully dedicated to my supervisor, **Prof. Dr. Zulfiqar Ali**, and my co-supervisor, **Dr. Sadaf ul Hassan**, whose scholarly guidance, and tireless mentorship enabled me to achieve my academic goals and strive for excellence.

Acknowledgements

“In the name of ALLAH, the most beneficent, the merciful, the only Creator”

First and foremost, I Thank **Allah Almighty**, who always blessed me with everything best! And granted me the ability to make another little involvement in the vast world of research and also to the teacher of the universe **Hazrat Muhammad (PBUH)** who is the ocean of knowledge and candle for every researcher!

صَلَّى اللهُ عَلَىٰ سَيِّدِنَا مُحَمَّدٍ

I am sincerely grateful to my supervisor **Prof. Dr. Zulfiqar Ali** for their enthusiastic guidance, sympathetic attitude, and enlightened supervision. I am also grateful to my co-supervisor **Dr. Sadaf Ul Hassan** for their efforts, hard work, and maintenance of professional integrity enabled me to complete my research work without any problem or hindrance. May Allah bless them with the best in this world and the world hereafter! **(AMEEN)**

I have no words to acknowledge the sacrifices, efforts, lot of prayers, guidance, unconditional love, and firm dedication of my father ‘**Arshad Khan’.**

رَبَّنَا اغْفِرْ لِي وَلِوَالِدَيَّ وَلِلْمُؤْمِنِينَ يَوْمَ يَقُومُ الْحِسَابُ

My sincere appreciation goes to the **COMSATS University Islamabad Lahore Campus,** especially the Head of Department, **Dr. Muhammad Shahid Nazir**, and all the respected faculty members for their academic guidance and moral support.

I extend my gratitude to my senior Ph.D. Scholar **Farah Kausar** for their unwavering support and invaluable help throughout my research.

I am incredibly appreciative of my family's constant encouragement and support. Their confidence in my skills has been a continual source of inspiration.

Finally, I am grateful to the **A15 Lab** and **Saqib Noor Chaudhary** for their cooperation in facilitating throughout this journey. I am deeply grateful to my friends, **Noor Zainab, Rimsha Saif, Hussain Ali Awan, Husnain Naqvi** and **Ayesha Siddiqa** for their companionship and encouragement throughout my research journey.

This thesis is the result of everyone's combined work and support, and I really appreciate all of your contributions to making this project a reality.

RASHID KHAN
CIIT/SP24-R06-025/LHR

Abstract

Eco Friendly Filler Modified Sustainable Polymer Composites for Improved Mechanical Performance

By

RASHID KHAN

This work presents a systematic investigation of kraft lignin as a sustainable bio-filler for elastomeric composites, focussing on chemical modification (nickel coordination), comprehensive physico-chemical characterisation, formulation into nitrile butadiene rubber (NBR) compounds, and comparison with conventional inorganic fillers. Motivated by the environmental and resource supply problems of petrochemical fillers, the study situates lignin within the circular bioeconomy paradigm and reviews current approaches to compatibility enhancement and performance optimisation of bio-fillers. The work details a reproducible protocol to synthesise nickel-coordinated lignin nanoparticles, and applies FTIR, UV–Vis and Raman spectroscopy to verify metal chelation and preservation of lignin's aromatic backbone. Dispersion, thermal stability and interfacial behaviour are quantitatively and qualitatively evaluated; modified lignin demonstrates reduced hydroxyl accessibility, characteristic spectral shifts consistent with Ni^{2+} coordination, and absorption features indicative of discrete chelate complexes rather than metallic aggregates. When incorporated into NBR matrices under controlled mixing and cure conditions, chemically modified lignin particularly following hydrophobization/compatibilisation strategies yields composite property profiles (hardness, abrasion resistance, and modulus) comparable to, and in specific metrics competitive with, carbon black and silica filled analogues. The manuscript identifies key process windows for filler loading and highlights residual challenges (agglomeration, polarity mismatch, thermal-processing limits) that determine the practical ceiling for lignin substitution in high-performance elastomers.

Table of Contents

List of Figures

List of Tables

List of Abbreviation

ISO	International Standard Organization
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
XRD	X-ray diffractometry
FTIR	Fourier transform infrared spectroscopy
TGA	Thermogravimetric analysis
UV	Ultraviolet/Visible spectroscopy
NBR	Nitrile Butadiene Rubber

Chapter 1

Introduction

1. Overview of Polymer

1.1 Historical Background of Polymers

In terms of industrial, commercial, and biomedical applications throughout modern civilization, polymer science development is among the key values in materials engineering that have revolutionized technological advances in the industry. Polymer materials are not new to human society, as early civilizations made use of natural polymers such as natural rubber, wool, cotton, and cellulose-based materials, without understanding their macromolecular structures. The precursors to modern advanced polymer systems are these primitive applications, as well as the history of the past two centuries of science, technological invention, and industrial expansion, which have broadly defined the history of materials science. [1], [2]

The polymer chemistry of modern times was founded in the early nineteenth century, when chemists began systematically developing derivatives of natural products. In his process of vulcanizing natural rubber, Charles Goodyear invented the vulcanization process in 1839, which significantly enhanced the properties of natural rubber, making it suitable for a broad range of applications as an elastomer that is easily manipulated due to temperature changes. In 1862, with the invention of Parke-sine, the first semi-synthetic polymer derived from the cellulose polymer, a precursor of celluloid, by Alexander Parkes, the replacement of natural polymers by synthetic ones began. Optionally, celluloid can be modified using chemistry to impart superior properties. [3], [4]

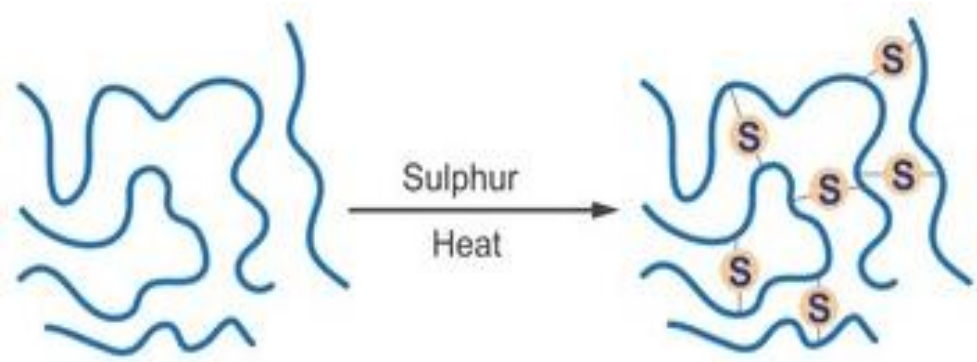

Figure 1.1: Vulcanization of Natural Rubber

Not until 1907 did a breakthrough in the science of synthetic polymers become possible. Leo Baekeland invented Bakelite, the first entirely synthetic polymer, by reacting methanol and formaldehyde under extremely restricted temperature and pressure conditions. Bakelite was made spectacular by its electrical conductivity, heat-conductivity, and molding capabilities, which form the foundation of the polymer revolution and are found in electrical conductors and radios, as well as in components of automobiles. This invention marked the Polymer Age of invention, a complete replacement of initially natural materials with entirely new materials, as it demonstrated that completely new materials could be synthesized from chemicals derived from fossil fuels. [5]

The 1920-1950 period is considered the golden age of polymer chemistry, marked by significant contributions to the field of theory that transformed the scientific understanding of macromolecular structures. The most significant theory followed this in the history of the macromolecular theory of the structure of polyposters, filed by Hermann Staudinger in 1920, who demonstrated that polymers were larger aggregates of molecular chains composed of repeating units bonded together in a covalent system and were no longer aggregates of small molecules bound together by weak intermolecular forces. It was a revolutionary theory to which the traditional scientific community was initially somewhat sceptical, having been accustomed to the long-standing theory of aggregation. Staudinger won the Nobel Prize in Chemistry in 1953 and introduced the science of polymer science as an independent and valid field of study. [6], [7]

The increase in the production and commercialization of polymers was historic during the interwar period and post-World War II, driven by industrial demand for new materials and the strategic value of synthetic materials during times of war. The other advancement is the control of polymerization reactions and the synthesis of stereo-regular polymers with controlled molecular architecture, which occurred in the 1950s with Karl Ziegler and Giulio Natta developing the Ziegler-Natta catalysts. This catalyst system led to the manufacture of high-density polyethylene and isotactic polypropylene, which exhibited higher mechanical properties compared to their predecessors, earning both scientists the Nobel Prize in Chemistry in 1963. The decades of 1940 to 1945 witnessed the world undergoing tremendous expansion in industrial production of polymers, commodity plastics, as well as engineering plastics, which

were being produced on a large scale that the world had never experienced before, as the requirements of industrializing economies rose. [8]

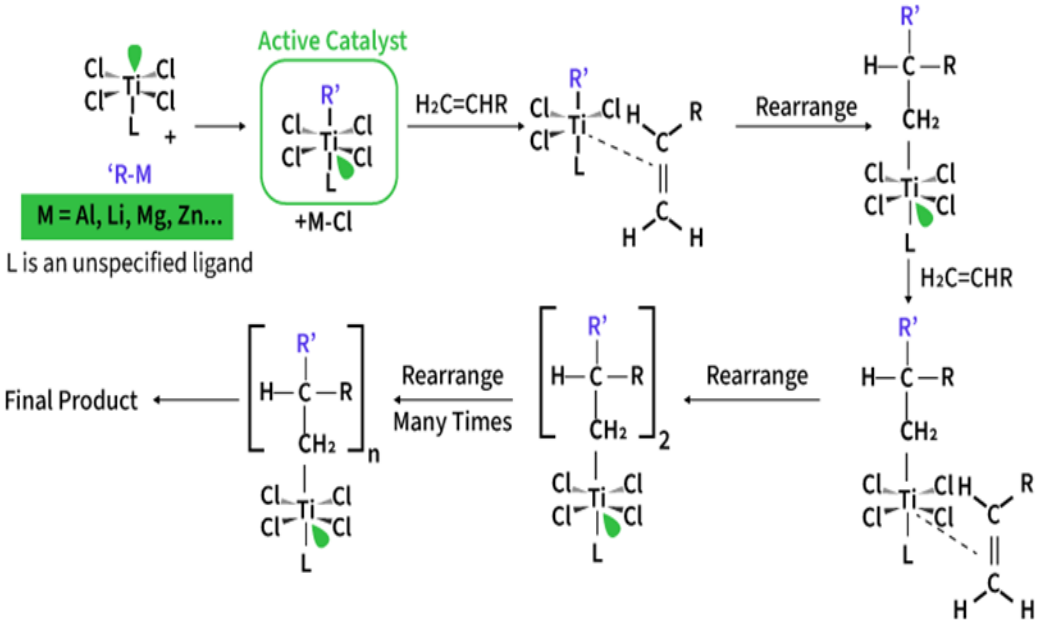

Figure 1.2: Mechanism of Ziegler-Natta Catalysis

A paradigm shift in increasing the sustainability of polymers has been experienced in the past few decades, as the growing alarm regarding environmental impact in the region of plastic pollution, as well as the pressing need to reduce the use of petroleum-based feedstock, can be traced. The contemporary era of the polymers industry has experienced phenomenal growth, and the worldwide market for polymers is still in its development, driven by the packaging segment, the automotive industry, the building sector, and the electronics industry. The main characteristics of this transformation are stricter environmental rules and regulations, heightened consumer awareness of how plastic waste should be managed, and spectacular advances in materials science that have enhanced the working capacity and environmental friendliness of polymer systems. [9], [10]

High-tech production technologies of polymers, including living polymerization processes to precisely control molecular weight, polymerization using the ring-opening process to prepare cyclic polymers, and click chemistry to provide easy access to functionalizing polymers, characterize modern polymer science. This is because a combination of computational modelling and artificial intelligence has been used to accelerate the discovery of polymers, enabling researchers to determine the characteristics of those polymers and optimize synthesis pathways at a level never

observed before. The shift toward environmentally friendly polymers is a typical trend in modern literature, and biodegradable polymers whose monomeric building blocks are produced from renewable sources, such as polylactic acid and polyhydroxyalkanoates, are gaining popularity in the packaging industries, as well as in the agricultural and biomedical industries. [11], [12]

The history of polymers, from primitive natural products to highly engineered polymers, depicts how humans have been on an endless search for materials that possess the properties of performance, economics, and eco-friendliness. Future research in polymers is increasingly geared towards the principles of a circular economy, focusing on designing polymers that can be recycled. This involves developing chemical recycling technologies, making them more effective and innovative, and creating end-of-life designs that cause minimal harm to the environment. It is hoped that, through the development of polymers, they will be at the forefront of addressing all types of urgent needs worldwide, such as mitigating climate change, conserving resources, and promoting sustainable development, without compromising the performance requirements of contemporary technological applications. [13], [14]

1.2 Classification of Polymers

Polymers are a highly heterogeneous group of materials that cannot be classified within a single unified group due to their complex molecular structures, wide range of properties, and extensive fields of use in various industrial activities. Polymers are typically classified according to several factors, including their source of supply, polymerization mode, molecular structure, backbone chain chemical composition, and thermal properties. The knowledge of such classification systems forms the basis of polymer science and engineering because it offers a systematic basis on which the properties of materials can be predicted, the selection of suitable processing methods, and the design of polymers for specific purposes. [15]

1.2.1 Classification on the Basis of Source

Polymers are generally classified into three main categories: natural polymers, semi-synthetic polymers, and synthetic polymers, based on their source of availability. There are natural polymers that are found in natural abundance and are biosynthesized by living organisms, such as plants, animals, and microorganisms, following very elaborate biochemical routes. Such biopolymers include proteins, such as collagen and

silk; polysaccharides, including cellulose, starch, and chitosan; polynucleotides, such as DNA and RNA; as well as natural rubber produced by the Hevea Brasiliensis trees. Natural polymers have been utilized by human civilization for thousands of years. They can be applied in various sectors, including food, pharmaceuticals, textiles, and biomedicine, due to their biocompatibility, biodegradability, and renewability. [16]

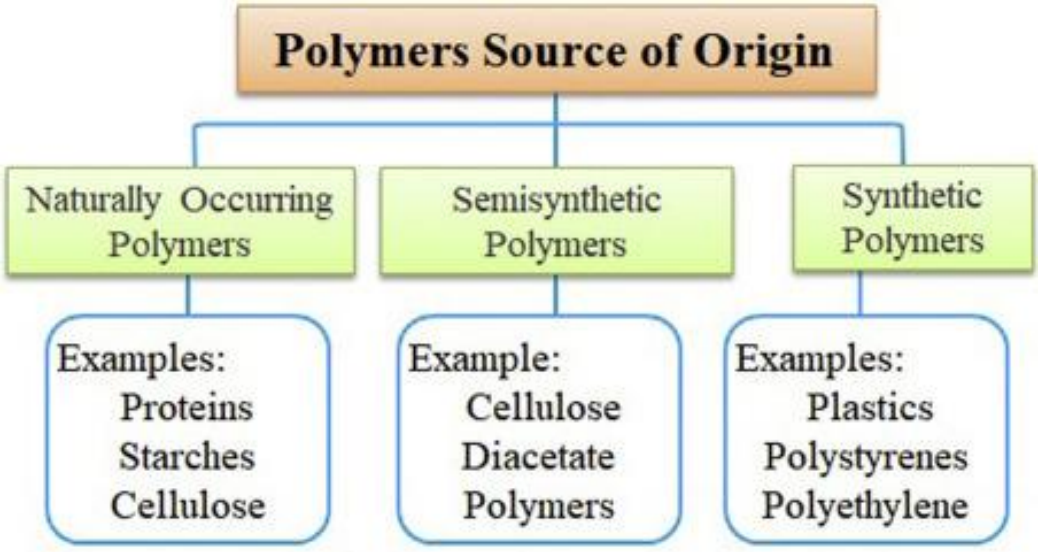

Figure 1.3: Origin-based classification of polymers

1.2.1.1 Natural Polymers

Natural polymers are macromolecules synthesized by living organisms by biosynthetic pathways, the most common polymeric materials on the planet, and play essential biological roles such as mechanical support, energy storage, genetic information transfer, and catalysis. These biopolymers are also constructed from renewable materials and possess inherent biocompatibility and biodegradability, thereby offering considerable potential for applications as a sustainable material. The most common natural polymer, cellulose, is the primary structural material of plant cell walls and is the biomass resultant of photosynthesis, amounting to approximately 1.5 trillion tons of biomass constructed each year. Starch, the primary energy storage molecule in plants, is another noteworthy polysaccharide. Additionally, chitin, the second-most commonly occurring polymer in nature, is a component of the crustacean exoskeleton and in the cell walls of fungi. Collagen, wool, and silk fibroin are protein-based natural polymers that offer exceptional mechanical properties with biological functionality. Hevea brasiliensis latex is an excellent natural rubber that has been used in various ways for centuries due to its exceptional elastic nature. [17]

1.2.1.2 Semi-Synthetic Polymers

Semi-synthetic polymers are the halfway products that lie between natural polymers and entirely synthetic polymers, since they are formed out of naturally occurring polymers but are then chemically processed to make them better or add new functionality. Examples of such cellulose derivatives are cellulose acetate, cellulose nitrate, and carboxymethyl cellulose: in all of them, the numerous and easily soluble hydroxyl groups of cellulose have undergone color-codiminatory alteration: the cellulose backbone has been esterified or etherified to produce compounds with better solubility, thermal stability, and mechanical strength. Another significant semi-synthetic material, less stable to air and water, but with vastly better thermal stability, mechanical strength, and elastic recovery than unmodified natural rubber, is vulcanized rubber, which is made by sulfur crosslinking of natural rubber. These changes typically involve regulated chemical reactions that alter the crystallinity, glass transition temperature, and processing characteristics of the polymer, while retaining the essential polymeric backbone based on renewable resources. Semi-synthetic polymers have also been widely used in textile fibers, packaging films, coatings, and pharmaceutical excipients. [18]

1.2.1.3 Synthetic Polymers

Synthetic polymers are strictly anthropogenic substances manufactured under controlled conditions at industrial plants through chemical polymerization, primarily using monomers of petroleum origin. Ever since the discovery of Bakelite in 1907, synthetic polymers have spread to encompass a vast range of materials, including commodity thermoplastics such as polyethylene, polypropylene, polystyrene, and polyvinyl chloride; engineering thermoplastics like nylon, polycarbonate, and polyetherimide; and high-performance polymers, such as polytetrafluoroethylene and polyetheretherketone. Synthetic polymers are prevalent in current material usage due to their property tunability, provided by molecular design, low costs resulting from economies of scale, and excellent performance properties, such as mechanical strength, chemical resistance, and dimensional stability. Their petroleum-based foundation, energy-intensive manufacturing capabilities, and inability to degrade in the environment have, however, given rise to significant sustainability dilemmas, leading

to the modern-day research trend of bio-based synthetic polymers made from renewable-sourced feeds and biodegradable synthetic alternatives. [19], [20]

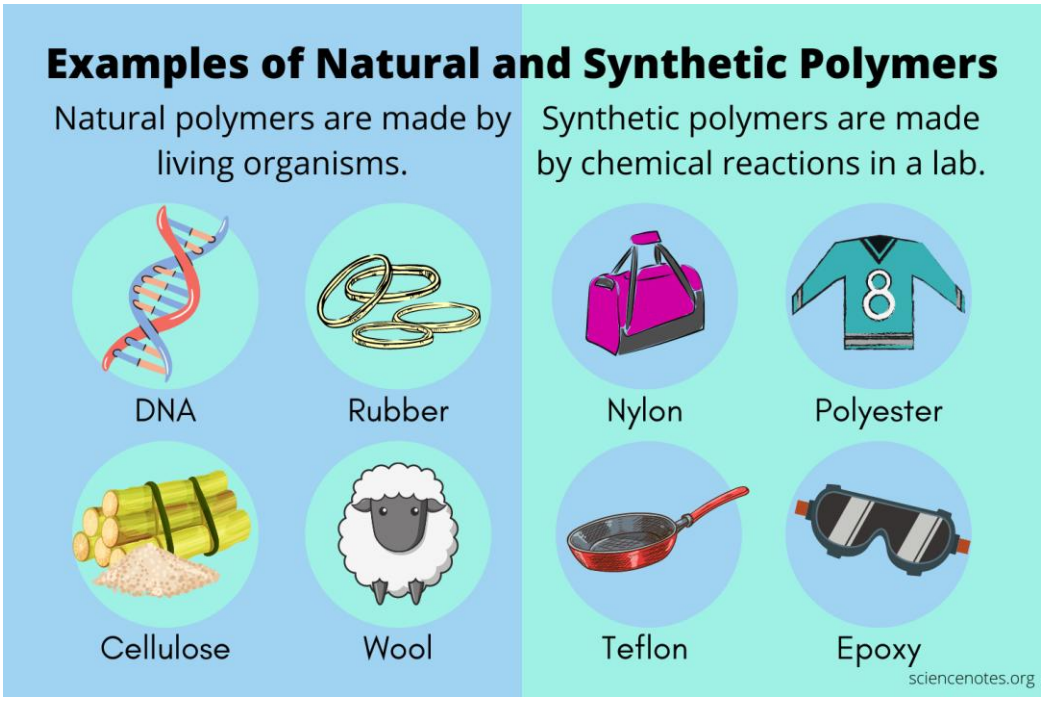

Figure 1.4: Examples of natural and synthetic polymers

1.2.2 Classification Based on Structure of a Monomer Chain

The molecular structure classification provides rich information on how polymer chains are spatially organized and how they are connected, which has a significant impact on mechanical properties, thermal behavior, and processing properties. This classification scheme (the macromolecular structure and connectivity of polymers) divides polymers into three main groups in terms of the topology and connectivity of their macromolecular structures. [21]

1.2.2.1 Linear Chain Polymers

Linear polymers are made up of unbranched and long chains of repeating units in an arrangement that then form a single chain, where the end of each chain is at one end of the molecule, and no side chains are attached to the backbone chain. The linear architecture enables the comfortable packing of chains in both amorphous and crystalline parts, thereby facilitating the occurrence of intermolecular forces through van der Waals forces, hydrogen bonding, or dipole-dipole interactions. They are high-density polyethylene, polyvinyl chloride, polytetrafluoroethylene, nylon, and polyethylene terephthalate. Linear polymers are generally more tensile, more

crystallized, have higher melting points, and are superior in their solubility resistance than branched polymers with the same chemical formula. The repetition of the chain structure allows the packing to occur closely, and crystalline domains are formed, which does not allow branching that causes steric hindrance and disturbs the crystalline order. Linear polymers are primarily thermoplastics, with the ability to melt and solidify easily, allowing for processing and recycling. [22], [23]

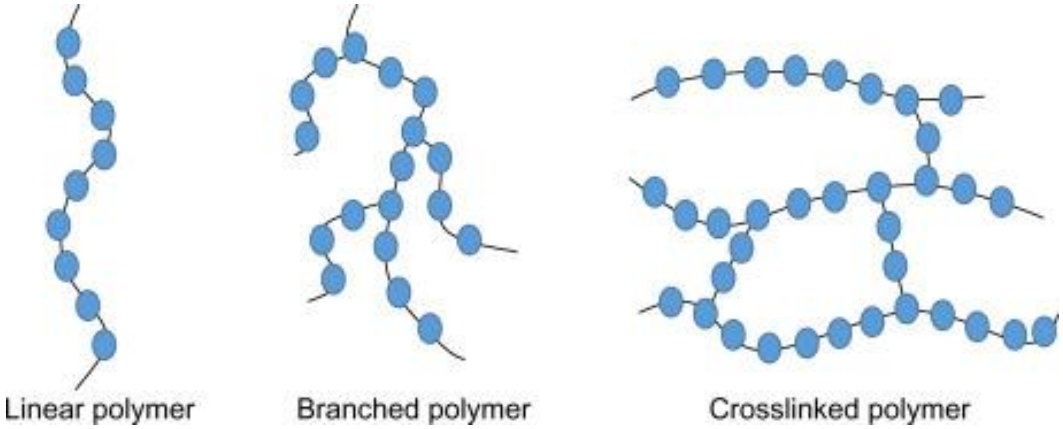

Figure 1.5: Linear, branched and cross-linked polymers

1.2.2.2 Branched Chain Polymers

The polymers with branched side chains have different lengths of extension entities extending out of the polymeric backbone, which interferes with the linear overall structure, forming a more complex three-dimensional structure. Branching may be either short-chain, and therefore include short side chains of 1-6 carbon atoms, or long-chain, with side chains of a similar length to the main chain. An example of a branched polymer is low-density polyethylene, which has many short-chain branches between them that interfere with crystalline packing, resulting in a lower density of the material. The density of linear high-density polyethylene is 0.97 g/cm³, while that of low-density polyethylene ranges from 0.91 to 0.93 g/cm³. Branching has a significant impact on the properties of polymers in general, reducing the crystal count, lowering the melt temperature and tensile strength, while boosting flexibility and impact strength, and lowering melt viscosity at high shear rates. The decreased efficiency of chain packing in branched polymers increases the amount of free volume, reducing density and modulus while enhancing processability. The introduction of branch-controlled permits enables the tailoring of the property to a specific application. [24]

1.2.2.3 Cross-Linked Polymers

Cross-linked or network polymers are polymers that have covalent bonds linking the various polymer chains through a variety of junction points, forming three-dimensional networks that inhibit molecular movement and chain slippage. Cross-linking may be obtained through various methods, such as chemical cross-linking using functional groups containing reactive groups, vulcanization with sulfur or peroxide, radiation cross-linking with high-energy photons or an electron beam, or by cross-linking multifunctional monomers during polymerization. This interlinked structure significantly modulates material characteristics, resulting in stiff, infusible, and insoluble materials that exhibit excellent dimensional stability, chemical resistance, and thermal stability. Examples of cross-linked polymers that are stronger and offer greater thermal stability than their linear counterparts in industry include vulcanized rubber, epoxy resin, phenol-formaldehyde (Bakelite), melamine-formaldehyde resins, and cross-linked polyethylene. The cross-linking level is directly proportional to the rigidity of the material. Highly cross-linked thermosets become very hard because the segregation of cross-links is minimal. In contrast, loosely cross-linked elastomers are flexible due to the high degree of mobility of their chain segments between cross-links. [25]

1.2.3 Classification based on Polymerization Mechanism

How the monomers interact to form polymers is another basic classification scheme, which splits polymerization reactions into two key categories: addition polymerization and condensation polymerization. These processes vary in their reaction routes, reaction dynamics, need to dispose of byproducts, and the products of the reactions. Knowledge of polymerization mechanisms is critical in regulating polymer molecular weight, structure, and properties during synthesis. [26]

1.2.3.1 Addition Polymerization

Combination polymerization, also known as chain-growth polymerization, is a type of polymerization that involves the successive addition of monomer units to an existing polymer chain via a reactive site, potentially without the elimination of any small molecules during the polymerization process. This process generally follows three clearly outlined steps, the first stage involves the production of a reactive species (free radical, cation or anion) which in turn reacts with the first unit of the monomers; the

second stage involves the addition of further units to the reactive center, and the third stage is termination which is attained by different mechanisms such as combining, disproportionation or transfer of chains. The addition polymerization is typical of monomers, which contain carbon-carbon double bonds or other reactive, unsaturated groups, allowing them to form new single bonds between monomers. Common examples include polyethylene, polypropylene, polystyrene, polyvinyl chloride, polyacrylonitrile, and polymethyl methacrylate. Addition polymers retain the chemical composition of the monomers, as they do not lose atoms during polymerization. The mechanism enables the formation of very high molecular weight polymers very early in the reaction, even when low amounts of monomers are converted. [27],[28]

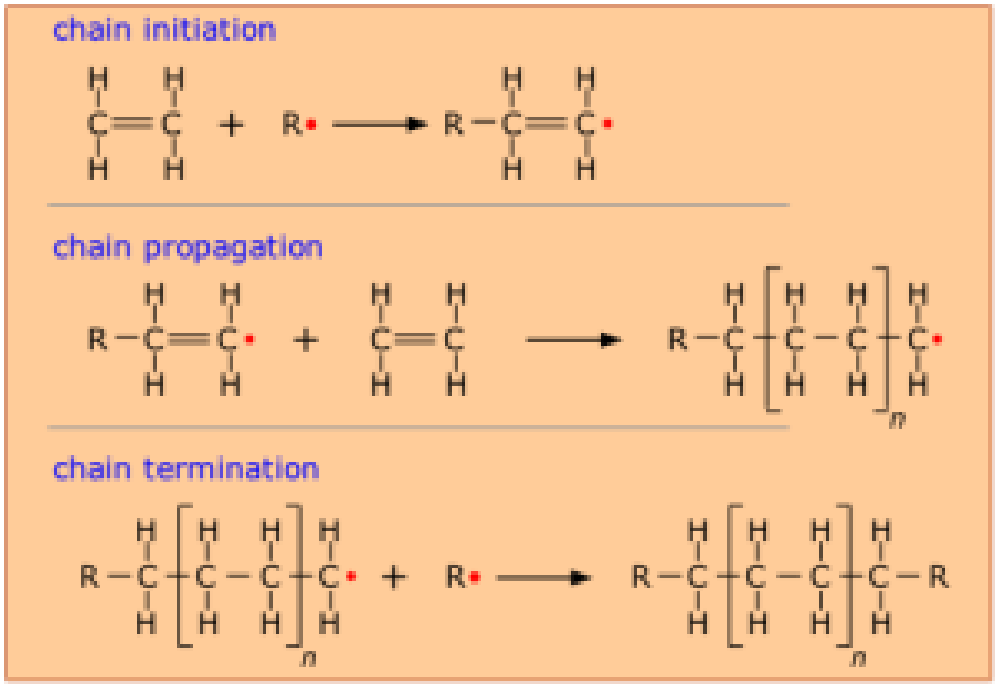

Figure 1.6: Free-radical mechanism for the formation of polyethylene

1.2.3.2 Condensation Polymerization

The behaviour of condensing a polymer causes the resulting substance to harden, indirectly decreasing its molecular mass. Also known as step-growth polymerization, condensation polymerization involves the reaction of bifunctional/multifunctional monomers with complementary reactive functional groups, and small molecules (water, methanol, hydrogen chloride, ammonia, etc.) are eliminated during each step of the condensation reaction. In contrast to addition polymerization, the molecular weight increases during the course of the reaction, and it requires very high monomer conversion (usually more than 98 percent) to obtain high-molecular-weight polymers.

Polymerization is a cumulative reaction in which repeated condensation reactions occur between any two molecular species in the reaction mixture, where either of the molecular species can be a monomer, oligomer, or a polymer chain. The most common functional group combinations known to form ester linkages (polyesters), amide linkages (polyamides), urethane linkages (polyurethanes), as well as carboxylic acid and alcohol groups, and carboxylic acid and amine groups. Some representative condensation polymers include polyethylene terephthalate, nylon 66, polycarbonates, polyurethanes, phenolic resins, and silicones. The heteroatoms in the backbone of condensation polymers are typically oxygen, nitrogen, or sulfur, and are polar, which contributes to their properties, including hydrogen bonding capabilities, elevated glass transition temperatures, and superior barrier properties compared to addition polymers based on hydrocarbons. [29], [30]

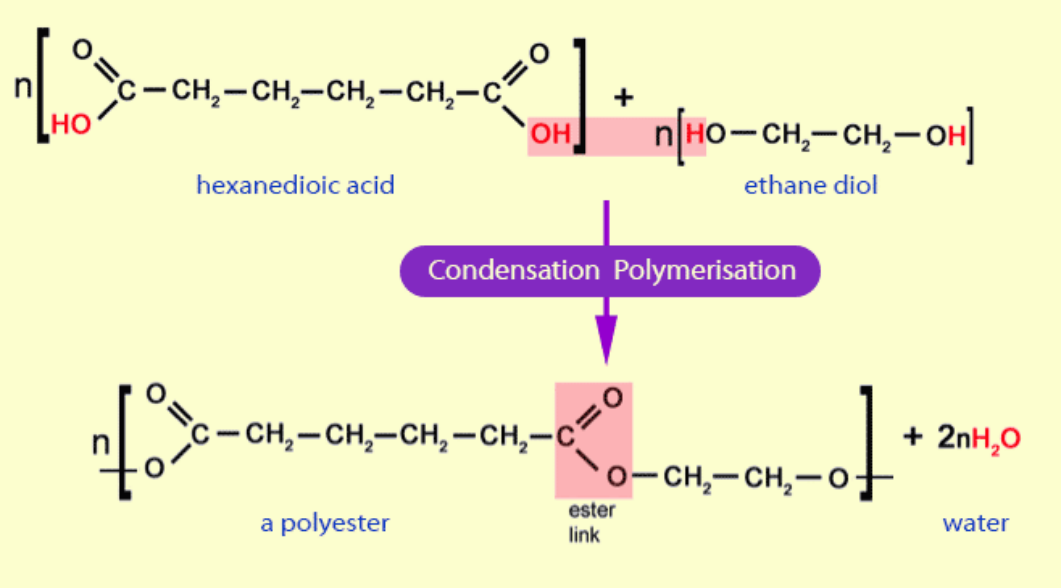

Figure 1.7: Condensation polymerization

1.2.4 Classification on the Basis of Backbone Chain

The chemical nature of the backbone structure of a polymer can be used to subdivide it into polymers with all-carbon backbones, heteroatomic polymers, and further classifications, including biodegradable and high-temperature-resistant polymers. The fundamental differences between chemical bonding, thermal stability and degradation mechanisms are represented in this classification. [31]

1.2.4.1 Organic Polymers

The backbones of organic polymers are carbon chains, as the majority of commercial synthetic polymers are based on hydrocarbon monomers. These materials consist of carbon-hydrogen bonds in the main chain, and such functional groups as oxygen, nitrogen, halogen, etc. might also be present as pendents. Pure hydrocarbon polymers are examples of polyethylene and polypropylene, whereas examples of polymers with different groups as substituents include polystyrene, polyvinyl acetate, and all other polymers made by attaching groups to the carbon backbone in vinyl polymers. Organic polymers are characterized by relatively low thermal stability (decomposition temperatures typically range from 250 to 400 °C), ease of processability, varying mechanical strength based on structure and crystallinity, and excellent electrical insulation. The covalent nature and low polarity that predominate in them usually lead to a hydrophobic nature, a low absorption rate by water, and strong resistance to acids and bases, but low resistance towards organic solvents. [32], [33]

1.2.4.2 Inorganic Polymers

Inorganic polymers have backbone structures composed of inorganic elements, as opposed to carbon, and exhibit entirely different characteristics compared to organic polymers, such as enhanced thermal stability, chemical resistance, and special electronic or optical properties. Polydimethylsiloxane (silicone) (which has a silicon-oxygen structure, with methyl groups of organic origin bound to silicon atoms) is the most commercially important inorganic polymer, which draws together the stability of inorganic backbones and from which the flexibility of organic substituents is obtained. Polyphosphazenes are phosphorus-nitrogen polymers that have two organic or halogen functional groups attached to the backbone, providing outstanding thermal stability, fire resistance, and biocompatibility. Polysulfides, polysilanes, polygermanes, and ceramic precursor polymers are examples of inorganic polymers. Organic polymers are typically much less thermally stable than inorganic polymers, with decomposition temperatures that can exceed 400-500°C or beyond. They exhibit excellent flame resistance without the need for flame retardants or stabilizers. In contrast, inorganic polymers possess unique optical or electronic properties, including semi conductivity or photoluminescence, as well as high weathering resistance. [34], [35]

1.2.4.3 Biodegradable Polymers

Biodegradable polymers are a specialized type of polymer that can break down into simpler substances through biological degradation by microorganisms, enzymes, or abiotic hydrolysis in environmental conditions. These materials address the issue of sustainability because they undergo limited degradation once all their utility has been exhausted, rather than persisting in the environment. Natural ones include biodegradable polymers such as starch, cellulose, chitosan, and proteins, as well as microbially produced polyhydroxyalkanoates. Synthetic ones include polylactic acid, polycaprolactone, polybutylene succinate, and poly(butylene adipate-co-terephthalate). See the figure below: Biodegradation is a process that generally occurs by breaking down macromolecules through ester, amide, or ether bonds in the polymer backbone, either by enzymatic or hydrolytic cleavage, resulting in monomers and oligomers that microorganisms can degrade. The speed of biodegradation of polymers is determined by polymer chemistry, crystallinity, molecular mass, environmental factors (temperature, humidity, pH, and microbial population), and physical form. Biodegradable polymers have applications in various fields, including packaging, agriculture, biomedical devices, and disposable products, where the elimination of products and their related waste at the end of their life is sought after. [36], [37]

1.2.4.4 High Temperature Polymers

High-temperature polymers are an elite category of materials designed to maintain mechanical integrity, dimensional stability, and functionality at high-service temperatures of more than 200-300 °C, which is significantly lower than those of conventional polymers. These substances are characterized by inflexible aromatic structures and high levels of conjugation, limited conformational mobility, elevated glass transition temperatures (typically above 250 °C), and high thermal stability. Major high-temperature polymer classes include polyimides (Tg > 350 °C), polyetherimides, polybenzimidazoles, polyetheretherketone, polyphenylene sulfide, and fluoropolymers such as polytetrafluoroethylene. The high thermal performance is attributed to the aromatic ring structures that provide backbone rigidity, strong intermolecular interactions through π-π stacking or hydrogen bonding, ladder or semi-ladder polymer architectures that limit bond rotation, and stable chemical bonding that withstands thermal cleavage. High-temperature polymers are vital in aerospace part usage, under-

hood automotive part usage, oil and gas equipment usage, semiconductor part fabrication, and in electrical insulation, where traditional polymers falter. [38], [39]

1.2.5 Determination of Classification by Molecular Forces

Polymers may be categorized based on the nature and strength of intermolecular forces that hold the polymer chain together, which are basic determinants of the influence of the polymer on physical properties, thermal transitions, and process ability. [40]

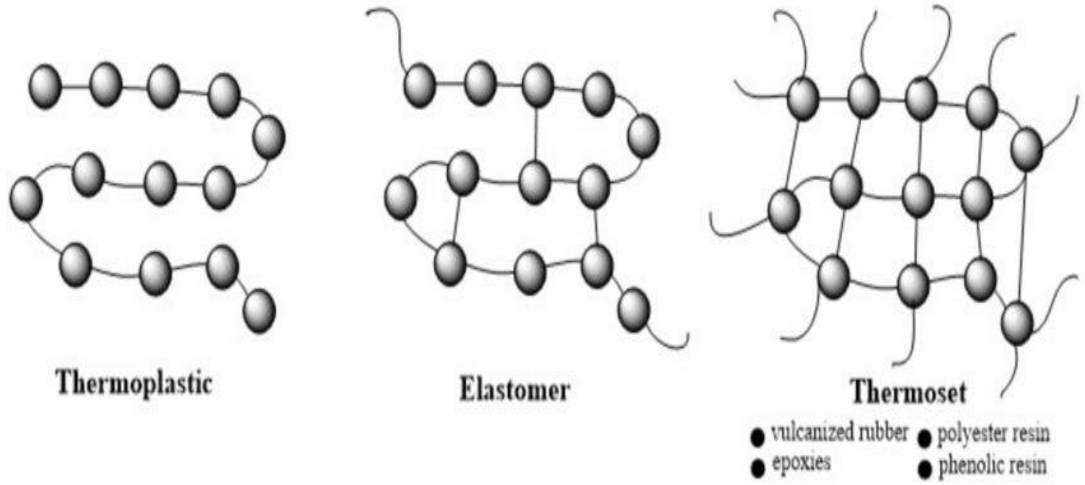

Figure 1.8: Thermoplastic, elastomer and thermoset polymer

1.2.5.1 Thermoplastic Polymers

Thermoplastic polymers are those that contain weak intermolecular forces holding together the linear or branched polymer chains, but not covalently cross-linked, such as van der Waals interactions, dipole-dipole forces, and hydrogen bonding. Such secondary forces can be countered by thermal energy. Thus, the material softens as it heats up and hardens when it cools, in a fully reversible process whereby it can be melted, remodeled, and refrozen into its solid state. This reprocessability is the inimitable benefit of thermoplastics, which makes recycling and remolding of scrap material easy. The thermoplastics may be further distilled into amorphous thermoplastics, which do not have any long-range molecular structure and are transparent (polystyrene, polycarbonate, poly(methyl methacrylate)) and semi-crystalline thermoplastics that have crystalline and amorphous zones and are characterized by high mechanical strength and chemical resistance (polyethylene, polypropylene, nylon, polyethylene terephthalate). The processing temperatures usually fall between 150-300 °C, based on the polymer, in which case the viscosity is doubled, enabling flow and molding activities. [41]

1.2.5.2 Thermosetting Polymers

Thermosetting polymers are chemically crosslinked, and therefore, they cannot be melted and reshaped once they have been formed into three-dimensional covalently bonded network structures. The heat, radiation, or other chemical catalysts cause reactions between the liquid or low-viscosity prepolymers through crosslinking, changing the liquid or low-viscosity prepolymers into rigid solid materials with an irreversible shape. Thermosets remain stable in terms of their dimensions and mechanical properties at high temperatures until they decompose, once they have been cured. Some of the common thermosets are the epoxy resins, phenolic resins, unsaturated polyester resins, polyurethanes, melamine-formaldehyde, and amino resins. The highly crosslinked structure is highly strengthened, offering extraordinary mechanical strength, dimensional stability, heat resistance (which typically retains properties up to 150-250 °C and beyond), resistance to solvents, acids, and bases, as well as electrical conductivity. Nonetheless, the irreversible crosslinking poses a significant challenge to recycling, which requires the development of chemical recycling, energy recovery through incineration, or innovative degradable chemistries for thermosets. [42]

1.2.5.3 Elastomers

Elastomers represent a special form of polymer that exhibits an extraordinary ability to bend and deform under stress (it can occur to a significant degree or even over 100-1000 percent of its length) and finally stretches almost entirely after pressure is removed. Structurally, elastomers consist of weakly cross-linked polymer networks in the amorphous state, characterized by high molecular mobility beyond their own glass transition temperature. This temperature should be sufficiently below the service temperature to allow sufficient chain mobility. The cross-links, which are formed by vulcanization or other methods of curing, inhibit permanent chain slippage and flow and permit large amounts of irreversible deformation by chain extension and orientation. Some of the important families of elastomers used in tire manufacturing, seals, gaskets, adhesives, and vibration damping include natural rubber, styrene-butadiene rubber, polybutadiene, neoprene, nitrile butadiene rubber, ethylene-propylene-diene rubber, and silicone rubber. The non-standard viscoelastic behavior is

a composite of both viscous flow and elastic deformation, offering energy dissipation, damping behavior, and flexible sealing properties. [43]

1.3 Sustainability Problem in Polymer and Rubber Industry

The petrochemical-based polymer sector is under increasing criticism, with several questions regarding its significant environmental impact throughout the entire lifecycle, from the extraction of feedstock materials to the final disposal of end products. The traditional methods used in making polymer products from petrochemical feedstock have a significant impact on the environment in various ways, including the production of greenhouse gases, energy consumption, the creation of toxic products, and long-term environmental pollution. The interpretation and solution of these sustainability issues are one of the most urgent needs in the field of modern science and engineering of polymers. [44]

1.3.1 Environment Effects of Petroleum-based Polymers

The expansion of virgin plastics derived from petroleum feedstocks has come to be seen as a significant contributor to global greenhouse gas emissions. This substantial environmental burden extends far beyond the visible plastic waste in both land and sea. The global production of primary plastics has contributed to greenhouse gas emissions in the atmosphere to the tune of 2.24 gigatonnes of carbon dioxide equivalent in 2019, according to recent comprehensive lifecycle assessments. Bottom-up modelling by leading research institutions, a proportion of which is alarming in view of the projected growth patterns of the plastic industry, with more conservative growth rates (2.5%/year) of the primary plastics in the future proportions of greenhouse gas emissions means that significant sources of production of primary plastics will exceed 4.75 gig With increased growth rates (4% per year) of the primary production of plastics, it would grow by more than threefold to 6.78 gigatonnes of CO_2 equivalent, representing 25-31% of the remaining carbon budget of the world to limit global warming to 1.5 ^{o}C. [45]

Massive greenhouse gas emissions from plastic manufacturing are due to various steps in the value chain prior to the polymerization process; about 75 percent of the total greenhouse gas emissions occur before the polymerization process. A closer examination of the sources of emissions shows that manufacturing of chemical precursors is primarily a source of about 26 percent of the total emissions, refining of

hydrocarbons and making plastics ingredients are the most significant sources of about 29 percent, and harvesting of crude oil and natural gas in the geological reserves leads to about 20 percent of plastic manufacturing emissions. The remaining emissions result from polymerization reactions, the conversion of raw materials into finished goods, and the transportation of goods along the supply chain. Cracking, in particular, the dominant technology used to produce olefins and aromatic compounds from petroleum feedstock's, namely steam cracking, is notably energy-intensive and has a significant impact on the cumulative carbon footprint of producing plastics in general. [46]

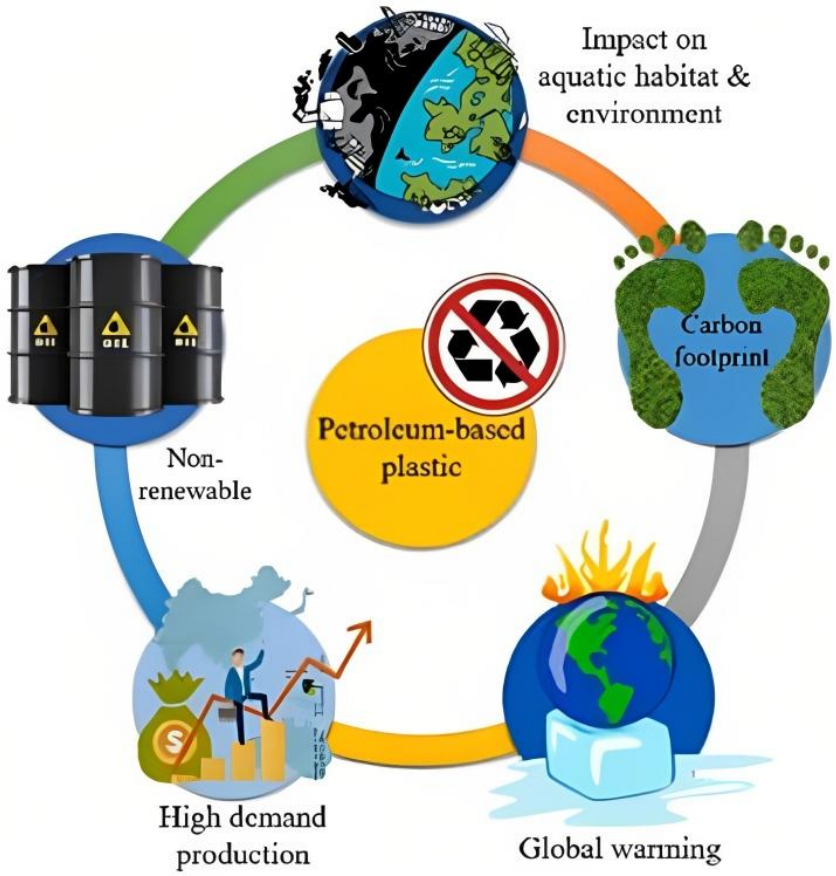

Figure 1.9: Environmental effects of petroleum-based plastic

In addition to carbon dioxide emissions, the polymers manufactured using petroleum result in the production of numerous other toxic byproducts and waste products that are hazardous to the environment and human health. During monomer production, polymerization reaction and downstream processing activities, volatile organic compounds, particulate matter, nitrogen oxides, sulfur dioxide, and toxic chemical intermediates are emitted. Air pollutants are capable of traveling great distances in the atmosphere, leading to the formation of tropospheric ozone, photochemical smog, and

acid rain that destroy the ecosystem. Polymer manufacturing plants can release aqueous effluents that include monomers not absorbed during production, raw materials used, catalysts, and toxic dyes. As such, they require extensive treatment of their wastewater prior to discharge into the environment. Polymer production, which accounts for an energy consumption of between 2.8-4.1 percent of the total world fossil fuel extraction, directly contributes to the global issues of anthropogenic climate change and resource depletion. [47]

The worst thing is that this environmental tenacity of traditional petroleum-based polymers persists even after disposal, because these synthetic materials are distinctly resistant to both biological and environmental degradation systems. The majority of commodity plastics, such as polyethylene, polypropylene, polystyrene, and polyvinyl chloride, take hundreds to thousands of years to decompose in the environment, where they accumulate in landfills, terrestrial biota, and mainly marine environments as a result of photodegradation and mechanical fragmentation, forming microplastic forms. The amount of microplastics in all environmental compartments has reached crisis proportions, with millions of tons of plastic materials entering the oceans per year, creating gigantic garbage fields like the Great Pacific Garbage Patch, and ecologically damaging oceans by entailing marine life and causing bioaccumulation in food chains, disrupting habitats, and releasing sorbed toxic substances into waterways. It has been reported in studies that microplastic particles have accumulated in all marine organisms (zooplankton to whales) as well as in terrestrial soils, aerosols, and human tissues (lungs, blood, organs), raising severe concerns about the well-being of the ecosystem and human health. [48]

There is also the manufacture of petroleum-based polymers, which produce toxic additives along with processing aids that contribute to environmental pollution. Phthalate plasticizers, which are commonly used in polyvinyl chloride to increase flexibility, are endocrine disruptors that can harm both human and wildlife health, and their reproductive and developmental toxicity is increasing exponentially. Polymers containing brominated flame retardants, antimicrobial agents, and UV stabilizers exhibit leaching effects during product use and disposal, leading to the accumulation of these compounds in environmental compartments and organisms. The inefficiency of existing polymer recycling methods, whereby most recyclable plastic commodities on Earth tend to end up in landfills and incineration, results in the generation of large

amounts of plastic waste in disposal channels, leading to a lasting environmental legacy of pollution. [49]

1.3.2 Requirement of Eco-Friendly and Renewable Materials

The growing environmental crisis behind traditional petroleum-based polymers has triggered an immediate, worldwide need to create and apply renewable, eco-friendly, and biodegradable polymer substitutes that can maintain performance while significantly reducing their overall environmental impact. The move toward sustainable materials is caused by many convergent factors such as a growing worry about resource depletion as oil deposits are drained, tightening environmental regulations aimed at lowering plastic pollution and greenhouse gas emissions, rising consumer consciousness and demand of sustainable products, corporate efforts to reduce carbon footprints and achieve the principles of a circular economy, and international laws and guidelines such as the negotiation of the proposed global plastic treaty under the auspices of the United Nations Environment Programme. [50]

The most promising way to achieve sustainable polymer systems that address not only the sustainability issues of renewable feedstock but also consider the issue of end-of-life degradation is through biodegradable polymers based on renewable biomass resources. These are polylactic acid, prepared using corn starch or sugarcane, polyhydroxyalkanoates prepared by microorganisms, polybutylene succinate, polycaprolactone, and a series of cellulose-based polymers that have the added benefit of containing renewable feedstock as well as biodegrading in proper environmental conditions. Enzymes or microorganisms degrade biopolymers into harmless compounds, such as water, carbon dioxide, and biomass, thereby reducing the environmental sustainability of traditional synthetic polymers in the long term. However, it must be remembered that the speed and nature of biodegradation largely depend on the chemistry of polymers, the degree of crystallinity, molecular weight and environmental factors, with specific bio-based polymers degrading fast in industrial composting plants with high temperature and white moisture levels but virtually remaining unchanged in the open oceans or soil with inappropriate microbial complexes and chemical characteristics. [51]

The use of renewable feedstocks to produce bio-based polymers addresses the depletion of resources. It offers the potential for minimizing greenhouse gas emissions through

the sequestration of carbon as biomass grows. The life cycle assessments have revealed that bioplastics made of first-generation feedstocks like corn starch or sugarcane need about 86 per cent less non-renewable energy as opposed to petrochemical plastics and second-generation bioplastics manufactured with non-food crops like agricultural waste and forestry residues have 25 per cent lower environmental impact in terms of non-renewable energy use than the first-generation bioplastics. Such renewable polymer platforms have the potential to significantly decrease the impact of polymer production on the carbon footprint, particularly in cases of sustainable agricultural production, effective biorefinery processing of waste energy, and the use of renewable energy sources in manufacturing plants. Sugarcane-based bio-based polyethylene produces results in less greenhouse gas emissions, approximately 140% lower than those generated by conventional polyethylene made with petrochemicals, and saves non-renewable energy by about 65%. [52]

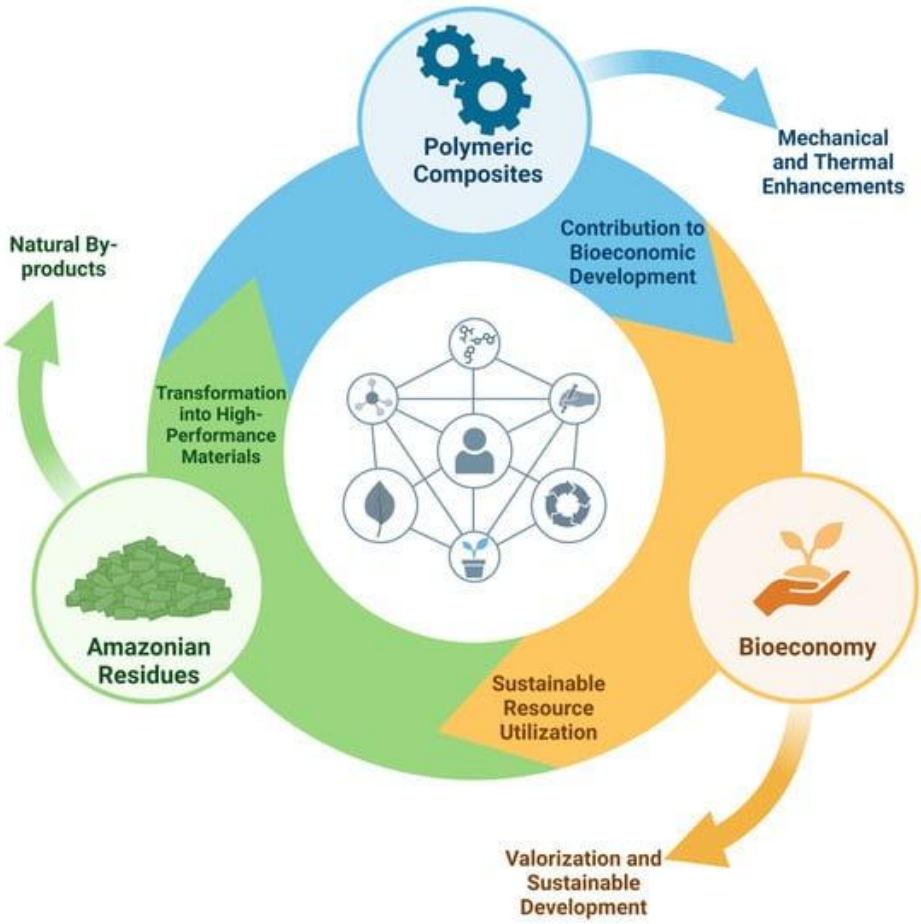

Figure 1.10: Scope of Eco-Friendly and Renewable Materials

Another important element of the sustainable materials transition is the use of natural fibers and bio-based fillers, which provide renewable alternatives to traditional synthetic fillers like carbon black and silica in composites such as polymers. Natural fibers, such as hemp, flax, jute, kenaf, sisal, and bamboo, possess favorable specific ratios of strength to weight, biodegradability, carbon sequestration during growth, and low environmental impact throughout production. Additionally, they are compostable or suitable for thermal treatment at the end of their life cycle. The biocomposites market has registered impressive growth rates, with market values standing at $ 4.46 billion USD in 2016 and projected to reach $10.89 billion USD by 2024, at a compound annual growth rate (CAGR) of 11.8%. The substantial market expansion indicates a growing appreciation of biocomposites in the automotive, construction, packaging, consumer products, and sporting equipment industries, driven by environmental concerns, regulatory actions, and technological advancements in fiber-matrix compatibility. [53]

Lignin, a byproduct of the paper pulping process and bioethanol production process, has particular promise in renewable filler polymer composites because of its extraordinarily natural abundance as the second most plentiful biopolymer on the list, behind cellulose. The technical lignins are produced in vast amounts worldwide, with kraft lignin, organosolv lignin, and lignosulfonates estimated to be obtained in quantities of 70-100 million tons annually during pulping and biorefining activities. The majority of technical lignin is currently vastly underutilized, with the large majority being used as a component in the recovery of energy by burning in pulping furnaces, rather than developing engineering-grade products from it. Lignin's chemical composition, which is both aromatic and phenolic, with reactive hydroxyl, carboxyl, and aliphatic hydroxyl groups, presents potential for chemical modification and reinforcement in polymer composites. The lignin engineering filler represents a promising prospect for the principles of the circular bioeconomy, utilizing currently underexploited waste streams to transform into marketable materials, while simultaneously reducing the use of petroleum-derived reinforcing substances. [54]

1.3.3 World Trends towards the Green Composites

A radical paradigm of sustainable, environmentally-friendly materials is occurring in the global composites sector as regulatory forces force companies to reduce their environmental footprint, consumer demands are shifting toward sustainable composites production, technological developments have led to significant improvements in the

performance schemes and the economics of green composites, and corporate sustainability priorities are consistent with international environmental regulations. Green composites (sometimes called biocomposites or eco-composites) are characterized as composite materials that use natural fibers as reinforcement and/or bio-based polymers as matrix materials and this has been shown to confer environmental benefits such as Biodegradability, renewability, lower carbon footprint, less energy use in their production and the capability of end-of-life compost production or thermal recovery than conventional synthetic fiber-reinforced composites. This is the key distinguishing feature of green composites, as they utilize renewable biological sources in all parts of the material structure, including the reinforcing fibers and the polymer materials, which enable the achievement of circular bioeconomy principles and significant decreases in reliance on fossil fuels. [55]

Figure 1.11: Bio-composites Processing and Degradation

The biocomposites marketplace has exhibited strong growth rate patterns across various regions worldwide, and market studies have prognosticated that the industry will grow to $ 20 billion by 2033, implying an average annual growth rate of more than 7 percent. In Europe and North America, this surge is particularly evident in the enforcement of stringent material regulations, such as the European Union's Single-Use Plastics Directive, Extended Producer Responsibility programs, and government subsidies for

bio-based materials, which have accelerated the shift to bio-based materials at a rapid pace. Within the European automotive sector, some of the top car manufacturers such as Mercedes-Benz, BMW, Volkswagen, and Volvo have actively used biocomposites by integrating hemp, flax, and kenaf fiber composites into the interiors of vehicles over the last twenty years and have achieved benefits in the form of a weight reduction, increased fuel efficiency, as well as the meeting of more stringent requirements of ever-stricter emissions mandates like the Euro emission regulations. [56]

Through recent developments, biocomposites have been developed as interior trim components and as more challenging structural and semi-structural uses, in which enhanced fiber-matrix adhesion with the aid of chemical treatments, including alkali treatment and silane coupling, the formulation of composite using hybrid-reinforcement, and the use of improved processing methods, including resin transfer molding and vacuum infusion. Similarly, the construction industry begins to enquire about the potential of biocomposites to help their activities in decking, window frames, wall paneling, roof insulation, and non-structural parts of the buildings that include Leadership in Energy and Environmental Design and Building Research Establishment Environmental Assessment Method, which encourage the use of sustainable materials with established environmental standards. Building-integrated biocomposites offer several benefits, including low thermal conductivity to provide energy-efficient insulation, a natural-fiber aesthetic, low density that reduces building structural load, and end-of-life compostability or thermal recovery. [57]

The packaging business is another significant area of growth for green composites, where biodegradable and compostable packaging materials are fast becoming popular alternatives to traditional petroleum-based plastics. The regulatory initiatives, such as the Single-Use Plastics Directive of the European Union, which prohibits certain types of plastic products and requires labeling of biodegradable ones with compostable marks, have produced considerable market forces behind innovative and sustainable packaging methods. Natural fiber-reinforced polylactic acid-based composites, or those filled with bio-derived fillers, are being increasingly used in food packaging, agricultural films, disposable tableware, cutlery, and single-use consumer products. These products offer greater sustainability through the use of renewable feedstock and the benefits of composting the end products in industrial composting facilities. Food packaging: The food packaging industry, in particular, has been a target for the

application of biocomposites due to the moisture and oxygen-barrier properties of these materials, thereby preserving the shelf life of perishable goods while protecting the environment. [58]

Along with these positive tendencies and market development, green composites face a variety of serious technical and economic challenges that need to be overcome in order to achieve mass penetration and compete with other time-tested composites based on petroleum. Cost competitiveness has become a consistent obstacle, as bio-based plastics and natural fiber composites are frequently higher in production costs than commodity petroleum-based plastics. However, the difference has been shrinking with relatively larger-scale production, the development of natural fiber supply chains, and fluctuations in petroleum prices. Limitations in the performance, such as moisture sensitivity of natural fibers as a result of hydrophilic hydroxyl groups, thermal instability of specific bio-based polymer when subjected to high-temperature processes, poor mechanical performance relative to glass or carbon fiber composite, and high batch-to-batch variability in natural fiber properties due to the variability of biological growth, are still a challenge to the technology. Natural fibers are known to vary in fiber length, diameter, crystallinity, and chemical composition in response to conditions in growing environments, when they are harvested, during storage, and in processing techniques, which hinder the attainment of uniform composite properties. [59]

Significant research towards food is aimed at overcoming such constraints by a variety of methods which involve physical and chemical modification of the surface of fibers in order to minimize moisture uptake and increase interfacial bonding, the incorporation of compatibilizing agents between the hydrophilic surface of the fiber and the hydrophobic polymer matrices, hybrid composite formulations (mixes of natural and synthetic fiber) to realize optimal property combinations, optimization of processing conditions such as temperature distributions and pressure cycling, and investigation of other matrix materials with higher thermal stability. The development of methods for treating fiber surfaces, including plasma treatment, enzyme modification, and grafting of vinyl monomers, has shown tremendous improvement in the fiber-matrix adhesion and subsequent mechanical properties of composites. The fact that natural fibers are utilized in circular bioeconomy closed-loop systems has strong sustainability merits, which makes them a worthwhile investment in research and development, despite present-day performance and economic issues. [60]

2. Polymer Composites Fillers that are Eco-Friendly and Bio-Based

2.1 Introduction to Natural and Renewable Fillers

Fillers play a crucial role in the world of composite materials. This shift in the world towards sustainable materials has highlighted the need to develop new types of filler systems based on renewable biological materials that can replace traditional synthetic fillers in polymer composites without compromising or even improving their mechanical properties. Some natural fillers, including plant materials like cellulose fibers, lignin, hemicellulose, and other agricultural residues, are an inexpensive and plentiful alternative to petroleum-based synthetic fillers such as carbon black or precipitated silica. The use of natural fillers in polymer matrices offers two environmental advantages: the utilization of renewable feedstock and reduced reliance on energy-demanding synthesis of synthetic fillers. Additionally, the incorporation of agricultural and forestry residues, which have potential for underuse, provides a valuable resource. [61]

The last ten years have seen a significant research and industrial interest in the use of plant-based biofillers due to the increasing global awareness of the issue of plastic waste collection, the necessity to mitigate climate change, and the realization that natural fillers can be used to provide the same technical capability as conventional synthetic fillers in most applications. Biofillers based on plants offer numerous technical benefits, including reduced density compared to mineral fillers, which allows for lightweight composite materials that do not require high-energy production sourcing and reduced fuel consumption on the road. Additionally, they exhibit biodegradability and lower production energy needs when compared to synthetic fillers, with no toxic processing chemicals or other byproducts. Unnatural fibers, such as flax, hemp, jute, kenaf, ramie, and sisal, have relatively high specific tensile strength and stiffness, combined with low density, making them preferred reinforcing materials for lightweight composite structures. Fiber crops can also offer significant sources of income to agricultural populations when cultivated, and the waste residues from fiber processing can find other uses as composite end products instead of being wasted. [62]

2.2 Benefits against Conventional Fillers (Carbon Black, Silica)

When compared using environmental, economic, and technical performance parameters, the natural filler has specific benefits over traditional synthetic fillers, such as carbon black and Precipitated Silica. The most commonly used filler in rubber composites is carbon black, which is partially burned or thermally broken down using petroleum feedstocks, producing large amounts of greenhouse gases and poisonous byproducts, such as polycyclic aromatic hydrocarbons, during production. Carbon black manufacturing is an energy-intensive process involving high temperatures. It produces considerable amounts of harmful pollution to the environment, such as air pollution by volatile organic compounds and PM. Although less energy-intensive than carbon black, precipitated silica still requires significant energy to mine, beneficiate, calcinate, and react to precipitation, which consumes energy resources and generates waste from mining. [63]

Natural fillers have significantly lower environmental impacts throughout their life cycle compared to synthetic fillers. Their lifecycle assessment shows that even in production using plant fibre-reinforced polymer composites, the equipment required is only 9.55 megajoules per kilogram of production energy, compared with 54.7 megajoules per kilogram of production energy in traditional glass-fibre-reinforced composites. Natural biofiller manufacturing results in minimal toxic waste generation, and biodegradable fillers can be recovered with ease at the end of life through various mechanisms, including industrial composting, anaerobic digestion, or thermal treatment with an associated energy credit. Natural fillers do not present the toxicological concerns that the use of carbon black poses, which has been designated as a probable human carcinogen, especially among workers in rubber processing plants and waste tire recycling processes, as well as nearby residents. [64]

Economically, natural fillers generally have lower raw material costs than their synthetic counterparts. When obtained as agricultural byproducts, such as rice husks, sugarcane bagasse, coconut shells, and wheat straw, natural fillers have a cost that is lower than the alternative disposal costs. The conversion of agricultural residues into engineering materials results in an economical value for the waste streams, minimizes environmental impacts, and reduces expenses associated with disposing of waste through landfills or open burning. Natural fiber production also serves the rural

agricultural economies by providing additional streams of crop value beyond primary food or feed production. [65]

Although natural fillers offer numerous benefits, they have significant technical limitations that have sporadically limited their use in high-performance applications. The over-saturated hydroxyl groups in cellulose and hemicelluloses contribute to the hydrophilic properties of plant-derived materials, resulting in increased moisture uptake and dimensional stability during moist conditions. This, in turn, reduces the mechanical strength and increases microbial colonization. Subject to natural conditions of growth, time of harvest, storage, and processing, the variability of natural materials is determined, which means that batch-to-batch inconsistency exists in fiber properties such as length, diameter, crystallinity, and chemical composition. Natural fillers exhibit low interfacial adhesion to hydrophobic polymer matrices due to a polarity mismatch, resulting in poor stress transfer through the interfaces between the filler and the polymer matrix, and consequently, suboptimal composite mechanical properties. The requirement for cellulose and hemicellulose components to regenerate thermally (up to approximately 200 °C), which limits the processing temperatures of most natural fillers, restricts the use of these materials with thermoplastics and thermosets that require higher processing temperatures. [66]

2.3 Limitations in Raw State

The technical shortcomings of polymer composite materials made from natural materials in their unmodified state necessitate the development of novel surface modification and compatibilization techniques that enable at least the performance-related characteristics of the material to be comparable to those of traditional engineering fillers using synthetic materials. The most significant limitation is the moisture sensitivity, as natural fillers are easily absorbed by water through their hydroxyl groups, which are hygroscopic in nature, leading to swelling, dimensional changes, and a decrease in mechanical properties. The amount of water absorbed by the filler is directly proportional to the filler surface area. It is especially troublesome in use in sensitive environments, such as in humid conditions or the presence of aqueous media, as seen in auto parts, outdoor building materials, and maritime use. High moisture levels promote the development of microbes, such as fungi and bacteria, on filler surfaces, leading to biodeterioration and, when combined with other factors,

composite failure. This can also cause stress corrosion and hydrolytic degradation of the matrix polymer, including polyesters and polyamides. [67]

The variability inherent in natural materials can pose numerous problems in the manufacturing process, such as a lack of uniformity in the properties of the composite across lots. This makes it challenging to establish consistent specifications and quality standards, and the process cannot be easily automated, as extensive sorting and grading must be employed. The aspect ratio (NPR), hollow lumen, and defects, as well as the cellulose crystallinity degree and chemical composition of natural fibers, differ significantly across species, growing conditions, harvest maturity, retting procedures, and the length of storage. This variability means that more strict incoming material characterisation and control processes are required (than synthetic fillers, which have characteristic and standardized properties). Abnormal geometry refers to the irregular fiber geometry with hollow lumens, pits, and surface roughness, which influences packing efficiency and forms stress concentration locations that may initiate fracture.[68]

The increased hydrophilicity of the natural fillers leads to poor interfacial adhesion between the hydrophilic fillers and the hydrophobic polymer matrix, due to the incompatibility of the empty spaces between the polar filler surface and the nonpolar polymer matrix, as well as the weakness of van der Waals interactions that inefficiently relay mechanical stress between the filler and the matrix. Mechanical interlocking at rough fiber surfaces offers low adhesion. With moist climatic conditions, hydrophilic fillers tend to adsorb water at the interface, forming a weak boundary layer of water-laden material with low mechanical strength. The moisture at the interface is considered a plasticizer of the polymer skeleton, further decreasing its mechanical properties. This low interfacial bonding typically leads to composite mechanical properties that are lower than predicted by the rule of mixtures, and strength and tensile modulus values are significantly lower than the anticipated values using basic composite theory. [69]

The thermal processing constraints place very stringent restrictions on the use of the natural filler, as cellulose becomes thermally degraded starting at around 150-200°C, with a high level of mass loss and properties becoming seriously impaired at higher temperatures. Hemicelluloses are even less resistant to heat; they begin to decompose at temperatures ranging from 120 to 150 °C. Such thermal stability constraints limit the use of natural filler composites to lower processing temperatures, far below those

required for many engineering thermoplastics and thermosets, and necessitate the use of low-temperature polymers or the development of new low-temperature processing methods. Long processing residence periods at high temperatures also contribute to a faster rate of thermal degradation of natural fillers. Aldehydes, ketones, and organic acids, which are byproducts of the thermal degradation of cellulose and hemicellulose, have the potential to catalyze undesired side reactions in polymer matrices and decrease composite properties. [70]

3 Lignin as an Environmentally-Friendly Bio-Filler

The third significant part of lignocellulosic biomass, at least compared to cellulose and hemicellulose, lignin is one of the most abundant, though least exploited, biopolymers currently present on the planet. It is estimated to be produced globally at 70-100 million tons each year through pulping and biorefining. Although lignin is a valuable resource with a rich biomass supply, it is not economically valued, with most of its resources being burned to generate energy in pulping plants instead of being used to produce engineering products of higher value. Another impressive circular bioeconomy prospect is the use of technical lignins as strengthening and functional fillers in polymer composites, which would convert otherwise waste-stream lignins into valuable products while simultaneously decreasing the use of petroleum-derived fillers and offer disposal options for underutilized biomass. [71]

3.1 Lignin Composition, Structure and Chemistry

Lignin is a three-dimensional, amorphous, aromatic biopolymer that is made mainly out of phenylpropane (C 3) units, made by three central monolignol units, which are para-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol which dehydrogenatively polymerizes during biosynthesis. The lignin is considered to have a complex pattern of carbon-carbon and ether chains and 3-O-4 anionic ether linkages are the most prevalent intermolecular associations within the polymer network and take up about 50-65 percent of the total number of linkages. Another notable linkage is the 4-etaher bonds, the biphenyl structures, and the carbon-carbon linkages by the condensed reaction. The heterogeneous lignin structure has a large proportion of reactive functional groups such as phenolic hydroxyl groups, aliphatic hydroxyl groups, carboxyl groups and methoxy group attached to aromatic rings. The molar mass of the native lignin is comparatively low (around 10-40 kDa) whereas the molar masses of technical lignins of industrial

extraction are higher (around 30-130 kDa) as a result of recondensing reactions during extraction processes.ing disposal options for underutilized biomass. [72]

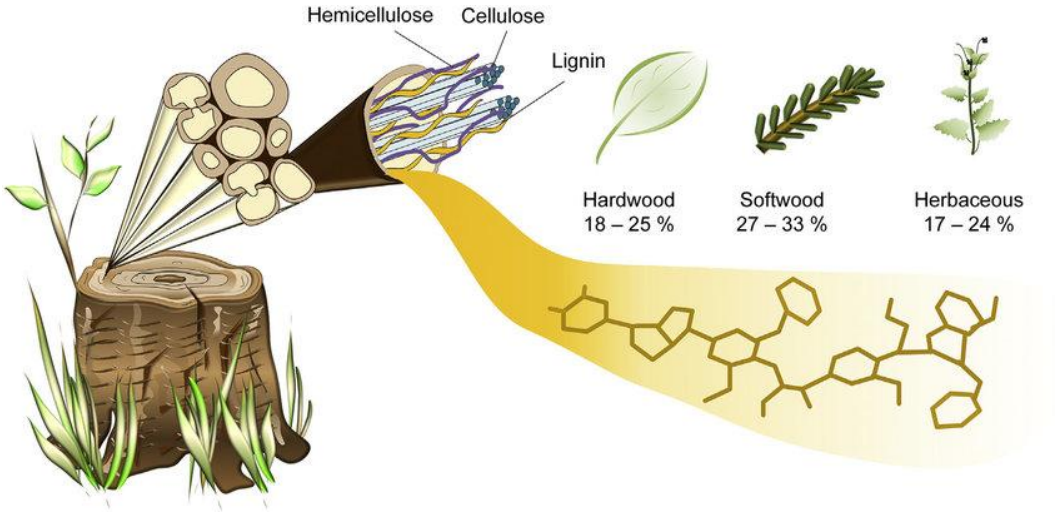

Figure 1.12: Lignocellulosic biomass schematic highlighting lignin content

Lignin chemical composition differs by the species of the plants and the type of tissue, and the softwood lignins (gymnosperms) use guaiacyl (G) units based on coniferyl alcohol as the most common monolignol, which leads to a more linear structure with fewer methoxy groups. Hardwood lignins (angiosperms) are relatively similar in the ratio of guaiacyl to syringyl (S) units formed from sinapyl alcohol, and thus are branched in more structures and have a higher proportion of methoxy groups. Furthermore, the lignins in grass and herbaceous plants have large percentages of p-hydroxyphenyl (H) functionalities of para-coumaryl alcohol, as well as G and S functionalities. The reactivity, thermal stability, and potential interaction of lignin with other polymers depend on the relative proportions of H, G, and S units present in the lignin; thus, what we know of lignin composition is necessary for the rational choice of material. Such changes include aliphatic and phenolic hydroxyl groups, which give the lignin a variety of sites on which it can be chemically modified and covalently bonded to other molecules, unlike chemically inert mineral fillers. [73]

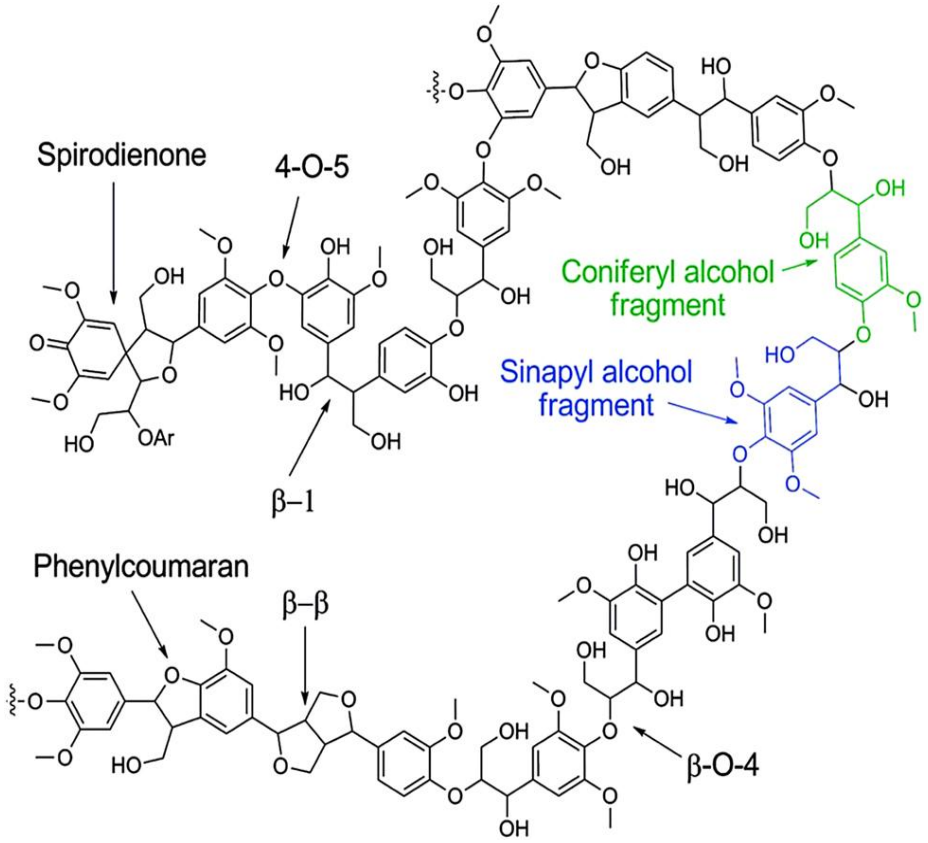

Figure 1.13: Schematic of lignin showing phenylpropanoid units and characteristic interunit linkages forming a highly crosslinked network

3.2 Types of Lignin

The technical lignins obtained after different industrial lignin extraction processes have varying structures, properties, and chemical compositions; thus, the lignin type needs to be carefully chosen for each application. The most common technical lignin in the world is the kraft lignin, which is a byproduct of the alkaline kraft process applied to delignify wood to make papermaking. The Kraft pulping process involves the addition of a sodium hydroxide and sodium sulfide solution under high pressure (170-180 °C) at a high temperature (170-180 °C) to the ether bonds of pulp fibres, breaking up the lignin, which is dissolved in the pulping solution. The pulping liquor then obtains lignins in kraft by employing different methods of precipitation and purification. Kraft Lignin has a comparatively lower sulfur content (1-4%), a broad molecular distribution, lower concentrations of reactive functional groups during pulping, and a low phenolic hydroxyl number compared to native lignin. The condensation reactions that occur during kraft pulping result in the formation of further carbon-carbon bonds, making

kraft lignin more condensed and less reactive compared to lignins formed by other extraction methods. [74]

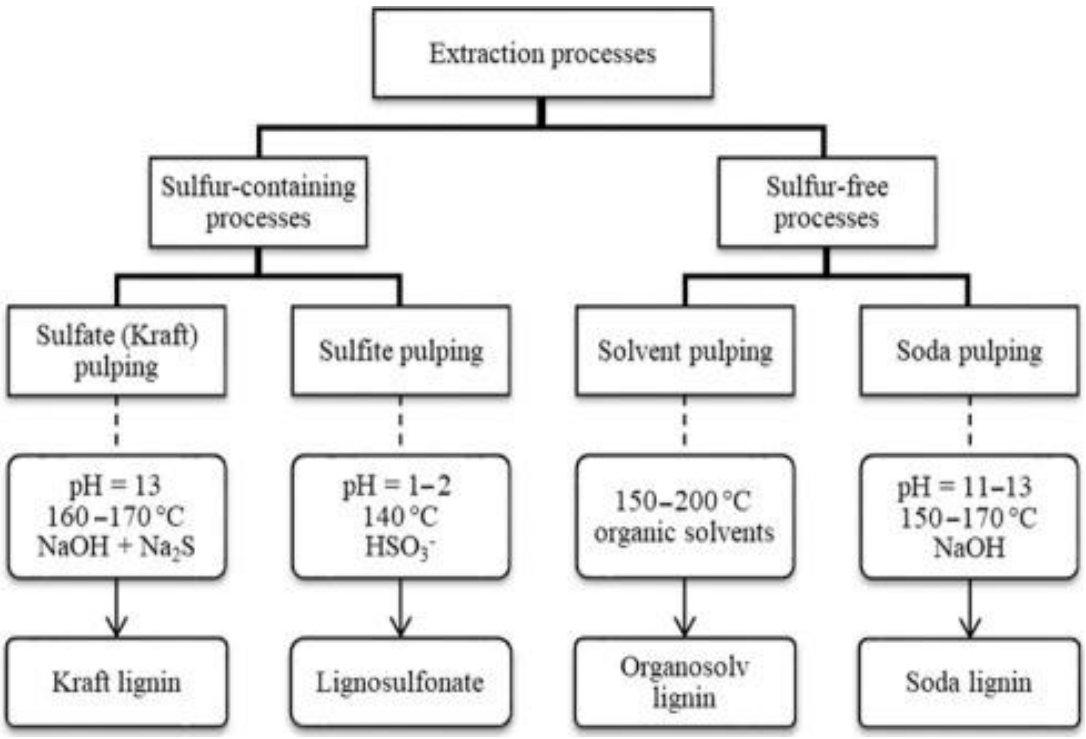

Figure 1.14: Schematic of lignin isolation routes, contrasting sulfur-based and sulfur-free pulping processes

Organosolv lignin is generated by pulping using organic solvents (usually ethanol) either singly or in the presence of organic or inorganic acid or alkali catalysts. This process requires milder conditions (150-190 °C) for lignin extraction compared to kraft pulping. Organosolv lignins are pricier than kraft lignins, but they have fewer ash and heavy metal impurities, fewer recondensation reactions during extraction, and thus preserve the natural lignin structure. They also have a higher content of phenolic hydroxyl groups, which enables enhanced chemical reactivity and a narrower molecular weight distribution. The reduced severity of the extraction and level of structural modification with respect to organosolv lignins make it especially appropriate for a range of applications demanding retained chemical reactivity and reactivity to covalent modification. The production of organosolv lignin is less economical than that of kraft lignin because the solvents are expensive and more complicated recovery systems are required. [75]

Soda lignin comes about as a result of alkaline pulping, just like kraft pulping, except that no sodium sulfide is added, as only sodium hydroxide is used as the delignification step. The soda lignins have intermediate qualities between the kraft lignins and organosolv lignins in that they contain a moderate amount of ash, a moderate amount of phenolic hydroxyl group, and structural change under alkali conditions, though not as brutal as kraft pulping. Lignosulfonates, which are obtained as byproducts of sulfite pulping processes, are technically distinct from neutral kraft and organosolv lignins and contain sulfonic acid groups that are created in the sulfite pulping process. The sulfonic acid groups make lignosulfonates more water-soluble than kraft or organosolv lignins, where they are beneficial but can be regarded as problematic in hydrophobic polymer matrix composites. The type of lignin used may substantially affect the characteristics of the composite, with organosolv lignins and soda lignins generally being more successful than kraft lignins in situations demanding positive interfacial adhesion and activity, as they contain more phenolic hydroxyls and are less structurally condensed. [76]

3.3 Physico-Chemical Properties on Composites

The physicochemical properties of lignin determine the types of applications it is suitable for in a polymer composite and dictate the kind of external modification needed to achieve the best composite output. Lignin has glass transition temperatures ranging from 130 to 190 °C, depending on its structure, moisture content, and measurement method. These temperatures are significantly lower than those of many polymer matrices used in processing and require careful management to prevent degradation. Thermal stability is also a property of lignin that depends on the type, with organosolv lignins tending to be more thermally stable compared to kraft lignins, as a result of lower condensation. Lignin has a high aromatic character, comprising about 70-75 percent of carbon atoms in aromatic rings, which is what gives it rigidity and may allow π-π stacking interactions, capable of increasing interfacial interactions with aromatic polymers. The phenolic hydroxyl group and aromatic structure of lignin, which confer antioxidant properties, can be utilized to stabilize polymer matrices against oxidative degradation, thereby reducing or eliminating the need for synthetic antioxidant additives. [77]

The lignin density is notably high (around 1.3-1.5 g/cm^3), yet comparable to most natural fibers, but very much in polymer matrices, which allows it to be used in much

higher lignin content with relatively minor density gains. The bulk density of lignin powders is a heavily dependent variable on the particle size and morphology of the powder, so a fine lignin powder (0.4-0.6 g/cm³) will have greater bulk density relative to a larger particle because the void volume between particles will result in 0.4-0.6 g/cm³. Lignin tends to absorb moisture variably, depending on the extraction method. Organosolv lignin tend to have relatively lower moisture uptake than Kraft lignin, primarily due to their lower phenolic hydroxyl content, although this remains relatively high compared to other customary fillers. Internal stress can occur in moisture-sensitive lignin-based composites when these composites are subjected to wet environments or following treatment with an aqueous system. The solubility of lignin is critically sensitive to the composition of the solvent, with certain lignin being soluble in alkaline water or organic solvents but insoluble in water, which has implications in how and where it can be used. [78]

3.4 Limitations of Unmodified Lignin in Polymers

2.4.1 Agglomeration and Non-Dispersion

Raw technical lignin experience extreme difficulties in the attainment of homogeneous dispersion in polymer matrices, mainly owing to the presence of strong intermolecular forces that lead to agglomeration of lignin particles, as well as the inability of hydrophobic polymers to wet the lignin particles. Lignin may agglomerate during mixing processes due to hydrogen bonding among hydroxyl functionalities on neighboring particles, van der Waals forces, and an insufficient interfacial energy balance with hydrophobic polymer matrices. The agglomeration produces large particle clusters that serve as stress concentration regions and initiation regions for mechanical failure, significantly decreasing the composite's mechanical properties to the extent that simple composite theory predicts. The agglomerated lignin particles also have a low specific surface area on which to interact with the polymer matrix, and thus, mechanical reinforcement and functional property advantages are limited. Oversized agglomerates may extend along more than one plane of composition, generating macro-scale defects, which enhance the initiation and spread of cracks through the material. [79]

The improper dispersion of the lignin material is even more of a problem with high filler loads, whereby, due to the high surface area and density of the lignin particle, there are agglomerated particle networks of percolated networks of lignin agglomerates

that hinder polymer flow during processing, in addition to providing continuous paths of crack propagation. The homogeneous dispersion of lignin requires the input of mechanical energy during composite processing, resulting from mixing operations. However, a large number of lignins could not withstand degradation under the high shear forces applied by the mixing equipment used in industrial applications. The viscosity attributed to agglomerated surface lignin particles increases the difficulty of processing, which necessitates higher temperatures that enhance both lignin degradation and polymer matrix thermal degradation. Poor dispersion causes batch-to-batch variability in composite properties, and quality control and specification verification are problematic when employed commercially. [80]

3.4.2 Polarity Mismatch with Rubber Matrices

The appropriate polarity of rubber tissue cannot be developed in the rubbers used for VAP cone production, which leads to the formation of the cone shape.

The irreconcilable nature of the lignin hydrophilic and rubber hydrophobic matrix is caused by inherent disparities in molecular polarity, chemical functionality, and intermolecular forces, which provide a poor filler-matrix interface that cannot readily transfer stress. Lignin molecules have many hydroxyl groups located on their polymer structure, forming numerous hydrogen bonding centers, which result in interactions with other polar molecules, such as water and other lignin molecules, but not with the nonpolar polymer backbone in elastomers. Natural rubber, nitrile rubber, and styrene butadiene rubber are mostly nonpolar hydrocarbon polymers that have little polar functionality and the ability to form hydrogen bonds with the hydroxyl groups of lignin. Thermodynamic incompatibility between polar and nonpolar elastomers results in a significant interfacial energy penalty, leading to phase separation and inefficient wetting of lignin particles by the elastomer matrix. [81]

The incompatible polarity can be observed as the inability of the lignin particles to interact well with the elastomer molecules, which causes the elastomer to selectively avoid wetting the lignin surfaces, leaving voids in the air and creating weak interfaces. The preferential absorption of moisture at the interface between lignin and elastomers forms hydrated boundary layers, which behave like weak phases with limited mechanical strength. The low interfacial adhesion will lead to a low stress transfer across the interface. The lignin particles are thus treated only as inert fillers that can

only benefit in terms of volume filling, but not stiffening. At the microscopic level, separate lignin particles do not disperse into primary particles, but instead continue to aggregate, further depleting the effective surface area and mechanical property advantages. Due to its rigid aromatic lignin structure, conformational accommodation at the interface with the elastomer matrix is challenging, as it is with flexible polymeric compatibilizers. [82]

3.4.3 Effect on Mechanical Properties

When unmodified lignin is incorporated into elastomeric matrices, it typically leads to a decrease in mechanical properties compared to those of traditionally filled elastomers, such as tensile strength, break elongation, resilience, and tear resistance. The low adhesion between lignin and elastomer matrices leads to stress concentration at the filler-matrix boundary and the development of cracks that propagate through the composite with every impact during mechanical loading. The mechanically reinforced property of unmodified lignin particles is such that they only have volume filling and densification effects, which are not generally strong enough to counter the degraded property caused by poor interfacial interaction. The tensile strength of elastomeric composites reinforced with lignin as it is, with no modification, is often significantly less than that of the unfilled elastomer, which demonstrates that the particles of lignin actually weaken the material, notwithstanding the mechanical hardness of the particles. The elongation at break typically decreases significantly with lignin loading, resulting in reduced chain movement in the elastomers and increased material brittleness. [83]

The resilience and rebound elasticity of elastomeric materials are greatly impaired by lignin, as its energy loss rises significantly, indicating poor stress transfer and mechanical damping in poorly bonded filler-matrix interactions. Lignin loading usually reduces the tear resistance, which is so critical in elastomeric materials, as the big agglomerated particles form crack initiation sites, where tears easily spread. Another important elastomer property is abrasion resistance, which can be slightly improved with lignin loading. The filler becomes sufficiently stiff, but is generally less effective than traditional fillers, such as carbon black and silica. When incorporated as an unmodified lignin, the processing properties of elastomeric compounds become inferior, such as elevated viscosity, greater processing temperatures that accelerate thermal degradation, and poor flow properties, thereby making them difficult to mold and shape. [84]

3.5 Lignin Modification Methods to Increase Compatibility

The significant restrictions of raw lignin in polymer composites necessitate the use of more complex chemical and physical modification strategies, which enhance the filler-matrix blend, improve thermal manipulability, increase chemical reactivity, and promote better dispersal within a hydrophobic polymer matrix. The systematic adjustment of lignin structure is a rational way of mechanically redesigning inconsistent biopolymer and nonpolar elastomeric matrices to enable lignin to act as a viable filler, offering mechanical strength equal to or superior to that of more conventional synthetic fillers. [85]

3.5.1 Chemical Modification Methods

The reason chemical modification methods are used is that nanobiosensors are sensitive to chemical degradation. The functional groups, molecular structure and intermolecular interactions in lignin are directly controlled by chemical modification, which allows the generation of customized properties depending on individual polymer matrix needs. Esterification, sulfonation, graft polymerization, and functionalization with coupling agents are the most widely researched chemical modifications, which have different benefits and drawbacks depending on the application context. [86]

3.5.1.1 Esterification

Esterification is one of the most general and most commonly used chemical modification methods of lignin, which consists of reacting the large number of hydroxyl groups in lignin (both phenolic and aliphatic) with an acid derivative or an anhydride to create ester bonds. The result of the reaction is that the polar hydrogen-bonding hydroxyl groups are modified by fewer polar ester functionalities, which increases hydrophobicity and lowers moisture pickup. However, this modification provides longer hydrocarbon chains, making the resin less polar and allowing compatibility with nonpolar polymer matrices. Reactions with acetic anhydride, fatty acid chlorides, or succinic anhydride have been shown to occur in high yields, with averages of over 80-90% of hydroxyl groups being converted efficiently to esters. The reaction between the hydroxyl groups in kraft lignin and the tall oil fatty acid (TOFA), a renewable byproduct of papermaking, introduces long alkyl chains on the lignin surface through the reaction with the acid chloride of the TOFA that increases its compatibility, significantly, with nonpolar polymer matrices. [87]

The altered esterified lignin has significantly improved dispersion in the elastomeric matrices, lower absorption by moisture, greater thermal stability by protecting the reactive hydroxyl groups, and improved covalent interactions with the polymer matrix by van der Waals binding between the long alkyl chains and possible 8 -interactions of aromatic rings on the lignin with aromatic groups on some polymers. Rearrangement to succinic acid provides additional carboxyl groups, which can be further functionalized or chelate metal groups, allowing for the addition of functionality beyond mere hydrophobicity. The temperature used in the course of the esterification reactions is also critical; high temperatures (100-150 °C) are necessary to reach the reaction equilibrium, where the formation of the product is required. However, this temperature should be closely monitored to prevent lignin from being thermally degraded. Systematic research has revealed temperature to be the most significant process variable in terms of its impact on the process variables and properties that result. Specifically, the higher the temperature, the higher the extent of the conversion; however, excessive levels may lead to thermal degradation. [88]

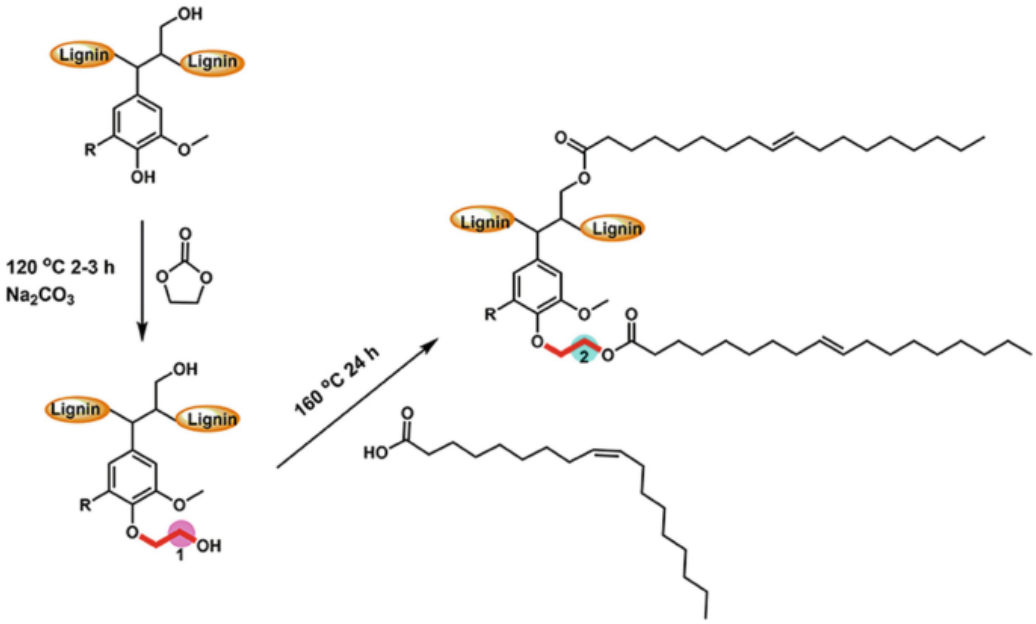

Figure 1.15: Esterification process of Lignin

3.5.1.2 Sulfonation

Sulfonation is another method of chemical modification that can be achieved by adding sulfonic acid groups to the lignin aromatic ring or hydroxyl groups, forming lignin derivatives that are more water-soluble and reactive. The sulfonated lignins have a higher charge density than the native lignin, allowing the lignin to interact with polar molecules through electrostatic interactions and perform analysis in applications that

require immersion in water. When the sulfonation of ball-milled lignin with sodium sulfite is conducted with the aid of microwaves, the quantities of reactive C-O active structures can be increased by several folds, which enhances the reactivity of the structure in subsequent cross-linking and polymerization reactions. The lignin pretreatment based on ball-milled lignin significantly enhances the sulfonation rate, which is proven to be more efficient due to an enhanced specific surface area and reactivity that proves to be synergistic when combining both mechanical and chemical changes. The sulfonated lignin would have greater solubility in organic solvents, superior reactivity for further functionalization, and the possibility of producing sulfonated lignin-based polymers with distinct characteristics. Although sulfonation induces a reduction in the inherent natural hydrophobicity of lignin, and thus, sulfonated lignin is no longer suited to hydrophobic polymer matrices unless enhanced with countermeasures that induce the recovery of such a hydrophobicity. [89]

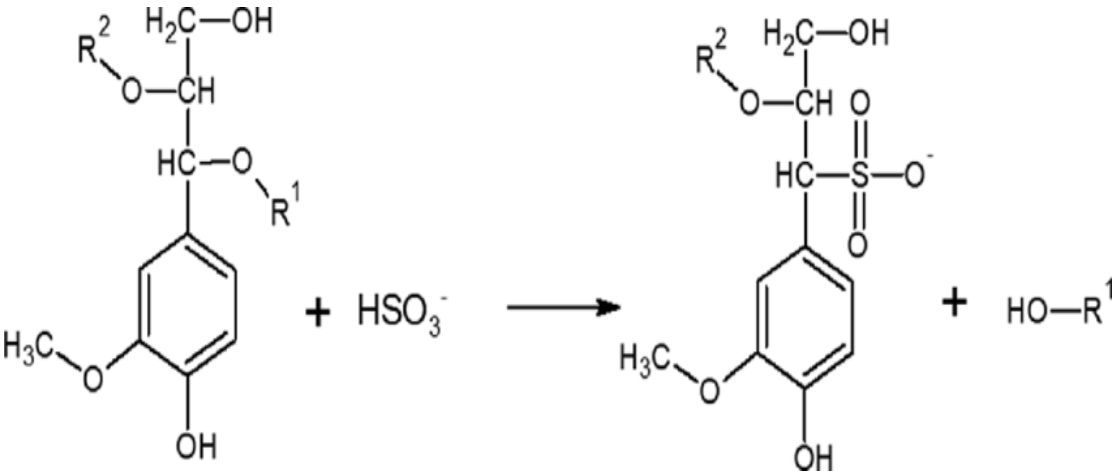

Figure 1.16: Sulfonation process of Lignin

3.5.1.3 Graft Polymerization

Graft polymerization is a strong modification method that involves the addition of synthetic polymer chains to the lignin backbone by grafting-from or grafting-onto methods, forming hybrid lignin polymer copolymers with characteristics of both materials. In grafting-based methods, artificial monomers are polymerized directly on surfaces located on lignin macromolecules, commonly through radical polymerization processes, such as atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT), or ring-opening polymerization (ROP). Grafting methods encompass the synthesis of existing polymer chains with reactive functional

groups, which then react covalently with lignin sites via efficient coupling chemistry, such as click chemistry or esterification. These methods have been effectively used to produce lignin-graft-polylactic acid copolymers, lignin-graft-polyethylene brassylate copolymers, and other high-end materials whose modulus values are three times greater when compared to the homopolymer controls. [90]

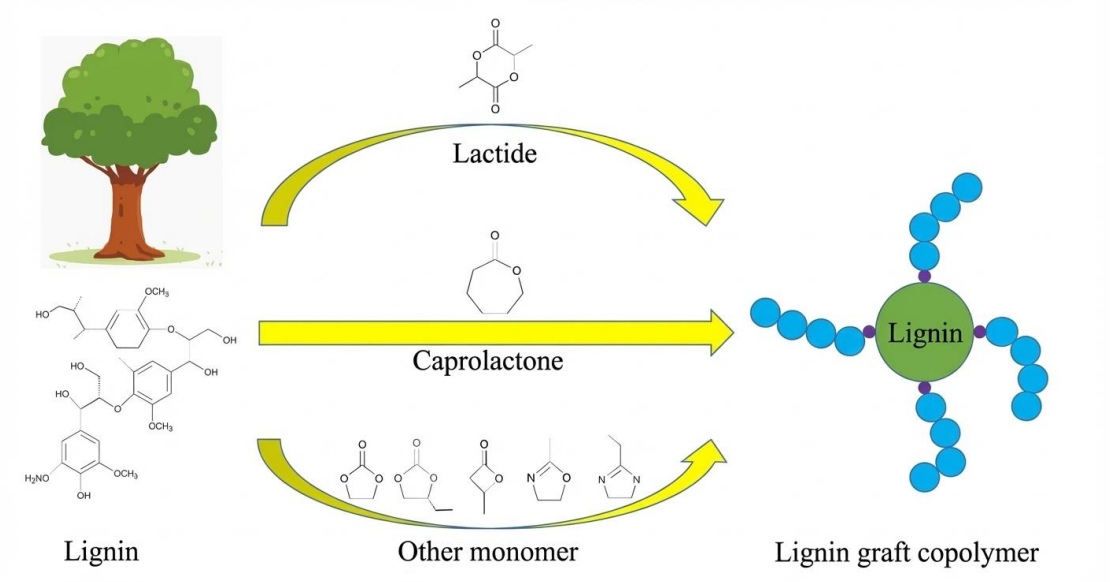

Figure 1.17: Grafting process of Lignin

Graft copolymerization enables deep modifications to lignin characteristics by the addition of synthetic polymer fragments with selected functionality, forming materials with a known structure, pre-established composition, and specific characteristics. Grafted polymer chains may be chosen to complement the hydrophobicity, functionality and molecular compatibility of the polymer matrix to which the grafted polymer chains find application in hybrid fillers that can have excellent interactions with the rest of the polymer that surrounds the filler. As an example, polylactic acid chain grafting onto lignin produces a filler that is only partially chemically similar to a PLA matrix, allowing for much better interaction at the interfaces and leading to far more impressive mechanical performance than unmodified lignin. Polymerization factors, such as reaction time, temperature, and monomer concentration, can be used to control the molecular weight of grafted polymers, which provides further tunability in optimizing properties. Nevertheless, graft copolymerization is a more complex and costly type of modification process than simple esterification, and it usually involves

specialized equipment, manipulation of reaction conditions, and further purification of the product. [91]

3.5.1.4 Metal Oxide (or Coupling Agent) Incorporation

Incorporation agents, such as metal oxides, can be incorporated with the reagents in one of the 33 reactions. The concept of functionalizing lignin using metal oxide nanoparticles or organic coupling agents is an alternative method for modifying lignin to enhance dispersion stability, introduce new functionalities, and increase interfacial interactions between the lignin and polymer matrices. Such metal oxides as titanium dioxide (TiO_2), zinc oxide (ZnO), and aluminum oxide (Al_2O_3) could be chemically attached to the surface of lignin through a reaction with surface hydroxyl groups, forming hybrid filler particles with greater qualities of lignin and metal oxides. Both metal oxide-modified lignins have been demonstrated to enhance UV protection, antimicrobial activity, and possible catalytic activity, and to grow as an addition to the mechanical reinforcement potential of the original lignin. Silane coupling agents that include sulfur have been established to react with lignin that comes through its hydrothermal treatment by utilizing the thiol-lignin reactions, instead of the standard silanol self-condensation, to synthesize modified lignins with enhanced levels of interfacial bonding to elastomeric matrices. The interaction process is direct carbon-sulfur bonding of lignin aromatic carbons and sulfur of the silane coupling agent to form covalent bonds, not through the siloxane consolidation standard method. [92]

Another significant functionalization strategy is the organosilanization of lignin, wherein silane functional groups are attached to the lignin surface, which can later be reacted with polymer matrices, epoxy resins, or silica surfaces to generate a covalent bond at the interface. This technique replicates the use of silane coupling agents in glass fiber-reinforced composites, an established technology that enhances fiber-matrix bonding. Silane functionality (methoxy, ethoxy, or chloroalkyl) can be tuned to make the silane reactive to specific polymer matrices suitable for a particular application, thereby allowing for customization. These coupling agent-based modifications often involve a lower capital outlay and more straightforward implementation than graft copolymerization, offering significant performance gains in the composites. [93]

3.5.2 Techniques of Physical and Surface Modifications

Physical routes to functionalization provide an alternative to chemical approaches that utilize mechanical, thermal, or surface treatment methods to modify the properties of lignin without creating new covalent lignin structures.

3.5.2.1 Ball Milling

One of the classic mechanical pretreatment methods used to control the particle size of lignin, providing more surface area and partially depolymerizing lignin through mechanical input of energy, is ball milling. This process forms activated lignin with greater reactivity and dispersibility capacity. Increasing to extreme levels of specific surface area and reactivity is achieved through the use of mechanical milling with planetary ball mills at high rotation speeds (600 rpm) over extended durations (3-7 hours), which generates particle size reduction from the original millimeter-sized crystals to microparticles or nanoparticles. The weakest β-O-4 linkages of lignin structure degrade during the milling process and lower molecular weight, as well as form carbon-centered radicals in the form of reactive radicals that can be involved in future chemical reactions. Increasing the time in a mill reduces the molecular weight but does not alter the number of hydroxyl groups. However, very long milling (more than 7 hours) can trigger some condensation reactions, producing recalcitrant structures. [94]

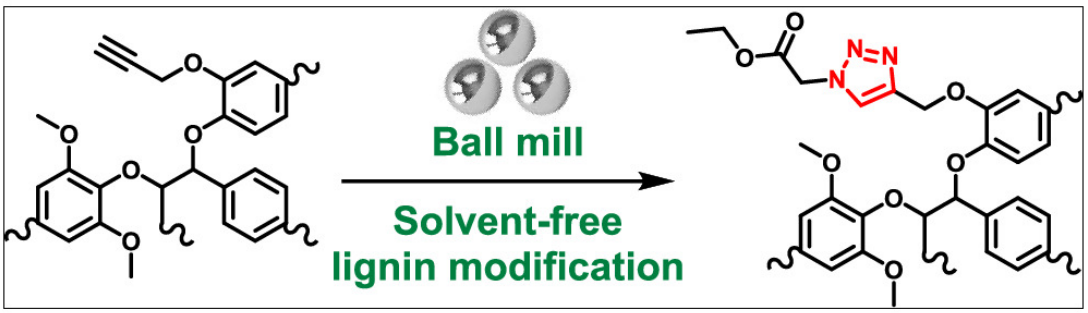

Figure 1.18: Ball Milling of Lignin

Mechanical activation of ball milling has a dramatic effect on the successive reactions of chemical modifications, making more areas reactive and in the formation of reactive sites by partial depolymerization. A combination of ball milling with chemical modification, such as sulfonation or esterification, exhibits synergistic behavior, yielding greatly enhanced results over chemical modification alone. This approach

achieves a high conversion rate and a more uniform distribution of the modification across the lignin particles. These microstructural alterations, caused by ball milling, such as an increase in porosity, a decrease in crystallinity, and the formation of defect sites in the lignin particle, contribute to the penetration and reaction of chemical reagents across the lignin particle. A smaller particle size enhances dispersion in polymer matrices, where the dispersion of nanoparticle lignins is superior to that of larger particles. However, due to their high surface energy, nanoparticles should not re-agglomerate during mixing. [95]

3.5.2.2 Thermal Treatment

Controlled thermal lignin treatment at controlled temperatures is a significant alteration strategy that affects lignin structure and properties through degradation and condensation reactions. Partial lignin degradation of a fraction of lignin is induced by mild thermal treatment at 160-210 ^{o}C and selects the most thermally labile of the 8 -O-4 linkages without altering the overall structure of lignin and hydroxyl group content. This incomplete degradation decreases the molecular weight, raises the proportion of reactive fragments and makes the molecule chemically accessible to further modifications. But a high temperature (>250 ^{o}C) leads to a rapid increase in thermal degradation and instigates demethoxylation by methoxy groups, produces condensation products with decreased reactivity, and may repolymerize lignin fragments into more complex condensed forms. Lignin thermal stability is also quite different between the types of lignins, with organosolv lignins possessing higher thermal stability than the kraft lignins because of reduced initial degree of structural condensation. [96]

Thermal treatment is able to simultaneously improve and diminish the utility of lignin based on the parameters of temperature and time. Transmission to hydroxyl groups Low temperature thermal treatment (160-180 degrees celsius and 3 hours) enhances the accessibility of hydroxyl groups and introduces reactive defects without suggesting widespread degradation or repolymerization, producing thermally activated lignin which is more reactive to chemical modification. An increase in temperature (210-250 ^{O}C) forms increasingly condensed structures with both adhesives and binders in which reduced reactivity and better structural stability is desirable. The thermal treatment parameters need to be optimized by balancing rival behaviors such as advantageous partial degradation rates against counterproductive condensation and re-polymerization. [97]

Solvent shifting and nanoprecipitation methods are potent strategies to transform technical lignins into colloidal lignin particles (CLPs) or stabilized lignin nanoparticles, thereby enhancing dispersion and providing new morphologies. Then, surface coat the lignin with valuable materials. The colloidal lignin particles produced by controlled precipitation of organic solvents into aqueous media exhibit the following morphologies. They are monodispersions with diameters ranging from 50 to 500 nanometers, the dispersion stability is high, and the surface hydroxyl groups remain available for further modification. The morphology of nanoparticles enhances interfacial interactions with polymer matrices, and the high surface area density and spherical form allow for mechanical interlocking and stress transfer across filler-matrix interfaces. [98]

The lignin nanoparticles are esterified with the long-chain fatty acids producing extended layers of hydrophobicity to the particle that result in a tremendous increase in the compatibility with nonpolar polymer matrices without compromising the mechanical properties and structural integrity of the underlying lignin core. Nanoparticles of lignin that have been esterified (esterified lignin nanoparticles (ELNPs) have been shown to experience much stronger interactions with surfaces having hydrophobic wax and polymer matrices than the lignin nanoparticles that are not adjusted in this manner. The hydrophobic surface layer decreases the moisture uptake, removes the thermodynamic incompatibility between the polar lignin and nonpolar matrices, and facilitates the compactness of the particles in the composite. ELNPs have also been utilized to create sustained-release formulations, protective coating and polymer composites where they have been utilized to form multifunctional materials due to their combination of hydrophobic external surfaces and polar internal cores. [99]

Surface modification of lignin nanoparticles with complementary polymers is another surface modification technique that allows for imparting specific functionality or enhancing compatibility with a given polymer matrix. To illustrate, a polyvinyl alcohol or other hydrogen-binding polymer coating on lignin nanoparticles can be used to enhance dispersion in hydroxyl-containing matrices or to provide lignin nanoparticles with specific sites of interaction with epoxy resins. Polymerization conditions and coating chemistry are both independent variables that can be manipulated to produce a

coating, which can then be tailored, allowing for comprehensive control over the ultimate filler characteristics. [100]

4 Nitrile Butadiene Rubber (NBR): Chemical Structure and Properties

4.1 Chemical Structure and Composition

Nitrile butadiene rubber, also acrylonitrile butadiene rubber and commercially referred to as NBR, Buna-N, or NBR, is a copolymer elastomer made by free radical copolymerization of two major monomers, namely, acrylonitrile (CH_2CHCN) and butadiene ($CH_2CH\text{-}CH{=}CH_2$). The proliferation of acrylonitrile and butadiene units within the macromolecular chain results in a random or pseudo-random distribution of units, forming a complex interwrapping microstructure that defines the profile of the material's characteristic properties: mechanical flexibility with high chemical resistance. The synthesis of NBR involves stringent control of the chemical composition to achieve an accurate acrylonitrile content, commonly referred to as ACN content, which constitutes the percentage of weight of acrylonitrile monomer units in the finished polymer. Typical commercial NBR grades have between 18 percent and 50 percent ACN content. Most general-purpose uses are made with NBR, which also contains about 33 percent ACN to compromise competing characteristics such as elasticity, oil resistance, and low-temperature flexibility. [101]

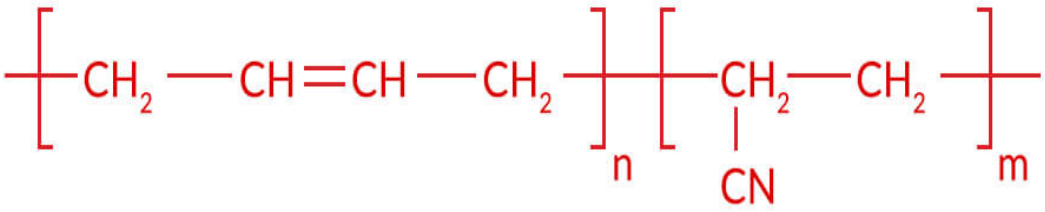

Figure 1.19: Structure of NBR

NBR polymerization is typically initiated through free radical mechanisms, typically introduced by organic peroxides or azo-based initiators, with the reaction conditions carefully regulated to achieve the required copolymer composition and molecular weight distribution. The NBR molecule may have a 1, 2- or 1, 4-microstructure, with 1, 4-linkages prevailing (approximately 90-95 percent of the butadiene monomers) to

provide good flexibility and elastomeric properties, and a few 1,2-linkages to achieve extra rigidity and thermal stability. Commercial NBR also has a wider molecular weight distribution than solution-synthesized polymers, with a molecular weight within the range of 200,000 to 500,000 g/mol, resulting in a spread of polymer chain lengths that affects flow characteristics and vulcanization rates. [102]

4.2 Mechanical, Thermal and Chemical Properties

The mechanical properties of NBR rubber are strongly dependent on ACN content, molecular weight, degree of vulcanization, and the addition of fillers, allowing for a tailor-made formulation of NBR with specific properties for various applications. Unvulcanized NBR has tensile strength of between 2-8MPa and break elongation of 300-600 percent, typical of uncrosslinked raw, uncrystallized elastomers with low mechanical strength. After vulcanization with sulfur and proper accelerators and activators, NBR crosslinks in controlled amounts that increase the mechanical properties dramatically, with tensile strength in vulcanized compounds of minimally reinforced compounds of 15-25 MPa hundred parts per hundred rubber (phr) and tensile strength of conventionally filled compounds 40 MPa hundred parts per hundred rubber (phr). Elongation at break of vulcanized NBR typically ranges between 200-400 percent, which does not alter the attribute of elasticity of the substance but gives it more mechanical strength. The Hardness values are expressed in Shore A units, ranging from 20 to 95 Shore A, according to formulation and cure conditions, which allow specific hardness requirements to be met for different seal, gasket, and vibration isolation applications. [103]

The acrylonitrile level has a significant effect on the NBR mechanical and thermal characteristics. ACN content of lower concentration (18-30 %) produces NBR with higher low-temperature flexibility and strength. The higher the reduction in ACN content, the lower the temperature of the glass transition, allowing it to be used at temperatures of less than -70 °C or below. Low ACN content, however, decreases the chemical resistance toward oils and solvents because the chemical interactions between the polar nitrile groups are fewer and weaker. The addition of higher concentrations of ACN content (40-50 %) significantly enhances resistance against petroleum-based oils, fuels, and other chemical solvents by rendering the rubber more polar and reactive towards the rubber backbone, at the expense of raising the glass transition temperature,

compromising low-temperature flexibility, and reducing hardness at the application temperature. [104]

The practical consensus on the content of most general-purpose NBR formulations typically uses about 33% ACN, which achieves satisfactory oil resistance while maintaining reasonably low-temperature performance and processing properties.

The thermal characteristics of NBR are glass transition temperature (Tg) with a typical range of values of -30 to -25 C of standard 33% ACN grades which allows elastomeric behavior at a wide intermediate range of temperature. The service temperature range is, however, considerably lower, with low static service usually limited to -40 to +250°C (-40 to +120 °C) with frequent short-term excursions of, say, 210 °C, which is well below the crucial thermal degradation. NBR also starts to degrade by oxidation at relatively high temperatures of between 150-155 °C in the form of polymer chain scission, the loss of volatile compounds, and the creation of crosslinked and plasticized degradation products which diminish mechanical properties. Antioxidant additives, metal oxide particles, and fillers that physically shield the elastomer matrix from atmospheric oxygen can significantly improve the thermal stability of NBR. [105]

The chemical compatibility of NBR is broad, encompassing excellent resistance to mineral oils, gasoline, diesel fuel, vegetable oils, and animal fats, as well as moderate resistance to most dilute acids and bases. This superior chemical resistance, which is due to the polar nitrile groups on the polymer backbone that allow solvent-polymer interactions between very hydrophobic elastomers and polar polymers, makes NBR the ideal choice of elastomer for seals, gaskets, hoses, and dynamic components exposed to petroleum-based fluids. NBR is also highly resistant to attack by ozone and oxygen, more so than most natural rubber and butadiene rubber compounds, but less resistant than tailored ozone-resistant rubbers, such as EPDM or chloroprene. The change in volume of NBR as a result of exposure to different solvents and oils can be measured using the American Society of Testing and Materials (ASTM) volumetric swell test, with NBR exhibiting swell indices less than 20 volume percent with several petroleum products, and thus showing little loss in properties even under the influence of chemicals. [106]

4.3 NBR Industrial Uses

Nitrile Butadiene rubber has been the elastomer material of choice for a wide variety of industrial and consumer applications, due to its unrivaled effectiveness in chemical resistance, mechanical properties, economy, and ease of processing over other elastomeric materials. The car industry is the most important consumer field of NBR, primarily for fuel system items that are in touch with gasoline and diesel, such as fuel injection seals, fuel pump gaskets, quick-disconnect connectors, and hoses that have to fulfill their functions despite decades of service exposure to constituents of fuels, and also thermal recycling. The rapid growth of the electric vehicle industry has also increased the demand for NBR products, as battery thermal management systems, electric motor cooling systems, and high-voltage electrical shielding systems all require elastomeric sealing products that can withstand various fluid exposures and thermal cycles. The oil and gas exploration and production sectors widely use NBR as both static seals (gaskets) and dynamic seals in underground equipment, wellhead construction, and fluid processing systems that operate at high temperatures and pressures and are in contact with crude oil, natural gas, produced water, and oil treatment fluids. [107]

In the production of industrial machinery and equipment, NBR-based products, such as pneumatic seals, hydraulic seals on actuators and pumps, covers on conveyor belts, and vibration-isolation mounts, are used in equipment where mineral oils, water, and mechanical forces are to be encountered. Pharmaceutical-grade NBR is used in equipment components, seals and gaskets in applications where pharmaceutical processing conditions and food-contact surfaces are required, in which case highly regulated standards and requirements, such as FDA compliance, are required. Specialty-grade NBR is being used more and more in aerospace and defense systems to manufacture fuel system components, hydraulic seals, and vibration dampers for aircraft that must meet stringent performance qualifications and specifications, including military requirements for thermal cycling, pressure cycling, and chemical exposure. NBR seals and gaskets used in the cabinets contain refrigeration units, dishwashers, and washing machines to carry water and refrigeration. [108]

The nitrile butadiene rubber (NBR) market worldwide has been showing healthy growth. The specialty NBR market is estimated at approximately 0.96 billion USD and is expected to rise to 1.45 billion USD by 2034, indicating a compound annual growth

rate of 4.70 %. This is due to the increasing automotive electrification, the greater use of industrial equipment in emerging economies, high-performance needs in aerospace and the military, and the rising use of fast-curing grades of NBR, which enable faster production and more efficient processes. NBR latex has also seen growth in the market in a similar trend, estimated at 2.8 billion USD in 2023 and expected to grow to 5.4 billion USD in 2030, due to the rising medical glove manufacturing, the rising Power of additional protective wear, and the rising number of applications in coating and adhesive formulations. [109]

4.4 NBR Composites Conventional NBR Limitations

4.4.1 Environmental Concerns

The NBR is used extensively in a variety of industrial applications. Which, although offering a high level of technical performance and affordability, raises considerable questions about its petroleum origin, manufacturing emissions, and management of its disposal at end-of-life. The complete synthesis of NBR uses monomers that are produced out of fossil fuels, acrylonitrile manufactured by the oxidation of acetylene, or acrolein. Which is created by reacting acetylene with ammonia, and butadiene manufactured as a by-product of crude oil refining or products obtained during petroleum refining. These monomers require a significant amount of energy to produce, as the processes of extracting raw materials, synthesizing them as chemicals, and purifying the monomers are energy-intensive, resulting in associated greenhouse gas emissions and contributing to climate change. NBR itself polymerization needs thermal energy to sustain reaction temperatures, solvents required to form free radical polymerization and water to cool and recover the products, which also adds to the overall environmental footprint of the material. [110]

4.4.2 Carbon Black Heavy Reliance

Another environmental liability and dependency on cost is the use of NBR with conventional fillers, mostly carbon black, to meet the mechanical properties required in demanding applications. Carbon black (prepared by the incomplete burning of petroleum products or coal tar in an energy-consuming partial oxidation process) is about 70 percent of all carbon black produced worldwide. It is the most commonly used filler for reinforcing elastomeric composites. Carbon black production emits high levels of greenhouse gas emissions, estimated at 5.55 metric tons of CO_2 equivalent per metric

ton of carbon black produced, which significantly contributes to the total carbon footprint of NBR-based composites. In addition to direct carbon emissions, the manufacturing of carbon blacks pollutes the air by producing volatile organic compounds, particulate matter, and other toxic products that need costly air pollution control systems. The dependence of the carbon black on the attainment of reasonable mechanical properties in NBR composites introduces vulnerability to supply chains to any fluctuations in petroleum prices and constrains sustainability enhancements not made through fundamental changes in the filler composition. [111]

4.4.3 Problems with Price and Sustainability

Both NBR elastomer and carbon black filler petroleum dependency cause the volatility of compounded costs, as the prices of the products are affected by the prices of crude oil and carbon black, respectively. The twofold dependence on petroleum inhibits manufacturers' ability to lower material costs or achieve sustainable growth by taking independent actions. Vulcanized NBR/carbon black composites pose significant technical and environmental challenges when it comes to disposing of them at the end of their life, as the three-dimensional sulfur crosslinked network structure is neither biodegradable nor environmentally degradable, meaning it will remain in landfills practically forever. Disposal techniques such as landfilling, incineration, or mechanical recycling/grinding each have current environmental issues. Although landfilling, with its low cost, is the most widely used disposal procedure due to its long-term environmental impacts, it is not without its drawbacks. Recycling of vulcanized NBR by mechanical methods forms ground rubber particles, which can be recycled partially (usually to a 10-20 percent level of recycled mass) into new vulcanized rubber compounds (non-demanding applications like playground surfacing or asphalt modification of roads can use these products) or reprocessed, or used in non-demanding recycling applications such as playground surfacing or asphalt modification. [112]

These issues of environmental sustainability of the traditional NBR composites have prompted investigation into various remedial solutions, such as fermentation of bio-based NBR using renewable sources of butadienes, adoption of alternative sustainable fillers such as lignin and natural fibers to replace traditional carbon black and studies of devulcanization technology that would allow the real recycling of vulcanized rubber products. Modern market laws are increasingly obliging the end-of-life effect to be taken into account, and schemes on extended producer responsibility in Europe and

other legislations recommend that manufacturers finance the collection and recycling of elastomeric materials. The regulatory bodies are mandating the creation of more environmentally friendly NBR compounds using bio-based materials, alternative fillings and enhanced recyclability. This will be a fundamental shift in the current approach toward the principles of the circular economy, particularly in the production and use of elastomer products. [113]

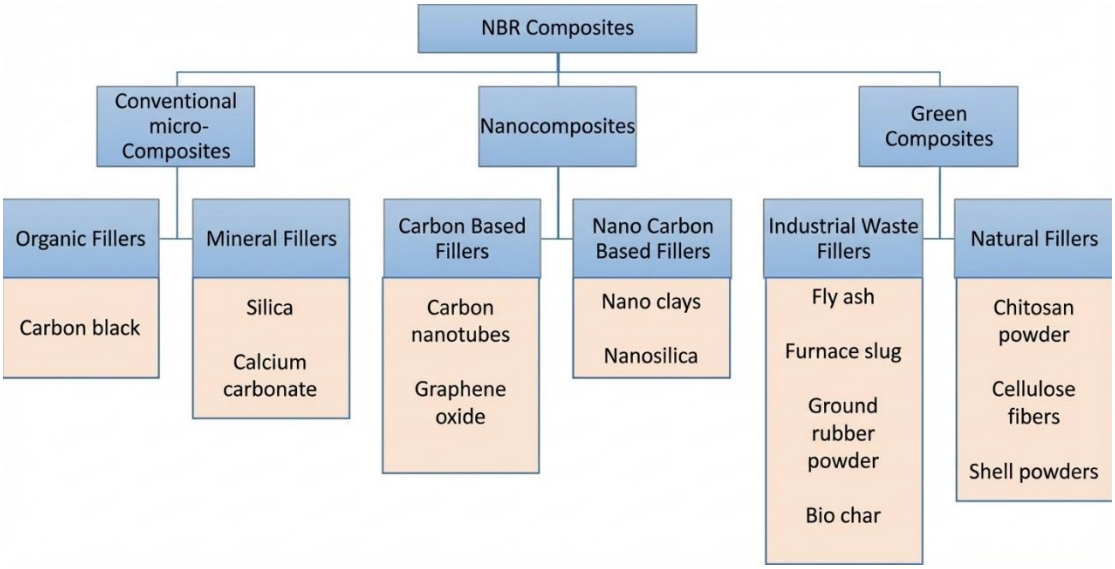

Figure 1.20: Classification chart of NBR composites into conventional, nano, and green types with associated filler categories (organic, mineral, carbon, nano-carbon, industrial waste, and natural).

5 Rubber Composites Fillers: Lignin

5.1 Trends in Mechanical Performance

Mostly, the nitrile butadiene rubber and natural rubber have shown remarkable results in improving mechanical properties compared to those of composites filled with unmodified lignin. In fact, they are near or even surpass the performance levels of composites with traditional carbon black and silica fillers. More recent systematic experiments that utilize chemically modified lignin types, especially esterified lignins and lignins functionalized with coupling agents, have shown significant improvements in the full range of mechanical property scales important in the field of engineering.

5.1.1 Tensile Strength

The tensile strength of modified lignin-filled elastomeric composites is positively affected by lignin loading and chemical modification, and the optimum formulation is comparable to that of standard filled rubbers. Epoxidized natural rubber (ENR)

composite with 25 percent epoxidized ENR as a compatibilizer with lignin showed an improvement in tensile strength values from 27.5 MPa to 36.2 MPa, equivalent to a 31.6 percent enhancement in tensile strength through a combination of epoxidation and an optimized process. This high-performance effectiveness arose due to the increased variety of interface sites between the polar epoxy groups positioned on the elastic mass and the reactive sites situated on the lignin, which correspondingly allowed improved stress transfer across the filler-matrix interface. Wet-mixing processing strategies far surpassed dry-mixing strategies, yielding composites with the highest tensile strengths of 36.2 MPa, rather than 22.9 MPa in their dry counterparts. This data illustrates the importance of ensuring good filler dispersion and interfacial development in composite preparation. [114]

5.1.2 Elongation at Break

Elongation at break, one of the most important elastomeric properties that determines the reversible deformation of the material before failure, exhibits interesting phenomena in lignin-filled composites, and the trend also depends on the lignin modification strategy, interfacial compatibility, and loading levels. The degrees of elongation at break of the epoxidized natural rubber/ lignin composites are 703.3 percent at a 25 percent epoxidation level, in contrast to 598.8 percent of the unmodified lignin composites, which is an increase of 17.5 percenton the unmodified composite through polymer modification and develops better filler-matrix bonds. The growing elongation, accompanied by increasing tensile strength, suggests that the material's toughness is enhanced and its brittleness is reduced due to improved interfacial bonding and stress dispersion. A high level of epoxidation, though (45 percent by degree), was reduced to lower values of elongation because high levels of self-crosslinking would be experienced, thereby inhibiting the movement of chains. The adhesive ability to retain elongation was consistently high in wet-mixed composites compared to their dry-mixed counterparts, highlighting the significance of proper filler dispersion in maintaining the elastomeric nature. [115]

5.1.3 Hardness

Shore A hardness is a standard variable of the stiffness of material, and its resistance to being deformed, which rises steadily in cases of lignin loading and chemical alteration, which is a calculable property conference on the practice of attaining application-

specific hardness aspects. The Shore A hardness values of the lignin-filled natural rubber composites were found to increase with the content of lignin in the natural rubber, ranging from about 50 to 65-75, with an optimum of 10-15 phr in filler incorporation and enhanced interfacial interactions. The increase in hardness can be attributed to the growing physical and chemical interactions that put chains into an immobile state, forming stiffer composites that can be used in applications that demand an enhanced ability to carry loads and lower compliance.

Such chemical modifications as esterification and treatment with coupling agents facilitate supplementary increments in hardness by incorporating rigid structural units and increasing cross-linking density at the filler-matrix interfaces. [116]

5.1.4 Abrasion Resistance

The addition of lignin typically yields an increase in abrasion resistance, which is important in tire tread compounds and elastomeric products subjected to mechanical wear, as the stiffness of the material and improved interactions between filler and matrix reduce particle pull-out and surface wear. The modified kraft lignin exhibited similar abrasion resistance to the traditional carbon black filler in polybutadiene rubber when used with proper compatibilization techniques, with a loss in volume approaching that of carbon black. The aromatic composition and surface properties of lignin also contribute to the development of better mechanical interlocks between rubber chains, compared to using unmodified lignin, and decrease the propensity for extracting filler particles during wear. Hybrid filler systems that incorporate lignin with carbon black or silica have shown synergies in terms of abrasion resistance and overall wear resistance, which is better than either of the filler components alone due to complementary reinforcements. [117]

5.1.5 Reinforcement Mechanisms

The reinforcement mechanisms of lignin-filled elastomeric composites involve multiple interrelated processes that function at various length scales. The hydrodynamic reinforcement due to the geometry and the volume filling of filler particles. The interfacial interactions between the surface functional groups of the filler particles and the rubber chains, as well as the possibility of strain-initiated crystallization in certain types of rubber-based systems.

5.2 Comparison to Traditional Fillers

5.2.1 Carbon Black

Carbon black has been the standard reinforcing filler of elastomeric composites due to its superior reinforcement effectiveness, well-established processing technologies, and refined surface properties achieved through high filler-matrix interactions. Nonetheless, the mechanical study shows that suitably treated lignins can achieve tensile strength, hardness, and modulus values that are similar to or higher than those of conventional carbon black under certain formulation conditions. Direct comparative research using kraft lignin, nitrogen-series carbon black, and precipitated silica as control fillers demonstrated. The lignin-filled composites, optimized for chemical modification and processing parameters and exhibited mechanical properties comparable to those of carbon black. [118]

5.2.2 Silica

The second significant reinforcing filler of elastomeric composites is precipitated silica, which offers the following benefits: high fuel, oil resistance, lower rolling resistance than carbon black (which is beneficial for tire fuel economy), and greater control over dynamic properties. However, silica naturally lacks hydrophobicity, which necessitates the mandatory addition of silane coupling agents (typically 4-8 phr, resulting in extra cost and complexity), is sensitive to moisture, resulting in property variations with environmental humidity, and is more costly than carbon black. Coupling agent-modified lignins may deliver a competitive property profile with silica-based systems, and remove the need to be concerned with moisture sensitivity with the inherent hydrophobicity, and may reduce processing costs through lower coupling agent requirements. [119]

Chapter 2

Literature Review

The article demonstrated that when 1 phr of aminosilane-modified graphene oxide (MGO) is added to NBR, tensile strength is improved by approximately 43.7 percent compared to neat NBR and 30.3 percent compared to GO-filled NBR, and abrasion loss is reduced by approximately 59 percent compared to both reference systems, which indicates how well chemically functionalized fillers improve mechanical and tribological performance. This is attributed to homogeneous dispersion of MGO, higher interfacial strength of shear (≈783 MPa versus ≈646 MPa of GO in MD pull-out experiments), and lower peel-off stress of interlayers of MGO (≈37% of GO) that collectively promote matrixfiller interactions rather than fillerfiller agglomeration. However, the research is limited to its petro-based graphene-oxide-based nanofiller, and hence its immediate applicability to the creation of completely sustainable NBR composites. [220]

The article demonstrates that the addition of silane-modified halloysite nanotubes (mHNTs) to SBR/NBR blends results in significant tensile strength (up to approximately 182 percent more than unfilled blend at 6 phr filler content) and 100% modulus (approximately 30 percent higher) and tear strength (approximately 85 percent higher) and hardness and abrasion resistance, with the best performance again being studied at about 6 phr filler content. These improvements can be ascribed to an increase in the density of crosslinks, better cure properties (lowering of the ts2 and t90, higher MH and cure rate index), and a more efficient interaction of the filler with the matrix due to superior dispersion and interfacial bondage of mHNTs than pristine HNTs. The study also demonstrates reduced solvent uptake and enhanced swelling resistance with increasing modified nanotube content, indicating a more tightly crosslinked and chemically resistant elastomer network. [121]

The article shows that surface-modified barium titanate (MBT, 30 vol%) markedly reinforces low-ACN NBR (20 wt%), increasing tensile strength from about 2.69 to 7.36 MPa and more than doubling tear strength, while maintaining acceptable elongation and hardness. These gains are attributed to the silane coupling agent lowering interfacial

tension, improving MBT dispersion, and creating stronger rubber–filler adhesion, which enhances stress transfer without needing additional carbon black or silica. However, as the acrylonitrile content of NBR increases, the interfacial tension between MBT and NBR rises, dispersion worsens, and the mechanical improvements become much smaller, indicating that the reinforcement effect is strongly dependent on matrix polarity and is not uniformly effective across all NBR grades. [122]

The article shows that adding a small amount of tea polyphenol (2 phr) to carbon-black-filled HNBR increases the 300% modulus by about 8.9%, tensile strength by 9.4%, tear strength by 18.5%, and reduces compression set by around 22.8%, while also cutting volume and mass change in transformer oil by roughly 48.1% and 57.1%, respectively. These improvements are attributed to TP acting as an interfacial bridge, where hydrogen bonding with nitrile groups and π–π interactions with carbon black improve filler dispersion, enlarge the interphase region, and build a polar network that slows oil diffusion. However, when TP content exceeds the optimal level, its plasticizing effect weakens the rubber–rubber network and slows vulcanization, so the mechanical benefits are not maintained at higher loadings. [123]

The article shows that incorporating multiwalled carbon nanotubes (up to about 2 vol%) into NR and NBR significantly enhances elastic modulus, tensile strength, and fracture toughness, with NR composites showing up to ~216% increase in tensile strength and ~169% increase in toughness, and NBR composites achieving higher absolute moduli and toughness values. These improvements are linked to strong filler–rubber interactions, with NR forming more chemical bonds to CNTs (reflected in higher Tg and improved thermal stability), whereas NBR relies more on physical interactions but provides superior dielectric properties, strain sensitivity (gauge factor up to ~39 000 at high strain), and electromechanical actuation under electric fields. However, above about 1.5–2 vol% CNT, aggregation reduces the incremental gains in mechanical and thermodynamic properties, so the reinforcement effect does not continue to increase at higher loadings. [124]

The article investigates NBR/PVC hybrid nanocomposites where 70 phr carbon black in a conventional formulation is partially replaced by COOH-functionalized graphene nanoplatelets, showing that a composition with 55 phr CB and 6 phr GNP increases stress at break by about 7%, 100% modulus by 42%, tear strength by 29%, and reduces swelling by roughly 20% compared with the CB-only composite, while also improving

hardness and compression set. These improvements are attributed to the high surface area of functionalized GNP, stronger interactions with the NBR/PVC matrix, formation of local CB–GNP hybrid filler networks, and more effective cross-linking between rubber and fillers, which together enhance stress transfer and restrict solvent uptake. However, at higher GNP loading (9 phr), graphene aggregation and interfacial defects appear in FESEM and the mechanical gains begin to decline, indicating that the reinforcing effect is strongly dependent on maintaining good dispersion and an optimal CB/GNP ratio. [125]

The article shows that mechanochemically devulcanized NBR/PVC waste powder (WNPP), prepared by solid-state shear milling and used to replace fresh NBR up to about 20 phr, can form robust co-vulcanized composites with strains around 700% and mechanical properties comparable to or better than those of neat NBR. These improvements are attributed to desulfurization-generated free chains in WNPP that co-vulcanize with the NBR matrix to produce dangling-chain-rich interfacial layers, enhancing interfacial adhesion and stress transfer without actually increasing the bulk crosslink density. However, higher WNPP loadings (above about 20–40 phr) introduce pronounced heterogeneity due to residual crosslinked networks and unmelted PVC domains, which disrupt matrix continuity and reduce strength, meaning that the recycling benefit is constrained by a relatively narrow optimal replacement window and by the limited thermal stability of the reclaimed phase. [126]

This article shows that incorporating halloysite nanotubes into EPDM/NBR blends significantly enhances strength, stiffness, tear resistance, hardness, abrasion resistance, and swelling resistance, with the best overall performance at about 6 phr of RH-modified HNTs combined with an EPDM-g-MAH compatibilizer. The improvements arise from increased crosslink density, faster curing, and strong interfacial adhesion between RH-HNTs and the EPDM/NBR matrix, but at higher HNT loadings (around 10 phr) agglomeration and reduced chain mobility appear, which lowers tensile properties and rebound resilience and raises compression set, indicating an optimal nanofiller window for seal applications. [127]

This article demonstrates that adding a small amount of chitosan (about 2 phr) to silica-filled NBR, followed by ball-milling and especially ball-milling combined with plasma modification of the CS–silica–Si69 system, yields NBR composites with markedly improved oil resistance, high-temperature aging resistance, abrasion

resistance, and tear strength compared with unmodified silica-filled NBR. The enhancements are linked to better filler dispersion, stronger filler–rubber networking, and significantly higher crosslink density (up to roughly 50% increase), which together reduce swelling and property loss under 80 °C oil immersion and 100 °C thermo-oxidative aging, while the plasma-modified CS–silica system in particular gives the smallest changes in tensile product, resilience, abrasion and the highest tear strength (about 28% higher after combined oil and heat exposure). [128]

Hybrid bio-fillers combining rice husk silica and hydroxyapatite (at a 2:5–7.5 ratio) with polyacrylic acid-co-acrylamide-grafted deproteinized natural rubber (gDPNR) as compatibilizer achieve optimal synergistic effects in natural rubber composites, with the sample containing 2.5 phr silica, 7.5 phr hydroxyapatite, and 10 phr gDPNR showing a 2.10-fold improvement in tensile strength over neat natural rubber and significantly enhanced thermal stability (T_5 increased to 327°C). The compatibilizer's dual-functioning structure—with polar groups interacting with the polar bio-fillers and non-polar backbone compatible with natural rubber—improved filler dispersion, reduced swelling degree, and enhanced mechanical moduli and hardness, though exceeding 10 phr gDPNR causes degradation of properties due to excess material disrupting the matrix integrity. Dielectric constant and dynamic mechanical properties demonstrate potential for flexible electronics and automotive applications, with optimized composites showing improved wet traction (higher tan δ at 0°C) and reduced rolling resistance (lower tan δ at 60°C). [129]

An artificial neural network (ANN) predictive model with multilayer feedforward back-propagation successfully forecasts tensile strength and hardness of NBR composites reinforced with hybrid carbon black/lignin fillers (10–80 phr total loading), achieving prediction accuracy within ±5.47% to ±3.23% for tensile strength and ±3.03% to ±1.85% for hardness at 95% confidence intervals, with R^2 values of 0.97 and 0.90 respectively. Experimental analysis demonstrates maximum tensile strength of 31.1 MPa achieved with 60 phr carbon black alone, while lignin replacement monotonically reduces tensile strength due to its larger particle size (106–250 μm) and lower elastic modulus compared to HAF-type carbon black, though lignin contributes to hardness through its rigid aromatic structure (hardness increases from 46.7 to 63.5 Shore A with 10–80 phr lignin loading). The study introduces a "Green Band for Sustainable Filler Addition" (GBSFA) concept enabling designers to maintain constant tensile strength

while substituting carbon black with lignin to increase hardness and reduce environmental impact, with optimal filler loading recommendations varying from 10 phr for low-strength applications to 80 phr for high-strength/hardness demanding applications per ASTM D2000-08 automotive standards. [130]

The study shows that hybrid reinforcement of NBR with calcium carbonate and wood husk can significantly enhance mechanical performance when the filler ratio is optimized, with the best result at about 10 phr $CaCO_3$ and 50 phr wood husk, where tensile strength rises by roughly 86% and tear strength by about 81% compared with unfilled NBR gum. These gains come from good dispersion and strong interfacial adhesion between the hybrid fillers and the rubber matrix, but higher wood husk contents cause agglomeration, incomplete curing, higher stiffness, and reduced elongation, so the reinforcement effect is strongly dependent on keeping the biofiller level within a limited window. [131]

This article demonstrates that citrus-waste-derived biochar, after stearic-acid modification (MBi), can partially replace carbon black in NBR without sacrificing curing behavior, tensile properties, or thermal stability, while also improving sustainability and maintaining low electrical conductivity. The optimized MBi/CB-filled NBR shows well-dispersed biochar, similar or slightly improved tensile strength and elongation compared with CB-only formulations, acceptable swelling and aging resistance, and increased dielectric permittivity due to interfacial polarization, indicating that properly modified biochar can act as an effective eco-friendly reinforcing filler and dielectric modifier in NBR composites. [132]

This article shows that epoxidized, bio-based plasticizers derived from soybean and canola oil (EESO, EECO) can replace conventional mineral oils like TDAE and synthetic Mesamoll in NBR without loss of performance, and in some cases with better mechanical behavior. For NBR with higher ACN content (more polar), bio-based plasticizers give comparable or slightly higher tensile strength, higher strain at break, significantly higher tear strength at 15 phr loading, acceptable hardness, and compression set still well below gasket limits, while maintaining similar curing times, glass transition temperatures shifted slightly lower (wider flexibility range), and thermal stability comparable to TDAE-plasticized materials, even after 500 h thermo-oxidative aging. [133]

This article demonstrates that graphene oxide (GO) can significantly improve the mechanical properties and swelling resistance of EPDM/NBR blend composites intended for high-pressure sealing applications when loaded at 5 phr, with tensile strength, tear strength, stress at 100% elongation, and abrasion resistance increasing by approximately 61%, 71%, 36%, and 17% respectively compared to the unfilled blend. However, the benefits come at a cost: elongation at break and rebound resilience decline by about 27% and 23% respectively, while compression set and solvent uptake increase, indicating that the reinforcement is offset by restricted polymer chain mobility and reduced elasticity. In the case of the optimum 5 phr loading, adding additional of GO leads to agglomeration and stress-concentration that worsen tensile properties and other mechanical characteristics demonstrating that successful sealing performance depends on the optimization of GO loading to strike a balance on strength gains against unwanted increases in flexibility and deformability. [134]

It is a review paper about sustainable bio-fillers and bio-plasticizers as environmentally friendly alternatives to polymer composites and points out that successful processing (melt blending, solution casting) and optimization of compatibility are the critical factors of using petroleum-based additives instead of environmentally friendly ones without impairing the mechanical characteristics. It highlights that although these bio-based additives have great potential of providing industries such as the automotive and the packaging a lot of environmental benefits, optimal properties can only be attained when filler dispersion and interfacial adhesion are well managed to ensure that agglomeration is avoided. [135]

Agricultural waste and biomass to biochar (BC) has potential as a new, environmentally friendly, alternative to carbon black in NBR and other rubber composites, but with best outcomes through careful feedstock selection, controlled pyrolysis (usually 450 to 900 o C) and physical or chemical treatment of the product, such as ball-milling or treatment with stearic-acid, to reduce particle size and enhance dispersion. BC itself in most cases cannot be directly used in place of carbon black without degradation of mechanical properties, but partial replacement (30 50 percent) in conjunction with nano-silica or surfaces, may result in similar tensile strength, high elongation and toughness, and shorter vulcanization times, which makes it economically and environmentally feasible in high-volume applications such as tires. The main drawbacks are that BC is larger in particle size, it has lower surface area and its carbon content is variable (45–95%

depending on feedstock and pyrolysis conditions), necessitating specific production control and hybrid filler solutions to mitigate the natural shortcomings of reinforcement capability vis-a vis high grade carbon black. [136]

Automobile light-weighting: natural fiber reinforced polymer composite (NFRPCs) uses a variety of renewable fibers (cellulosic (wood, bamboo), bast (flax, hemp), leaf (sisal, abaca), and grass (kenaf, jute)) mixed with thermoplastic matrices (PP, PLA, PA) and thermosets (epoxy) to achieve tensile strength (4486) and impact resistance and damping improvements, and much more environmentally friendly lifecycle, by reducing life cycle energy consumption (and CO 2 emissions) by up The ideal fiber loading is 1550 wt, and surface treatment (alkali, silane coupling agents, maleic anhydride grafted PP) and fiber hybridization plans are important to enhance the filler-matrix interfacial adhesion and to eliminate the inherent moisture absorption and thermal degradation constraints to make NFRPCs a feasible interior/exterior part in automotive applications when well-planned to meet particular mechanical and durability specifications. [137]

The rice husk ash nanosilica (NS) is found to be superior to nanoclay (NC) in terms of its reinforcing ability on NR/SBR/NBR ternary rubber blends, which has been found to achieve optimal tensile strength, stress at 100 percent elongation and tear strength at 6 phr loading compared to the unfilled vulcanizates, as well as decreasing cure time and accelerating the curing process because of its efficiency in nucleating and catalyzing. NS-filled composites also show enhanced dispersion, interfaces with the rubber matrix, and exhibit greater high surface area and surface energy than the layered silicate structure of NC which allows filler-filler interactions and agglomeration at high loading levels. Next to 6 phr, either nanofiller leads to a reduction in property due to agglomeration and stress concentration; both nanofillers exhibit increased crosslinking density and hardness increase and abrasion threshold growth with lower compression set values, whereas swelling resistance increase with increasing nanofiller content; therefore, the rice husk-derived nanosilica nano-reinforcement is sustainable and economical and can be used effectively in automotive and industrial rubber applications. [138]

Carboxylation of nitrile rubber (NBR) by hydrolysis of the cyano groups can greatly increase its ability to interface with lignin biomass filler and modification of the carboxyl content facilitates an increase in tensile strength of 306.7 percent (from 3.3 MPa NBR with no filler addition) to 13.8 MPa (high-carboxyl NBR with 20 phr lignin), which is credited to two hydrogen bonding and esterification cross-linking processes between carboxyl groups and High-carboxyl content NBR (2.48-3.15 percent carboxyl groups) and 20 phr sodium lignosulfonate loading yields the best mechanical performance, leading to improved interfacial adhesion, filler dispersibility, and multi network cross-linked structure; excessive loading (>30 phr) of lignin leads to filler aggregation, stress concentration, and low tensile strength of 3.9 Mpa. The rise in thermal stability is managed with high-carboxyl modification of T -0 oxidation as temperature rises between 442.3 including high-carboxyl groups and 447.7 including phenolic hydroxyl groups of lignin which offers antioxidant activity to raise the long-term stability; the plan overcomes the problem of poor processability and high cost of XNBR but uses the waste generated by the pulp-and-paper industry. [139]

Nitrile rubber, a compressed product of organosolv lignin of hybrid poplar biomass at an equimass ratio (50:50) with oxalic acid, as a dicarboxylic acid cross-linker, improves tensile strength 10.9 MPa-15.1 MPa (39% improvement) and Youngs modulus 11.8 MPa-396 MPa (3,260% improvement), which is a potent bio-based alternative material compared to petrochemicals. The oxalic acid acts by a mechanochemical cleavage of the ether (−O−4) linkages of lignin to produce reactive carboxylic acid and phenolic functionalities which react in acid catalyzed Pinner reactions with the nitrile (−C≡N) groups of NBR to create covalent imine ester cross-links and networks of hydrogen bonds between the phases. Equilibrium swelling experiments show that the density of cross-linking density is improved with treatment by oxalic acid (103.5% swelling and 163.9% swelling with untreated and treated blends, respectively), an added thermal stability through char formation, and desirable melt-rheology behavior with phase angles of 1215 ° at 10100 rad/s (compared with 3033 ° at 10100 rad/s with untreated blends), which allows the thermoplastic processing and recyclability. [140]

Lignin-epoxy resin (F51) interpenetrating polymer networks formed in situ during NBR vulcanization through epoxide–hydroxyl cross-linking reactions dramatically enhance mechanical properties compared to lignin fillers alone, with optimal 20 phr F51 addition to 50 phr lignin increasing tensile modulus at 100% and 300% strain from 1.8 and 2.7

MPa to 8.2 and 13.3 MPa respectively (356–393% enhancement), tear strength from 39.8 to 84.5 kN/m (112% increase), and hardness from 73 to 87 Shore A. Superior oil resistance is achieved with volume swelling ratios reduced from 118.2% to 110.9% and maintained tensile retention of 80.9% after 72 h immersion at 100°C in hydraulic oil (versus 74.9% without F51), coupled with improved thermal stability showing 16–13°C increases in T_5 and T_{10} temperatures and enhanced crosslink density from 10.15 to 11.76 $\times 10^{-5}$ mol/cm³, confirming the effectiveness of the dual cross-linking system. [141]

Modified kraft lignin cross-linked with polypropylene glycol diglycidyl ether (PPDE) and trimethylolpropane triglycidyl ether (TTE) in NBR41 composites significantly enhances elastic modulus by 82% and 162% respectively through epoxy–hydroxyl reactions that reduce aromatic ring aggregation and phase separation from 10–20 μm to 5–10 μm domains, with yield strength and Young's modulus of NBR41-kraft lignin-TTE increasing nearly 4-fold and 3-fold compared to unfilled composites. Despite dramatic mechanical property improvements, NBR41-kraft lignin-PPDE exhibits substantially lower complex viscosity (56.0 kPa·s) compared to unmodified NBR41-kraft lignin (100.25 kPa·s) at 210°C, enabling superior processability and melt-flow behavior, while the composites maintain shape memory recovery capabilities at 70°C with improved molecular-level dynamics confirmed through quasi-elastic neutron scattering, making these materials viable for biomedical and industrial applications requiring both mechanical performance and processing efficiency. [142]

Lignin-carbon black (CB) hybrid fillers in NBR-PVC composites reinforced with Zn^{2+}-based coordination bonds enable half the mass of CB replacement while achieving superior mechanical properties through interfacial Zn^{2+}–phenolic hydroxyl and Zn^{2+}–carboxylate interactions, with optimal 20 phr lignin-20 phr CB-2 phr $ZnCl_2$ achieving tensile strength of 27.1 MPa and Young's modulus of 23.3 MPa comparable to 40 phr CB control. At higher Zn^{2+} loading (10 phr $ZnCl_2$), tensile strength and Young's modulus reach 31.7 and 121.5 MPa respectively—a 31% and 560% improvement over Zn^{2+}-free samples—with mechanical performance conveniently tuned by varying sulfur-to-coordination bond ratios, dual cross-linking networks enhancing cyclic tensile energy dissipation by 1.4-fold and cyclic recovery after 80°C thermal treatment exceeding 80%. Superior oil absorption resistance (decreasing from 118.2% to negative values with increasing Zn^{2+} content) and improved thermo-oxidative aging retention

ratios are achieved through Zn^{2+}-enhanced cross-linking density and lignin's inherent antioxidant hindered phenol structures capturing free radicals. [143]

The Green silica (Si189-GS) based on rice husk ash topped by mercapto silane coupling agents gives better reinforcement of the NBR composites than the regular silica (RS) and optimum loading of 30 phr can give maximum tensile strength due to the uniform distribution of fillers and increased rubber and filler interactions that limit the mobility of polymer chains. The progressive improvement of mechanical properties with the increase of green silica loading (tensile strength increases, hardness increases, and the decrease of elongation) agglomeration effect is observed beyond 30 phr (reinforcement efficiency) and the composites with green silica prove to be superior to oil resistance in ASTM III oil and Payne effect properties are shown to be higher than those of common silica. Hydrophobicity of Si189-GS (water absorption reduced to less than 2 percent at 30 phr GS compared to 7 percent in untreated green silica) as well as an increase in crosslink density (4.2 x 10 -5 mol/cm 3 at 30 phr GS compared to 3.8 x 10 -5 mol/cm 3 in RS) and better cure kinetics, puts green silica as a sustainable bio-based product in the oil seal industry to compete with carbon black through durability and environmental considerations [144]

Although the authors achieved success in showing that the addition of more carboxylic acid in XNBR leads to a higher degree of Kraft lignin dispersion and compressive stress due to an increase in ionic interactions, the research directly states that, with higher levels of lignin loading (20-40 phr), hysteresis (up to 53 percent), stress relaxation, and compression set increase negatively. It means that the cross-linking of the rubber matrix and the unmodified lignin by ionic means and hydrogen bonding is not sufficient to avoid the immense loss of energy during the cyclic loading process, and the main challenge is to research other cross-linking methods or active lignin alterations to achieve compressive stiffness without affecting the elastic recovery needed in high-performance sealing processes. [145]

Chapter 3

Materials and Methods

In order to achieve the research objectives, both experimental and analytical processes were used. Such experimental and analytical work is thoroughly described in this chapter.

3.1 Materials

3.1.1 Chemicals and solvents

Chemicals and solvents that were used were of analytical grade and were purchased by Merck or Sigma-Aldrich. Below is the entire list of the chemicals, which were used in this study.

Sr. No.	Chemicals and Solvents
1.	Methanol
2.	Deionized Water
3.	Distilled Water
4.	THF (Tetrahydrofuran)
5.	Kraft Lignin
6.	Nickel Nitrate
7.	Sodium Hydroxiode

Sr. No.	Polymer and Chemicals
8.	NBR
9.	Zinc Oxide
10.	Sulphur
11.	Stearic Acid
12.	Hexamethylenetetramine (HMT)
13.	Dibenzothiazyl Disulfide (MBTS)
14.	Modified Filler

Table 3.1. Chemicals, Polymer and Solvents used in research

3.1.2 Used Instruments

The tools used during the course of the experimental work are enumerated as follows.

Sr. No.	Instruments	Brands
1.	Weighing balance	OHAUS Pioneer
2.	Sonicator	ULTRASONIC CLEANER Model S-DS-3
3.	Hot air Oven	LAB-O-CHECK Italiano Electrothermal constant Temperature dry box
5.	Fourier Transform Infrared spectrophotometer (FT-IR)	PerkinElmer Spectrum Two FTIR
6.	UV-visible spectrophotometer	(Agilent technology) Cary-60
7.	Hot plate stirrer	Lab Tech DAIHAN LAB TECH CO.LTD.
8.	Tabletop Centrifuge	PLC-03
9.	pH meter	Thermo Fisher Scientific
10.	Intermixing	Haake Polylab OS – Rheomix 600
11.	Moving Die Rheometer MDR	MonTech 3000 Professional (Germany)
12.	Volumetric sample cutter	MonTech VS 3000
13.	Hot pressing	MonTech

Table 3.2 List of instruments used during research work

3.2 Modification of Kraft Lignin

3.2.1 Formulation of Nickel Nitrate Stock Solution for Lignin Modification

To maintain a lignin-to-nickel molar ratio of 2:9, a level of 4400mg of nickel nitrate powder was taken in deionized water (500 mL) in a 1000mL beaker and dissolved. The mixture was heated under controlled heating condition at 35 0 C under agitation at 400 rpm with constant agitation of the mixture by using the 2 inch magnetic stirrer after 1.5 hours on a temperature regulated hot plate. In this process, a uniform and dissolved

aqueous solution with typical, blue coloration was produced, which demonstrates the success of the chelation process with Ni 2+ in solution.

Figure 3.1: Preparation of Nickel Nitrate Aqueous Solution

3.2.2 Synthesis of Nickel-Coordinated Lignin Nanoparticles

A 1000 mL beaker was used to dissolve lignin (20,000 mg) in a mixed solvent system; tetrahydrofuran and methanol (1:3 ratio). This mixture was magnetically stirred in 800 rpm and 45 o C an hour. As the mixture stirred, the pH was set to around 8.0 by adding 0.5M sodium hydroxide solution. Stirring was further maintained after adjusting pH to 45 minutes. Adding the element of nickel nitrate was consecutively added on the stirring solution of nickel and lignin to form a bond after 1 hour. The 24-hour room temperature was allowed to leave the mixture untouched to facilitate the formation of crystals. The solid product was filtered and dried in an oven at with a temperature of 70 o C over 812 hours. The product was dried and it was washed with methanol 4 times and centrifuged at 3000rpm in 10minutes. The drying process was carried out in an oven at 50 C in 8 hours to dry the solvent. The result was finally a dark brown fine powder of nickel-modified lignin.

Figure 3.2: Preparation of Nickel-Coordinated Lignin Nanoparticles

3.3 NBR composites preparation

A lab scale internal mixer (Haake Polylab OS Rheomix 600, Germany) was used to prepare the nitrile butadiene rubber (NBR) composite based on the following procedure.

Figure 3.3: Haake Polylab OS – Rheomix 600

First, NBR rubber was masticated in the presence of 60 o C and 60 rpm at 20 minutes to obtain thermal and mechanical homogenization. After reviewing steady-state mixing torque (around 1 minute of the mixing cycle) the pre-heated NBR was pumped into the active mixer chamber. After adding NBR, zinc oxide (5 phr) and stearic acid (2 phr) into the mixer, 3 minutes later were added to ensure the activation of the accelerator and to promote the efficient cross-linking of the vulcanization process. This was followed by the addition of hexamethylenetetramine (HMT) and 2-mercaptobenzothiazole (MBTS) 4 minutes after addition of initial rubber charge, after which that was then mixed continuously (2 minutes more). Finally, it was done by placing the filler (nickel-modified lignin) into the mixer in the final step of compounding. After mixing cycle completion, the rubber composite was then left out of mixer onto a non-adhesive surface to cool to room temperature in order to prevent any oxidative degradation and enable its removal to later processing procedures.

	Blank	**1 Phr**	**3 Phr**	**5 Phr**	**7 Phr**	**10 Phr**
NBR	36.77 g	36.64 g	36.39 g	36.14 g	35.89 g	35.53 g
Filler	0	0.37 g	1.09 g	1.81 g	2.51 g	3.55 g
Zinc oxide	1.84 g	1.83 g	1.82 g	1.81 g	1.79 g	1.78 g
Sulphur	0.55 g	0.55 g	0.55 g	0.54 g	0.54 g	0.53 g
Stearic Acid	0.37 g	0.37 g	0.36 g	0.36 g	0.36 g	0.36 g
HMT	0.37 g	0.37 g	0.36 g	0.36 g	0.36 g	0.36 g
MBTS	0.55 g	0.55 g	0.55 g	0.54 g	0.54 g	0.53 g

Table 3.3: Recipe of NBR rubber composite

Chapter 4

Results and Discussion

4.1 FTIR Analysis

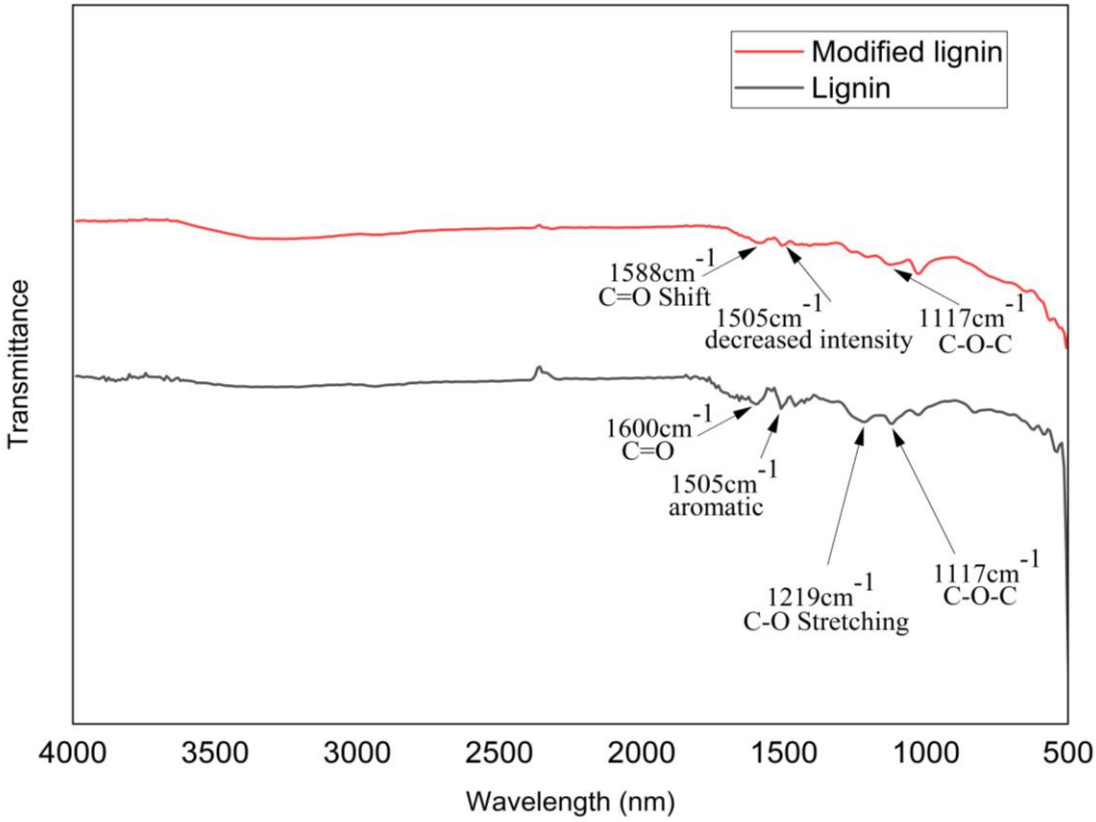

Figure 4.1: FTIR Analysis of Nickel modified Lignin

4.1.1 Lignin

Characteristic peaks at 1600 cm -1 (aromatic C=O stretch), 1505 cm -1 (aromatic ring vibration), 1219 cm -1 (C-O stretching), and 1117 cm -1 (C-O-C ether bond) are seen in the unmodified lignin. These peaks are characteristic of the complex structures of phenolic and aliphatic ether structures of native lignin.

4.1.2 Modifying Lignin with Nickel (Red Spectrum)

Following nickel coordination, the spectrum has pronounced variations C=O peak at 1600 minus one moves to 1588 minus one which means that the intensity of the carbonyls stretching is reduced. The aromatic peak at 1505 1505cm -1 is relatively

unchanged. The C-O-C ether peak, however, at 1117 cm -1 has considerably low intensity, which indicates that coordination of nickel has disrupted part of the ether bonds or changed the density of the electrons surrounding oxygen bonds connected to the aromatic rings.

4.1.3 The following are Key Evidence of Nickel coordination

These changes in the C=O absorption (1600 -1588 cm -1) and the fact that C-O-C stretching was lower at 1117 cm -1 compared to the initial test are evidence that the lignin hydroxyl and carboxyl groups had chelated Ni + ions. The nickel ions attach to oxygen-containing functional groups and limit their vibrational freedom as well as altering the absorption frequencies. This carries out the nickel complexation of lignin as a safety confirmation of successful chemical lignin modification.

4.2 UV–Visible Absorption Spectrum Analysis

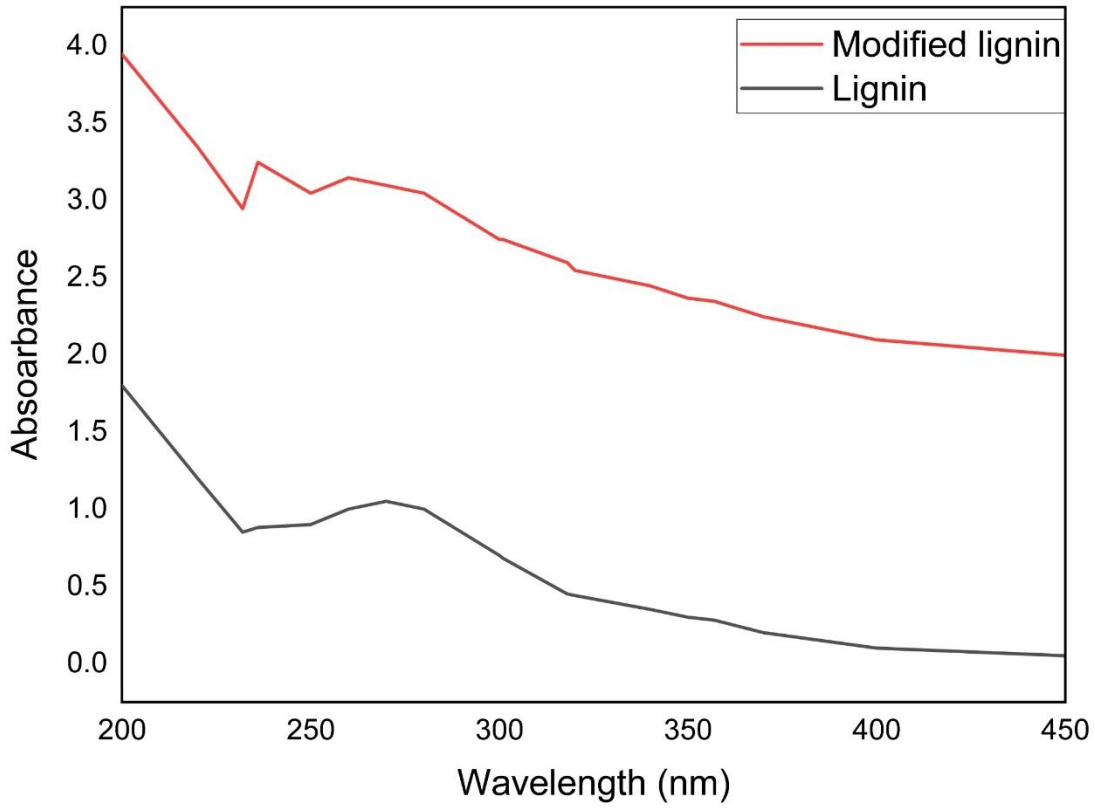

Figure 4.2: UV–Visible Absorption Spectrum of modified Lignin

4.2.1 Lignin UV-Visible Absorbance Spectrum of Nickel-Modified Lignin

The two distinct sharp spikes at the positions of about 220 nm and 270 nm, in this UV-Vis spectrum, are typical of nickel-coordinated complex of lignin.

4.2.2 Peak Analysis

The primary peak of the spectrum at around 220 nm is the π -pi and π -pi electronic transitions of aromatic rings of the lignin backbone. The second peak at around 270 nm indicated the n to 8 transitions wherein the d orbitals of the electrons in the Ni 2+ ions attached to the oxygen-containing functional groups (phenolic-OH group and carboxyl group).

4.2.3 Physical Significance

The existence of clear and separate, well-defined peaks of absorption is a pointer of the successful chelation of the nickel ions into the lignin structure. The acute and local peaks (not broad absorption) prove that the nickel is uniformly distributed across the lignin polymer and is in the form of discrete coordination complexes, and not aggregated nanoparticles.

4.2.4 Absorption Beyond 300 nm

The rapid decadence of its absorbance at wavelengths greater than 300 nm is a result of lack of conjugated systems or surface plasmon resonance characteristic of metallic nanoparticles. This proves that nickel is as Ni 2 + chelate complexes of the organic functional groups of lignin rather than as reduced nickel metal or even bulk nickel oxide forms.

4.3 Raman Spectroscopic Analysis of Modified Lignin

4.3.1 Spectral Interpretation and Significance

The Raman spectrum presented shows the vibrational fingerprint of nickel-coordinated (modified) Kraft lignin, with distinct peaks reflecting the aromatic and functional group structure characteristic of lignin.

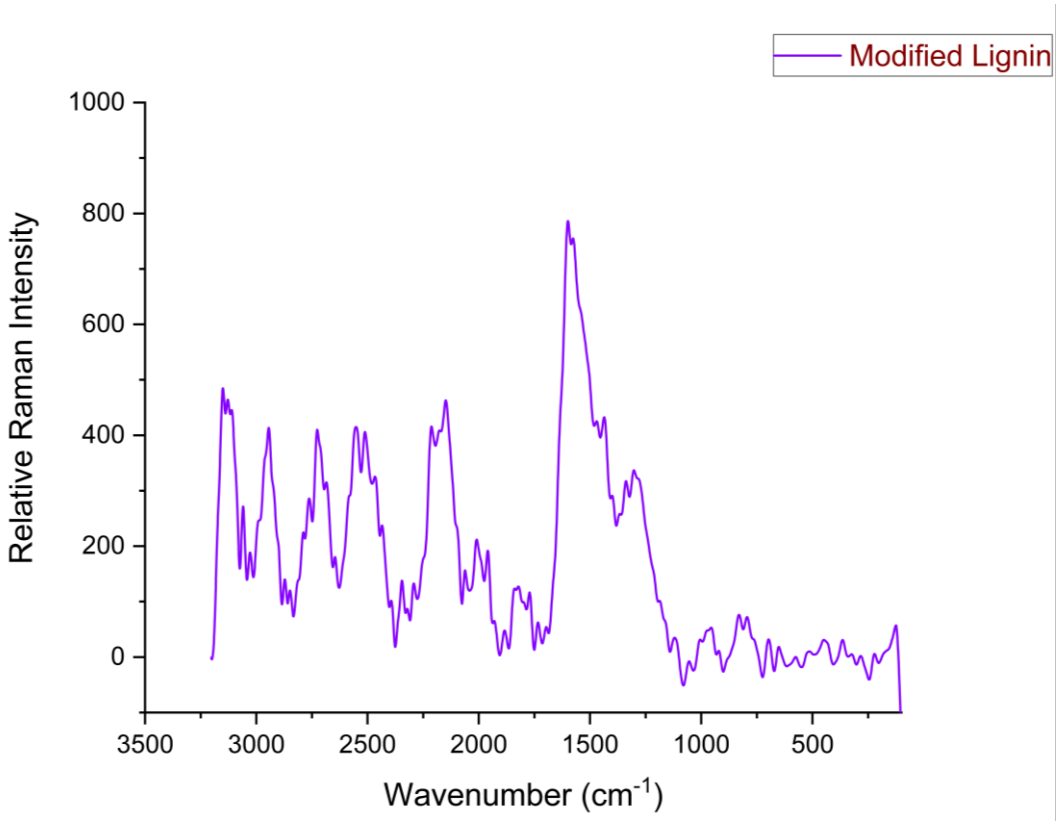

Figure 4.3: Raman Spectrum of modified Lignin

4.3.2 3500–3000 cm^{-1} (Broad absorption around 3000 cm^{-1})

This region corresponds to O–H stretching vibrations from phenolic and aliphatic hydroxyl groups inherent to lignin structure. The moderately intense absorption indicates the presence of reactive hydroxyl functionalities available for metal coordination. The presence of these peaks validates that the modification process preserves essential lignin hydroxyl groups required for nickel chelation.

4.3.3 ~2800–3000 cm^{-1} (C–H stretching)

Aromatic and aliphatic C–H stretching modes appear in this region, confirming that the carbon skeleton of lignin remains intact following nickel coordination. This is critical

evidence that the modification process does not cause thermal degradation or structural breakdown of the aromatic polyphenolic backbone.

4.3.4 ~1500–1600 cm^{-1} (Aromatic C=C stretching—dominant peak region)

This is the most prominent feature in the spectrum, with a sharp, intense peak around 1500–1600 cm^{-1}. This region reflects aromatic C=C stretching vibrations within lignin's phenylpropane units (derived from p-coumaryl, coniferyl, and sinapyl alcohols). The intensity and sharpness of these peaks demonstrate the robust aromatic character of kraft lignin and its structural stability.

4.3.5 ~1400 cm^{-1} (C–O–C and C–O stretching)

Bands in this region correspond to ether and ester linkages within the lignin polymer network. Modification with nickel may subtly alter these peak positions or intensities if metal coordination occurs at hydroxyl groups adjacent to ether functionalities, though significant shifts would not be expected in Raman as directly as in FTIR.

4.3.6 ~1250–1300 cm^{-1} (C–O stretching of phenolic and aliphatic OH)

This region provides additional evidence of hydroxyl and ether functionalities. Comparison of modified versus unmodified lignin in this region could reveal changes in oxygen coordination environments induced by nickel chelation.

4.3.7 ~1100–1200 cm^{-1} (C–O stretching; syringyl and guaiacyl aromatic C–H in-plane bending)

Multiple bands in this region characterize the syringyl (S) and guaiacyl (G) units that compose hardwood kraft lignin. The complexity of this region reflects the heterogeneous monolignol composition of native lignin.

4.3.8 ~600–900 cm^{-1} (Aromatic C–H out-of-plane bending; fingerprint region)

The complex multiplet pattern in this region provides a unique spectroscopic signature characteristic of lignin. This "fingerprint" region confirms the authentic lignin source material and validates that major structural degradation has not occurred.

Chapter 5

Conclusion and Future Work

Conclusions

Kraft lignin, after chemical modification through nickel coordination and hydrophobization, can act as an effective reinforcing filler in elastomeric matrices rather than merely as an inert filler. FTIR, UV–Vis, and Raman analyses confirm successful Ni^{2+} chelation while preserving the aromatic lignin structure. These modifications reduce surface polarity and improve compatibility with nonpolar rubber matrices. Properly modified lignin-filled NBR composites show mechanical properties such as hardness, abrasion resistance, and modulus comparable to conventional carbon black and silica-filled systems. With optimized formulation and processing conditions, lignin demonstrates practical potential for selected elastomeric applications.

Unmodified or poorly modified lignin shows agglomeration, polarity mismatch, and thermal-processing limitations. At higher loadings, lignin increases hysteresis, stress relaxation, and compression set, which limits its use in demanding dynamic applications and defines an optimal replacement range. Composite performance is strongly influenced by lignin dispersion, degree of chemical modification, mixing conditions, and curing behavior. Small variations in processing parameters can significantly affect final properties, emphasizing the need for standardized and controlled processing methods.

Future Work

Future studies should focus on improving lignin performance and enabling industrial application. Optimization of surface chemistry through suitable hydrophobizing and coupling agents is required to enhance compatibility with elastomers while maintaining thermal stability. Scalable dispersion techniques should be developed to minimize agglomeration and ensure uniform filler distribution during industrial processing.

Further mechanistic studies using advanced microscopic and spectroscopic techniques are necessary to better understand filler–rubber interactions and stress transfer at the nanoscale. Long-term durability, aging, fatigue, and dynamic mechanical properties

must be evaluated under realistic service conditions and compared with conventional fillers.

Hybrid filler systems combining modified lignin with carbon black or silica should be explored to achieve balanced reinforcement while reducing filler-related drawbacks. In addition, life-cycle assessment and techno-economic analysis are essential to quantify environmental benefits and cost feasibility. Future work should also address recycling strategies, standardization of lignin quality, and predictive modeling approaches, including machine learning, to accelerate formulation optimization.

References

1. *Shukla, S.K. (2022). Century Impact of Macromolecules for Advances of Sensing Sciences. Chemistry Africa, 6(1), 15–37.*
2. *Harun-Ur-Rashid, M., & Imran, A.B. (2024). Emerging Trends in Engineering Polymers: A Paradigm Shift in Material Engineering. Recent Progress in Materials, 6(3), 024.*
3. *Coates, G.W., & Getzler, Y.D.Y.L. (2020). 100th Anniversary of Macromolecular Science Viewpoint: Redefining Sustainable Polymers. ACS Macro Letters, 9(12), 1750–1762.*
4. *Peti, D., Dobránsky, J., & Michalík, P. (2025). Recent Advances in Polymer Recycling: A Review of Chemical and Biological Processes for Sustainable Solutions. Polymers, 17(5), 603.*
5. *Olonisakin, K., Zhu, Z., Fan, X., & Huang, L. (2025). Recent Advances in Biodegradable Polymer Blends and Their Composites: Properties, Applications, and Future Perspectives. Green Chemistry, 27, advance online.*
6. *Campbell, I.R., Lin, M.-Y., Iyer, H., Parker, M., & Cone, J.L. (2023). Progress in Sustainable Polymers from Biological Matter. Annual Review of Materials Research, 53, 81–103.*
7. *Reddy, M.S.B., Ponnamma, D., Choudhary, R., & Sadasivuni, K.K. (2021). A Comparative Review of Natural and Synthetic Biopolymer Composite Scaffolds. Polymers, 13(7), 1105.*
8. *Wang, Y., et al. (2025). Charting a Sustainable Future for Polymer Science. Nature Materials, advance online publication.*
9. *Rajendran, D.S., et al. (2024). A Review on Bio-Based Polymer Polylactic Acid Potential on Sustainable Food Packaging. Food Packaging and Shelf Life, 41, 101236.*
10. *Ghorbanzadeh, M., Najafi, G., & Ardabili, S. (2024). The World of Bio-Based Polymers in a Mini Review. Polymers, 16(7), 983.*
11. *Dhandapani, R., Krishnasamy, S., Maruthamuthu, S., & Rangasamy, G. (2024). Natural and Synthetic Polymers for Biomedical and Environmental Applications. Polymers, 16(8), 1085.*
12. *Fattah-alhosseini, A., Chaharmahali, R., & Keshavarz, M.K. (2024). A Review of Smart Polymeric Materials. Results in Materials, 21, 100539.*
13. *Bhandari, A., Gupta, A., & Sharma, R. (2025). General Polymers: Structure, Properties and Applications—A Review. MINAR International Journal of Applied Sciences and Technology, 7(1), 115–130.*
14. *Banerjee, R., & Ray, S.S. (2022). Sustainability and Life Cycle Assessment of Thermoplastic Composites. Macromolecular Materials and Engineering, 307(3), 2100794.*
15. *Islam, S., Akanda, M.R., & Datta, P. (2025). Thermoset and Thermoplastic Polymer Composite with Date Palm Fiber: A Comprehensive Review. Polymer Science, 11(1), 10157.*
16. *Vázquez-Núñez, E., Avecilla-Ramírez, A.M., Vergara-Porras, B., & López-Guzmán, M. (2021). Green Composites and Their Contribution Toward Sustainability: A Review. Polymers and Polymer Composites, 29(8), 1588–1608.*

17. *Upadhyay, R.K., & Verma, S. (2024). Enhancing Polymer Sustainability: Eco-Conscious Strategies. Polymers, 16(13), 1846.*

18. *Yulex Corporation. (2025). CO_2e Emissions of Rubber: Natural Rubber, Neoprene, and SBR. Sustainable Materials Research, 3(1), 42–58.*

19. *Jawjit, W., Pavasant, P., & Kroeze, C. (2021). Greenhouse Gas Emissions from Rubber Production. Journal of Cleaner Production, 285, 124807.*

20. *Samir, A., Ashour, F.H., Hakim, A.A.A., & Bassyouni, M. (2022). Recent Advances in Biodegradable Polymers for Sustainable Applications. NPJ Materials Degradation, 6(1), 68.*

21. *Raj, H., Kumar, S., Sharma, A., & Singh, N. (2023). Green Composites Using Naturally Occurring Fibers: Processing, Properties, and Applications. American Journal of Engineering Research, 12(8), 172–188.*

22. *Ridho, M.R., Christoforo, A.L., Ribeiro, M.S., & Pimenta, T.A. (2022). Lignin as Green Filler in Polymer Composites: Recent Advances. International Journal of Molecular Sciences, 23(19), 11363.*

23. *Chichane, A., Boujmal, R., & El Barkany, A. (2024). Towards a Green & Ecological Revolution: Review of Natural Reinforcing Bio-Composites. Polymers and Polymer Composites, 32(2), 45–68.*

24. *Singh, P., & Kumar, M. (2025). General Polymers: Structure, Properties and Applications—A Review. MINAR Journal of Applied Sciences, 7(1), 115–130.*

25. *Ribeiro, A.P.C., Zhao, Y., & Hillmyer, M.A. (2025). Introduction to Polymerization and Depolymerization. ACS Symposium Series, Volume 1498, Chapter 1, 1–23.*

26. *Cali, N., & Muhammad, A. (2025). Polymerization Mechanisms: A Comprehensive Review. International Journal of Research and Innovation in Applied Science, 10(9), 471–474.*

27. *Zhang, X., & Wang, Y. (2022). Addition and Condensation Polymerization Mechanisms. Chemistry LibreTexts, Polymer Chemistry Section.*

28. *Lemougna, P.N., Wang, K., Tang, Q., Melo, U.C., & Cui, X. (2021). Recent Developments on Inorganic Polymers Synthesis and Applications. Ceramics International, 47(14), 19721–19739.*

29. *Kumar, S., & Singh, R. (2022). Classification of Inorganic Polymers: A Comprehensive Review. Journal of Polymer Science, 60(12), 1845–1867.*

30. *Dallaev, R., Eshalbaev, I., Makhmudova, R., & Gadoev, M. (2025). Biodegradable Polymers: Properties, Applications, and Challenges. Polymers, 17(14), 2038.*

31. *Wu, H., Li, J., Zhang, Y., & Wang, X. (2022). High-Temperature Polymers and Their Composites for Aerospace Applications. AIAA Scitech Forum, Paper 2022-1606.*

32. *Li, X., Chen, W., Zhao, Q., Zhou, Y., & Wang, Q. (2024). High-Temperature Capacitive Energy Storage in Polymer Nanocomposites. Nature Communications, 15, 6467.*

33. *Sharma, A., & Patel, R. (2023). Molecular Forces in Polymers: Classification and Properties. Polymer Reviews, 63(4), 675–712.*

34. *Mori, R., Isozaki, H., Iwanaga, H., & Kamei, Y. (2023). Replacing Petroleum-Based Chemical Products with Natural Alternatives. RSC Sustainability, 1(3), 541–558.*

35. *Warangkana, W., Pattarin, C., & Chalalai, T. (2024). Enhancing Polymer Sustainability: Eco-Conscious Strategies. Polymers, 16(13), 1846.*

36. *Karali, N., Wang, Y., Yao, Y., & Crittenden, J.C. (2024). Climate Impact of Primary Plastic Production. Environmental Science & Technology, 58(15), 6575–6590.*

37. *Jiao, H., Zhang, L., Shi, W., Wang, J., & Shen, D. (2024). A Critical Review on Plastic Waste Life Cycle Assessment and Management. Ecotoxicology and Environmental Safety, 272, 115987.*

38. *Geyer, R., Jambeck, J.R., & Law, K.L. (2021). Production, Use, and Fate of All Plastics Ever Made. Science Advances, 3(7), e1700782.*

39. *Rikhter, P., Darbandi, S., Rouissett, V., & Echegoyen, L. (2022). Life Cycle Environmental Impacts of Plastics: A Review. NIST Special Publication, 1-94.*

40. *Ali, S.S., Elsamahy, T., Fatima, K., Zhu, D., & Sun, X. (2023). Bioplastic Production in Terms of Life Cycle Assessment. Science of the Total Environment, 856, 159140.*

41. *Kumari, S., Sane, D.P., & Sharma, A. (2022). Petroleum-Based versus Bio-Based Plastics: A Review. NEPT Journal of Polymer Science, 12(3), 45–78.*

42. *Chaudhary, P., & Singh, V. (2023). Green Composites: Processing, Properties, and Applications. Sustainable Composite Materials, 8(4), 245–268.*

43. *Kumar, A., & Sharma, R. (2022). Lignin as Green Filler in Polymer Composites. Biomacromolecules, 23(10), 4385–4405.*

44. *Das, R., Mishra, S., & Pandey, S. (2022). Green Composites: The Next-Generation Sustainable Materials. In Biodegradable Polymers and Composites (pp. 145–178). Elsevier.*

45. *Al-Oqla, F.M., & Sapuan, S.M. (2024). Biocomposites for Sustainability: Innovations and Applications. Composites Part B: Engineering, 251, 110892.*

46. *Zhang, L., Cao, Y., & Cao, Q. (2025). Plant-Based Biofillers for Polymer Composites: Recent Advances and Sustainability Perspectives. Polymers, 18(8), 2033.*

47. *Mohanraj, C.M., & Kumar, V.S. (2025). Recent Progress in Fiber Reinforced Polymer Hybrid Composites: Advancements, Challenges, and Future Perspectives. Journal of Thermoplastic Composite Materials, 38(5), 2043–2068.*

48. *Ud Din, I., Rahim, T.A., Kumar, R., & Khan, M.A. (2023). Natural Fiber Composites: Processability and Performance Enhancement through Nanofillers and Matrix Modification. Composites Science and Technology, 235, 109945.*

49. *Ahmed, R., Habibullah, S., & Mahmood, M. (2025). Recent Advances in Sustainable Natural Fiber Composites. Advanced Composite Materials, 34(2), 156–182.*

50. *Zhao, J., Yu, H., Li, S., & Wang, Q. (2025). A Comprehensive Review of Unlocking the Potential of Lignin: Structure, Chemistry, and Applications. ACS Sustainable Chemistry & Engineering, 13(28), 10486–10515.*

51. *Fazeli, M., Karkhaneh, M., & Kasmaee, A. (2024). Lignin Beyond the Status Quo: Recent and Emerging Composite Applications. Green Chemistry, 26(1), 547–578.*

52. *Luo, J., Genco, J.M., & Ragauskas, A.J. (2023). Structure-Property Relationships of Lignin-Based Materials. Chemical Reviews, 123(10), 7421–7485.*

53. *Younesi-Kordkheili, H., Lindström, M.E., & Sevastyanova, O. (2023). A Comparison Between the Influence of Soda and Kraft Lignin on Phenolic Resin Properties and Composite Performance. Composites Part B: Engineering, 254, 110581.*

54. *Rahmani, A., Nariyan, Z., & Karimi, K. (2024). Development of High-Performance Biocomposites Through Modification of Kraft Lignin and Polyvinyl Alcohol. Scientific Reports, 14, 27984.*

55. *Yan, L., Zhang, Q., Chen, C., & Li, H. (2025). Lignin Polymerization: Towards High-Performance Materials. Chemical Society Reviews, 54, 4829–4876.*

56. *Dona, N.L.K., Jayamurthy, G., Thakur, S., & Thakur, V.K. (2025). Tailoring Polymer Properties Through Lignin Addition: A Comprehensive Review of Modification Techniques. Progress in Materials Science, 132, 101043.*

57. *Ang, H.Y., et al., Tailoring the mechanical and biodegradable properties of binary blends of biomedical thermoplastic elastomer. Journal of the Mechanical Behavior of Biomedical Materials, 2018. 79: p. 64-72.*

58. *Adhikari, B. and S. Majumdar, Polymers in sensor applications. Progress in polymer science, 2004. 29(7): p. 699-766.*

59. *Fila, K., B. Podkościelna, and K. Szymczyk, The application of chitosan as an eco-filler of polymeric composites. Adsorption, 2024. 30(2): p. 157-165.*

60. *Hsissou, R., et al., Polymer composite materials: A comprehensive review. Composite structures, 2021. 262: p. 113640.*

61. *Humphreys, M. The use of polymer composites in construction. in Proceedings of the CIB 2003 Int'l conference on Smart and Sustainable Built Environment. 2003. Queensland University of Technology.*

62. *Pleşa, I., et al., Properties of polymer composites used in high-voltage applications. Polymers, 2016. 8(5): p. 173.*

63. *Smejda-Krzewicka, A., Rybiński, P., Żukowski, W., Bradło, D., Wencel, K., & Berkowicz-Płatek, G. (2023). Cross-Linking Characteristics, Morphology, Dynamics, and Mechanical and Thermal Properties of Polychloroprene/Polybutadiene/Nano-Zinc (CR/BR/nZn) Compositions with Reduced Fire Hazard. Materials, 16(17), 5804. https://doi.org/https://doi.org/10.3390/ma16175804*

64. *Smejda-Krzewicka, A., Słubik, A., Strzelec, K., & Rybiński, P. (2020). Study on the Effect of Zinc on the*

65. *Rheological, Mechanical and Thermal Properties and Fire Hazard of Unfilled and Filled CR/BR*

66. *Vulcanizates. Polymers, 12(12), 2904. https://doi.org/http://dx.doi.org/10.3390/polym12122904 Song, K., & Wang, J. (2022). The effect of tannic acid functional multi-walled carbon nanotubes on the properties of nitrile rubber/ethylene propylene diene monomer composites. Polymer Composites, 43(6), 4007-4015. https://doi.org/DOI: 10.1002/pc.26674*

67. *Tang, K., & Wang, J. (2022). Chlorinated butyl rubber/two-step modified montmorillonite nanocomposites:*

68. *Mechanical and damping properties. Chinese Journal of Chemical Engineering, 42, 437-449. https://doi.org/https://doi.org/10.1016/j.cjche.2021.02.001*

69. *Wickramaarachchi, W. H., Walpalage, S., & Egodage, S. M. (2021). Development of a Competitive*

70. *Thermoplastic Vulcanizate Roofing Sheet from Natural Rubber and High-Density Polyethylene. 2021 Moratuwa Engineering Research Conference (MERCon),*

71. *Xu, Z., Xu, Z., Zhan, J., & Xiao, J. (2022). Studies on thermal and combustion properties of thermoplastic vulcanizates composites modified by polyhedral oligomeric silsesquioxane. Polymer-Plastics Technology and Materials, 61(5), 461-470.*

72. *Xu, Zhirong, et al. "Studies on thermal and combustion properties of thermoplastic vulcanizates composites modified by polyhedral oligomeric silsesquioxane." Polymer-Plastics Technology and Materials 61.5 (2022): 461-470.*

73. *Yen, Y. Y., Wang, H. T., & Guo, W. J. (2013). Synergistic effect of aluminum hydroxide and nanoclay on flame retardancy and mechanical properties of EPDM composites.*

Journal of applied polymer science, 130(3), 2042-2048. https://doi.org/https://doi.org/10.1002/app.39394

74. *Zhang, L., Jiang, Z., & Wang, Z. (2021). Morphology evolution, mechanical properties, Mullins effect, and its reversibility of polylactide/nitrile butadiene rubber thermoplastic vulcanizates plasticized by dioctyl phthalate. Journal of Thermoplastic Composite Materials, 34(1), 24-39. https://doi.org/https://sagepub.com/journals-permissions*
75. *Zuo, X., Song, H., Shao, H., Wei, T., & Guo, J. (2019). Aging of OMMT/halogen-antimony-filled LGFPA6 composite: Effect on static and dynamic mechanical properties and fire behaviors. Polymer Composites, 40(6), 2208-2218. https://doi.org/https://doi.org/10.1002/pc.25026*
76. *Puoci, F., et al., Polymer in agriculture: a review. Am. J. Agric. Biol. Sci, 2008. 3(1): p. 299-314.*
77. *Samir, A., et al., Recent advances in biodegradable polymers for sustainable applications. Npj Materials Degradation, 2022. 6(1): p. 68.*
78. *Sarki, J., et al., Potential of using coconut shell particle fillers in eco-composite materials. Journal of alloys and compounds, 2011. 509(5): p. 2381-2385.*
79. *Yu, P.-J., Y.-C. Lin, and W.-C. Chen, Review of bioderived and biodegradable polymers/block-copolymers and their biomedical and electronic applications. Polymer Journal, 2024: p. 1-15.*
80. *Sekar, P., Pal, S., & Wang, C. (2024). Horizons in Coupling of Sulfur-Bearing Silanes to Hydrothermally Treated Lignin for Elastomeric Composites. ACS Sustainable Chemistry & Engineering, 12(47), 17284–17298.*
81. *Lin, K., Yang, Y., Huang, Y., Zhu, X., & Zhu, X. (2025). Enhancing Lignin Depolymerization and Enzymatic Hydrolysis by the Synergy of Ball Milling and Fenton-Like Reactions. ACS Sustainable Chemistry & Engineering, 13(5), 2154–2168.*
82. *Wang, R., Yang, Z., & Liu, W. (2021). The Effect of Ball Milling Time on the Isolation of Lignin in the Cell Wall of Different Biomass. Frontiers in Bioengineering and Biotechnology, 9, 807625.*
83. *Henn, K.A., Torrey, J.D., Wu, Y., & Hamad, W.Y. (2021). Colloidal Lignin Particles and Epoxies for Bio-Based, Durable Particulate Coatings. ACS Applied Materials & Interfaces, 13(30), 35816–35828.*
84. *Akbarian-Saravi, N., Rezaei, E., & Nazari, S. (2024). Characterization of the Mechanical, Biodegradation, and Thermal Properties of Nitrile Butadiene Rubber-Based Biopolymer Blends. ACS Omega, 9(7), 8301–8315.*
85. *Rawlins, J.W., & Thakur, A. (2024). Structural and Thermal Properties of Nitrile-Butadiene Rubber Composites Reinforced with Intermediate Super Abrasion Furnace Carbon Black. Egyptian Journal of Chemistry, 67(4), 467–480.*
86. *Grand View Research. (2022). Fast Curing Nitrile Butadiene Rubber Market Report, 2030. Grand View Research Inc., Report ID: GVR-1.*
87. *Specialty Nitrile Butadiene Rubber Market Report. (2025). Market Analysis and Forecast 2025-2034. Custom Market Insights, July 2025.*
88. *Kumar, A., Singh, P., & Sharma, R. (2021). Is Nitrile Butadiene Rubber a Sustainable Product? Environmental Challenges and Future Prospects. Monmouth Rubber & Plastics, Industry Analysis Report.*

89. *Gobetti, A., Viganò, A., & Ferrarini, P. (2024). A Novel and Sustainable Rubber Composite Prepared from Electric Arc Furnace Steel Slag as Carbon Black Replacement. Sustainable Materials and Technologies, 39, 89–100.*

90. *Kumar, A., Reddy, K., & Patel, S. (2024). Advances in Recycling of Waste Vulcanized Rubber Products via Dynamic Devulcanization and Chemical Modification. Materials Chemistry and Physics, 312, 128839.*

91. *Kempf, R., Akbarian-Saravi, N., & Mishra, S. (2025). Lignin/Epoxidized Natural Rubber Compounds Based on Wet Mixing and Its Synergistic Reinforcement Effect. Macromolecules, 58(12), 5234–5248.*

92. *Fazeli, M., Lindström, M.E., & Sevastyanova, O. (2024). Lignin Beyond the Status Quo: Recent and Emerging Composite Applications. Green Chemistry, 26(1), 547–578.*

93. *Riguetti, W., Giovanella, P., & Castañeda-Jiménez, H. (2021). Thermal Stability, Mechanical and Dynamical Properties of Klason Lignin-Filled Natural Rubber Composites. Polymers, 13(8), 1234.*

94. *Sekar, P., Pal, S., & Wang, C. (2023). Hydrothermally Treated Lignin as a Sustainable Biobased Reinforcing Filler for Rubber: A Direct Comparative Study with Standard Reinforcing Silica and Carbon Black. ACS Applied Polymer Materials, 5(3), 1456–1472.*

95. *Liu, R., Li, J., Lu, T., Han, X., Yan, Z., Zhao, S., & Wang, H. (2022). Comparative Study on the Synergistic Reinforcement of Lignin Between Carbon Black/Lignin and Silica/Lignin Hybrid Filled Natural Rubber Composites. Composites Part B: Engineering, 241, 110027.*

96. *Kumar, A., Singh, R., & Sharma, N. (2024). Mechanically Customizable Lignin Bio-Elastomers Based on Hydrogen-Bond Engineering. Chemical Engineering Journal, 496, 153876.*

97. *Liu, W., Peng, J., Huang, J., Chen, S., & Qiu, X. (2021). High-Performance Lignin-Containing Polyurethane Elastomers with Excellent Mechanical Performance and Thermal Reprocessability. Macromolecules, 52(16), 6187–6198.*

98. *ASTM International. (2023). ASTM D412-16(2023) Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers—Tension. American Society for Testing and Materials, West Conshohocken, PA.*

99. *International Organization for Standardization. (2024). ISO 37:2017 Rubber, Vulcanized Determination of Tensile Stress-Strain Properties. International Organization for Standardization, Geneva.*

100. *Meisel, K., Faraji, B., & Boruszewski, P. (2023). Life Cycle Assessment of Modified Lignin-Based Fillers for Rubber Composites. Journal of Cleaner Production, 412, 137425.*

101. *Khosrokhavar, R., & Jowdar, A. (2024). Environmental Impact Assessment of Lignin-Based Fillers: A Comprehensive Review of Life Cycle Analysis Studies. Sustainable Materials and Technologies, 41, 101428.*

102. *Adhikari, B. and S. Majumdar (2004). "Polymers in sensor applications." Progress in polymer science 29(7): 699-766.*

103. *Fila, K., et al. (2024). "The application of chitosan as an eco-filler of polymeric composites." Adsorption 30(2): 157-165.*

104. *Hsissou, R., et al. (2021). "Polymer composite materials: A comprehensive review." Composite structures 262: 113640.*

105. *Humphreys, M. (2003). The use of polymer composites in construction. Proceedings of the CIB 2003 Int'l conference on Smart and Sustainable Built Environment, Queensland University of Technology.*

106. *Pleşa, I., et al. (2016). "Properties of polymer composites used in high-voltage applications." Polymers 8(5): 173.*

107. *Puoci, F., et al. (2008). "Polymer in agriculture: a review." Am. J. Agric. Biol. Sci 3(1): 299-314.*

108. *Sarki, J., et al. (2011). "Potential of using coconut shell particle fillers in eco-composite materials." Journal of alloys and compounds 509(5): 2381-2385.*

109. *Zhang, N., et al., Rubber-like and biodegradable poly (vinyl alcohol) composites with triple networks for high-efficiency solvent barrier. Composites Science and Technology, 2023. 231: p. 109801.*

110. *Sun, N., M. Di, and Y. Liu, Lignin-containing polyurethane elastomers with enhanced mechanical properties via hydrogen bond interactions. International Journal of Biological Macromolecules, 2021. 184: p. 1-8.*

111. *Van de Velde, K. and P. Kiekens, Biopolymers: overview of several properties and consequences on their applicatiosns. Polymer testing, 2002. 21(4): p. 433-442.*

112. *Sarki, J., et al., Potential of using coconut shell particle fillers in eco-composite materials. Journal of alloys and compounds, 2011. 509(5): p. 2381-2385.*

113. *Masłowski, M., J. Miedzianowska, and K. Strzelec, Natural rubber composites filled with crop residues as an alternative to vulcanizates with common fillers. Polymers, 2019. 11(6): p. 972.*

114. *Liao, C., et al., Synergistic modification of polylactic acid by oxidized straw fibers and degradable elastomers: A green composite with good strength and toughness. International Journal of Biological Macromolecules, 2022. 221: p. 773-783.*

115. *Kupka, V., et al., Biodegradation of polyurethane-polyhydroxybutyrate elastomeric composite investigated from morphological and structural viewpoint. Journal of Applied Polymer Science, 2019. 136(1): p. 46909.*

116. *Ghiaskar, A. and H. Taghipoor, Investigating mechanical properties and energy absorption of elastomeric polymer nanocomposites containing cellulose nanofibers in tensile, quasi-static compression, and high strain rate tests. Physica Scripta, 2024. 99(8): p. 085963.*

117. *Banerjee, S.S., et al., Water-responsive and mechanically adaptive natural rubber composites by in situ modification of mineral filler structures. The Journal of Physical Chemistry B, 2019. 123(24): p. 5168-5175.*

118. *Araujo-Morera, J., et al., Solving the Dichotomy between Self-Healing and Mechanical Properties in Rubber Composites by Combining Reinforcing and Sustainable Fillers. Macromolecular Materials and Engineering, 2022. 307(10): p. 2200261.*

119. *Yu, P.-J., Y.-C. Lin, and W.-C. Chen, Review of bioderived and biodegradable polymers/block-copolymers and their biomedical and electronic applications. Polymer Journal, 2024: p. 1-15.*

120. *Suyambulingam, Indran, et al. "Introduction to polymer composites-Historical aspects and building blocks." Sustainable Fillers/Plasticizers for Polymer Composites. Elsevier Science Ltd, 2025. 1-25.*

121. *Krishna, Ajay, et al. "Influence of wood husk and CaCO3 on the mechanical properties of nitrile butadiene rubber." Macromolecular Symposia. Vol. 402. No. 1. 2022.*

122. *Yang, Bin, et al. "Aminosilane modified graphene oxide for reinforcing nitrile butadiene rubber: Experiments and molecular dynamic simulations." Composites Science and Technology 235 (2023): 109956.*

123. *Koriem, Adel A., et al. "Management of agricultural waste to manufacture biochar: An alternative reinforcing filler for carbon black in nitrile butadiene rubber composites." Journal of Cleaner Production 428 (2023): 139360.*

124. *Rahman, Md Mahbubur, et al. "Influence of bio-based plasticizers on the properties of NBR materials." Materials 13.9 (2020): 2095.*

125. *Karthikeyan, K., S. Vishvanathperumal, and Ajith Damodaran. "Impact of halloysite nanotubes on the curing characteristics, mechanical performance, and swelling resistance of SBR/NBR nanocomposites." Journal of Polymer Research 32.2 (2025): 62.*

126. *Vishvanathperumal, S., and A. Kannan. "Effect of graphene oxide (GO) on the mechanical properties of ethylene-propylene-diene monomer/acrylonitrile butadiene rubber (EPNBR) blend composites." Journal of Polymer Research 32.4 (2025): 145.*

127. *Subramanian, N., K. Senthilvel, and B. Prabu. "Studies on the morphology and physico-mechanical properties of NBR/PVC hybrid nanocomposites." Materials Today: Proceedings 38 (2021): 2810-2816.*

128. *Subramanian, N., K. Senthilvel, and B. Prabu. "Studies on the morphology and physico-mechanical properties of NBR/PVC hybrid nanocomposites." Materials Today: Proceedings 38 (2021): 2810-2816.*

129. *Zhu, Suoshi, Jiacong Guo, and Jun Zhang. "Enhancement of mechanical strength associated with interfacial tension between barium titanate and acrylonitrile–butadiene rubber with different acrylonitrile contents by surface modification." Journal of Applied Polymer Science 135.9 (2018): 45936.*

130. *Yin, Hang, et al. "Enhancing Mechanical Properties and Oil Resistance of Carbon Black/Hydrogenated Nitrile Butadiene Rubber Composites via Tea Polyphenol-Assisted Interfacial Modification." ACS omega 10.35 (2025): 39649-39657.*

131. *Alam, Md Najib, et al. "Critical role of rubber functionalities on the mechanical and electrical responses of carbon nanotube-based electroactive rubber composites." Polymers 17.2 (2025): 127.*

132. *Arockiasamy, Felix Sahayaraj, et al. "Processing and application of bio-fillers/bio-plasticizers and their effects in polymeric composites." Sustainable Fillers/Plasticizers for Polymer Composites. Elsevier Science Ltd, 2025. 237-255.*

133. *Campos, Gustavo Ninho, et al. "Mechanical Performance Under Compressive Load of Carboxylated Nitrile Rubber and Kraft Lignin Composites." Polymer Composites (2025).*

134. *Sathishkumar, N., S. Anandha Kumar, and G. Harichandran. "Effects of Green Silica on Nitrile Butadiene Rubber Composite on Its Enhanced Mechanical Characteristics." Polymers for Advanced Technologies 36.6 (2025): e70219.*

135. *Karunanayake, Laleen, et al. "Role and potential of biochar as a sustainable alternative reinforcing filler to carbon black in rubber composites." Biochar 7.1 (2025): 1-27.*

136. *Inphonlek, Supharat, et al. "Synergistic Effects of Hybrid Bio-Fillers and Modified Natural Rubber on Natural Rubber Composite Properties." Polymers 17.5 (2025): 632.*

137. *Skosana, Sifiso John, Caroline Khoathane, and Thomas Malwela. "Driving towards sustainability: A review of natural fiber reinforced polymer composites for eco-friendly automotive light-weighting." Journal of Thermoplastic Composite Materials 38.2 (2025): 754-780.*

138. *Srinivas, J., et al. "A comparative study on the influence of nanoclay and nanosilica on the mechanical properties of NR/SBR/NBR ternary rubber nanocomposites." Journal of Polymer Research 32.5 (2025): 187.*

139. *Zheng, Hongbing, and Dongmei Yue. "Effect of carboxyl content on mechanical properties of lignin/carboxylated nitrile rubber compounds." Polymers 17.17 (2025): 2332.*

140. *Ghosh, Arun. "Enhancing the Performance of Lignin/Acrylonitrile Butadiene Hybrid Materials Using Dicarboxylic Acids." Journal of Applied Polymer Science 142.10 (2025): e56572.*

141. *Kachirayil, Antony J., et al. "Learning based model for predicting mechanical properties and sustainable filler band for NBR composites using lignin and carbon black." Materials Research Express 11.9 (2024): 095101.*

142. *Nathan, K. Senthil, et al. "Study on the effect of halloysite nanotubes on the mechanical properties and swelling resistance of ethylene-propylene diene monomer (EPDM)/nitrile butadiene rubber (NBR) blend nanocomposites." Materials Research Express 11.11 (2024): 115306.*

143. *Wang, Haixu, et al. "Lignin-reinforced nitrile rubber/poly (vinyl chloride) composites via metal coordination interactions." Industrial & Engineering Chemistry Research 58.51 (2019): 23114-23123.*

144. *Yu, Peng, et al. "Enhanced oil resistance and mechanical properties of nitrile butadiene rubber/lignin composites modified by epoxy resin." Journal of Applied Polymer Science 133.4 (2016).*

145. *Osti, Naresh C., et al. "Sustainable Shape Memory Elastomers with Reduced Melt Viscosity and Enhanced Stiffness." ACS Applied Polymer Materials 7.4 (2025): 2554-2566.*

146. *Xiao, Yao, et al. "Preparation of oil resistant and high-temperature resistant NBR composites by chitosan/silica/coupling agent modification." Polymer Engineering & Science 65.2 (2025): 492-505.*