The effect of inorganic flame-retardant fillers on the flammability properties of environmentally friendly biopolymer/sawdust fibre biocomposites

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August 2025

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DECLARATION OF INDEPENDENT WORK

DECLARATION WITH REGARD TO INDEPENDENT WORK

I, **Sylvia Tlholohelo Sikhosana**, identity number ____________ and student number _________, do hereby declare that this research project submitted to the Central University of Technology, Free State for the Doctor of Philosophy: Environmental Health, is my own independent work; and complies with the Code of Academic Integrity, as well as other relevant policies, procedures, rules and regulations of the Central University of Technology, Free State; and has not been submitted before to any institution by myself of any other person in fulfilment (or partial fulfilment) of the requirements for the attainment of any qualification.

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ABSTRACT

The rapid accumulation of biomass waste, and the effect of non-degradable materials on the ecosystem have compelled scientific communities to explore sustainable alternatives. Moreover, growing concerns about fire safety and environmental sustainability have driven significant research into bio-based flame-retardant polymer composites. This thesis focuses on repurposing agro-industrial wastes —particularly sawdust (SD) and sugarcane bagasse (SB) —as reinforcing agents in biodegradable polymer matrices such as polybutylene succinate (PBS) and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH). It therefore addresses the challenges of environmental sustainability and performance through hybrid fibre systems and inorganic flame retardants, including halloysite nanotubes (HS) and expandable graphite (EG). Both natural fibres were incorporated at 10 wt% into PBS and PHBH to develop eco-friendly hybrid composites. These composites were melt-mixed using a TE-30 co-rotating twin-screw extruder, with the heating-zone temperatures ranging from 120 to 160 °C from the hopper to the die set. To counter the inherent flammability of these materials, flame-retardant fillers, EG (only in PBS), and HNT (in both systems) were incorporated at a concentration of 3 wt%. The effects of these additives on the morphology, thermal stability, flammability, dynamic mechanical properties, and rheological behaviour of the resulting composites were investigated. Two experimental studies were conducted on reinforcing PBS and PHBH with SD and SB. In the first study, PBS was reinforced via melt compounding with SD and SB, both individually and as a hybrid composite, together with HS and EG. The rheological analysis demonstrated an increase in complex viscosity, addressing PBS's limitations in melt processing. The hybrid composite (PBS/SB/SD) exhibited improved morphology, as SD effectively encapsulated SB. More so, the hybrid composite (PBS/SB/SD) displayed enhanced morphology, as the sawdust effectively encapsulated the sugarcane bagasse. Meanwhile, HS and EG enhanced stiffness and crystallisation, although toughness and impact resistance decreased due to poor fibre-matrix adhesion. In the second study, PHBH was reinforced in a similar manner, revealing comparable trends with variations in matrix-fibre interactions. The SD exhibited better dispersion and compatibility with PHBH than the SB. Additionally, the inclusion of halloysite clay enhanced interfacial adhesion in the PHBH/SD/SB/HS hybrid composite. All composites showed improved stiffness, viscosity, and storage modulus compared to pristine PHBH, with the best thermal stability observed in the PHBH/SB/SD/HS system. Despite these enhancements in thermal and rheological properties, mechanical properties such as elongation at break and impact resilience were found to be reduced.

DEDICATIONS

- **To God**, I am eternally grateful for the gift of life, your endless mercy, and unwavering love. Through every challenge, you have been my strength and guide, illuminating my path with your wisdom and grace. Your unfailing support has been my anchor, and your blessings have sustained me throughout this journey. I dedicate this milestone to you, my Creator, who makes all things possible. Thank you for walking with me every step of the way and for your boundless faithfulness that has never wavered.

- **To my beloved daughters, Palesa Meva, Tshiamo Sikhosana, and Khumo Sikhosana**, I am deeply grateful for your unwavering love, support, and understanding throughout this journey. Your patience and encouragement have been a constant source of strength, and I truly could not have done this without you. In every challenge, you stood by me with smiles and comforting words. God has listened to the sincere prayers from your hearts, and through His grace, He has granted your wishes. This achievement is not just mine; it is **ours**.

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ABBREVIATIONS AND SYMBOLS

pH	Acidity or Basicity	T_c	Cooling Temperature
Al_2O_3	Aluminum oxide	pKa	Acid dissociation constant
As^{5+}	Arsenate	A	Alpha
As^{3+}	Arsenite	Θ	Angle
Cd^{2+}	Cadmium ions	$\approx$	Approximately
$Ca(OH)_2$	Calcium hydroxide	@	At
Ca^{2+}.	Calcium ion	B	Beta
CaO	Calcium oxide	CP	Centipoise unit/viscosity
CO_2	Carbon dioxide	η^*	Complex viscosity
Co	Carbon Monoxide	°C	Degrees Celsius
Cr^{3+}	Chromium (III)	~	Equivalent
EVA	Ethylene vinyl acetate	GPa	Gigapascals
EP	Ethylene-propylene copolymer	T_g	Glass transition temperature
Fe	Iron	G	Grams
Fe_2O_3	Iron (III) oxide or ferric oxide	g/cm	Grams per centimetre (often appears as g/cm^3 for density or g/cm^2 for area mass density)
La_2O_3	Lanthanum (III) oxide or lanthana	g/mol	Grams per mole
Pb^{2+}	Lead ions	Hz	Hertz
Mg^{2+}	Magnesium ion	kg/hr	Kilograms per hour
Mn	Manganese	KJ/m^2	Kilojoules per square meter
BRN	Metaverse	kN	Kilonewton
MDL	Moldovan Leu	kN	Kilonewton
Viz.	namely" or "more specifically	MPa	Mega Pascals
Ni^{2+}	Nickel ion	Mm	Micrometer
P_2O_5	Phosphorus pentoxide	Mg	Milligrams
PP	Polypropylene	mL/min	Millilitres per minute

PS	Polystyrene	mm	Millimetre
K^+	Potassium	nm	Nanometre
KOH	Potassium hydroxide	%	Percentage
K_2O	Potassium oxide	rpm	Revolutions per minute
SiO_2	Silicon dioxide	ε_b	Strain at break
UV	Ultraviolet	σ_b	Stress at break
H_2O	Water	σ_y	Stress at yield
Zn^{2+}	Zink ions	™	Trademark
ZrO_2	Zirconium oxide or zirconia	wt.%	Weight percentage or percentage by weight
		E	Young's modulus

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CHAPTER 1

Introduction

1.1. General overview

1.1.1. Agricultural waste: farming and forestry residues

Modern agricultural technology has undoubtedly increased crop production. It has also brought about adverse effects on the environment, society, and the economy. Agricultural development often leads to waste from intensive farming methods and chemical abuse, significantly impacting rural and global environments (Obi *et al*., 2016; Phiri *et al*., 2023). Agricultural activities generate significant amounts of waste, with humans producing 150 billion metric tonnes annually through intensive farming, harvesting, cultivation, and related industrial processes (Phiri *et al*., 2023). Due to limited financial and technical resources for harvesting, storage, and cooling, underdeveloped countries generate large amounts of waste from very early in the supply chain. Regrettably, only small portions of agro-industrial waste are repurposed, with most of it being improperly disposed of through random burning or landfilling. These practices present significant environmental and health risks, such as soil and water contamination, air pollution from decomposition gases, and the depletion of potentially valuable resources (Dey *et al*., 2021; Obi *et al*., 2016; Phiri *et al*., 2023). Notably, the agricultural sector is responsible for producing about 21-37% of greenhouse gases (Bala *et al*., 2023).

The growing concerns about environmental sustainability and depletion of natural resources have therefore led to increased emphasis on effective agro-waste management and valorisation. Agricultural waste valorisation involves reusing and recycling waste into valuable products or energy rather than treating it as a disposable byproduct. This approach not only reduces waste and emissions but also creates value through environmental conservation efforts. Waste valorisation and repurposing are global trends that help reduce landfill waste while conserving natural resources by converting waste into useful products, thereby reducing the demand for new raw materials. Agro-industrial residues have the potential to produce sustainable energy and bio-products as illustrated in **Figure 1.1**. When treated properly, biowaste can be used for energy generation, soil enrichment, and pollution control. It can also be utilised in various applications such as bio-based composites, biodegradable packaging, biofuels, fertilisers, animal feed, and as a source of cellulose for textiles and paper products. Additionally, it can be used in wastewater treatment, bioplastics, and in the development of flame-retardant materials and eco-friendly insulation for buildings. Recently, nanotechnological and biotechnological innovations have emerged as green approaches to improve the stability and utility of agricultural food waste, further advancing waste valuation efforts (Capanoglu *et al*., 2022; Giurea *et al*., 2024; Rana *et al*., 2024).

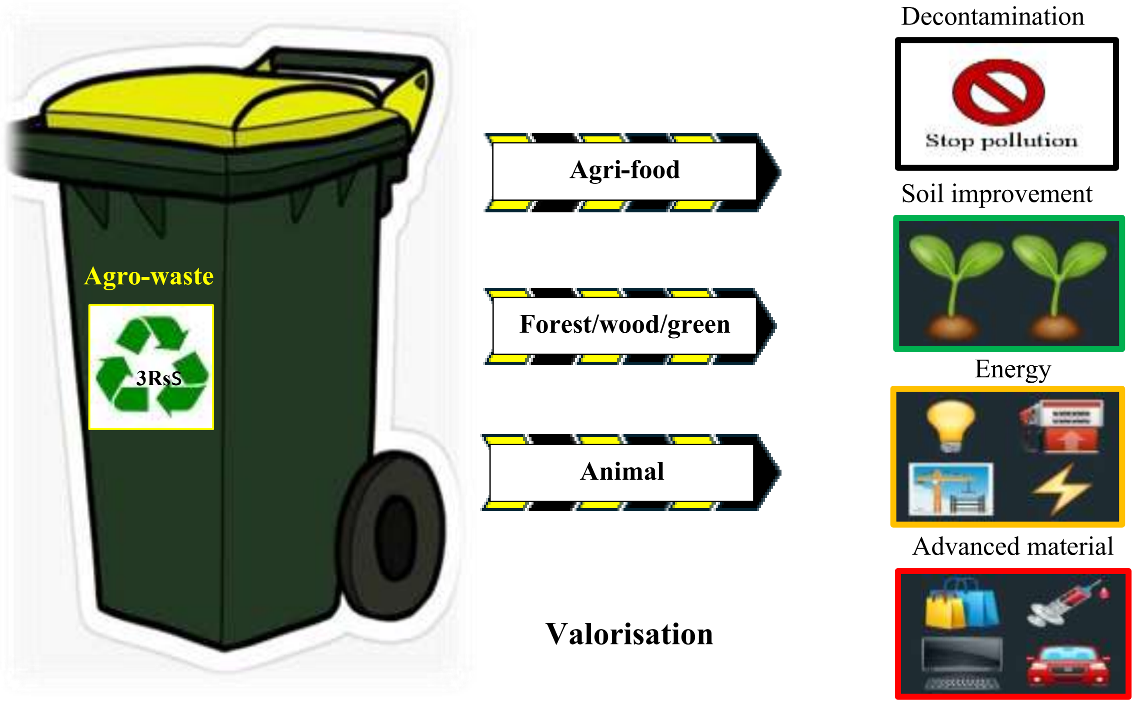

Figure 1.1. Valorisation and repurposing of agricultural waste

Agricultural waste, which includes farming and forestry residues, can be categorised into different groups, each with unique sources and characteristics. These include biosolids, animal wastes, plant biomass, wood, and green wastes, each derived from various activities. Observably, plant biomass makes up a big portion of the biowaste, particularly in agrarian economies. Agricultural residues, such as sugarcane bagasse, rice and wheat straw, corn stover, and rice husks, are often left in fields after harvest, where they are used for fodder, landfill material, or simply incinerated. Forestry operations and urban landscaping generate significant amounts of wood and green waste, such as tree branches, bark, sawdust, and leaves. These materials often end up in landfills or are incinerated, but they can be repurposed into valuable bio-products (Dey *et al*., 2021; Ginni *et al*., 2021). Lignocellulosic biomass comprises a significant portion of agricultural waste, consisting of approximately 35%–55% cellulose, 25%–40% hemicellulose, and 15%–25% lignin, in addition to small amounts of extractives, protein, and ash (Bala *et al*., 2023). The specific composition of these components varies based on factors such as plant species, growth conditions, biomass age, and the specific part of the plant used. Also, environmental factors like climate, soil quality, and harvesting methods can also influence the proportion of cellulose, hemicellulose, and lignin in the biomass. Various technologies are available for converting and utilising agrowaste, including physical methods such as grinding and pyrolysis, chemical processes such as alkali or acid hydrolysis, biological treatments involving enzymes or bacteria, and the use of green solvents like ionic liquids. Products obtained from the valorisation of agro-waste include biochar (used for soil enhancement and carbon sequestration), cellulose (for bioplastics, paper, and textiles), lignin (for adhesives and biofuels), and bioethanol (a renewable fuel); thus demonstrating their potential applications in sustainable agriculture, energy, and material sciences (Bala *et al*., 2023; Dey *et al*., 2021; Xu *et al*., 2018).

1.1.2. Polymers derived from biomass

Two main opportunities for deriving value from agricultural waste have been identified: recycling non-organic materials and improving the management of organic waste, such as biomass. With its rich structural and chemical composition and easily tunable properties, agro-waste serves as an ideal source of building block for biopolymers and can effectively function as a matrix, reinforcement, or filler in composite materials (Vianna *et al*., 2024). Commercial biopolymers (**Figure 1.2**) can be produced directly from natural materials such as cellulose or starch, or through the fermentation and polymerisation of bio-based monomers (De *et al*., 2023). Common examples include polylactic acid (PLA), polyhydroxyalkanoates (PHAs), polybutylene succinate (PBS) which are produced using corn starch, microbial fermentation, and bio-based succinic acid, respectively. Additionally, cellulose-based biopolymers extracted from plant cell walls and polycaprolactone (PCL), a biodegradable polyester, are frequently used in various sustainable applications. They consist of long chains of repeating units, typically featuring elements like carbon, hydrogen, oxygen, and occasionally nitrogen or sulphur. Biopolymers are biodegradable and present a sustainable alternative to fossil-based polymers, thus offer reduced environmental impact and a lower carbon footprint. Biopolymers can be classified by origin, monomeric units, and properties such as heat responsiveness. These materials can be used to create environmentally friendly biocomposites by incorporating various organic and inorganic fillers or reinforcements using different fabrication methods, including compression moulding, injection moulding, extrusion, and resin transfer moulding, among others (Phiri *et al*., 2023; Naser *et al*., 2021).

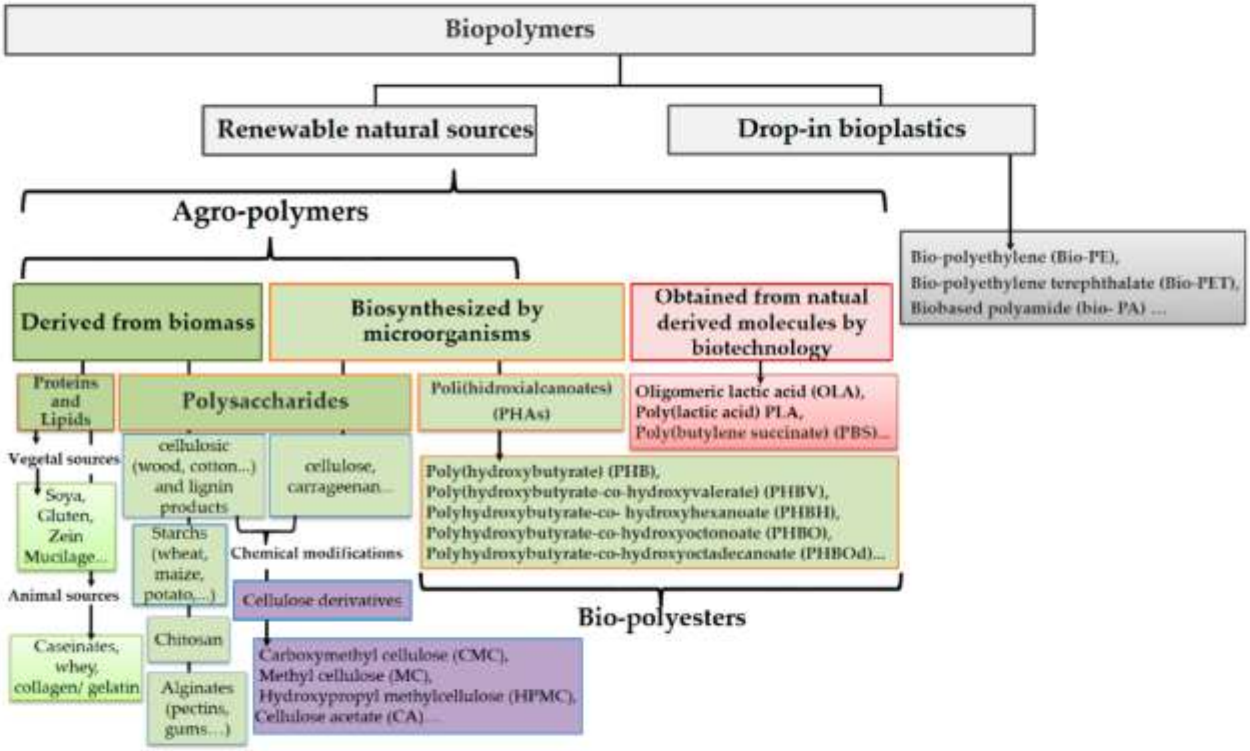

Figure 1.2. Classes of biopolymers and their method of synthesis (Balart *et al*., 2021) Open access

1.1.3. Organic fillers

When processed into fine particulate powders, agro-waste materials exhibit significant potential as fillers in biopolymer composite materials, which improve the properties of biopolymer matrices that render them inferior for advanced applications. Moreover, these natural materials can be chemically modified to enhance their compatibility with various matrices, improving the overall performance of the composite (Khalid *et al*., 2021; Ortega *et al*., 2021). Fillers can be either reinforcing or non-reinforcing, depending on their intended purpose (Saleh *et al*., 2019). Even in minute quantities (e.g., from 0.5%), these processed materials offer promising mechanical and structural enhancements, making them viable alternatives to conventional reinforcement materials in various applications (Kandpal *et al***.**, 2021). Typically, examples include cellulose, lignin, and biochar as presented in **Figure 1.3**. In their natural states, these materials play critical structural and protective roles. For instance, cellulose, a primary component of plant cell walls, provides mechanical strength and rigidity. Lignin, found in the spaces between plant cell walls, thereby acting as a binder, giving plants structural integrity and resistance to environmental stresses. In addition, biochar, a product of biomass pyrolysis, is a carbon-rich material that enhances soil fertility and sequesters carbon in nature. When incorporated into a composite matrix, these agro-waste derivatives transfer similar properties: cellulose contributes to mechanical strength, lignin improves bonding and durability, and biochar enhances thermal stability and possibly provides fire resistance due to its carbon content (Joseph & Babaremu, 2019; Ortega *et al*., 2021).

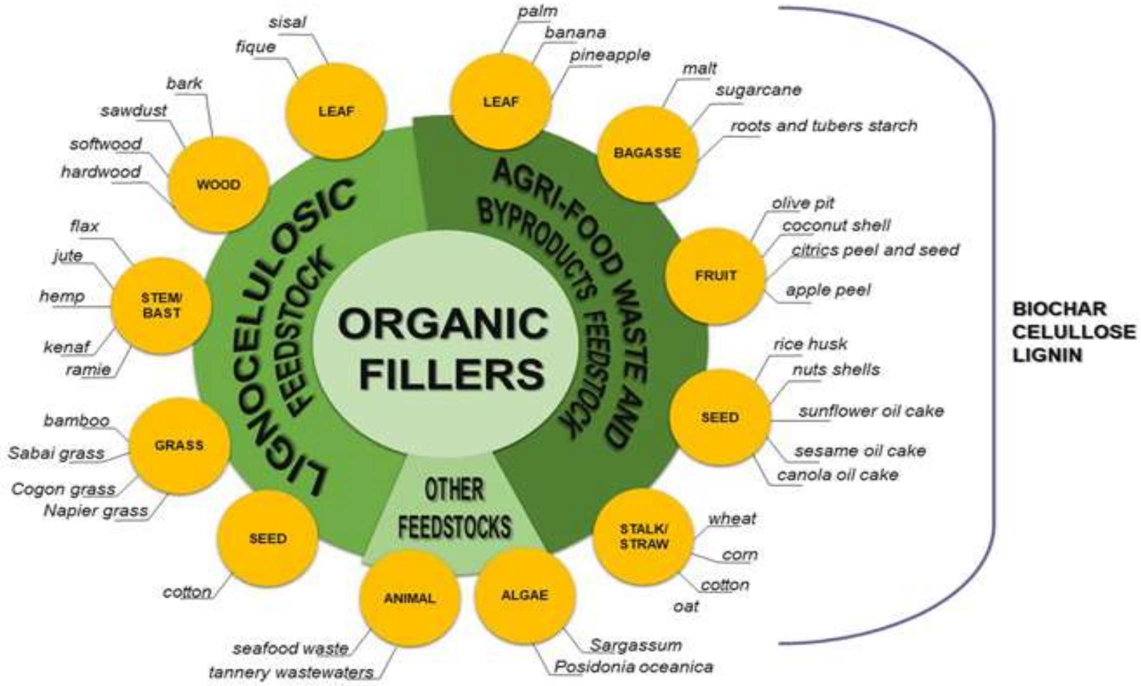

Figure 1.3. Main sources and examples of organic fillers (Ortega *et al*., 2021) Open access

1.1.4. Flame retardant-biocomposites

Composites made of natural fibres and bioplastics are becoming increasingly popular due to the rising environmental awareness, concerns for environmental sustainability, and the growing global waste problem. The shift towards using more environmentally friendly materials will help preserve ecological balance by reducing non-biodegradable waste through reuse (Orgeta *et al*., 2021; Sindhu *et al*., 2014; Xie *et al*., 2016). Significant progress has been made in creating biodegradable plastics from renewable sources, resulting in biodegradable materials with properties similar to oil-based polymers. As a result, fibre-reinforced biopolymer composites are being utilised in various applications as viable alternatives (Kumar *et al*., 2017; Singh *et al*., 2023). These composites offer advantages such as high stiffness, increased strength, better fatigue performance, improved corrosion resistance, low thermal expansion, low energy consumption during manufacturing, and nonmagnetic properties. However, a major drawback of fibre-reinforced composites is their susceptibility to heat and flame damage (Mazela *et al*., 2020; Mochane *et al*., 2019). The high flammability of these composites is largely influenced by the presence of cellulose and volatile compounds found in plant fibres and biopolymers (Phonphuak & Chindapracirt, 2015). Likewise, their use in advanced engineering applications is limited due to the risk of igniting during a fire, thus failing to satisfy strict industry fire protection standards. Therefore, research is needed to develop and introduce flame-retardants in the polymer-fibre matrices to enhance their flame resistance (Kmeťová *et al*., 2024; Mazela *et al*., 2020; Mochane *et al*., 2019; Murad *et al*., 2025; Shamsuri *et al*., 2023).

In the past, halogenated fire retardants have produced excellent results, but their major drawback is their potential to cause toxicity and damage environment when burned. The implementation of regulatory standards requires more environmentally friendly products; hence research initiatives have focused on the development of inorganic, non-hazardous fire retardants. Inorganic flame protective fillers possess exceptional thermophysical and mechanical properties (Feng *et al*., 2023). They are low-density carbon materials with a range of unique properties including developed specific surface, binder-free pressing capacity, stability to aggressive media, and low thermal conductivity. Many inorganic fire-retardant additives, such as expandable graphite (EG), clays, and phytic acid, act as intumescents. Intumescents create a voluminous, insulating protective layer through carbonisation and simultaneous foaming, preventing material combustion during a fire (Mazela *et al*., 2020; Mngomezulu *et al*., 2018; Spieß *et al*., 2021). **Figure 1.4** presents a graphic detail of intumescent flame-retardant filler. In cases where their protective prowess is insufficient for the intended purpose, one or more supporting additives can be included for a synergistic effect. The combined effect of flame-retardant fillers in natural fibre-reinforced materials enhances the flammability resistance of the composite more effectively than a single flame-retardant agent (Mochane *et al*., 2019). While it is important to identify and incorporate suitable flame-retardant additives, it is also crucial to ensure that they are compatible with the system because incompatibility can have a negative impact on the mechanical properties of the composites. It is noteworthy that inorganic fillers can potentially affect not only the combustion properties but also the general properties of the hybrid system. They are a promising class of materials for use in both research and industry (Chun *et al*., 2020; Mochane *et al*., 2019; Spieß *et al*., 2021). Although numerous studies have been conducted, there are still many gaps in fire retardant applications where innovative solutions such as an additional carbon source (lignin, starch, graphite, *etc*.) could be used in biopolymer systems (Chun *et al*., 2020; Mazela *et al*., 2020). Therefore, this study seeks to repurpose farming and forestry waste, specifically sugarcane bagasse and sawdust, through the production of flame-retardant biopolymer composites by incorporating inorganic fillers for use in advanced applications.

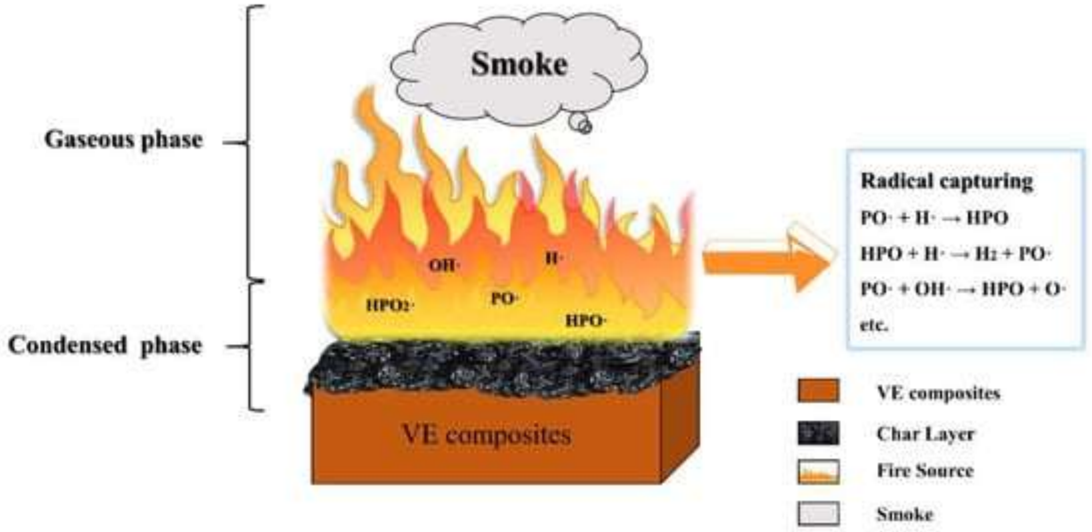

Figure 1.4. The mechanism of an intumescent flame-retardant filler (Xu *et al*., 2022) Open access

1.2. Research problem

Improper disposal and accumulation of lignocellulose waste lead to water effluent acidification and increased chemical oxygen demand, land contamination by leachates, and the emission of greenhouse gases into the atmosphere (Hallers *et al*., 2021; Mohanty *et al*., 2016; Wibowo *et al*., 2023). The high toxicity and enormous amount of polluted materials pose hurdles to remediation efforts (Hallers *et al*., 2021), creating a breeding ground for pests and diseases (Wibowo *et al*., 2023).

The sub-problems in relation to the problem statement are shown below.

(i) Lignocellulosic materials are environmentally friendly but very combustible, limiting their use in advanced applications. Thermal decomposition releases flammable volatiles, and evenly integrating flame-retardant chemicals is difficult due to their hydrophilicity. Moreover, high flame-retardant loadings can compromise mechanical properties, posing challenges in meeting fire safety regulations (Mazela *et al*., 2020; Mochane *et al*., 2019).

(ii) Blending fibres, polymers, and flame retardants are crucial for achieving desired material properties when making fibre-reinforced polymer composites. However, immiscibility, where components do not mix well, can significantly affect performance and the distribution of flame-retardant additives. Over time, phase separation can worsen due to environmental factors, reducing the durability of the material (Chun *et al*., 2020; Mochane *et al*., 2019; Spieß *et al*., 2021).

1.3. Research aims

The study aims to investigate the effect of halloysite (HS) and expandable graphite (EG) and their synergy on the properties of biopolymer composites, including polybutylene succinate (PBS) and Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH), reinforced with sawdust and sugarcane bagasse fibres.

1.4. Research objectives

The research objectives for this study are to present:

(i) Expandable graphite on the flammability properties of PBS/Sawdust fibres composites.
(ii) Clay on the flammability properties of PBS/Sawdust fibre composites.
(iii) Phytic acid on flammability properties of PBS/Sawdust fibre composites.
(iv) Expandable graphite on the flammability properties of PBS/Sawdust fibre/Sugarcane bagasse composites.
(v) Clay on the flammability properties of PBS/Sawdust fibre/sugarcane bagasse composites.
(vi) Phytic acid on flammability properties of PBS/Sawdust fibre/sugarcane bagasse composites.
(vii) Synergistic effect of the above inorganic fillers on the flammability properties of PBS/Sawdust fibre composites.

The same objectives above will be applied to PHBH.

1.5. Thesis organisation

This thesis is divided into eight chapters. Chapter 1 introduces the research problem, objectives, and scope of the study. Chapter 2 presents a focused discussion on phytic acid, highlighting its relevance and application as a bio-based flame retardant. Both chapters two and three are literature reviews. While chapter 3 examines sawdust as a natural fibre for polymer composites, chapter 4 explores the potential of sugarcane bagasse as a reinforcing filler. Chapters 5 through 7 comprise the core experimental work. Chapter 5 investigates PBS-based composites that incorporate natural fibre fillers. Chapter 6 focuses on PHBH-based systems, and chapter 7 evaluates the flammability performance of the developed composites across both matrix systems. In chapter 8, the researcher synthesises the main findings, draws overarching conclusions, and outlines recommendations for future research.

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CHAPTER 2

Phytic acid: A novel phosphate bio-based flame retardant

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Abstract

The development and application of sustainable flame-retardant agents have become a research hotspot due to the urgent need for eco-friendly materials and the demand for a sustainable environmental protection. Phytic acid has gained popularity as a natural substance that is present in plant seeds with the potential to be a bio-based flame retardant. Its distinct structure, which consists of six phosphate groups, connected to a myoinositol core, confers inherent flame retardancy, making it a suitable candidate for fire safety in polymeric materials. Phytic acid can be added to polymer matrices through physical mixing, chemical grafting, or covalent bonding. This alters the thermal and mechanical properties of the resulting flame-retardant composite, as well as its fire performance. Ongoing research aims to maximize the potential of phytic acid in different polymeric systems, with the goal of creating safe, eco-friendly, and sustainable materials for fire safety applications in fields, such as: construction, automotive, electronics, and textiles.

Keywords: Phytic acid; biobased filler; phosphate; flame retardancy; synergy

2.1. Introduction

Flame retardants refer to a class of materials that are specifically created to decrease the flammability of other materials (Babrauskas *et al*., 2014). Flame retardant materials are widely used to enhance fire safety and adhere to fire safety rules and regulations in various products and materials, such as: plastics, textiles, electronics, furniture, and building materials. These materials have, the abilities to halt the combustion process, create a protection heat shield, and emit gases that extinguish flames when exposed to high temperatures. The importance of these materials cannot be overstated, since they play a critical role in increasing fire safety across various settings, including homes, workplaces, public areas, and numerous industries. They provide occupants with additional time for effective evacuation and firefighting efforts and this extra time has been proven to be extremely crucial (Babrauskas *et al*., 2014; Hull *et al*., 2011; Shen *et al*, 2022; Trovato *et al*., 2023). Some industries are governed by stringent fire safety rules that necessitate the use of flame-retardant materials for certain applications. Manufacturers can use flame retardants to comply with certain laws and standards (Yang *et al*., 2021). Since most polymer materials burn easily, they are usually mixed with flame retardants to ensure their safe usage (Babrauskas *et al*., 2014; Kim *et al*., 2021). The addition of flame retardants is crucial in improving the fire resistance of flammable polymers. These materials help lower the potential for polymer combustion and the production of toxic fumes, which are essential for the safe development and use of new materials (Hull *et al*., 2011; Krishnadevi & Selvaraj, 2015; Yang *et al*., 2019). In the past, halogenated fire-retardant fillers were commonly used because of their effectiveness in preventing fires. However, they have several significant drawbacks and environmental concerns. Halogenated compounds remain in the environment for a long time after their disposal and they can release harmful substances into the air and water, leading to pollution and posing long-term risks to ecosystems. Additionally, some fire-retardant fillers containing halogens, e.g., chlorinated or brominated compounds, have been found to contribute to ozone depletion, if released into the atmosphere. As a result, they have been subject to regulatory restrictions and have been phased out or banned (Chen *et al*., 2019; Hull *et al*., 2011; Mazela *et al*., 2020; Yang *et al*., 2019; Yang *et al*., 2021). Lately, there has been a shift towards creating and utilizing halogen-free substitutes for flame-retardant fillers. Both the industry and academia are making efforts to develop more ecofriendly and sustainable flame-retardant materials (Ahmad *et al*., 2022). These alternatives are better for the environment, and they pose fewer health risks, while providing sufficient and effective fire protection. One effective method for achieving the necessary flame-retardant properties is to incorporate additives that contain nitrogen, phosphorous, or silica. Research on various bio-based materials, such as: chitosan, lignin, phytic acid, polydopamine, tannic acid, and *β*-cyclodextrin, has gained considerable attention from different bio-based research groups. Due to its intrinsic phosphate-based flame-retardant characteristics and its renewable origin, phytic acid has emerged as a particularly fascinating alternative among these choices (Ahmad *et al*., 2022; He *et al*., 2021; Mazela *et al*., 2020; Velencoso *et al*., 2018; Wang *et al*., 2022). The purpose of this chapter is to explore the potential of phytic acid in creating sustainable and high-performing flame-retardant materials. The chapter discusses the history of phytic acid and its reinforcement with polymers and/or polymer/fibre composites.

2.2. History: Phytic acid: A novel phosphate bio-based flame retardant and its applications

Pfeffer was, in 1872, the first to recognise phytic acid, which is also known as inositol hexakisphosphate (IP6), inositol polyphosphate, or phytate when in the salt form, and in 1903, Posternak introduced the word "phytine". Nassar *et al*. (2021) reported that in 1914, Anderson, (1914) was the first scientist to describe the structure of IP6. Subsequently, in 1969, Johnson and Tate confirmed this structural depiction by using the nuclear magnetic resonance spectroscopy Nassar *et al*. (2021), reported that IP6 is a saturated cyclic acid and the phosphate ester of inositol, which has a high density of negative charges due to its six phosphate groups that become partially ionized at a physiological pH, where the negative charges are counter-balanced by cations. Nassar *et al*. (2021) further explained that IP6 is in abundance in plants and that it has a significant nutritional role, acting as the principal storage form of phosphorus in many plant tissues, especially bran and seeds. Reddy *et al*. (1982) and Schlemmer *et al*. (2009) further explained that IP6 is a source of myoinositol as in animal cells since it has a high concentration, ranging from 10 to 100 μM in Mammalian cells and this depends on factors, such as the cell type and developmental stage. Schlemmer *et al*. (2009) and Gupta *et al*. (2015), have reported that due to the IP6 strong binding affinity to dietary minerals, it also serves as a potent nutrient. However, other studies have indicated that when iron or zinc binds to IP6, insoluble precipitates are formed, contributing to the deficiencies of these elements in people whose diets rely on foods for their mineral intake. In the year 1983, Graf, played a significant role in researching the characteristics and potential applications of IP6. Notably, Graf was among the pioneering researchers to provide an extensive account of the metal chelation and antioxidant properties that are associated with IP6. Graf's research highlighted the merits of IP6, including its cost-effectiveness, inert nature, non-toxicity, and its abundance (Graf, 1983; Nassar *et al*., 2021). Moreover, it could be easily obtained from various plant sources, through the relatively straightforward procedures (Chen *et al*., 2019).

Despite the limited existing research, Nassar *et al*. (2021) reported indications of IP6's potential in oral care applications. Graf (1983) demonstrated that IP6 possesses the capability to enhance the physical and chemical attributes of dental cements when used as an additive. Prosser *et al*. (1983) study, concluded that the resultant cement low vulnerability to early attack by water and acid, as well as the better adhesion to enamel when compared with dentine, are due to the lower mineral content of the latter. The mechanical properties of zinc phosphate cements (Posternak,1903), also improved with the addition of IP6. The study demonstrated that by increasing the IP6 concentration from 0 to 2%, resulted in a doubling of the compressive strength (Nassar *et al*., 2021). Substituting a portion of phosphoric acid with between 3–5% IP6, yielded the maximum compressive strength achievable (Nassar *et al*., 2021). Gbureck *et al*. (2004), reported that the addition of IP6 alone, triggered a swift reaction and brought about a short and controllable setting time. By adjusting the ratio of IP6 to phosphoric acid or by manipulating the water content, allowed for achieving a more practical setting time.

Ongoing clinical trials are actively working on advancing these attributes (Gbureck *et al*., 2004; Posternak,1903). In 2017, a study by Meininger *et al*. (2017) highlighted that IP6 exhibited a setting-retarding effect on di-calcium phosphate cements. This effect was crucial to meet the clinical requirement for cement handling time, which typically sets in less than a minute in an environment without retardants. Meininger *et al*. (2017) suggested that IP6 achieves this outcome by absorbing di-calcium phosphate crystals within the cement, thereby slowing down the crystal growth and reducing the maximum temperature reached during the setting process. In the context of brushite cements, IP6 was utilized as a retarder to achieve the highest cement strength, hence resulting in values surpassing those attained with retardant-free cement. Furthermore, Meininger *et al*., (2017), emphasized the fact that cements incorporating with IP6, displayed a notably improved compatibility with osteoblast cells in comparison to citric-acid-containing cement. Furthermore, research that was conducted by Hurle *et al*. in 2018 focused on the influence of IP6 on the hydration mechanism and setting kinetics of brushite cements (Velencoso *et al*., 2018). Their findings were consistent with the observations of Meininger *et al*. (2017) and Hurle *et al*., (2018), demonstrating that controlled concentrations of IP6 acted as a retarder for the cement setting reaction. This effect translated to enhanced mechanical performance, as reported by Hurle *et al*. (2018), resulting in a cement that was composed of a crystalline structure, known as monetite. In 2015, phytic acid (IP6) was introduced as a natural chelating agent to assist in overcoming the deleterious effects of Ethylenediaminetetaacetic acid (EDTA). It has shown various benefits in medicine and the food industry as a preservative. It is claimed to possess anti-cariogenic and anti-plaque effects because of its inherent ability to prevent dissolution of enamel (Afshan *et al*., 2020). Moreover, it was reported that IP6 is more biocompatible and less cytotoxic than EDTA with considerable smear layer removal ability (He *et al*., 2020).

In a recent report, Afshan *et al*. (2020) indicated that due to these advantages, 1% IP6 was proposed as an alternative chelating agent. Properties, such as: its effect on microhardness, its removal ability of in-tracanal medication, effect on dentine bond, chelating efficacy, calcium loss from root dentine, effect on dental pulp stem cells, effect on calcium silicate-based cements, antimicrobial effect and its role in regenerative endodontics, have been reported previously by Afshan *et al*. (2020). However, literature on its erosive potential and smear removal ability of a 1% IP6, was reported (Kalçay, 2018). Kalçay (2018) reported on a better erosion performance of dentine with a 1% IP6 when compared to a 17% EDTA. Nassar *et al*. (2021) reported equal or better smear removal of IP6 when compared to 17% EDTA. In contrast, however, Jagzap *et al*. (2017) reported a less effective smear removal by IP6. This contrary evidence warrants a study on IP6 with a known pH. Therefore, the objective of this study was to compare the erosive potential and smear layer removal ability of a pH=3, 1% IP6 with 17% EDTA, by using both as final irrigants at different time intervals (Afshan *et al*., 2020). Boot *et al*. (2021) reported that the phytic acid extraction methods may be applied to various types of grain, as well as biological and vegetable sources. The extraction method includes phytic acid solubilization and acidic dissociation from related proteins or mixed salts. Phytic acid is largely ionized under physiological pH conditions, thereby, becoming negatively charged and thus, reacting easily with positively charged substances, e.g., proteins. Based on the forementioned, different phytic acid extraction conditions have been studied by using different acid solutions.

In 1970, Wheeler and Ferrel conducted the first studies on the investigation of organic phosphorus extraction from wheat and wheat fractions and they found out that 0.3 mol L^{-1} trichloroacetic acid (50 mL), under mechanical shaking for 30 min or occasional manual swirling for 45 min, was more extraction-efficient than 6 mol L^{-1} hydrochloric acid, extracting ~88% of total phosphorus. There has been recent potential industry application, i.e., the use of phytic acid for imparting long-lasting flame-retardant properties to fabrics (Wheeler & Ferrel, 1971). Bloot *et al.* (2021) reported on the different approaches, based on the use of phytic acid as a bio-based phosphorus flame retardant that have been applied to develop fabrics, such as: cotton, wool, silk, cellulosic fibres, and nonwoven fabric with flame retardant properties or heat and smoke suppressing ability (Cheng *et al.*, 2016; Cheng *et al.*, 2017; Cheng *et al.*, 2019; Cheng *et al.*, 2020; Liu *et al.*, 2018; Thota *et al.*, 2019; Zhou *et al.*, 2020). In conclusion, the historical path of flame-retardant development has seen remarkable shifts towards the environmentally friendly and sustainable solutions. The emergence of phytic acid as a novel phosphate bio-based flame retardant, represents a significant milestone in this journey. With its roots in traditional practices and its application in modern research, phytic acid offers a unique blend of historical wisdom and scientific innovations.

2.3. Structure and properties

Phytic acid (PA) is a natural plant compound, known as Myo-inositol-1,2,3,4,5,6-hexakisphosphate, and **Figure 2.1** shows its structure. It can be found in different forms because it possesses 12 interchangeable protons that enable it to interact with multivalent cations and positively charged proteins. One of the several myo-inositol (Ins) phosphorylated derivatives, is classified as a cyclic alcohol that offers the carbon backbones that are required for phytic acid production. The chemical formula for phytic acid is: $C_6H_{18}O_{24}P_6$, and it has a molar mass of 660.04 g mol. The phosphate groups are axially connected to carbons 1, 3, 4, 5, and 6 and equatorially bonded to carbon 2, according to X-ray crystallographic study (Feil, 2001; Nissar *et al.*, 2017; Oatway *et al.*, 2001; Sarkhel & Roy, 2022; Wang & Guo, 2021).

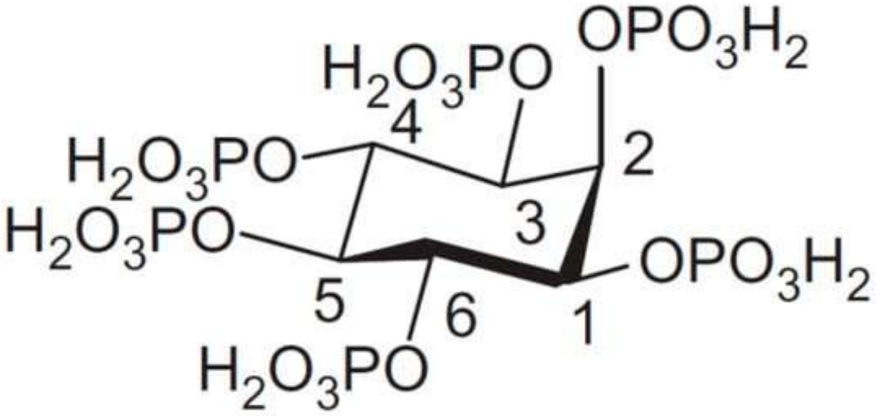

Figure 2.1. Basic structure of phytic acid (Marolt & Kolar, 2021) Open access

The calcium salt of PA is called phytate, while the calcium/magnesium salt is known as phytin. In accordance with the physiological pH and the metal ions available, phytic acid can exist as free acid, phytate, or phytin. Most of the work done on phytic acid systems, has utilized interchangeably, these types of phytic acid. Inositol and inorganic phosphates are produced when phytic acid is completely hydrolyzed. Because the phytic acid molecule is inert and extremely stable, it may be kept as a solid for months or years in neutral or alkaline aqueous solutions, without producing any by-products of breakdown (Bloot *et al*., 2021; Feil, 2001; Oatway *et al*., 2001). Phytic acid exhibits a significant affinity with polyvalent cations in the declining stability order, shown below: Cu^{2+} is followed by Zn^{2+}, Ni^{2+}, Co, Mn, Fe, and Ca. Such cations are chelated by phytic acid, resulting in the formation of water-insoluble phytate salts. The most prevalent mono- and divalent cations, are K^+, Mg^{2+}, and Ca^{2+}. Protein and starch can interact with phytic acid, either directly or indirectly. For many years, phytic acid was regarded as an anti-nutrient. However, several research, using both human and animal models, have shown how phytic acid can prevent a variety of diseases. In the eukaryotic species, phytic acid is everywhere, and lower in concentrations of myo-inositol with fewer phosphate groups (IP1-5) and are important for controlling crucial cellular processes, such as: cell division, cellular differentiation, exocytosis, and endocytosis (Hídvég & Lásztity, 2002; Nissar *et al*., 2017; Sarkhel & Roy, 2022; Wang & Guo, 2021). **Table 2.1** illustrates the physiochemical properties of phytic acid.

Table 2.1. Physiochemical properties of phytic acid (Nissar *et al*., 2017; Marolt & Kolar, 2017; Hussain *et al*., 2021)

Molecular Formula	$C_6H_{18}O_{24}P_6$
Molar Mass	660.04 g/moℓ
Density	1.432g/mL at 25°C
Melting Point	<25°C
Boiling Point	105°C
Flash Point	673.9°C
Solubility	It is soluble in water, ethanol, and acetone but almost insoluble in ether, benzene, and chloroform.
Vapor Pressure	0.039Pa at 60°C
Appearance	Light yellow to light brown serous liquid.
Specific Gravity	1.282
Merck	14,7387
pKa	1.13±0.10 (Predicted)
BRN	2201952
Storage Condition	2-8°C
Refractive Index	*n*20/D 1.4
MDL	MFCD00082309
Physical and Chemical Properties	Trait light yellow to light brown serous liquid. Soluble in water, ethanol and acetone, almost insoluble in ether, benzene and chloroform.

2.4. Phytic acid/polymer composites

To evaluate the effectiveness of flame-retardant properties on polymers, various tests, such as the: limiting oxygen index (LOI), vertical burning test (UL 94), thermogravimetric analysis (TGA), and the cone calorimeter tests are conducted. The LOI measures the minimum oxygen needed to support the burning of a polymer; it happens in a controlled atmospheric environment (Liu *et al*., 2021). High values of LOI, results in the best performance of flame retardancy. The UL 94 test measures the flammability of plastic materials. UL 94 has various ratings that are used to explain its results. These ratings include, *viz*: V-0 (flame extinguishes within 10 seconds with no flame drippings), V-1 (flame burns out within 30 seconds with no flame drippings) and V-2 (burns out within 30 seconds with drippings). For the best flame retardancy results, the material needs to attain a V-0 UL 94 rating (Marti *et al*., 2018). The thermogravimetric analysis measures the changes in weight (thermal degradation) of a material when heated in controlled atmospheric conditions (Ng *et al.*, 2018). The monitored changes in weight of a sample are then, recorded down so that they can be plotted against time and/or temperature in order to derive/generate the TGA curve (Hull *et al*., 2011). The cone calorimeter tests are used to measure the fire response behaviors of materials (Schartel & Hull, 2007). It relies on the fact that the heat release from the combustion of a material is dependent on the oxygen needed to sustain the combustion. It measures parameters, such as: the heat release rate (HRR), peak heat release rate (PHRR), total heat release (THR), temperature of maximum heat release rate (T_{max}), ignition time, flame spread, smoke production, and other parameters related to the combustion process of a material (Schartel *et al*., 2005; Schartel & Hull, 2007). A recent study on phytic acid (PA) conducted by Cheng *et al*. (2016), showed that PA greatly improved the flame-retardant properties of polylactic acid (PLA) fabric. The untreated PLA fabric exhibited an LOI value of 26.3% and the PLA that was treated with 250 g/L (PLA-250) had a higher value of 36.1%, which clearly indicated an improvement of flame-retardant efficacy. **Figure 2.2** shows the vertical burning tests of PLA fabrics that have been treated with 0,100 and 250 g/L of PA. The black colour represents the average length of the char with respect to the PLA fabrics. It can be observed that the burnt area of the fabrics became smaller with an increase in the content of PA. The cone calorimeter tests, showed that the pHRR and the HRC values decreased with an increase in the PA content. The pHRR value of the untreated fabric was 463.6 W/g, while the treated fabrics of PLA-100 and PLA-250 were 329.7 and 279 W/g, respectively. From these outcomes, it can be deduced that the treated fabric can reduce the flame spread and exhibit a low fire risk when exposed to fire. The TGA showed that the onset temperature for pure PLA is 309 °C compared to the treated fabric of PLA-100 and PLA-250 331 °C and 323 °C respectively. The char residue increased with an increase in PA content in PLA. These results indicate that PA served as an effective char forming agent, which greatly improved the flame-retardant properties of PLA.

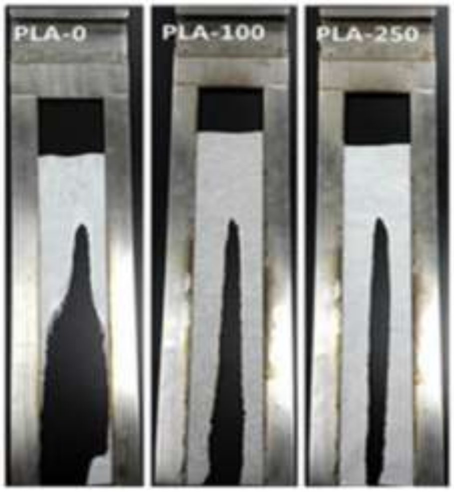

Figure 2.2. Vertical burning tests of PLA treated with 0, 100 and 250 PA (Cheng *et al*., 2016) Open access

Gao *et al*. (2019) conducted a study on the effectiveness of phytic acid salt that was prepared *via* the salt formation reaction between phytic acid and piperazine (PHYPI) as a flame retardant in a polypropylene (PP) matrix. The mechanism of PP/PHYPI is illustrated in **Figure 2.3** and the dehydration of phytic acid as well as the breakdown of ionic bonds in PHYPI, happened at the same time during the initial phase. This led to the production of non-flammable volatile substances, e.g., H_2O. Significantly, some thermally stable structures, such as P-N-C and P-O-C, were produced in this stage, which resulted in enabling the charring process of PP/PHYPI composite (Gao *et al*., 2019; Liu *et al*., 2023), which clearly indicated the success and suitability of PA as a flame retardant in PP.

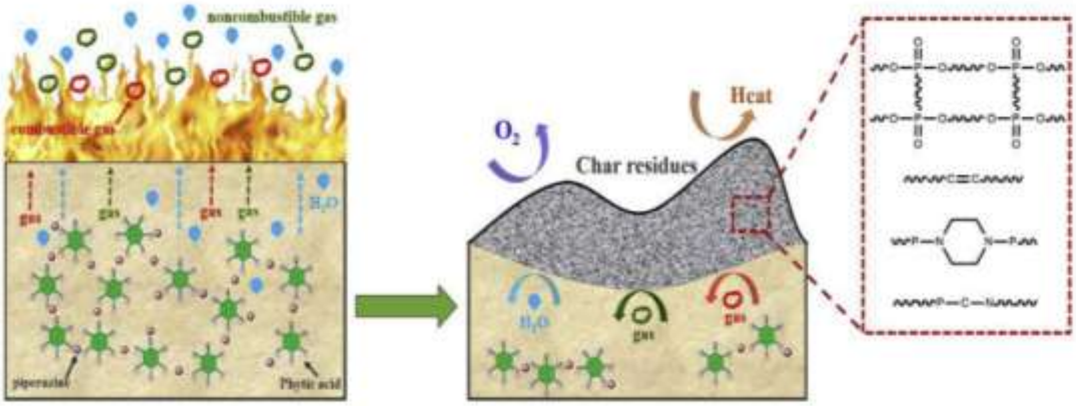

Figure 2.3. The mechanism of PHYPI on the flame retardancy of PP (Gao *et al*., 2019) Open access

Phytic acid, as a flame retardant, can be applied in more than one industry, and it can be applied in plastics, wool, wood, cotton, and various types of materials. Wool and cotton are two naturally occurring fabrics that have been extensively, used in upholstery, clothing, and industrial applications. These fabrics are mostly used because they provide softness and comfort, can absorb moisture, are biocompatible and they possess breathability properties. However, like most materials, they have low thermal stability, and they are fire hazard-prone when exposed to flames (Sykam *et al*., 2021). A recent study of PA and wool demonstrated that the wool's LOI values increased with an increase in the content of PA (Cheng *et al*., 2016). Wool with PA exhibited a higher LOI value of ~35.2% when compared to the untreated wool that recorded an LOI value of ~23.6%. This study employed the pyrolysis combustion flow calorimetry (PCFC), which is a testing technique that measures the heat release rate and combustion qualities of materials, during pyrolysis and combustion processes. The peak heat release rate of the untreated wool was ~131.7, while for the wool-40, wool-80 and wool-120, the values were: 89.8, 80.7 and 76.6 W/g, which exhibited reductions of 31.8%, 38.7% and 41.7%, respectively. According to the data, it can be concluded that PA significantly improved that flame retardancy of wool (Cheng *et al*., 2016). Polyamide 66 is a synthetic fibrous material that is broadly used by civilians and the military because of its ability to absorb and retain dye, good mechanical properties, and resistance to chemicals and shrinkage. However, its application in various industries, is limited because its flammability and melt-dripping tendencies, when exposed to flames or fire, which pose danger to human health and properties (Liu *et al.*, 2021). Liu *et al.*, 2021 reported on the flammability properties of phytic acid (labelled IP_6)/polyamide 66 (PA) fabric *via* the pad dry method (see **Figure 2.4**).

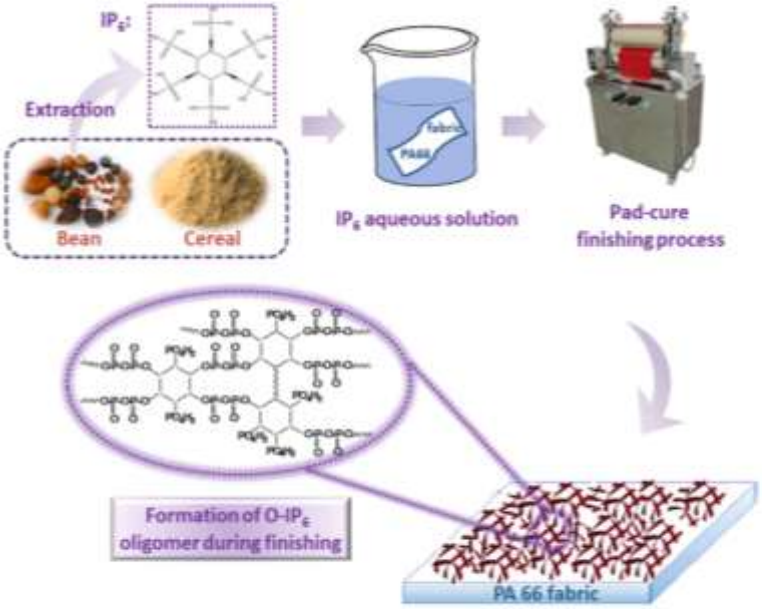

Figure 2.4. Step by step scheme displaying method of preparation for polyamide 66 incorporated in phytic acid (Liu *et al.*, 2021) Open access

Table 2.2 shows the LOI results for polyamide 66 that has been coated with phytic acid. The untreated PA fabric had the lowest LOI value of 19.6% when compared to the fabrics that were coated with phytic acid (IP6), which recorded the highest LOI value of 32.3%. It can also be observed that the LOI value is directly proportional to the content of IP6 content that was added; hence, an increase in the content of IP6, resulted in an increase in the LOI value, indicating an improvement in the flame retardancy properties of the material under test.

Table 2.2. LOI values for IP$_6$/PA fabric blends (Liu *et al.*, 2021)

Sample	**IP$_6$ concentration/%**	**LOI value/%**
Untreated PA fabric	0	19.6
25IP$_6$-PA fabric	15	26.3
25IP$_6$-PA fabric	25	31.8
35IP$_6$-PA fabric	35	32.3

The vertical burning test revealed that the char length of the untreated PA fabric was 18.1 with an associated dripping during combustion process, and it was also reported that the 15IP6-PA fabric had a char length of ~21.4 with no dripping. This can be attributed to the possibility that the melt dripping that occurred during the combustion of the polymer substrate, redirected the heat and fire away from the sample. However, the 25 and 35 IP_6-PA samples showed excellent vertical burning tests results, with a char length of ~12.5 and ~11.9, respectively and with no dripping, effectively proving the fact that phytic acid can improve the flammability characteristics of polyamide 66.

2.5. The synergy of phytic acid with other flame-retardant fillers

An improvement in the flammability of polymers by incorporating green flame-retardant fillers is a step forward, but the use of a single filler material may not meet or guarantee the universally acceptable safety standards. The addition of supporting additives to the phytic acid systems, can enhance the protective ability of these materials, thereby, resulting in a synergistic effect. By combining two or more flame-retardant fillers, the flammability resistance of the resultant product can significantly, be enhanced. Synergism can result in a more robust flame-retardant system, which is critical in areas, such as: construction, electronics, transportation, and textile manufacturing, where fire safety is important. The combination of flame-retardant fillers can prevent or delay ignition and hence, reduce the generation of the associated harmful gases and smokes during combustion. The use of different (hybrid) flame-retardant fillers together, can result in superior formulations that require low contents of the individual filler loadings, resulting in cost savings, while preserving or even increasing fire performance (Costes *et al*., 2017; Mokhena *et al*., 2022; Wang *et al*., 2022; Wang *et al*., 2022). The incorporation of non-combustible fillers to a polymer, not only decreases the flammability of the polymer, but it can also increase the heat capacity, thermal conductivity, reflectivity, and emissivity of the material. Phosphorus-based flame retardants, e.g., phytic acid can act in both the gas and condensed phases during a fire out-brake (Özer *et al*., 2022; Trovato *et al.,* 2023; Wang *et al*., 2022). The ability of phosphorous to adopt a range of oxidation states, allows the phosphorus-based flame retardants to exhibit different flame-retardant mechanisms, i.e., both the gas and condensed phases. This means that they can work in the gaseous phase by creating phosphorous radicals, such as $PO^•$, $PO_2^•$, and $HPO_2^•$, which trap the highly reactive radicals $H^•$ and $OH^•$, while in the condensed phase phosphorous promotes char formation (Velencoso *et al*., 2018). Due to its characteristic decomposition nature at elevated temperatures (± 200°C), phytic acid reduces the flammability of materials by absorbing heat and releasing water vapor, thereby diluting combustible gases. Additionally, phytic acid promotes the formation of a protective char layer on the surface of the polymer and hence, hindering the accessibility of oxygen and further inhibiting combustion (Mokhena *et al*., 2022; Velencoso *et al*., 2018). As an emerging environmentally friendly phosphorous-based biomass flame retardant, phytic acid has an obvious developmental potential in the flame-retardancy of polymers. **Figure 2.5** illustrates the interaction of phytic acid with other flame-retardant fillers (Liu *et al*., 2023). However, recent studies have revealed the fact that the use of phytic acid alone as a flame-retardant additive, does not work well. When used alone, phytic acid induces the decomposition of the composites and, in some cases, increases their hygroscopic behaviours. In addition, its flame-retardant efficiency is low, and its application spectrum is limited (Costes *et al*., 2017; Liu *et al*., 2023; Yang *et al*., 2021). To improve its flame-retardant abilities, phytic acid is commonly used in conjunction with other materials. For instance, improved properties have been reported in composites made of PLA, phytic acid, and lignin combinations (Costes *et al*., 2017). The presence of both phytic acid and lignin effectively, limited the thermal degradation of PLA and composite hygroscopic tendency. Not only that, but they also managed to significantly, reduce ~44%, the pHRR in the cone calorimeter test, thereby achieving a V-2 classification in the UL-94 test. Furthermore, certain combinations have been proven to enhance mechanical properties, e.g., increasing elongation-at-break from a mere 3.1%, to an impressive 12.6%.

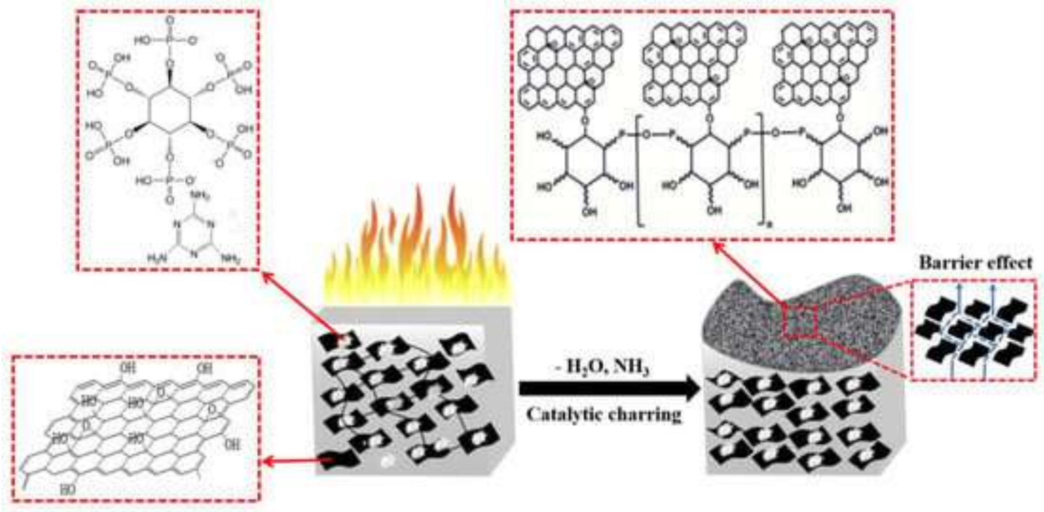

Figure 2.5. Schematic illustration of flame-retardant mechanism. GO and PA derivatives as synergistic flame retardant (Yang *et al*., 2021) Open access

To create efficient flame-retardant formulations, it is critical to understand and maximize their combinations (Wang *et al*., 2022). Synergistic combinations of flame-retardant fillers often, act through different mechanisms to address the various stages of the fire triangle, *viz*: heat, fuel, and oxygen (**Figure 2.6**). This comprehensive approach provides a more effective barrier against fire. The ability to mix and match various flame-retardant fillers, allows for the tailoring of fire performance to suit specific application requirements and regulatory standards (Malucelli, 2020). Phytic acid is a strong acid that exhibits six negatively charged phosphate groups in its structure and often, it chelates and/or forms stable complexes with metal ions to improve the flammability properties the material (Liu *et al*., 2023). Some examples of the metal-based fire retardants that have been used with phytic acid, include those containing zinc, iron, or aluminium compounds, which have been studied through various techniques, including spectrophotometry, potentiometry, and NMR in conjunction with computational data analysis. The stability and solubility of the ion–phytate complexes, are influenced by the specific cation, pH value, phytate-to-cation molar ratio, and the presence of other compounds in the solution. These compounds have been paired with various polymer matrices for their efficacies as flame-retardants (Liu *et al*., 2023; Marolt *et al*., 2020; Wang *et al*, 2022).

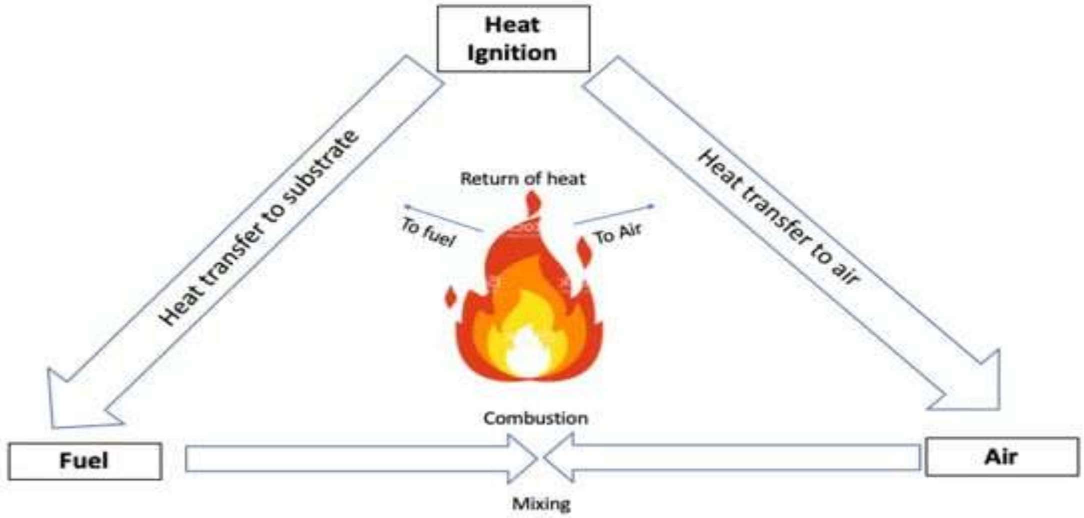

Figure 2.6. A self-sustaining combustion cycle (i.e., Emman's fire triangle) for flammable materials (Malucelli, 2020) Open access

Nonetheless, the most common and the frequently explored systems are those of phytic acid and nitrogen-containing compounds, fondly known as the P-N system (Yang *et al*., 2019; Velencoso *et al*., 2018). When nitrogen and phosphorous are combined, the two elements have a synergistic effect that greatly improves the flame retardance efficiency of the resulting product. The synergism between phytic acid and nitrogen-containing compounds, exhibits excellent flame-retardant properties, high thermal stability, high LOI values, and low smoke production. Mokhena *et al*. (2022) reported on the different nitrogen-containing substances, including melamine, amino acids, DNA, and proteins, that have proven to be ideal P-N systems, adequate for the enhancement of the overall fire resistance performance of the resulting products. Depending on the polymer matrix, the efficiency of the synergy between phytic acid and other flame-retardant additives can vary. Different polymers have different combustion characteristics, thermal properties, and interactions with flame retardant compositions/chemicals (Wilén & Pfaendner, 2013). Phytic acid and its derivatives as composite modifiers, are commonly used to improve the fire safety of EP, cotton, PLA, PP, EVA, and other materials (Wang *et al*., 2022; Yang *et al*., 2019). Zhou *et al*. (2023), reported on the flame retardancy characteristics of phytic acid-functionalized graphene oxide (PA-GO), incorporated into the rigid polyurethane foam. **Figure 2.7** illustrates a synthetic route for PA-GO flame retardant filler.

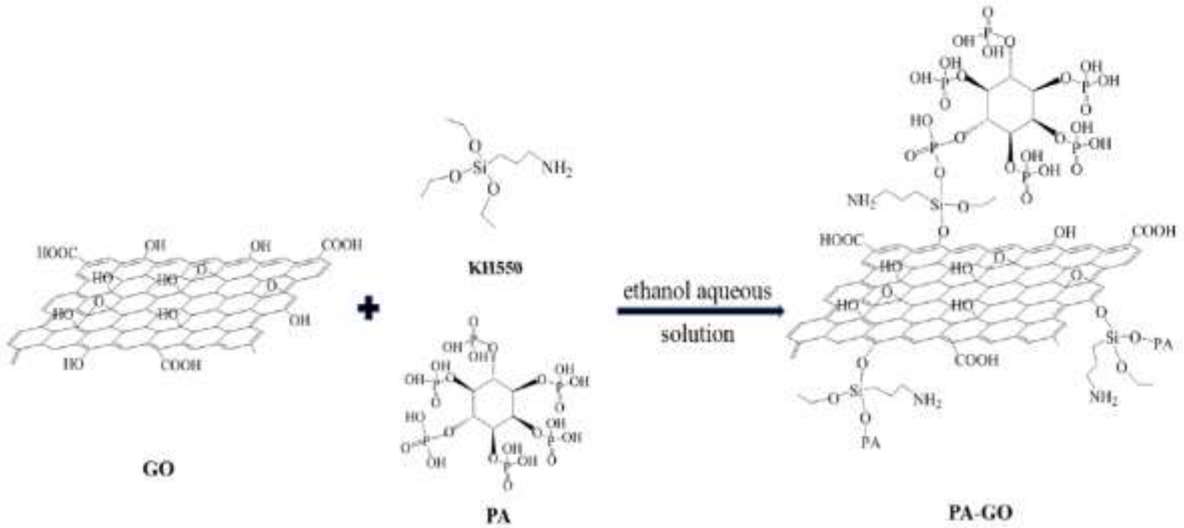

Figure 2.7. Schematic drawings of the formation of PA-GO (Zhou *et al*., 2023) Open access

The flammability properties of PA-GO, in synergy with expandable graphite (EG) and ammonium phosphate incorporated in rigid polyurethane foam (RPUF), were analysed for their limiting oxygen index (LOI), by using the UL-94 vertical combustion tester and cone calorimeter. The LOI of the neat RPUF was ~18.4%, however with the incorporation of the 12 wt.% IFR, i.e., 9 wt.%

EG and 3.0 wt.% GO, increased the LOI value to ~25.7%. There was a reduction in the LOI value (*viz* 25.9%) of the hybrid composite consisting of 0.3 wt.% GO together with 12 wt.%, which is associated with poor dispersion of the fillers within the RPUF. From the cone calorimeter results, the PHRR of neat RPUF was recorded to be 84.32 kW/m^2 and the PHRR of the RPUF-1 (9.0 wt.% EG + 3.0 APP) was recorded to be 35.94. A noticeable reduction was observed for the RPUF-3 (9.0 wt.% APP +0.3 PA-GO), with a reduction of ~18.71 kW/m^2 in the PHRR. The spread of fire was relatively slow in the RPUF, which was associated with the effective synergy between PA-GO and an enhanced dispersion within the RPUF matrix. Similar results were obtained in the THR study, whereby the RPUF-3 samples showed a lower THR value (*viz* 9.16 MJ/m^2) when compared with the RPUF-0 with a THR value of 18.46 MJ/m^2 **(Figure 2.8)**.

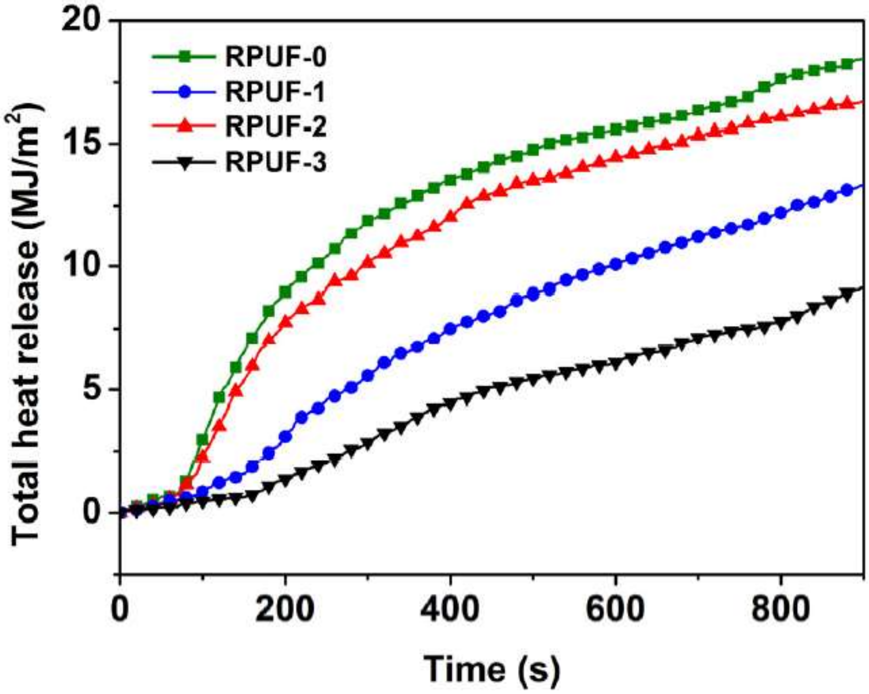

Figure 2.8. Total heat release (THR) of all the investigated samples (Zhou *et al*., 2023) Open access

Furthermore, Wang *et al*. (2019) reported on the synergistic effect of phytic acid and melamine, incorporated into epoxy resin (EP). It is known that the melamine can produce non-flammable nitrogen-containing compounds, which can inhibit flammability. Neat epoxy (EP) recorded an LOI value of 24%, whereas the LOI value of the EP/PAMA (bio-based organic-inorganic hyperbranched hybrid) (EP-6), reached a value of 29.7%. Neat epoxy recorded a PHRR value of 1050.5 kW/m^2, while the EP-6 samples showed a reduction of 62.3% (PHRR=395.6 kW/m^2) (**Figure 2.8**). The THR of neat epoxy was observed to be 101 MJ/m^2, while the addition of the flame-retardant filler, reduced the value to 91 MJ/m^2 (**Figure 2.9**). This is associated with the incorporation of nano layered PAMA, which reduced the flammability of the system. The PAMA formed a continuous and compact device, which can prevent heat from entering the systems and also block the volatile products from leaving the system, and as a result, enhanced the flame resistance of the composite.

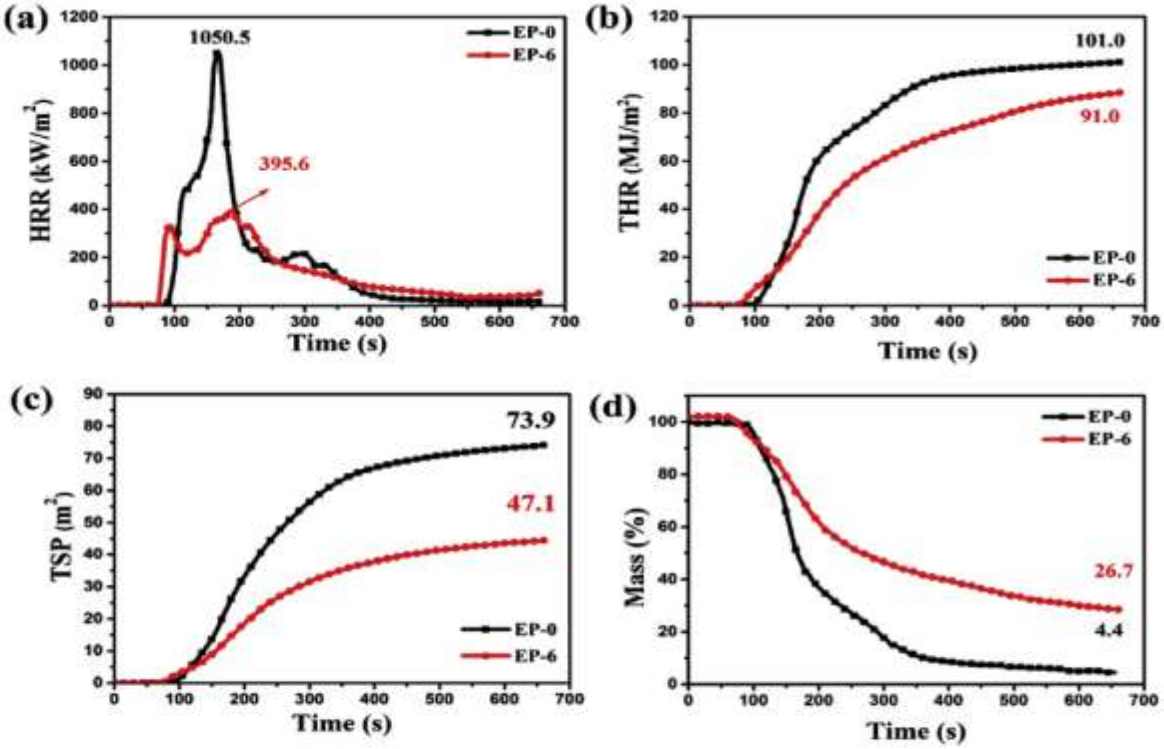

Figure 2.9. The (a) HRR, b) THR, c) TSP and d) of the investigated samples (Wang *et al*., 2019)

2.6. Phytic acid fibre hybrid systems

Hybridisation opens-up new alternatives for improving the function of composite materials, particularly in sophisticated applications, by increasing the composites toughness or impact resistance. In addition, hybrid composites provide more design freedom than the non-hybrid composites, resulting in a synergetic effect that no single material can equal. The synergetic effect can be achieved in a variety of ways, including fibre selection, suitable fibre combination and orientation, and hybrid system interaction. Hybridisation is a design technique for fibre-reinforced composite materials that involves combining two or more fibres of different groups within a single matrix to manipulate the desired properties (Nurazzi *et al*., 2021). They may be made from an admixture of natural and synthetic fibres, synthetic and synthetic fibres, or natural fibre and carbonaceous materials. Owing to their diverse properties of low production cost, high strength-to-weight ratio, and simple manufacturing process, hybrid natural fibre composite materials are useful in various structural and engineering applications. The utilisation of hybrid natural fibre polymer composites in advanced applications, is usually hindered by their high flammability. High cellulose levels can enhance the risks of high flammability, while high lignin levels are responsible for char formation (Phonphuak & Chindapracirt, 2015). It is noteworthy that inorganic fillers, e.g., phytic acid can potentially affect, not only the combustion properties, but also the general properties of the hybrid system. Apart from their potential flame-retardant capabilities, phytic acid and its derivatives have also been utilized as modifiers to increase dispersion and consequently, the overall qualities of the final products (Mochane *et al*., 2019). The unique molecular structure of phytic acid, adds to its remarkable chelating ability to interact, in a variety of ways, with metallic ions or cationic polymers. The rich phosphate groups in phytic acid can induce mineralisation of material surfaces to build a robust biomineralised skeleton and hence, improving a composite performance. Phytic acid can thus, bridge biopolymers and filler reinforcement *via* a significant interfacial chelation and an efficient electrostatic attraction, thereby, resulting in a strong biopolymer-based composite (Jin *et al*., 2020). Zhang *et al*. (2021) employed phytic acid to modify hemp fiber (HF-P) as a green flame retardant for vehicle parts containing unsaturated polyester resins (UPR). Phytic acid, in combination with melamine cyanurate, were used to modify hemp fiber to enhance the flame resistance of the resulting composites. The flammability properties of the composites were analysed with the LOI test and cone calorimeter test. The LOI value of the neat UPR was recorded to be 19.5% (**Figure 2.10**), while the addition of 3% hemp fiber slightly, reduced the value to 19.2% (**Figure 2.10**) The reduction in LOI value is an indication of the high flammability of the composite system. The synergy of phytic acid and melamine cyanurate, revealed an LOI value of 26.3% (**Figure 2.10**).

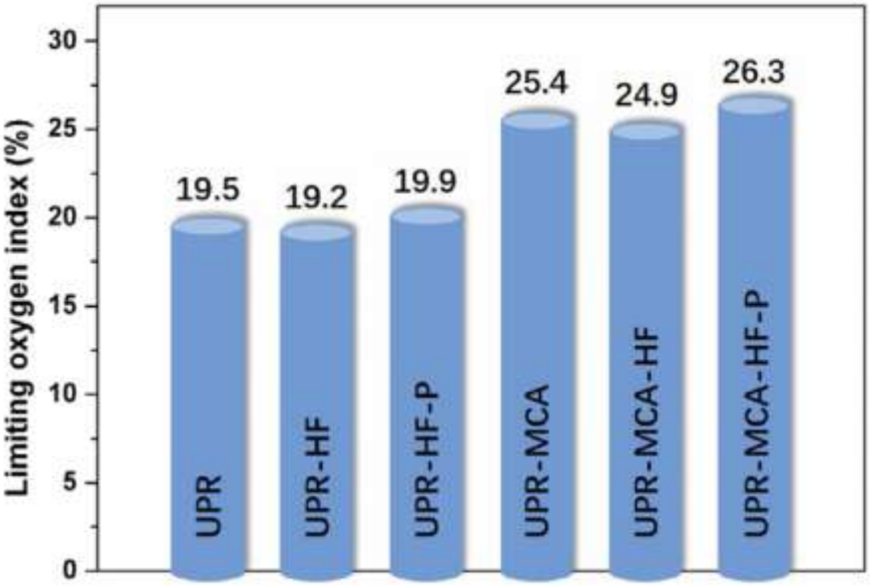

Figure 2.10: Limiting oxygen index (LOI) of the investigated samples (Zhang *et al*., 2021) Open access

The cone calorimeter test of the investigated samples recorded a PHRR value of 751.3 kW/m^2 and with the incorporation of the hemp fibre, raised the PHRR value to 756.9 kW/m^2. The incorporation of MCA and hemp fibre-phytic acid into the neat UPR, reduced the peak heat release rate (PHRR) to 237.2 kW/m^2 (see **Figure 2.11a**). Furthermore, the UPR/MCA/HF-P composite showed a lower THR value (**Figure 2.11b**). The improvement in flammability resistance was associated with the HF-P, acting as a skeleton for the expansion of the carbon layer formed from the MCA and the matrix. The expanded and continuous char layer, can prevent the pyrolysis products from entering the UPR matrix and thereby, enhancing the flammability resistance.

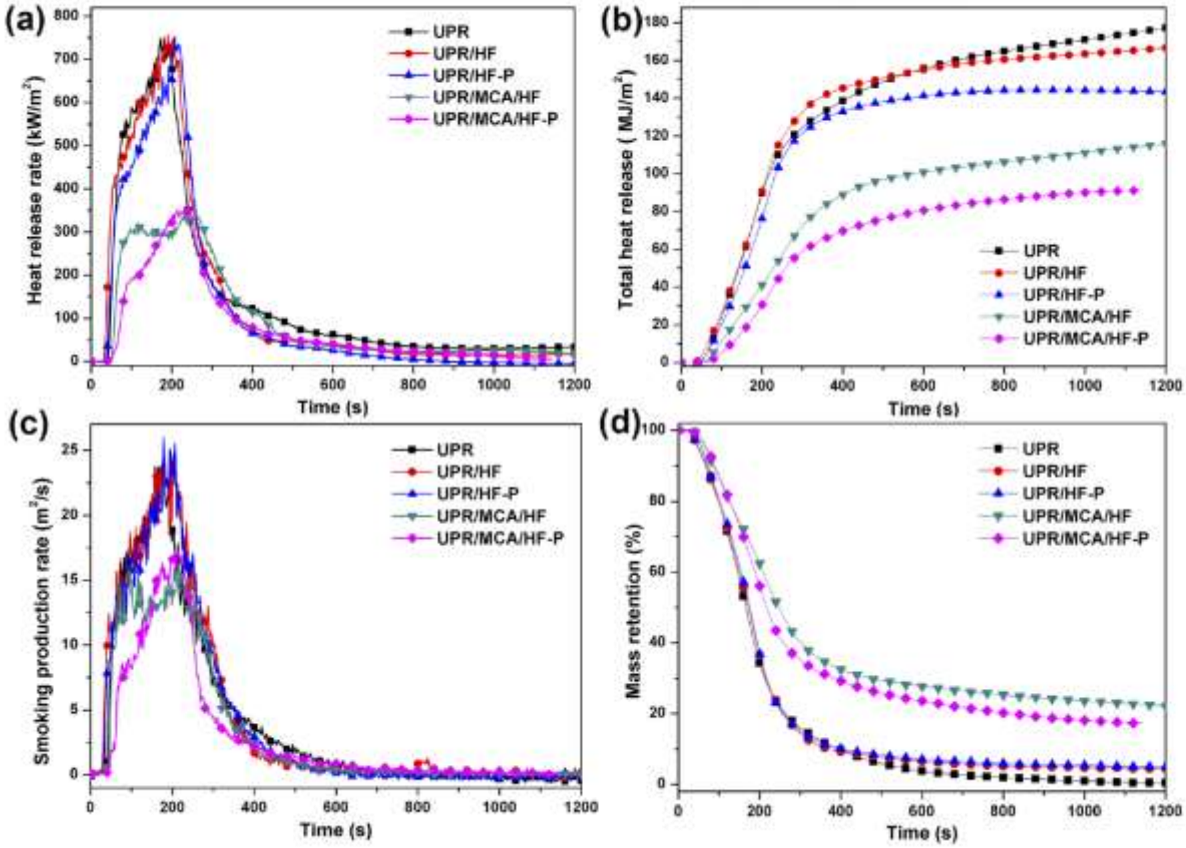

Figure 2.11. a) HRR, b) THR, c) SPR and d) mass retention of all the investigated samples (Zhang *et al*., 2021). Open access

2.7. Conclusions

The use of phytic acid as a flame-retardant agent is an area of ongoing research. One of the primary benefits of using phytic acid as a flame retardant, lies in its eco-friendliness nature: it is derived from renewable plant sources and it is biodegradable, making it a more sustainable option in comparison to some traditional chemical flame retardants. Although research into phytic acid as a bioflame retardant is still in its rudimentary stages, phytic acid has been studied for use as a flame retardant in polymers and other materials. Its potential ascribes to its ability to form char and release phosphorous compounds when exposed to heat, which helps to reduce the flammability of materials. The potential synergies between phytic acid and other flame-retardant compounds, have also been studied. So far, the most important or prominent synergies are the P-N complexes. By combining phytic acid with other additives or materials could enhance its effectiveness in reducing flammability, and in some cases, a UL-94 V rating of V0, has been achieved. There are concerns, however, over its compatibility with some matrices and only limited studies on its use in fibre-fibre hybrid systems are available. If research continues to expand and it shows promising results, there could be potential applications in various industries, such as: construction, textiles, electronics, and automotive, where flame-resistant materials are of necessity and required.

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CHAPTER 3

Sawdust as a byproduct of wood processing: properties, applications and a reinforcing filler in hybrid polymer composites

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Abstract

There is a sizeable amount of sawdust produced from wood industries such as timber and furniture. In the past, sawdust has been utilized as a fuel source and in the manufacturing of furniture. Based on the limited use of sawdust, there is plenty of sawdust accessible from the industries. Sawdust is the material of choice due to its cost-effectiveness, environmental friendliness, and biodegradability. However, if sawdust is not appropriately disposed or utilised better, it may have negative impact on the aquatic life and organic products. As a result, this review paper discusses the best possible methods or proper routes for the utilisation of sawdust to benefit the environment, society, and the economy at large. Sawdust possesses superior capabilities as reinforcing fillers in various polymer matrices for advanced applications. This paper provides an in-depth discussion on the sawdust hybrid composites in comparison to other natural fibre hybrid composites. The applications of various sawdust hybrid polymer composites for specific systems are also mentioned. Furthermore, the morphology and preparation of the sawdust/polymer composites and/or sawdust hybrid polymer composites are also discussed, since it is well known that the properties of the natural fibre composites are affected by the preparation method and the resultant morphology. Based on the above, the current paper also plays a critical role in providing more information about the waste-to-value-added products.

Keywords: Natural fibre; wood-waste; sawdust; hybrid systems; polymer composites

Highlights

- Fabrication of the sawdust reinforced plastic composites for 21 century applications. The resultant composites need less energy and have less carbon footprint.
- In depth discussion on the morphology of the sawdust/polymer composites and their hybrid polymer composites.
- Comparison of the sawdust/polymer hybrid polymer composites with other natural fibre hybrid polymer composites for specific applications.
- Overall, the paper provides an insight information on waste to profit: suitable methods for utilizing sawdust to meet societal needs.

3.1. Introduction

The demand for lightweight materials has prompted scientists to invest more research into natural fibre-reinforced plastic matrices. The fabrication of natural fibre composites explored the possibility of enhancing the properties of the materials and reducing their ecological footprint. Currently, researchers have utilized agricultural, and forestry wastes such as bagasse, rice husks and sawdust (SD), as reinforcing fillers in various polymer matrices (Arjmandi *et al*., 2015; Deepan *et al*., 2022; Ganesan *et al*., 2021; Ismail *et al*., 2022; Prasad *et al*., 2020; Sombatsompop *et al*., 2006; Suhot *et al*., 2021; Zafeer *et al*., 2003). The reason behind the utilisation of agricultural and forestry waste is due to the accumulation of industrial wastes because of quick increase in population and industrialisation (Ahmed *et al*., 2018). Wood waste has emerged as one of the wastes systems that requires serious attention in terms of recycling and effective utilisation since it accumulates in various areas such as household activities, factories, and mills (Abdel-Shafy & Mansour, 2018; Ahmed *et al*., 2018). Globally, there is a slow progress for the effective recycling of wood waste (Ahmed *et al*., 2018). According to statistics, the United States of America (USA) produces approximately 64.05 million tonnes/year of wood waste, with 25.76 million tonnes/year being non-recycled wood waste (United States Environmental Protection Agency, 2023). Furthermore, Pakistan and Australia produced 1.73 and 4.51 million tonnes of wood waste yearly, respectively (Fabien, 2023; Sattar *et al*., 2023). In addition, the quantities of non-recycled wood waste were reported to be 346,189 (Pakistan) and 1.74 million tonnes/year (Australia) (Fabien, 2023; Sattar *et al*., 2023). Wood is a renewable material that is useful in various applications such as paper, timber, and construction (Sattar *et al*., 2023). Wood is a renewable material that is useful in various applications such as paper, timber, and construction (Ramage *et al*., 2017). Chemically, wood is a biomaterial consisting of cellulose, hemicellulose, and lignin. **Table 3.1** summarises various residues produced in the processing of wood, with sawdust being the most dominant byproduct from various processing methods.

Table 3.1. Selective sources and various types of residues produced in wood processing, reproduced from (Pandey *et al*., 2022).

Sawmilling	Bark, split wood, **sawdust,** trimmings
Particleboard production	**Sawdust,** bark, sander dust, panel trim
Forest function	Needless, leaves**, sawdust,** branches
Plywood manufacturing	**Sawdust,** core, bark, panel trim

Sawdust produced from timber-based industries is used as a source of energy in manufacturing. However, the energy production process produces large amounts of wood-ash with unfavourable environmental impact (Jaya *et al*., 2018). Furthermore, wood ash is made up of particulate matter (e.g. carbon particles, heavy metals, polycyclic aromatic hydrocarbons (PAHs), *etc*.) which can easily cause air bore through winds which might present respiratory health complications. Based on the above concerns, there is a need to convert wood sawdust into valuable products. Sawdust has emerged as a potential reinforcing filler for various polymer matrices. Such composites are favoured because of good mechanical properties, positive environmental impact, and dimensional stability. Therefore, this review paper discusses an overview of bio-fibres, their applications, the history of sawdust and a comparison of sawdust hybrid composites with other natural fibre hybrid systems. Furthermore, various sawdust polymer hybrid systems are also reported in relation to their applications. The morphology and preparation of the sawdust polymer and/or hybrids system are also discussed.

3.2. An overview on bio-fibres

Fibres are substances distinguished by their flexibility, fineness, and high length-to thickness ratio (De Araújo *et al.*, 2011). Based on their source, they are classified as natural, synthetic, or inorganic, as shown in **Figure 3.1**. Glass and carbon fibres are the most commonly used synthetic fibres, and glass fibres are the most widely used of all synthetic fibres because they offer excellent strength and durability, thermal stability, impact resistance, chemical, friction, and wear properties. Other synthetic fibres, such as aramid, basalt, polyacrylonitrile, and polyethylene terephthalate, among others, provide similar benefits but are rarely used due to their toxicity to both humans and the environment (Karim *et al.*, 2023; Mohd-Bakhori *et al.*, 2022; Rajak *et al.*, 2019; Rajak *et al.*, 2022; Unterweger *et al.*, 2013). Although the utilisation of synthetic fibres makes good economic sense, safety concerns remain an issue, thus the interest in fibres obtainable from various biological sources such as plants (cotton, sisal, hemp, kenaf, jute, *etc.*) and animals (sheep, butterflies, spiders, *etc.*), that represent both economic and environmental sustainability, have become an option (Jiang *et al.*, 2020; John *et al.*, 2008; Kumar *et al.*, 2017; Mahir *et al.*, 2019; Mann *et al.*, 2023).

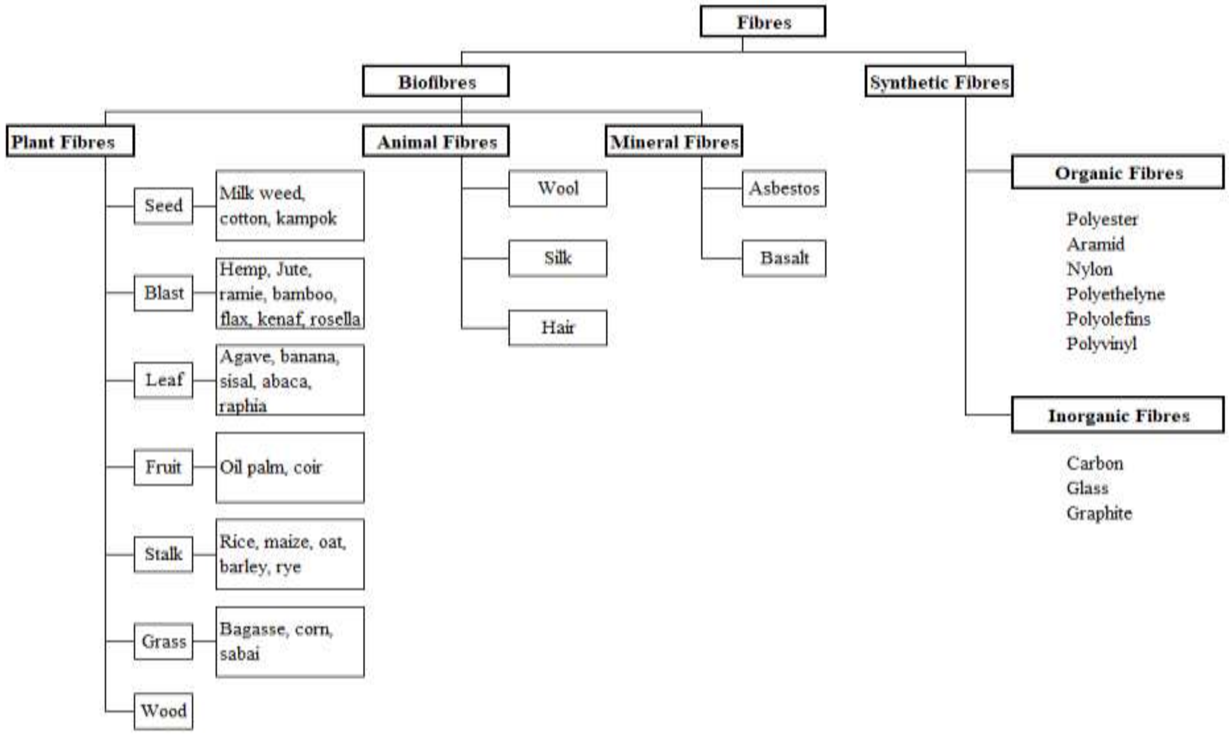

Figure 3.1. Classification of fibres, a reproduction from (Jiang *et al.*, 2019)

In recent years, synthetic fibres such as glass have dominated the fibre market (Thomason, 2019). However, concerns about the continuous use of toxic and non-renewable resources have led to a demand for sustainable materials, resulting in a renewed and growing interest in bio-fibres (Shah, 2013). Stringent environmental regulations are forcing researchers across the globe to develop environmentally friendly materials, and fibres from natural resources offer significant properties with potential applications in modern industry (Rajak *et al*., 2019). Plant fibres, which are perceived as eco-friendly sustainable materials, are increasingly being used in a variety of markets, particularly as reinforcements and/or fillers in various composite matrices (Elfaleh *et al*., 2023; Khalid *et al*., 2021; Maiti *et al*., 2022; Shah, 2013; Suárez *et al*., 2021). **Figure 3.2** shows popular countries in the field of natural fibres. Asian countries, especially those in tropical regions (e.g., People's Republic of China and India), lead in natural fibre production due to abundant resources such as jute, sisal, coir, and bamboo. Traditional knowledge and expertise in working with natural fibres have been passed down through generations, providing a basis for innovation and advancement (Elfaleh *et al*., 2023).

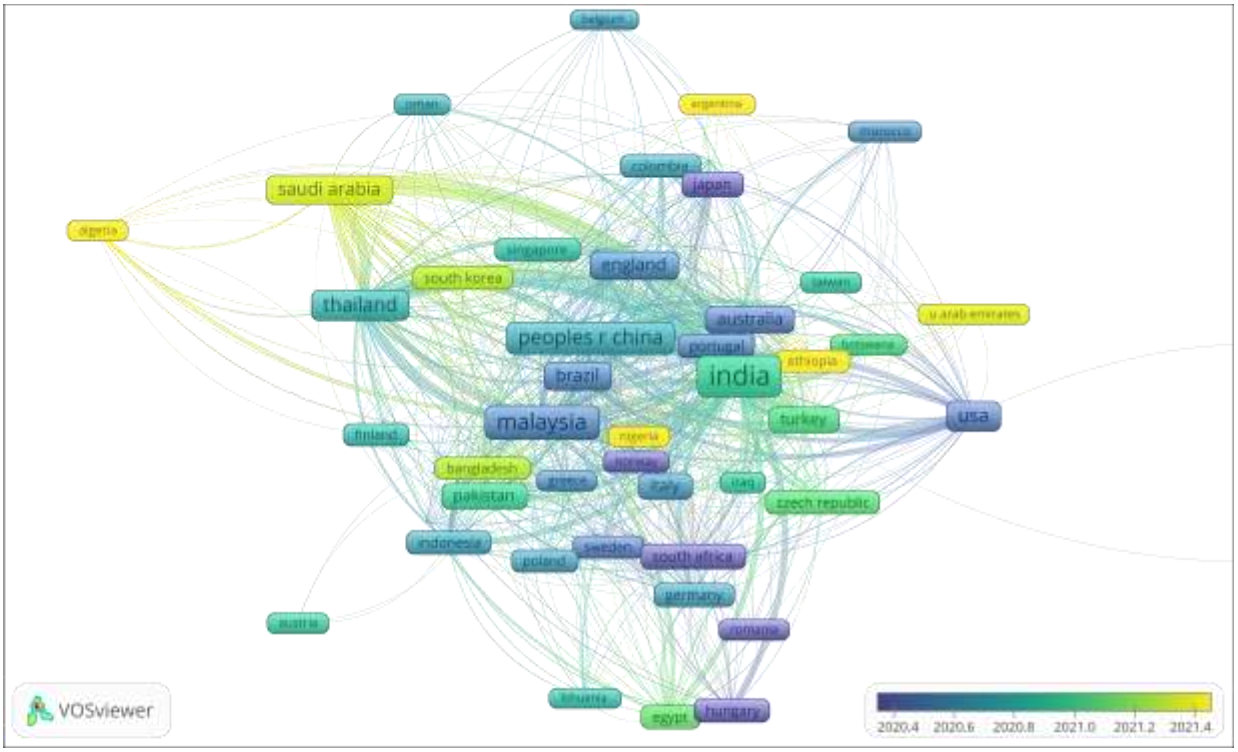

Figure 3.2. Selective countries in the field of natural fibre, (data collected on the 7th of May 2023).

The plant fibre market is now a lucrative enterprise with numerous applications across industries (Bogoeva-Gaceva *et al*., 2007). The automotive and construction industries are at the forefront of utilizing natural fibre-reinforced polymer composites, capitalizing on their distinct benefits to suit changing industry demands and consumer preferences. In the automotive industry, where lightweight and eco-friendly materials are urgently needed, natural fibre composites offer a compelling solution. Bio-fibre-based composites can drastically reduce weight, up to 30% in some cases, and provide substantial reductions of about 20% for automotive parts (Ismail *et al*., 2022). This weight reduction is crucial for improving fuel efficiency and reducing emissions, in line with strict environmental regulations and consumer preferences for environmentally friendly vehicles. In construction, similar demands for lightweight and sustainable materials exist, driving the adoption of natural fibre composites for applications such as roofing, insulation, and structural components (Bogoeva-Gaceva *et al*., 2007; Ismail *et al*., 2022; Rajak *et al*., 2019). The growing interest in bio-fibre applications is primarily motivated by the advantages of biodegradability and biocompatibility, abundance, cost-effectiveness, insulation, and tunability (feasible to modifications) (Jiang *et al*., 2020; Kumar *et al*., 2017; Phonphuak & Chindapracirt, 2015). Plant fibres have the lowest density of any structural fibre and possess higher specific strength and stiffness compared to glass fibres at a lower cost (Djafari Petroudy *et al*., 2017). They offer the lowest possible carbon footprint due to fewer and less harmful emissions released during processing in comparison to other materials. Moreover, these fibres are generated by repeating monomeric units, consisting of carbon (C), oxygen (O), hydrogen (H), and nitrogen (N) (Kabir *et al*., 2020; Mohanty *et al*., 2005; Phonphuak & Chindapracirt, 2015; Shankar and Rhim, 2021). Recyclability is another contributing factor to the sustainability of fibres (Jiang *et al*., 2020). These fibres are not only easy to handle and work with, but they are also gentle on mixing and moulding equipment. The employment of bio-fibres as an eco-friendly and cost-effective alternative to synthetic fibres will aid in the preservation of ecological balance by reducing non-biodegradable waste through reuse while at the same time generating revenue (Barón *et al*., 2009; Prodanović *et al*., 2017; Sindhu *et al*., 2014; Xie *et al*., 2016). The use of plant fibres can be traced back to prehistoric times when the Egyptians used them as reinforcing materials in bricks and the Babylonians used them for burial purposes (Mwaikambo, 2006). Plant materials, such as paper reed, cotton, and linen fibres have been used throughout the existence of mankind to make clothing, paper, pottery, *etc*. To date, they remain the primary source of materials in textile, food, bioethanol production, building, and construction and automotive, among others (Baley *et al*., 2021; Junio *et al*., 2023; Mwaikambo, 2006). The dawn of civilization saw scientist Hendry Ford develop an automobile body out of hemp fibres, which inspired Mercedes-Benz and BMW to incorporate the same fibres into modern car components (Mwaikambo, 2006). **Figure 3.3** depicts a typical procedure for using bio-fibres to make car inner door panels for automobiles. A mat made entirely of bio-fibres, or a 50/50 blend of bio-fibres and any suitable polymer matrix can be produced. This mat can be moulded into any desired shape and laminated with plastic or leather film, or it can be adorned however desired (Peças *et al*., 2018). By employing these materials, weight savings of 20 to 50% in interiors can be achieved, significantly increasing the environmental performance rating of automobiles (Zhang & Xu, 2022).

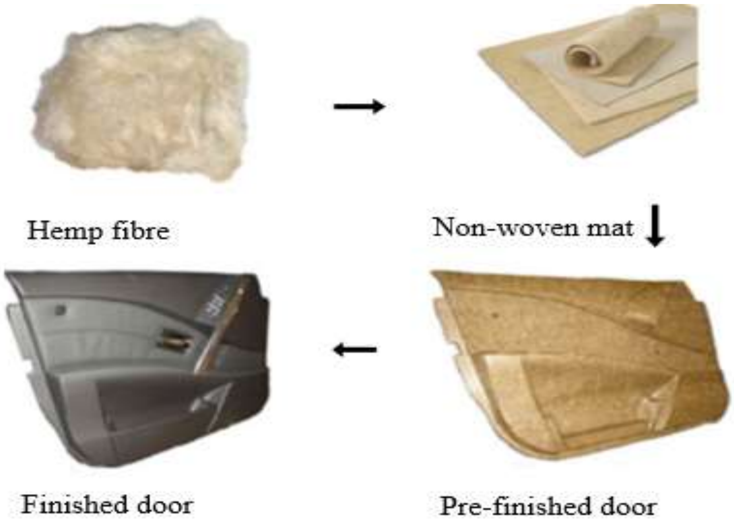

Figure 3.3. A typical procedure for fabrication of car inner door panels (Peças *et al*., 2018) Open access

Historically, plant fibres were predominantly employed as the main matrix, with thermoplastics serving as fillers in minor proportions (Elseify *et al*., 2021; Mwaikambo, 2006; Peças *et al*., 2018). However, recent research has explored alternative trends. These long, thin, and flexible strands of material can also be employed as both fillers and/or reinforcement in technological developments to improve the qualities of biodegradable polymers. Some of the most commonly used commercial fibres include flax, hemp, and kenaf, and they are often in conjunction with eco-friendly matrices such as polypropylene, epoxy, and polylactic acid (PLA), to name a few (Lendvai *et al*., 2022;

Maiti *et al*., 2022; Shah, 2013; Sarwar *et al*. 2020; Ramesh, 2016). Most automakers now use bio-fibres in their creations to reduce vehicle weight, production costs, and environmental effects while leveraging these characteristics as a competitive marketing advantage (Peças *et al*., 2018; Zhang & Xu, 2022). Presented in **Table 3.2** are the motor producers who adopted fibres from unconventional sources to produce interior car components. The different parts produced among others include inner door panels, seat covers and insulation *etc*.

Table 3.2. Selective applications of natural fibres in automotives produced with information from (Designboom, 2023; Olham *et al.*, 2021; Peças *et al.*, 2018; Schmiedel *et al.*, 2023).

Automotive manufacturer companies/ Car manufacturing companies? (Models)	**Door panels**	**Seat Parks**	**Boot liners**	**Spare wheel lining/cover**	**Instrument panels**	**Insulation**	**Others**
Renault (Twingo, Clio)							Dashboard area including other rigid parts (Not specified)
Ford (Mondeo, Focus, Ford fusion, Lincoln)	✓	✓	✓				
Volkswagen (Golf, Passat, Bora)	✓	✓	✓				Trunk lid
Audi (A2, A3, A4, A6, A8)	✓	✓	✓	✓			Hat holder/rack
Citron (C5)	✓						
Mercedes-Benz (C, S, E, A class truck & Vision EQXX)		✓					Bumper, wheel, box, roof cover, glove box, internal engine cover
General Motors (Chevrolet – Impala, Cadillac De Ville)		✓	✓		✓		Back-shelf trim panels
BMW (3, 5, 7 & i3 series)	✓	✓	✓		✓	✓	Foot well covers, dashboard
Fiat (Alfa Romeo 146, Brava, Punto, Marea)	✓						
Opel-Astra	✓						Hat racks and spare tire covers
Daimler-Chrysler (A, C, E, S)	✓						Dashboard, windshield, window pillar panel cover, business table
LOTUS (Eco Elise)	✓	✓					Spoiler, mats
Peugeot (406)	✓	✓					
Rover 2000 and other models							Back shelf/panel storage system
Mitsubishi	✓		✓			✓	
Toyota (Brevis, Harrier, Celsior, Raum)							
SAAB (9S)	✓	✓					
Volvo (C70, V70)		✓					Natural foams,
Vauxhall (Corsa, Astra)				✓		✓	
Porsche (18 Cayman GT4 Club sport)	✓						Body panels, rear wing

Scientists often draw inspiration from nature and employ biological compounds as design cues for advanced materials. Nature provides bio-fibres with a wide range of shapes, sizes, densities, and microfibril angles. Plant fibres represent a class of macro-molecular biomass materials that can be further developed and widely used, thus the vast interest to incorporate them into composite materials. The molecular structure and functional motifs of natural materials can be reproduced in artificial materials to give a blueprint for various functionalities. Besides cotton, all plant fibres have three basic components, i.e., lignin, cellulose, and hemicellulose, which are crucial for structural support and plant survival (Kim *et al*., 2023; Novaes *et al*., 2010; Ochoa-Villarreal *et al*., 2012; Saba *et al*., 2015; Singh *et al*., 2020). They range from linear to highly branched structures with versatile features that permit modifications. Bio-fibres can be easily processed using a variety of green production techniques, including melt moulding, freeze-drying, phase separation, gas foaming or high-pressure processing, electrospinning, and/or a combination of some of these techniques. The usage of organic fillers that meet the majority of material design and development requirements to substitute synthetic fillers could result in both economic and sustainable development (Farah *et al*., 2016; Pawar *et al*., 2012; Sampath *et al*., 2016). Cellulose is the major plant polysaccharide, followed by hemicellulose and lignin respectively (Singh *et al*., 2020). It is a chiral molecule composed of glucose monomer units linked by 1–4 linkages. The cellulose polymer chain is stabilized by the terminal reducing and non-reducing sugar units. Due to strong hydrogen bonds between hydroxyl group networks that form the cellulose molecule, the fibres are crystal line, which is currently a significant area of research (Ergun *et al*., 2016; Joseph *et al*., 2020; Lisuzzo *et al*., 2021). Cellulose has been widely used as a raw material to produce commercial plastics and/or as a filler to overcome limitations in other polymers, predominantly in the tissue engineering and packaging industries (Hivechi *et al*., 2020; Ramos *et al*., 2018; Singh *et al*., 2020). Furthermore, cellulose contains an inherent structural characteristic that enables the molecule to be modified to perform the desired function anywhere in the industry. Surface modification of cellulose allows for substitution of hydroxyl functional groups with other functional groups. This chemical variability is especially important for the current global drive to replace non-biodegradable petroleum-based commodities with more environmentally friendly products. As a result, cellulose has found use in water purification, fibre, membrane, film, and sensor production in the form of nanofibrous membranes, in addition to other industrial uses (Liu *et al*., 2021; Ramos *et al*., 2018; Rojas, 2013).

According to Panthapulakkal *et al*. (2017) and Gregory *et al*. (1999), hemicellulose is a branched polysaccharide composed of sugar monomers such as glucose, xylose, mannose, galactose, and arabinose, as well as uronic acids. Its constituents are known as "cross-linking glucans" because they can establish hydrogen bonds with cellulose and lignin. Unlike cellulose, they do not form microfibrils. Hemicellulose has a more open structure, several side branch groups, and is non-crystalline. Carboxymethyl, acylated, and cationic hemicelluloses, which contain a lot of free hydroxyl groups, are good candidates for chemical modification via cross-linking, esterification, etherification, and other methods. In reality, modified hemicellulose has outstanding water resistance, thermoplasticity, and other properties. Chemically modified hemicelluloses could be used to create materials with distinct properties, increasing the value of biopolymers. These reactions alter characteristics of hemicellulose, allowing it to be employed in a range of applications such as medicine, films, hydrogels, and conductive polymers. Recent developments include food packaging due to functional properties like tensile strength and barrier properties, which can be improved (Chen *et al*., 2016; Hosseinaei *et al*., 2012; Hu *et al*., 2020; Norrrahim *et al*., 2021; Ye *et al*., 2018). Lignin is a biomacromolecule with a cross-linked polyphenol and numerous functional groups that provide multiple crosslinking sites with other compounds. The three-dimensional network structure of lignin allows for significant chemical modification (Vinardell *et al*., 2017). Due to the presence of phenolic, hydroxyl, and methyl groups, lignin is an excellent candidate for the development of new materials. Pure lignin contains phenolic hydroxyl groups (PhOH) that can deprotonate and adsorb numerous metal ions, whereas kraft lignin (a modified version) contains carboxyl groups (-COOH) that can also ion-exchange with metal ions as a result of the oxidative bleaching process. Due to these unique properties, lignin can be directly used as a binder, natural oxidant, ultraviolet (UV) protectant, and decontaminant (Antonino *et al*., 2021; Li *et al*., 2022; Liu *et al*., 2018; Mandlekar *et al*., 2018; Santander *et al*., 2021). Thus, there are numerous reports on the development of its blends for: (i) heavy metal polluted water decontamination through cation exchange (Santander *et al*., 2021); (ii) preparation of UV-based antimicrobial food packaging composites using lignin as a reducing agent and a stabilizer (Li *et al*., 2022); (iii) and novel flame retardants with concurrent excellent smoke-suppression properties among others (Mandlekar *et al*., 2018). Typically, plant fibres are found in nature as composites of cellulose and hemicellulose embedded in a lignin matrix, with varied proportions of the readily identifiable constituent (Jiang *et al*., 2019; Phonphuak & Chindapracirt, 2015). The cellulose fibrils are aligned along the length of the fibre, resulting in maximum tensile strength, flexural, and rigidity. Weak van der Waals and hydro gen bonds hold these components together. The cellulose molecules are hydrogen-bonded to hemicellulose. The cellulose-hemicellulose structure is then strengthened by lignin covalently linked to hemicellulose. The hydrophobic lignin fills voids in the cellulose–hemicellulose network as a coupling agent. Lignin stiffens the cellulose–hemicellulose network, protecting cellulose fibres from biological attack and environmental stress. While lignin and cellulose regulate water intake, hemicellulose influences the thermal and recyclable properties of plant fibres (John *et al*., 2008; Vermaas *et al*., 2019; Yang *et al*., 2019). These biological cues are commonly employed as a guide for creating new materials in modern societies (Kim *et al*., 2023; van Beilen & Poirier, 2008). The basic components have a considerable influence on the characteristics of lignocellulosic fibres. Because of their filler and/or reinforcement capabilities, these components have been employed both individually and as a unit in a variety of matrices (Yang *et al*., 2019; Zarna *et al*., 2021). One of the major problems that researchers have had to deal with is the hydrophilicity of the fibres (Elfaleh *et al*., 2023; Girijappa *et al*., 2019; Kabir *et al*., 2012). However, if cellulose and hemicellulose are generally occluded or capsuled by hydrophobic lignin, this could render the fibre biscuit hydrophobic because the other components are unavailable to establish interactions unless studied in the absence of lignin (Poovaiah *et al*., 2014). Nonetheless, because of the complexity of the structures some constituents, especially lignin, this concept is not fully understood. Although the primary purpose has been to remove lignin and hemicellulose for better results, some authors believe the combined effect has better prospects (Jiang *et al*., 2019).

3.3. Sawdust history

The production of bio-fibre-based commodities came to a near-halt with the introduction of synthetic fibres in the nineteen forties (van Beilen & Poirier, 2007). However, critical conversations about natural resource preservation and recycling in the nineties sparked renewed interest in renewable materials (Moshood *et al*., 2022). Recent developments in environmental consciousness have piqued their research interest, and their significance has grown (Rodrigues Pereira de Paula *et al*., 2020). Various bio-fibres with significant commercial value have been gracing the same markets as glass fibres. Kenaf, sisal, and hemp are a few examples of such bio-fibres. Wood fibres are not new, but their popularity has increased in recent years, putting them on the list of emerging fibres alongside coir, *hibiscus*, and *bagasse* (Kozłowski *et al*., 2020). Like other important fibres, sawdust does not only offer low-cost and less dense products. In many cases, improved mechanical properties suited for engineering applications are achieved in the presence of sawdust (Lendvai *et al*., 2022; Mahesh *et al*., 2022; Nair *et al*., 2018; Olaiya *et al*., 2023; Rodrigues Pereira de Paula *et al*., 2020). Another intriguing attribute to consider is the biodegradability of sawdust. Although its decomposition depends on variables like wood type, composition, environmental conditions, *etc*., sawdust can generally break down within six months of soil exposure (Lennox *et al*., 2019). When combined with bioplastics, the composites can degrade within 6 to 12 months. This rapid degradation, in contrast to the decades-long persistence of traditional plastics, renders them well-suited for circular material use and aligns with current sustainability efforts (Ortega *et al*., 2021).

Sawdust is a versatile, low-cost, and easily accessible lignocellulosic bio-waste. It is a tiny, powdery wood debris generated by sawing and sanding in lumber mills and other related businesses. Sawdust is a byproduct of timber processes such as cutting, sizing, re-sizing, edging, trimming, and smoothing (Setyono & Valiyaveettil, 2014; Mwango and Kambole, 2019). Vegetation produces thousands of tons of energy-rich lignocellulosic materials daily, which offer enormous potential for the long-term synthesis of chemicals and fuels (Isikgor *et al*., 2015). Despite its widespread use as animal feed and in the creation of biofertilizers, sawdust management remains a challenge with prevalent aesthetic consequences, especially in developing countries. The forestry industry is the largest producer of copious sawdust (Padam *et al*., 2012). Typically, every 100 kg of wood treated in a sawmill yields 12-25 kg of sawdust. Softwood generally produces less residues or sawdust than hardwood, and the interior wood parts usually result in less sawdust than the leaves and bark. On average, wood sawing results in 12–25 % dust (Varma *et al*., 2019).

Material wastage is a common phenomenon in many machining and manufacturing activities, making lumber waste management challenging. Most wood enterprises exist and aim to earn profits at the lowest possible cost, but waste extraction and disposal are additional expenses (Agrawal *et al*., 2013; El-Haggar, 2007). Wood waste refers to mechanically shredded wood residues, which include sawdust, hog fuel, bark, chips, slabs, shavings, trimmings, and mill ends, among others (see, **Figure 3.4**) (Jahan *et al*., 2022). Offcuts and chips are frequently utilised in commercial sawmills, as well as by workers and communities, to generate steam for kiln drying and fuel. The bark and shavings are mostly used as beds or bedding in nurseries and animal farms. Shavings and sawdust, on the other hand, are the most underutilized wood waste parts. Approximately 20 – 70% of sawdust along with some shavings and chips have to be disposed of if not mixed with chips for biofuel. Due to a lack of suitable disposal options, the majority of this waste is routinely discharged into the environment without treatment. Common disposal methods include burning, heaping at mill margins, and disposal alongside roadways and bodies of water (Charis *et al*., 2019; Ferede *et al*., 2020; Hillig *et al*., 2007; O'Dwyer *et al*., 2018; Phonphuak *et al*., 2015).

Figure 3.4. Different wood waste (Jahan *et al*., 2022) Open Access

Waste burning, in open fires or through incineration, emits pollutants into the atmosphere, which can impair both human health and the environment (Sharma *et al*., 2013). Incinerating sawdust releases noxious fumes and gases, including sulphur oxides (SOx), carbon monoxide (CO), nitrogen oxides (NOx), volatile organic compounds (VOCs), and particulate emissions, depending on its source and composition. In addition, the ash residue left after burning may be harmful if not handled and disposed of correctly. Nitrogen and sulphur oxides constitute substantial portions of emissions. These gases contribute to the formation of photochemical smog, an atmospheric phenomenon defined by a complex mixture of pollutants that not only degrades air quality but also actively depletes natural ozone levels in the atmosphere, worsening environmental issues. Generally, burning of bio-waste leads to acidification and eutrophication. These pollutants can cause acid rain and harm the surrounding ecosystems by increasing soil and water acidity levels. These events can have detrimental effects on both terrestrial and aquatic habitats. Additionally, the ash and particulate matter from incineration can contribute to nutrient overload in water bodies, further exacerbating eutrophication and disrupting ecological balances (Adegoke *et al*. 2022; Deac *et al*., 2016; Sharma *et al*., 2013; von Schneidemesser *et al*., 2015).

On the other hand, sawdust disposed of in formal and informal landfills is subject to chemical, physical, and biological reactions and transformations during which nutrients, elements, and gases are released. These come into contact with water and other undesirable substances to create leachate (Vaverková *et al*., 2020). Leachate is defined as any contaminated liquid that is generated by percolating through a solid waste disposal site and moving into surface areas (Sridhar *et al*., 2020). Leachate negatively impacts groundwater, surface water, soil, and plants, as indicated with red arrows in **Figure 3.5**. Landfill leachate alters the physicochemical parameters and heavy metal concentration in surface water, groundwater, soil, and plants. They exhibit biodegradable and non-biodegradable organic matter, compounds, humic substances, ammonia, nitrogen, heavy metals, and chlorinated salts. Improper landfill leachate management may have negative consequences for both the environment (biodiversity) and public health (Hredoy *et al*., 2022). The potential impacts of sawdust landfilling are illustrated in **Figure 3.5**. This figure highlights key water quality indicators that can be affected by the leachate produced from sawdust decomposition in a landfill, including Dissolved Oxygen (DO), Total Dissolved Solids (TDS), Electrical Conductivity (EC), and Total Hardness (TH). Generally, improper handling and management of waste, including sawdust, pollutes the eco system and emits noxious fumes and gases into the atmosphere, thereby contributing to global warming and its emission back to humanity, resulting in environmental hazards. Hence, researchers are researching ways of converting sawdust into value-added goods to provide a green, clean, and sustainable environment while also contributing to the global waste management system (Adegoke *et al*. 2022; Deac *et al*., 2016; Hredoy *et al*., 2022; Vaverková *et al*., 2020).

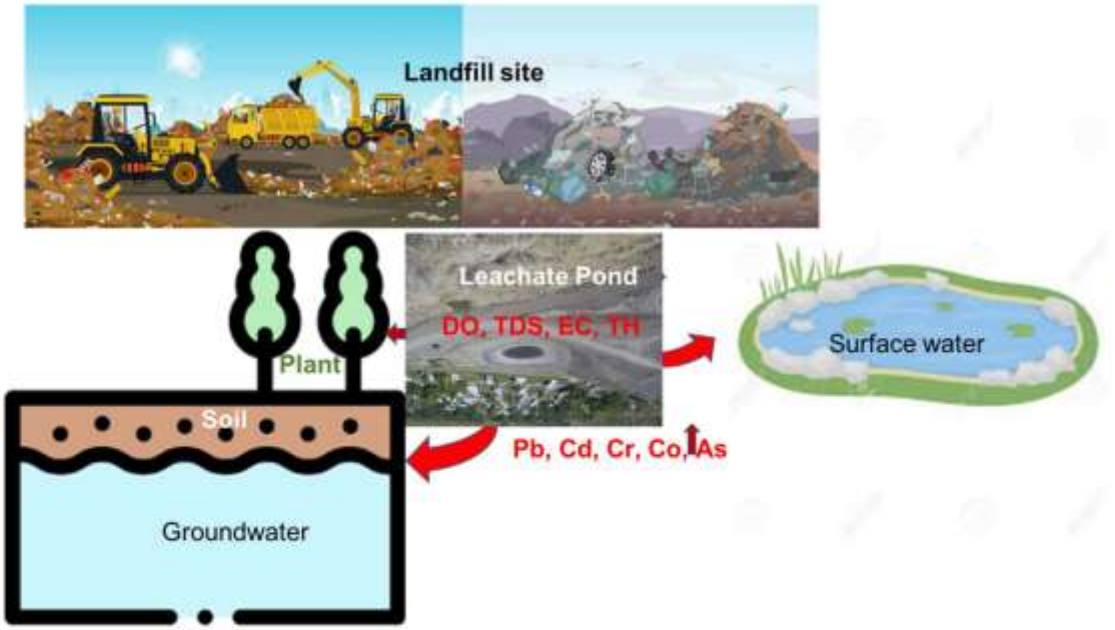

Figure 3.5. Effects of landfill leachate on the surrounding eco-systems (Hredoy *et al*., 2022) Open Access

3.4. General applications of sawdust

Traditionally, wood residues were considered "little to no economic value byproducts". However, nowadays wood residues are treated as a valuable resource from which energy, fuel, and other profitable goods can be derived (Rominiyi *et al*., 2017). Sawdust, for example, is widely regarded as a polluting timber-industrial waste, but it has the potential to become a valuable commodity as a raw material in the manufacturing industries (Charis *et al*., 2019; Ferede *et al*., 2020; Jahan *et al*., 2022; Maharani *et al*., 2010). Sawdust is a low-cost energy source, an excellent adsorbent for extracting heavy metals and other impurities from water, and an inexpensive building material (Setyono & Valiyaveettil, 2014; Turgut *et al*., 2007). As such, the energy industry burns it directly or indirectly to produce wood gas, briquettes, pellets, and other products, whereas the building and construction sector uses it to manufacture wood boards, light construction materials such as shelves, notice boards, walls, and roof sheeting for mobile homes, and as an insulator in the refrigerating system and cold conservation (Charis *et al*., 2019; Rominiyi *et al*., 2017). Furthermore, as an absorbent, it has been widely utilized to contain or clean up surface oil spillages (Rubasinghe *et al*., 2013) and as an alternative point-of-entry (PoU) water treatment in areas where modern water treatment methods are out of reach for people (Udokpoh & Nnaji, 2023).

Sawdust is composed of various functional groups such as nitrogen (-N), oxygen (-O), sulphur (-S), and phosphorus (-P), conferring the ability for effective removal of environmental pollutants. These groups are essential in facilitating pollutant removal mechanisms like hydrogen bonding, where the polar groups on the sawdust surface interact with polar contaminants, and ion exchange, where positively charged metal ions in solution are exchanged with negatively charged functional groups on the sawdust surface, aiding in the purification of soil or water systems (Setyono & Valiyaveettil, 2014; Tan *et al*., 2021). A systematic review by Setyono and Valiyaveettil (2014) revealed that unmodified and modified sawdust can be used to remove different impurities from wastewater including. **Figure 3.6** is an illustrative example of the removal of arsenic ions (As^{3+} and As^{5+}) from aqueous solutions with renewable metal oxides (La_2O_3/ZrO_2)-sawdust hybrid composites. The dominant adsorption mechanisms differed for both hybrids. Electrostatic interactions were found to be more prevalent for La_2O_3-sawdust, while ligand exchange was more common for ZrO_2-sawdust. The ZrO_2-sawdust composite exhibited extraction capacities of approximately 12 mg/g for $As5^{+}$ and 29 mg/g for As^{3+}, while La_2O_3-sawdust composites demonstrated higher capacities of about 22 mg/g for As^{5+} and 28 mg/g for As^{3+} (Setyono & Valiyaveettil, 2014). Moreover, ZrO_2 and sawdust composites were able to regenerate with an efficiency of approximately 50%, whereas La_2O_3 and sawdust could be fully reused without any loss in adsorption efficiency.

Figure 3.6. Removing arsenic pollutants with modified sawdust (Setyono & Valiyaveettil, 2014) Copyrights American Chemical Society

Besides making domestic fires and firing up power plants, due to its high cellulose content, sawdust can be used as a raw material in the production of bioethanol. Bioethanol is a clean, green, and renewable energy produced from lignocellulosic biorefinery that has attracted attention as a substitute for petroleum and fossil fuels while relieving environmental and energy crises (Nwakaire *et al*., 2013). According to Amaefule *et al*. (2023), bioethanol can be used as fuel on its own or combined with gasoline. Bioethanol, both in pure form and blended with gasoline, serves as a versatile fuel option, commonly used in flexible fuel vehicles in countries like Brazil and the United States. Blends such as E-10, E-15, and E-85 offer varying ethanol concentrations. Its use can replace gasoline additives, offering strong stopping power and other benefits like biodegradability, sulphur-free nature, and less hazardous by-products from incomplete oxidation. As the most utilised biofuel globally, bioethanol finds applications not only in transportation but also in domestic cooking, fuel blending, hydrogen production, and as a precursor for various chemical products. In a two-part bioethanol production study (Amaefule *et al*., 2023), different particle sizes of sawdust (212 µm, 300 µm, and 500 µm) were preheated, hydrolysed with H_2SO_4, and fermented with two species of yeast, i.e., *Saccharomyces cerevisiae* and *Saccharomyces chevalieri*. Distillation recovered bioethanol of varying weight, pH, density, viscosity, flash point, and heating value, with alcohol content consistently at 69%.

Sawdust is a durable and decay-resistant material that can serve as a long-lasting substitute for traditional building materials (Batool *et al*., 2023; Olaiya *et al*., 2023). Cultrone *et al*. (2020) investigated the effects of incorporating sawdust as an additive to clayed earth used in brick production. The sawdust, sieved to remove larger grains, is mixed in varying proportions (2.5%, 5%, and 10%) with the clay for experimentation. The bricks were handcrafted due to the demand for less standardized products in construction and restoration projects. Handmade bricks are preferred for their versatility in size, shape, and finish compared to industrially extruded ones. The manufacturing process involves moulding the clay/sawdust mixture, cutting it into cubes, and firing at temperatures ranging from 800 °C to 1100 °C. Slow cooling prevents cracking during the transition of quartz types. After firing, the bricks are submerged in water to eliminate CaO grains, which otherwise could lead to cracking due to lime blowing. The resulting bricks were lighter in weight with better thermal insulation, for which extensive vitrification was not required. This method would enable them to be fired at lower temperatures, so reducing energy costs.

Sawdust comes in a variety of sizes and shapes to suit a wider range of industrial applications. A range of factors, including the source (wood type and geographical location) and manufacturing process, influence the physical and chemical qualities of sawdust. Its composition differs significantly depending on the type of processed tree species (Chávez-Rosales *et al*., 2021; Turgut *et al*., 2007). **Table 3.3** summarises the typical sawdust composition based on the source. The shape, dimension, and amount of dust produced are all influenced by the physical and chemical properties of the sawed and abraded wood, as well as the form, dimension, sharpness of cutting instruments, and technological circumstances of sawing and sand abrading operations (Mračková *et al*., 2016). Saw blades play a critical role in determining particle size, typically classed as oversized, coarse, pin, or fine particle-sized, with diameters of >850 m, 500-850 m, 400-500 m, and 177-400 m, respectively (Bello, 2017). Sawdust has features similar to wood, but because it is in particle form, some of its structural properties are modified. However, sawdust can be reformed into wood and imitate it in some applications when necessary. When sawdust is used as an energy source, it can produce the same amount of heat as other fuels, making it an adequate wood substitute. Sawdust is a versatile material that can be moulded into different shapes and sizes using various techniques, making it an ideal material for advanced designs (Rominiyi *et al.*, 2017; Udokpoh & Nnaji, 2023).

Table 3.3. Chemical composition of sawdust

Plant Source	Classification	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Extractives (%)	Reference
Hevia sawdust	Hardwood	39	29	28	4	(Ali *et al.*, 2013)
Palm Pressed Fiber (PPF)	Grass like (neither soft or hardwood)	50.38	16.48	19.46	13.68	(Carrillo-Parra *et al.*, 2020)
Meranti wood	Hardwood	53.00	18.50	32.4	2.5	(Ahmad *et al.*, 2016)
Maple wood	Hardwood	60.15	17.71	11.61	10.53	(James *et al.*, 2014)
Pine wood	Softwood	44	26	26	4	(Rusanen *et al.*, 2018)
Eucolyptus Grandis	Hardwood	41.6	19.6	27.0	7.3	(Chen *et al.*, 2020)

Research trends have shown that sawdust and its derivatives can be used as alternatives in the production of sustainable engineering materials for a variety of applications (Ahmad *et al.*, 2016; Ali *et al.*, 2013; Carrillo-Parra *et al.*, 2020; Chen *et al.*, 2020; James *et al.*, 2014; Rusanen *et al.*, 2018). Ideally, it can be used as reinforcing materials in inferior bioplastics to provide the requisite superior physical and mechanical properties for a wide range of technical applications, while also addressing the issues of depleting fuel supplies and environmental degradation (Islam *et al.*, 2019;

Pannu *et al*., 2021; Raja *et al*., 2022; Raja *et al*., 2022; Rangappa *et al*., 2022). Sawdust has been predominantly used in building and construction as a filler for more than four decades (Olaiya *et al*., 2023). Besides substituting sand in concrete, other sawdust composites include particleboard, floor slabs, panels, attic, and brick. Introducing sawdust as an intriguing biological waste and transforming it into a resource for sustainable remediation technologies might increase its application spectrum in varied applications (Mwango & Kambole, 2019; Setyono & Valiyaveettil, 2014).

3.5. A brief discussion on hybrid systems

The term composite is Latin derived, *composĭtus* used to describe a multi-phase combination material made up of two or more materials with significantly diverse chemical and physical properties through an interface (Borah *et al*., 2016). The composite material not only retains the main properties of the original materials but also possesses new properties that none of the original components have (Saba *et al*., 2015; Safdari & Al-Haik, 2018; Wang *et al*., 2014; Zarna *et al*., 2021). The two most commonly mentioned composite phases are the matrix and the filler. However, an additional transitional phase called the interface exists between the phases. The arrangement of both matrix and filler through interface of the composites is illustrated in **Figure 3.7**. During composite formation, the matrix is represented by a continuous, homogeneous and/or isotropic phase, with a lower modulus and high elasticity (such as polymers extracted from plants) polymers, carbon, ceramics, or metals. The filler, which is usually in the form of short or long fibres with much higher physical and mechanical qualities, is surrounded by the matrix. Generally, the scattered phase is stronger than the continuous phase, and it is responsible for enhancing one or more properties of the matrix (Jaiswal *et al*., 2019; Safdari & Al-Haik, 2018; Wijesinghe *et al*., 2020).

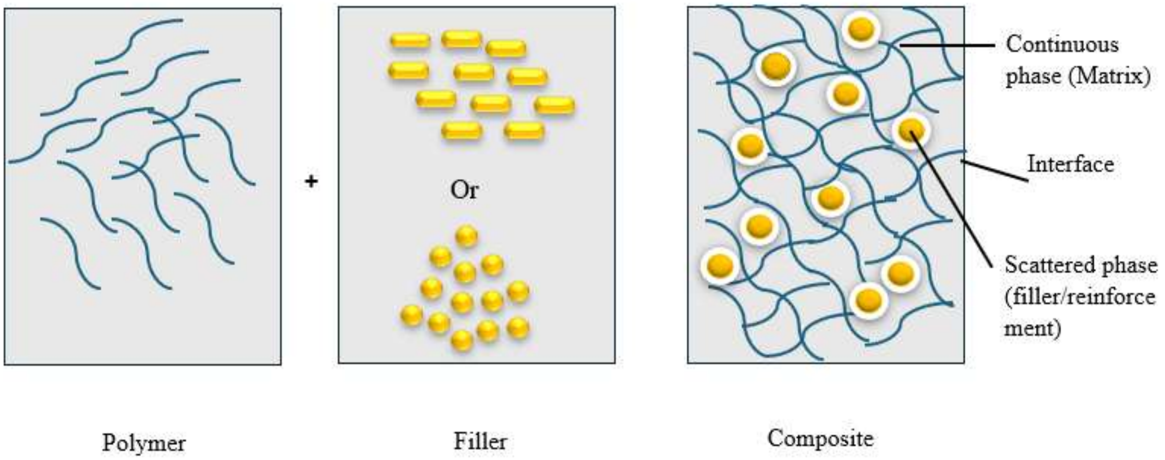

Figure 3.7. Arrangement of both matrix and filler through interface of the composite

The range of prospective engineering material requirements is diverse and particular and almost impossible to meet with a single material (Allwood *et al*., 2013). Combining two or more materials with distinct properties to create a composite material leads to improved properties than the individual components. Several natural and synthetic additives have been incorporated in various matrices to create novel inorganic and/or organic combination composites suitable for different engineering applications (Park & Seo, 2011; Wang *et al*., 2014). The different materials work together to give the composite unique properties. Generally, the composite material will have better and/or improved qualities than any of the components alone. Thus, composite materials have superior mechanical and physical properties, making them more suitable for a wide range of applications than individual composite components (Carey, 2017; Knight & Curliss, 2003; Linganiso & Anandjiwala, 2016). They are also versatile with unique characteristics such as high strength and modulus-to-weight ratio, ease of processing, and cost-effectiveness. As such, they are in high demand for practical applications in major industries, including aerospace, automobile, thermal and acoustic insulation, packaging, sports, defence, construction works, *etc.* (Maiti *et al*., 2022; Ravishankar *et al*., 2019). One of the most significant advancements in material history has been the creation of composite materials and related design and manufacturing processes. The emphasis in engineering and research has turned away from monolithic materials and toward natural and/or synthetic fibre-reinforced materials. The fundamental advantage of using composite materials in advanced applications over single materials is that a composite is a multiphase material made up of two or more physically separate and mechanically separable components.

Furthermore, composites are made by carefully mixing the ingredients to ensure homogeneous dispersion, resulting in perfect qualities (Ahmad & Zhou, 2022; Cheung *et al*., 2009; Zweben, 2015). Finally, the mechanical properties of composites outperform those of individual components, and in some situations, are distinct from constituent properties (Ostolaza *et al*., 2023). In recent years, natural fibres have attracted research interest from relevant stakeholders as alternative reinforcing materials in polymer composites over conventional glass and carbon fibres. Natural fibres exhibit superior mechanical properties such as flexibility, stiffness and modulus to glass fibres. However, despite natural fibres offering several attractive features as potential substitutes in composites, they are still relatively inferior to synthetic fibres. This limits the use of natural fibre-based composites in certain advanced applications (Jiang *et al*., 2020; Kumar *et al*., 2017; Kumar *et al*., 2021; Mahir *et al*., 2019; Mann *et al*., 2023). Although fibre-reinforced composites have acquired market share in advanced applications, the key limiting factors that impede the use of natural fibres in composite materials are low mechanical characteristics and water absorption. Bio-fibres, particularly plant-based fibres, absorb a lot of moisture, resulting in composites with low mechanical strength (Feng *et al*., 2019; Nurazzi *et al*., 2021). A possible remediation technique for improving the characteristics of fibre composites is hybridisation, which is the outcome of a combination of many phases in which at least two varying additives are combined with the matrix. By integrating two or more fibre types, these hybrid composites provide a superior combination of physical and mechanical qualities than non-hybrid composites. The three basic types of hybrid composites are synthetic/synthetic, synthetic/natural, and natural/natural hybridization. Synthetic/natural fibre-reinforced hybrid composites are the most commonly investigated hybrid composites due to their superior mechanical performance. Current trends, on the other hand, favour natural/natural hybridization, owing to the necessity to achieve a balance between environmental friendliness and mechanical strength. Through hybridisation, the synergy of merging the particular benefits of each reinforcement and/or filler, general traits, and overall performance of the final composite can be improved (Bouhfid *et al*., 2019; Mochane *et al*., 2019; Shamsuyeva *et al*., 2019; Seydibeyoğlu *et al*., 2023; Swolfs *et al*., 2014). The physical and mechanical properties of forestry and agricultural biowaste are diverse and vary greatly based on the origins and compositions of organic materials, ranging from soft to pliable plant matter (Ramage *et al*., 2017; Thapliyal *et al*., 2023). Various factors, such as moisture content, cellular structure, and decomposition stage, affect the properties of biological waste. These traits have recently inspired some researchers to develop hybrid composites by combining multiple forms of bio-fibre. The hybrid approach maximises the potential of both additions and in some cases, a synergistic impact may emerge (Bouhfid *et al*., 2019; Mochane *et al*., 2019; Shamsuyeva *et al*., 2019; Seydibeyoğlu *et al*., 2023; Swolfs *et al*., 2014). Sawdust fibre hybrid systems are currently among the most researched natural fibre hybrid systems. In addition to their superior flexibility, stiffness, and modulus comparable to glass fibres, sawdust fibres are eco-friendly and relatively cheaper. Sawdust-improved systems are durable, making them ideal candidates for sophisticated engineering applications that demand high-strength materials with flexibility (Islam *et al*., 2019; Pannu *et al*., 2021; Raja *et al*., 2022; Raja *et al*., 2022; Rangappa *et al*., 2022). Traditional sawdust composite systems have shortfalls that limit their applicability; nevertheless, pairing sawdust with other complementary fibres in selected matrices guarantees improved properties and hence viability in various applications (Ismail *et al*., 2021; Ismail *et al*., 2022). While the hybrid system can use multiple fibres, a combination of only two types of fibre would be most effective. In principle, the hybridisation of sawdust composites enables a balance between composite performance and cost unattainable with the single fibre (Jayamani *et al*., 2020). Sawdust composite can be moulded into different shapes and sizes using various processing techniques, making it a versatile engineering material. The resulting composites are lightweight and easy to work with, therefore ideal for use in applications where weight is a consideration (Lendvai *et al*., 2022; Olaiya *et al*., 2023). Over the years, researchers have evaluated the performance of numerous hybrid systems comprising sawdust and other natural fibres. A summary of selected studies and their findings are shown in **Table 3.4**. The hybrid composites in **Table 3.4** have demonstrated outstanding qualities when the fibre is paired with its counterpart or another reinforcement(s). Overall, properties such as mechanical (tensile, flexural, impact strength, *etc.*), thermal, dimensional stability, morphological features, and moisture absorption were improved. In addition, the hybrids can be suitable for building and construction, textiles, automotive, and packaging among other applications (Ahmed *et al*., 2018; Lendvai *et al*., 2022; Olaiya *et al*., 2023; Raja *et al*., 2022; Raja *et al*., 2022).

Table 3.4. Selective studies on sawdust polymer hybrid composites and other hybrid systems

Sawdust (SD) fibre hybrids	**Other fibre hybrids**	**Fabrication and optimum effective fibre concentration: Sawdust (A) and other fibres (B)**	**Effects of the fibre combinations on the properties of composites**	**Recommended Application**	**References**
SD/Banyan/Epoxy	Ramie/Banyan/Epoxy	**A.** Sawdust/banyan fiber(s) epoxy hybrid were prepared by hand layup process. Better mechanical properties were obtained with ratios: (2% sawdust + 38% banyan) loading whereas the least was observed at (13 sawdust + 37% banyan).	– Improved tensile and flexural strength with high energy absorption capacity. – SEM images revealed poor adhesion between the fibers and polymer matrix.	–	(Raja *et al*., 2022)
		B. Hand layup method was used to fabricate 50% of the fillers (woven mats) and 50% of the polymer matrix. Optimum results were obtained at 37.5 + 12.5 wt. % banyan/ramie fibre composition.	– Increased storage modulus leading to improved stiffness and overall properties. – SEM images revealed remarkable bonding between the fibres and epoxy.	– Helmets and car interiors	(Raja *et al*., 2022)
SD/Chicken Feathers/Epoxy	Ceiba Pentandra bark fiber/Chicken feather fiber/ Epoxy	**A.** The composites were prepared by an extruder. The best results were obtained with a combination of chicken feathers (CF) and sawdust (SD) at a composition, 80H-10CF-10SD.	– Sawdust and chicken feather enhanced the mechanical properties. The enhancement in mechanical properties was observed through impact, flexural and tensile strength. – Thermal properties were also improved.	–	(Uppalapati *et al*., 2018; Uppalapati *et al*., 2020)
		B. The bioepoxy (BE) composites were prepared by solvent casting and	– Better mechanical performance and improved	–	

		compression moulding. Composition – 36.36/9.09/54.54 CPF/C/BE and 18.18/18.18/9.09/54.54 CFF/CPF/C/BE wt.% were studied.	thermal stability for the fabricated composites. – Better interfacial interaction between the filler(s) and bioepoxy resin matrix. – CPF/C/BE showed better mechanical properties than CFF/CPF/C/BE composites.		(Rangappa *et al*., 2022)
SD/Cotton/Polypropylene	Jute/Cotton/Polypropylene	**A.** Hot pressed hybrid composites fabricated at different fibre loads (between 10 and 20 wt. %). A layer of cotton fabric was spread over the entire cross-section, with a consistent amount for all samples. Optimal performance was observed at 15 & 20 wt.%. **B.** Composites were prepared by blending and compression moulding. Better performance of the composites was achieved at 30 wt.% filler loading.	– The mechanical properties (Tensile and flexural strength) of the composites improved when reinforced with cotton. – The increase in natural filler contents led to a substantial increase in water absorption at 20% fabric/wood-sawdust. – Outstanding results in terms of transmission loss and sound absorption in comparison to single fibre reinforced composites. – Chemically stable composites.	– – Acoustic – noise reduction field	(Ayrilmis *et al*., 2017; Islam *et al*., 2019) (Azieyanti & Faris, 2020)
SD/Coir/Epoxy	Sisal/Coir/Epoxy	**A.** The epoxy fibre composites were fabricated using the hand layup technique at varying filler and reinforcement loading. The addition of sawdust improved the mechanical properties of the composites up to a certain	– The addition of filler material improved the tensile, flexural, and hardness properties of the specimen up to a certain percentage, enhancing overall mechanical characteristics. – Higher water absorption with the addition of sawdust was	–	(Nair *et al*., 2018)

		degree. Higher filler percentage (>5%) increased resistance to resin penetration, rendering specimen redundant.	observed due to the hydrophilic nature of sawdust and coir.		
		B. The fibre composites were compression moulded. Better mechanical performance was achieved with the 20/15/65 Sisal/Coir/epoxy composites when the fibres were pre-treated with 5% NaOH.	– The sisal and coir fibres improved the tensile, flexural and impact properties of natural composites. – SEM – hybridization improves reinforcement and adherence of epoxy resin.	– Aerospace and automobile industries for their interior parts.	(Akash Sreenivasa Rao *et al.*, 2016)
SD/Rice husk/Polylactic acid	Banana/Rice husk/ Polylactic acid	**A.** Fibre reinforced polylactic acid composites were injection moulded at compositions between 2.5 and 10 wt.%), with banana to rice husk ratios of 1:1. Improved performance was observed at maximum loading of 10 wt.% (where 5 wt.% is banana fiber and 5 wt.% is rice husk).	– Significant improvement in their ability to resist deformation but reduced mechanical strength. – The fibres improved the overall crystallinity of the polymer by acting as nucleating agents	–	(Lendvai *et al.*, 2022)
		B. Composites of weight percentages ranging from 10 to 40 and banana to rice ratios of 1:1 were prepared by extrusion. Maximum results were obtained with a fiber composition of 40 wt.%.	– The mechanical properties, i.e. tensile and flexural strength of the composites, were 2.5 times higher. – Impact strength also doubled.	–	(Pannu *et al.*, 2021)

SD/Jute/Epoxy	Oil palm empty fruit bunches (EFB)/Jute/Epoxy	**A.** Hand layup in five different composition combinations 80/20. The matrix was kept constant at 20% while the composition of SD ranged from 0-40% and Jute 80-40. Better mechanical performance was observed at 30 wt.% SD loading.	– Flexural and impact strength improved. – Jute fibres resulted in increased water absorption in comparison to sawdust.	– Partition walls	(Mahesh *et al*., 2022)
		B. Hybrid composites prepared in a stack up mould. The matrix was kept constant at 60% while fibre combination varied from 10-40 wt.%. Reduced quantities of the fibres (1:4) led to improved strength and stiffness.	– Improved flexural, impact and tensile strength. – Morphological analysis showed poor compatibility between the fibres and matrix (cracks, debonding).	–	(Jawaid *et al*., 2010)
SD/Flax/Epoxy	Kevlar/Flax/Epoxy	**A.** Sawdust/Flax fiber(s) epoxy hybrid were prepared by hand layup technique and studied.	– Overall mechanical properties improved. Enhanced tensile, flexural and impact strength.	Automotive interior, furniture with complex shapes	(Terciu & Curtu, 2012)
		B. Kevlar/flax fiber/epoxy hybrids were created via hand layup and compression moulding. Kevlar at a concentration of 25 wt.% resulted in a twofold increase in the resistance to failure of the composites.	– Improved the strength, stiffness, and moisture absorption of flax composites.	–	(Sarwar *et al*. 2020)

3.6. Preparation and morphology of sawdust composites and/or hybrids

Sawdust composites are made by combining sawdust with a binder or matrix material to create a composite with enhanced properties. Properties of these composites can be further advanced through hybridisation with additional materials such as fibres, reinforcements, or nanoparticles (Andrew & Dhakal, 2022; Rashid *et al*., 2024). The production method typically involves mixing the sawdust with the binder or matrix using various techniques such as compression moulding, extrusion, resin transfer moulding, thermoforming moulding or injection moulding, depending on the desired shape and properties of the completed product (Jawaid *et al*., 2010; Lendvai *et al*., 2022; Uppalapati *et al*., 2018; Uppalapati *et al*., 2020). In compression moulding, for example, the mixture of sawdust and binder is placed into a mould and subjected to heat and pressure to combine the composite (Elsheikh *et al*., 2022). During the preparation, additional additives such as plasticizers, coupling agents, or fillers can be incorporated to improve specific properties including flexibility, adhesion, or strength (Ghaffar *et al*., 2018). Many matrices, including polymers, can be used to create sawdust composites or hybrid systems, and the selection of the matrix depends on the desired qualities of the composite, the processing technique, and the intended application (Boey *et al*., 2022). Thermosetting, thermoplastic, and biopolymer matrices are a few of the most popular types of polymer matrices currently explored for sawdust (Masuelli *et al*., 2013). Thermosetting resins such as epoxy, phenolic, and polyester resins are the most widely employed for sawdust composites (Andrew & Dhakal, 2022). They undergo a curing process where they are initially liquid or semi-liquid and eventually harden due to a chemical crosslinking reaction. They offer high dimensional stability, excellent chemical resistance, and mechanical qualities (Muc *et al*, 2019). Epoxy resins, in particular, are known for their great strength and adhesion (Su *et al*., 2011). Thermoplastic polymers such as polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), and polyethylene terephthalate (PET) are also popular choices for sawdust composites. Thermoplastics offer good toughness, flexibility, and ease of processing (Dybka-Stępień *et al*., 2021). Bio-based polymers have gained popularity in the production of sawdust composites due to growing demand for environmentally friendly materials (Najafi *et al*., 2006; Yashas *et al*., 2022). Polymers derived from natural resources, such as starch, cellulose, lignin, or soy protein, can be used as matrices. These bio-based polymers have several advantages, including biodegradability, renewable supply, and low environmental impact. As such, there is a growing interest in sawdust composites based on bio-based polymers such as polylactic acid (PLA), polyhydroxyalkanoates (PHA) and polybutylene succinate (PBS) that exhibit enhanced stiffness and impact resistance compared to pure plastics (Lendvai *et al*., 2022; Petchwattana *et al*., 2017; Tian *et al*., 2021). These composites can be applied in different industries, including automobile components, building materials (such as decking and fences), furniture, packaging materials, and consumer items (Jaya *et al*., 2016; Schwarzkopf & Michael 2016). The morphology of sawdust hybrid composites refers to the structure and arrangement of the components within the composite (Ismail *et al*., 2021; Jaya *et al*., 2016). Generally, sawdust particles are spread throughout the binder matrix. The distribution and orientation of sawdust particles in the composites have a significant impact on the mechanical, thermal, and physical qualities of the finished product. For uniform characteristics, sawdust particles must be distributed evenly throughout the matrix. The physical properties of the sawdust particles influence the total composite strength, stiffness, and durability (Ismail *et al*., 2021; Mochane *et al*., 2019; Seydibeyoğlu *et al*., 2023; Swolfs *et al*., 2014). For instance, the shape and size of sawdust particles influence the mechanical characteristics and homogeneity of composites. Smaller particle sizes often result in better interfacial bonding between the matrix and sawdust particles, leading to improved mechanical strength and stiffness of the composite (Jaya *et al*., 2016; Khalil *et al*., 2006; Manaila *et al*., 2016). Also, sawdust is believed to possess a high moisture content, which influences composite processing and performance. Increased moisture levels in the composite mixture tend to impede flowability, producing processing difficulties. It can also induce dimensional instability and reduce the strength of the final product (Elfaleh *et al*., 2023; Girijappa *et al*., 2019; Kabir *et al*., 2012; Rahman *et al*., 2013). Various pre-treatment approaches, such as those shown in **Table 3.5**, can be used to modify the surface properties of sawdust and improve its compatibility. These treatments can improve the interfacial adhesion of sawdust and matrix, resulting in desirable mechanical characteristics and water resistance of composites (Elfaleh *et al*., 2023; Ferede *et al*., 2020; Girijappa *et al*., 2019).

Table 3.5. Possible pre-treatment for sawdust fibres to improve fibre/matrix interactions for better properties

Type	**Treatment**	**Short description**	**Outcomes of possible modifications**	**References**
Chemical	Alkaline	The alkaline reagent is used to clean the surface of plant fibres and modify the cellulose structure. This is known as alkalization, and it reduces the lignin content.	• Improved fibre-matrix adhesion, thermal stability and heat resistivity.	(Elfaleh *et al*., 2023; Ferede *et al*., 2020; Girijappa *et al*., 2019)
	Silane	Involves immersing the natural fibres in a saline solution for a specific duration, allowing the salt to interact with the fibre surface.	• Reduce the moisture regain. • Improved tensile strength.	(Elfaleh *et al*., 2023; Girijappa *et al*., 2019)
	Acetylation	Involves treating fibres with acetic anhydride or acetyl chloride in the presence of a catalyst. The acetylating agent reacts with the hydroxyl groups (-OH) present in the fibre molecules substituting the hydrogen atoms with acetyl groups.	• Improve tensile and flexural strength.	(Girijappa *et al*., 2019)
	Peroxide	The peroxides decomposed to form free radicals that react with the hydrogen group of the cellulose fibres and polymer matrix.	• Mechanical properties.	(Girijappa *et al*., 2019)
	Benzoylation	Benzoylation is used to decrease the hydrophilic nature of the fibres.	• Improve hydrophobicity. • The thermal stability of the treated fibres was higher than that of the untreated fibres.	(Girijappa *et al*., 2019)
	Potassium Permanganate (KMnO4)	The chemical reagent potassium permanganate is utilized to change the interfacial contact between the fibre and matrix.	• Homogeneity in the mixture, improving morphology contributing to enhanced mechanical properties.	(Girijappa *et al*., 2019)

Subcritical water		Subjecting fibres to a liquid water treatment at temperatures and pressures below its critical point can help soften and swell the fibres, making them more flexible and easier to process.	• Good dispersion leading to improved morphology. • Enhanced fibre-matrix interactions.	(Cheng *et al*., 2021; Novo *et al*., 2015)
Supercritical water		Supercritical water exhibits unique solvent characteristics at high temperatures and pressures (374°C and 22.1 MPa), allowing for effective lignin degradation and solubilization. This delignification procedure improves the cleanliness and cellulose content of the fibres, making it more appropriate for a variety of uses.	• Improved thermal stability. • Reduced moisture content • Enhanced adsorption properties.	(Louw *et al*., 2016)
Grafting		Grafting is a process of attaching certain chemical moieties or functional groups to the surface of sawdust fibres. This treatment serves multiple functions and can improve the characteristics and performance of the composites.	• Improves fibre wettability by hydrophilic matrix materials, allowing for greater fibre dispersion and wetting within the matrix. Improved hydrophilicity can also make interactions with water-based systems easier, such as in biocompatible or biomaterial applications.	(Manaila *et al*., 2016)
Enzymatic		Enzymes can selectively degrade certain components of lignocellulosic, such as lignin and hemicellulose, while preserving the cellulose structure.	• Better dispersion within the matrix (enhanced morphology) • Improved mechanical properties.	(Patil *et al*., 2019)

Besides pre-treatments, overall optimisation of processing techniques and parameters in the production of sawdust hybrids or composites is crucial for achieving desirable mechanical, thermal, and physical properties, thus ensuring efficient and sustainable use of sawdust as a renewable resource (Alarifi, 2023; Sumesh *et al*., 2020). Processing conditions and techniques have a significant effect on the properties of sawdust composites and/or hybrid systems (Shesan *et al*., 2019). Certain elements, such as the degree of homogeneity of the fibre, wettability of the fibre, fibre length, fibre volume fraction, processing parameters, and fibre orientation, must be taken into account in order to generate high-quality sawdust fibre composites (Alarifi, 2023; Madueke *et al*., 2022; Routray *et al*., 2020; Le & Pickering, 2014; Shesan *et al*., 2019). **Table 3.6** summarises some of the key factors and their impact.

Table 3.6. Core factors affecting the morphology of sawdust composites (adapted from Alarifi, 2023; Madueke *et al*., 2022; Routray *et al*., 2020; Le & Pickering, 2014; Shesan *et al*., 2019).

Factors	**Influence or effect**
Fibre content (Volume fraction of the fibre)	• The content or concentration (volume fraction) of sawdust and other reinforcing elements affects the morphology of the composites. • Increased reinforcement or filler content can result in more densely packed structures, affecting the arrangement and distribution of the particles. • Fibre content optimisation is necessary to achieve a balance between processability and better composite qualities (Good results have been obtained between 10 – 40 wt. %).
Fibre orientation	• Fibre orientation influences the degree of dispersion within the matrix. • Well-aligned and uniformly distributed fibres result in sawdust composites with improved mechanical properties due to enhanced load transfer along the fibre direction. • Poor fibre dispersion and alignment, on the other hand, might result in weak interfacial bonding and lower mechanical performance.
Particle size	• The particle size of sawdust and other reinforcing materials in the composite can greatly impact the morphology. • Smaller particle sizes often result in better particle dispersion within the matrix thus a more homogeneous morphology. • Controlling particle size distribution is critical to preventing particle agglomeration or clustering, which can impair the mechanical properties of the composite.

Choice of the matrix	• Various matrices and reinforcing agents have different interactions and compatibility, which can affect particle dispersion and the overall morphology of the composite. • The matrix choice depends on the desired properties of the composite and the intended application. • The matrix or binder must be compatible with the sawdust particles and provide sufficient adhesion and cohesion to form a strong composite. • Thermosetting resins (e.g., epoxy, phenolic), thermoplastics (e.g., polypropylene, polyethylene), and bio-based polymers (e.g., starch, lignin) are common matrices for sawdust composites.
Additives	• Introducing additives such as plasticisers, coupling agents, or fillers can alter the morphology of sawdust hybrid composites. • Their addition can modify the rheological properties of the matrix, encourage interfacial bonding, or improve specific qualities. • However, excessive, or improper use of the additives may lead to morphological defects, including agglomeration or phase separation.
Fibre/matrix interface (Interfacial bonding)	• The binding strength between the sawdust particles and the matrix material is critical for producing the desired shape. • Surface treatment of sawdust particles, compatibility of matrix and reinforcing materials, and usage of coupling agents can all affect interfacial bonding. • Strong interfacial bonding improves load transfer and the overall mechanical performance of the composite.
Processing techniques and parameters.	• Different techniques, such as compression moulding, extrusion, or injection moulding, have varying effects on particle dispersion and orientation. • These methods use varying processing conditions or parameters even when processing the same material. • Changes in parameters such as mixing speed, pressure, and temperature can all have an impact on the properties of the composite. • Proper control of processing parameters is crucial to achieving the desired morphology.

3.7. Degradation of sawdust-reinforced biocomposites

Disposing of plastics at the end of application remains a challenge as available dumping sites are approaching exhaustion. In addition, conventional plastics are resistant to degradation in different media such as soil, water, and composts (Mtibe *et al*., 2021). Natural fibres are biodegradable, and this is one of main reasons they are incorporated in polymer matrices to impart biodegradability and hasten their degradation rates. Therefore, incorporating lignocellulosic waste materials such as sawdust could accelerate the degradation rates of various polymer matrices. Degradation of sawdust-reinforced polymer composites is controlled by factors such as hydrophilicity of the fibres, which determines water absorption of the composites; the source of sawdust also affects degradation of natural-fibre reinforced composites (Kumar *et al*., 2019). The material properties, such as load-bearing properties, tend to decrease as a result of degradation. Fakhrul and Islam (2013) investigated the biodegradability of PP/sawdust (5%) and PP/wheat flour (5%) composites exposed to different degradation conditions including moist soil, water, salt solution, and normal environmental conditions (moisture, temperature, sunlight, and wind). The water absorption tests indicated higher water absorption by sawdust-reinforced PP than its PP/wheat flour counterpart, and this was attributed to highly hydrophilic nature of sawdust compared to wheat flour. Hydrophilic materials with high water absorption rates are likely to degrade faster through hydrolysis and microbial attack. In this case, PP/sawdust composites showed faster degradation rates, which were also confirmed by greater reduction in tensile properties of exposed sawdust-based composites compared to PP/wheat flour composites. Haque and Islam (2024) evaluated the degradability of two epoxy-based composites containing sawdust and jute fibre at 5 wt.%. The biodegradation of the composites was conducted by keeping the samples in the drainage for a period of one year. The composites demonstrated higher water absorption than the neat epoxy sample, with the jute-based composite showing higher absorption capacity than the sawdust composite. After one year, the samples were brownish, with many cavities noticed in the composites.

These changes were attributed to swelling of the fibres and microbial attack. The tensile strength declined after one year of drain water exposure by 40 and 57% in sawdust and jute fibre-based composites, respectively. This indicated that jute fibre offered a higher degradation rate than sawdust, and this was attributed to lower lignin content in jute, which rendered it more prone to microbial attack and degradation. Abdel-Hakim *et al*. (2021) reported an increasing trend in weight loss of sawdust-reinforced expanded polystyrene (EPS) buried under soil for 90 days. The composites were prepared by incorporating sawdust at concentrations ranging from 20 to 80%. Neat EPS did not show any weight loss after 90 days of burial in soil. The percentage weight loss decreased with increasing the amount of sawdust in composites. For example, the weight loss reached 2 and 6.3% in the composite containing 20 and 80% of sawdust, respectively. Dhal *et al*. (2023) developed composites of PLA/PCL reinforced with sawdust at concentrations of 10, 20, and 30%, and evaluated their compostability. The time taken to degrade 10% of the materials decreased with increasing loading of sawdust, while time taken to degrade 50% of the material decreased with up to 20% of sawdust and increased again at 30% filler. In addition, time taken to degrade 90% of the material was not significantly affected compared to neat blend matrices. Prachayawarakorn and Hanchana (2017) buried the composites of modified starch reinforced with sawdust under soil and evaluated changes in the mechanical response of the buried specimen after four weeks. The assessed mechanical properties (modulus, stress at maximum load) declined drastically as a result of burial in soil. The observed decrease was attributed to increased water uptake of the composites in the presence of sawdust, which facilitated degradation of the composites and subsequent decrease in mechanical properties. Islam and Islam (2015) prepared the injection-moulded composites based on modified sawdust and recycled polyethylene. The composites prepared with unmodified sawdust showed higher water uptake, whereas treated sawdust composites showed less water uptake and swelling, attributed to reduced hydrophilicity of sawdust. Consequently, though weight loss increased with number of burial days, the weight loss of untreated sawdust-based composites was higher. Incorporating sawdust as hydrophilic material into polymer matrices serves as a viable strategy to enhance their degradation rates.

3.8. Conclusion and future recommendations

There is a huge pressure globally to reduce waste by recycling and reusing by-products of processing. The forest industry has produced wood, and the byproduct of wood processing is sawdust. Sawdust is inexpensive, abundant and, a lignocellulosic compound that can be easily converted into reusable materials. Due to its biodegradability, eco-friendliness and low weight, sawdust has been utilized as a reinforcing filler in various polymer matrices. The resultant sawdust polymer composites depend on the preparation method and sawdust distribution within the polymer matrix, which have significant impact on the mechanical, thermal, and physical qualities of the finished product. Furthermore, various factors are playing a key role in the morphology of the sawdust/polymer composites and/or the hybrid systems, such as the type of the polymer, content of the sawdust within the matrix, particle size of the sawdust, and synergy of sawdust with other natural fibres. The particle size of sawdust and other reinforcing materials in the composite can greatly impact the morphology, while smaller particle sizes often result in better matrix dispersion, thus, a more homogeneous morphology. In most cases, there seems to be a poor interfacial adhesion between the sawdust and polymer matrix, which affects the properties of the resultant composites. There are possible treatments for sawdust to improve its adhesion with polymers, such as alkaline, silane, and acetylation. A careful inspection of the comparison of sawdust with other natural fibre hybrid composites showed that the sawdust hybrid system can compete with the well-known hybrid composites. In all the hybrid systems, there is a common component for the purpose of comparison, for an example, the common factor is one of the fibres and a polymer matrix. In most of the sawdust hybrid systems reported in these review paper, there is a significant improvement in the mechanical properties of the hybrid systems. Based on the improvements, one can conclude that the sawdust hybrid systems can compete with well-known natural fibre hybrid systems, whereby they may be used in applications such as helmets, car interiors, and aerospace. For future purposes, more of the sawdust hybrid "green composites" based on the biopolymers such as polycaprolactone (PCL), polybutylene succinate (PBS) and polylactic acid (PLA) are needed, since majority of the sawdust hybrid systems are fabricated from epoxy matrix.

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CHAPTER 4

Sugarcane bagasse hybrid system biocomposites: preparation, properties and applications – A review

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This chapter will be submitted as:

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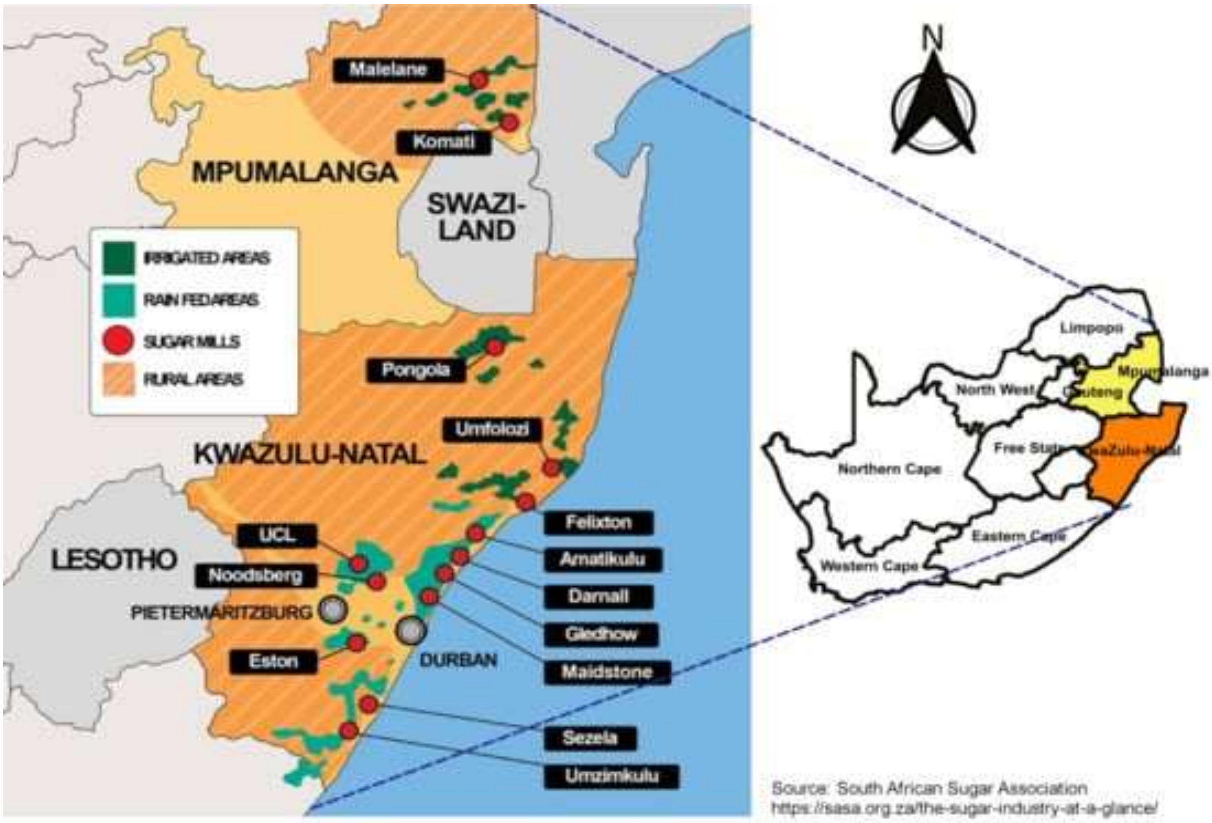
Abstract

In most developing countries, waste management systems remain in their rudimentary stages, contributing significantly to factors that drive global warming. South Africa is among the top cultivators of sugarcane globally and the leading producer in Africa, with sugar production as its primary focus. The remnant, sugarcane bagasse, has limited application and often ends up in the environment, where it can harm plants and animals. Sugarcane bagasse can be incorporated into polymers to produce valuable hybrid composites that can be moulded into various shapes for a wide range of applications. Some growing environmental concerns have driven the development of innovative green materials that cause minimal pollution. Natural fibres —particularly those derived from sugarcane bagasse— have recently attracted significant attention due to their numerous benefits, including abundance, biodegradability, processing flexibility, low health hazards, relatively high tensile and flexural modulus, low density, affordability, and recyclability. These fibres can be chemically modified by adding a specific functional group to their surface or by altering their chemistry. These modifications have been shown to improve matrix adhesion and the mechanical characteristics of composite materials.

4.1. Introduction

South Africa was listed among the top 20 sugarcane producers in 2020, alongside Brazil and India (Nunes *et al*., 2020). The country produces about 20 million tonnes of sugarcane annually, making it one of the largest producers of this crop in Africa, followed by Nigeria and Uganda. In South Africa, sugarcane is mainly grown in two provinces, namely KwaZulu-Natal and Mpumalanga, and **Figure 4.1** shows the distribution of sugarcane farms in these two provinces. The KwaZulu-Natal Province has around 22,949 registered sugarcane growers, with about 14 million supply sections. These supply sections extend from southern KwaZulu-Natal to Mpumalanga Lowveld, as shown in **Figure 4.1** (Mnisi & Dlamini, 2012). The sugarcane produced in these plantations is an essential raw material for sugar and alcohol mills. However, these mills cannot process the entire crop, leaving about 30% of a pulpy, fibrous residue after use (Seroka *et al.*, 2022). This agricultural residue, known as bagasse, is often regarded as waste, with approximately 7 million tonnes produced annually, and negatively impacting the environment (Mnisi & Dlamini, 2012; Seroka *et al.*, 2022).



Source: South African Sugar Association https://sasa.org.za/the-sugar-industry-at-a-glance/

Figure 4.1. Sugarcane plantations in Mpumalanga and Kwazulu Natal, South Africa (Mahmud Md. & Anannya, 2021) Open access

Sugarcane bagasse is therefore considered one of the largest natural fibre resources with potential for innovative technologies (Huang *et al.*, 2012). Nevertheless, its potential benefits can quickly transform into environmental hazards if mismanaged. Improper disposal and inadequate lignocellulosic waste treatment can lead to soil and water contamination, posing a threat to local ecosystems and biodiversity. Sugarcane bagasse holds immense potential for sustainable applications, but this potential can be compromised if it is not managed with due diligence (Ajala *et al.*, 2021; Antunes *et al.*, 2022; Haghdan *et al.*, 2016; Raza *et al.*, 2021;

Ungureanu *et al*., 2022). As South Africa and the rest of the world strive to balance economic development and environmental preservation, it is necessary to understand the role of sugarcane bagasse (Iwuozor *et al*., 2023). Reviewing current waste management techniques and providing long-term solutions to avoid potential concerns is therefore crucial. One such idea is to use sugarcane bagasse as a substitute material to produce fillers and/or reinforcement for large-scale commodity polymers, which can help reduce reliance on petroleum and polymer goods while easing the burden on waste management systems (Huang *et al*., 2012; Iwuozor *et al*., 2023; Józó *et al*., 2022; Shah *et al*., 2013).

Meanwhile, recycling and reusing industrial waste residues are an effective strategy for minimising the disposal of environmentally unfriendly waste. The latest trends focus on the valorisation of industrial agricultural wastes as a solution to the growing problem of inadequate disposal of agro-waste residues (Singh *et al*., 2021; Srivastava *et al*., 2023). Thus, the development of hybrid composites through reinforcements in material science. When fibres and polymers are combined, they create composite materials that exhibit improved strength, durability, and sustainability. These fibre polymer hybrid systems possess some enhanced mechanical, thermal, and environmental properties and find applications in various industries, contributing to advancements in materials science and technology. Advancements in the processing of sugarcane bagasse have created numerous possibilities for the sugarcane industry. By reusing this waste material, the industry has unlocked the potential for innovative technologies and value-added bioproducts that can be applied in various practical applications. Sugarcane bagasse has the potential to play a significant role in sustainable resource management (Iwuozor *et al*., 2023; Kumar *et al*., 2021; Loh *et al*., 2013; Shah *et al*., 2013). This review aims to comprehensively examine the significance and applications of sugarcane bagasse reinforced polymer hybrid systems. It delves into the latest research, methodologies, and advancements in this field, shedding light on the potential of these hybrid materials to address challenges in waste management, environmental conservation, and the development of high-performance materials.

4.2. General overview of sugarcane bagasse

Sugarcane, a crop with a history dating back to 8000 BC, belongs to the Saccharum genus, comprising six species (Nunes *et al*., 2020). Sugarcane is a tall grass originating in Southeast Asia and is now widely cultivated in tropical countries. The commercial species, *Saccharum* *officinarum L*, is typically grown in warm, sunny climates, although slightly cooler conditions are preferred during the harvesting season. The global sugarcane production reached 1.84 billion tonnes in 2017, and this variety was predominantly used for sugar production, although other applications exist (Seroka *et al*., 2022). Brazil, for instance, has been utilising sugarcane for sugar production for centuries, while in more contemporary times, it has been used to generate ethanol and electricity through an integrated plant (Brienzo *et al*., 2016). Sugarcane, a member of the *Poaceae* family, resembles other monocotyledons in stem structure, but its stem is solid rather than hollow. While the stems are the primary source of sugar juice and bagasse, the leaves and other plant parts can also be utilised for energy generation, particularly in co-generation systems. Sugarcane composition is typically in the range of 86% to 92% juice and 8% to 14% fibrous material, with this varying depending on several factors, including plant variety, number of tips and leaves, maturation, harvesting period, burning before harvesting, and whether the harvest was mechanised or manual (Kabeyi & Olanrewaju, 2023). Climatic factors, such as rainfall during plant growth, also influence sugarcane yield and quality. The sugar production process involves cleaning, crushing, and milling the plant to extract juice, which is then heated, clarified, and filtered to separate sucrose. The resulting syrup is concentrated through evaporation, then crystallised to form sugar, and separated from the remaining liquid. This process is summarised in **Figure 4.2**. The residue, known as bagasse, is a matted cellulose fibre that constitutes about one-third of the plant. It is a sustainable energy and the fuel resource for the sugar milling industry. Sugarcane bagasse is a versatile waste material with numerous practical applications, and a vital contributor to sustainable resource management (Loh *et al*., 2013; Oleszek *et al*., 2023; Vinass *et al*., 2021).

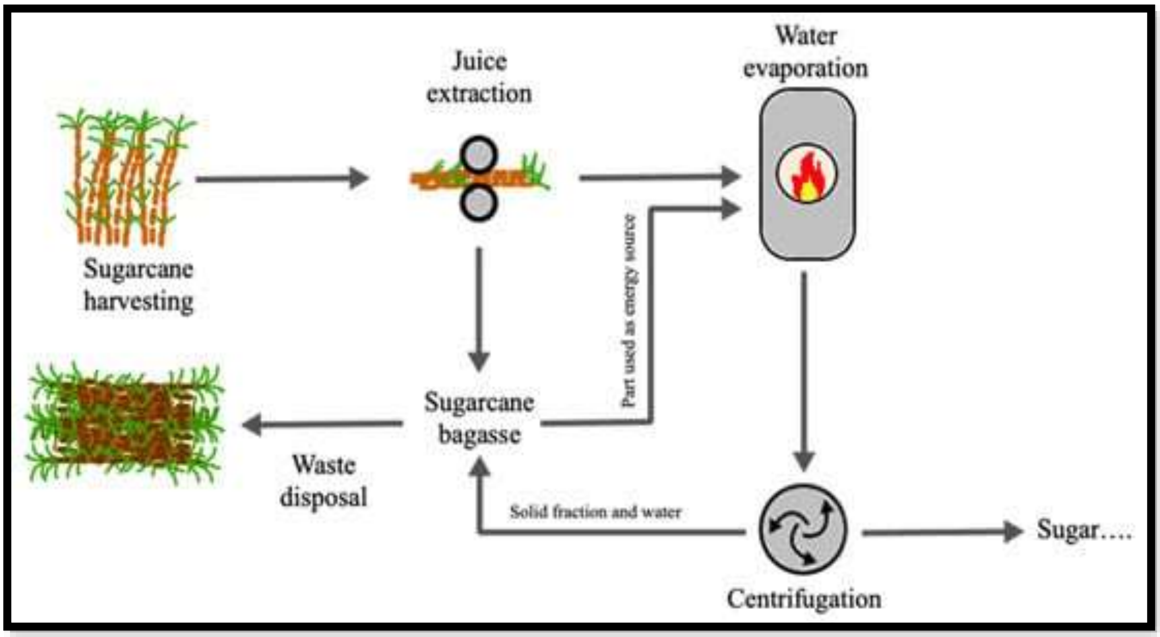


Figure 4.2. Sugar production simplified (Nunes *et al*., 2020) Open access

The fibrous residue is a significant agricultural waste, and it is produced globally. Typically, the extraction of one tonne of sugarcane generates 250-280 kg of bagasse (Haghdan *et al*., 2016; Oleszek *et al*., 2023; Rabelo *et al*., 2011). Bagasse, like other lignocellulosic fibres, is a composite mixture of cellulose, hemicellulose, lignin, ash, and wax (Bahrami *et al*., 2020; Kobetičová *et al*., 2021; Srivastava *et al*., 2022; Wang *et al*., 2023). These components are linked or bound by hydrogen bonds and some other covalent bonds. The amount of fibre produced depends on factors such as the length and diameter of the stems, the number of nodes, and the distance between nodes. Cellulose, the primary component of sugarcane bagasse, is composed of glucose units, while hemicellulose is mainly composed of xylose units with small amounts of arabinose. Notably, cellulose is a crucial component for improving the strength and modulus of fibres, while hemicellulose is in charge of biological and thermal degradation and has high water absorption (2.6 times higher than lignin). Lignin mainly controls UV and fire degradation and is a complex substance made up of aromatic phenolic compounds that provide stiffness to the sugarcane fibre. In addition, small amounts of inorganic compounds such as calcium and silica are present in the cellular structures, but they do not significantly affect the overall fibre composition. Ash, an inorganic compound, is also found in the bagasse structure. The chemical composition of natural fibres is crucial for their performance and application, and the relative amounts depend on the variety of the cane, the age, and the size of the stems. Meanwhile, factors such as age, climate, soil conditions and methods of extraction also play a critical role. Each component can induce different types of susceptibility to natural fibres, such as biological, chemical, mechanical, thermal, photochemical, and aqueous (Ahmad & Zhou, 2022; Bahrami *et al*., 2020; Huang *et al*., 2012; Yang *et al*., 2019). **Table 4.1** shows the varying compositions of the different constituents of sugarcane bagasse, while **Table 4.2** shows compositions derived from treatment.

Table 4.1. Chemical composition of sugarcane bagasse

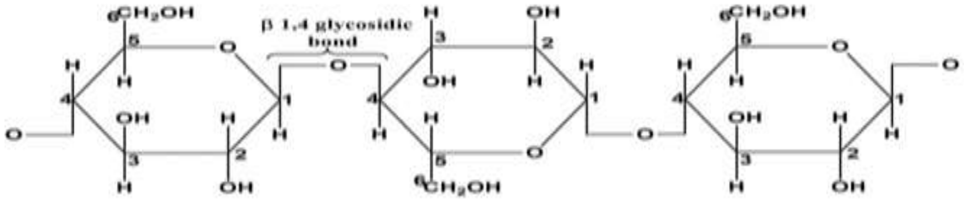
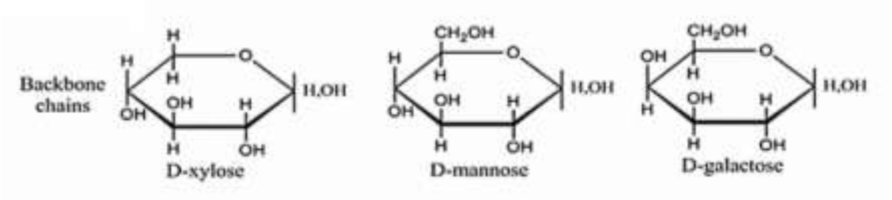
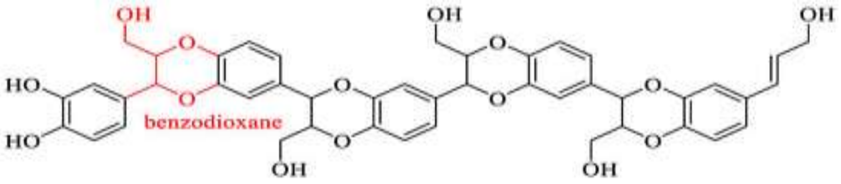
Components	**Percentage Composition (%)**	**Structure**	**Ref.**
Cellulose	27–54		Srivastava *et al*., 2022
Hemicellulose	19–33		Bahrami *et al*., 2020
Lignin	14–24		Wang *et al*., 2023
Ash	1–5	—	Kobetičová *et al*., 2021
Waxes and fats	2-5	—	Qin *et al*., 2023

Table 4.2. The influence of different treatments (extraction) on the composition of sugarcane bagasse (Motaung & Anandjiwala, 2015)

Sample	**Cellulose (%)**	**Hemicellulose (%)**	**Lignin (%)**
Untreated sugarcane bagasse	48.75 ± 0.14	(1) ± 0.75	2.78 ± 1.34
NaOH treated Sugarcane bagasse	54.90 ± 0.18	39.80 ± 1.81	2.51 ± 0.12
H_2SO_4 treated Sugarcane bagasse	66.0 ± 0.11	32.80 ± 0.12	1.49 ± 0.51

Understanding the general properties of sugarcane bagasse —chemical, physical, and mechanical— is essential for developing new commercial applications. These properties directly impact its suitability for various industrial uses. Knowledge of its physical characteristics, such as its strength, flexibility, density, and related parameters, enables industries to select it for specific applications based on their requirements. Sugarcane bagasse consists of pith, fibre, and rind particles, which exhibit unique morphologies and sizes. The outer rind contains longer and finer fibre bundles, while the inner pith has short fibres. Fibres are cylindrical, pith particles are spongy and spherical, and rind material is rectangular with a high length-to-width aspect ratio. Pith particles contribute to the overall porosity and lightweight nature of the material, while the rind is relatively dense compared to the pith and contains a higher concentration of lignin, providing additional strength and durability to the sugarcane stalk (Vinass *et al*., 2021; Wirawan *et al*., 2010). **Table 4.3** highlights some of the features that maybe necessary for maximising its utilisation/exploitation in advanced applications.

Table 4.3. Mechanical properties of sugarcane bagasse fibres (Vinass *et al*., 2021; Wirawan *et al*., 2010)

Fibre	**Density (g/cm^3)**	**Elongation (%)**	**Tensile Strength (MPa)**	**Young's Modulus (GPa)**
Bagasse	1.1–1.6	6.3–7.9	170–350	5.1–6.2
Pith	0.32–0.34	1.823	2.194	1.195
Rind	0.72–0.76	4.24	8.68	2.0

Due to its increased cellulose content, high yields and annual regeneration capacity, sugarcane bagasse is being used in numerous applications. For instance, it is currently employed in conventional applications such as energy production through burning, electricity generation, and pulp and paper production **Figure 4.3**. Additionally, this material is an excellent raw material for creating biofuels such as ethanol, promoting cleaner and more sustainable energy solutions (Brienzo *et al*., 2016; Bušić *et al*., 2018; Loh *et al*., 2013; Xu *et al*., 2018). Other uses include protein-enriched cattle feed; however, some of these processes are still in their infancy and demonstrate uneconomical results, limiting their widespread use in industries. The low heating value of sugarcane bagasse makes burning it as fuel an inefficient process (Kabeyi & Olanrewaju *et al*., 2023). According to Ungureanu *et al*. (2022), approximately 85% of sugarcane bagasse is burnt as fuel, but there are still some excess remains, necessitating the development of innovative applications to use this byproduct and decrease landfill waste. Approximately 9% of bagasse is used in ethanol production, but the process is inefficient, making it critical to increase the economic value of sugarcane bagasse. As a result, the residual sugarcane bagasse has an adverse effect on the ecosystem. One promising option is to employ sugarcane bagasse in composites, and thereby allow this bioresource to be utilised more efficiently. Its environmentally friendly qualities also make it perfect for producing biodegradable products such as disposable plates, bowls, and packaging materials, offering a greener alternative to typical single-use plastic (Singh *et al*., 2021; Singh *et al*., 2022; Zafeer Mohd. *et al*., 2023).

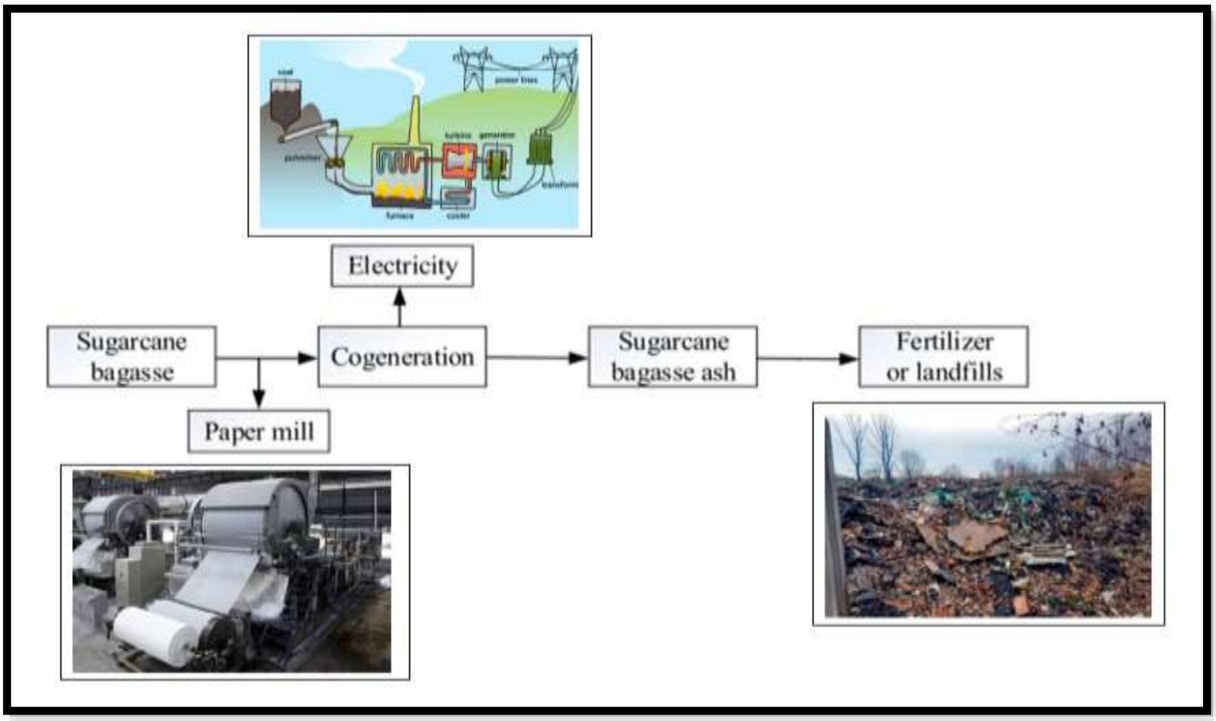


Figure 4.3. Common applications of sugarcane bagasse (Xu *et al*., 2018) Open access

4.3. Sugarcane bagasse hybrid composites

The trend of transforming agricultural waste into a sustainable resource is gaining momentum. Lignocellulosic materials, derived from sources such as wood, agricultural residues, and plants, are abundant and renewable. This attribute makes them sustainable alternatives to non-renewable options, contributing to environmentally friendly practices (Verma *et al*., 2012; Yang *et al*., 2019; Zarna *et al*., 2021). Using reinforcement derived from recycled sources represents an ideal approach to sustainable composite production, and it offers an innovative solution to the global challenge of waste management. By adopting this alternative approach, industries can significantly reduce their ecological footprint by repurposing waste materials into valuable components for composite materials. This does not only address environmental concerns but it also contributes to the circular economy by promoting more responsible and sustainable manufacturing practices. Using agricultural waste for material development offers several benefits, such as easy and safe disposal at the end of the service life and fabrication of lightweight and eco-friendly materials, particularly composites with desirable properties for advanced applications (Iwuozor *et al*., 2023; Józó *et al*., 2022; Kumar *et al*., 2021; Loh *et al*., 2013; Shah *et al*., 2013).

Meanwhile, wood, cotton, jute, and sugarcane bagasse are some examples of natural reinforcements that can be used in conjunction with plastics to create polymeric composite practices (Jiang *et al*., 2020; Mann *et al*., 2023; Verma *et al*., 2012; Yang *et al*., 2019; Zarna *et al*., 2021). Composite materials are created by combining two or more components to produce a unique set of features. One of the materials is made up of stiff, long fibres, and the polymer is a binder or "matrix" that holds the fibres in place. Sugarcane bagasse can be selected based on desired characteristics, and the reinforcing matrix can be metal, ceramic, or polymer (Zafeer Mohd.*et al*., 2023). Polymers, when used as binders, protect natural fibres from damage, act as load carriers, and enhance composite properties. They are lightweight, rigid, and strong in the direction of reinforcements. Composite materials are classified into three basic categories: particulate, structural and fibrous composites, with various sub-divisions (**Figure 4.4)** (Suriani *et al*., 2021). Natural plant fibres can be employed in a variety of forms, including woven mats, chopped fibres, and powders, to create polymer matrix composites in place of standard reinforcement materials like glass or carbon fibres. These fibres are as strong and durable as traditional materials, but they are also biodegradable, have a longer life cycle, and are resistant to insects and decay (Syduzzaman *et al*., 2020). Generally, natural fibres improve the mechanical performance of composites by increasing toughness, reducing polymer deformation, and raising the elastic modulus. The composites are well-suited for a variety of industries due to their environmental benefits and low density when compared to traditional composites. Since the late 1980s and early 1990s, composite materials have been the most prominent emerging materials, steadily growing in both volume and range of applications, while continuously penetrating new markets. Today, modern composite materials make up a significant proportion of the engineered materials market, ranging from everyday products to sophisticated niche applications (Zhang *et al*., 2023).

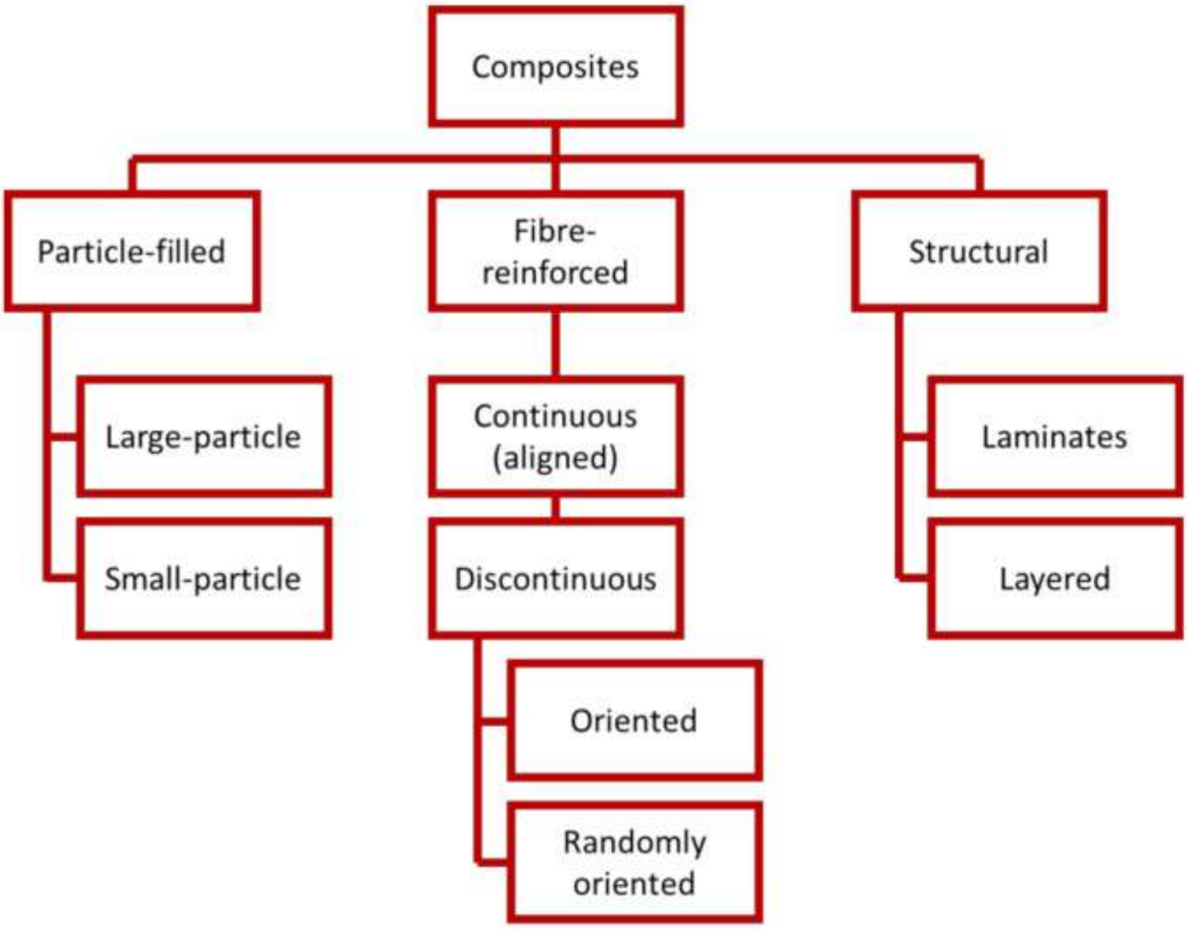


Figure 4.4. Classification of composites (Suriani *et al*., 2021) Open access

Natural fibres, including sugarcane bagasse, offer many advantages as filler or reinforcement materials, but working with them in polymer matrices can be challenging, and thereby requires innovative solutions. One of the main issues with natural fibre polymer composites is the lack of interfacial adhesion between the fibre and the matrix. In addition, natural fibres have a high moisture absorption rate, which results in a high swelling rate and degradation. They also exhibit inferior resistance to fire and chemicals, and they likewise have inferior mechanical properties to commercial fibres. These issues can therefore be addressed through hybridisation. Research focus has shifted from traditional composite systems, which include thermoplastic polymers reinforced with natural fibres, to more advanced systems called hybrid composites. Hybridisation is the strategic blending of different types of fibres, such as glass, carbon, aramid, or natural fibres, to leverage their respective strengths and qualities. The procedure involves introducing a complementary fibre and/or other filler material to the polymer-bagasse mixture to enhance mechanical, thermal, and other desirable properties. The combination of multiple fibres and polymers allows for the synergistic utilisation of the strengths of both components. **Figure 4.5** illustrates possible topologies for hybrid fibre-reinforced biocomposites. These composites, which combine synthetic and/or natural fibres with polymer matrices, exhibit improved properties compared to their individual constituents. These composites can be cost-effective, and they are also suitable for a variety of applications, such as automotive components, construction materials, packaging, and storage devices (Bouhfid *et al*., 2019; Mochane *et al*., 2019; Seydibeyoğlu *et al*., 2023; Shamsuyeva *et al*., 2019; Swolfs *et al*., 2014).

Figure 4.5. Possible fibre polymer combinations in hybridisation (Bahrami *et al*., 2020) Open access

Sugarcane-based hybrid systems with varied compositions and enhanced properties have been developed over time using different methods, depending on the intended application. **Figure 4.6** depicts the typical procedure followed for developing composite mixtures. Melt mixing, injection moulding, spraying, lay-up, resin transfer moulding, compression moulding, pressing, and stir casting are some of the procedures being used (Cao *et al*., 2006; Mustapha *et al*., 2022; Saba *et al*., 2015; Vilay *et al*., 2008). Therefore, lightweight materials with adequate specific mechanical properties have been formed with such natural fibre-based raw materials as reinforcements (Hemath-Kumar *et al*., 2017; Velmurugan *et al*., 2023). For instance, Hemath-Kumar *et al*. (2017) fabricated and investigated the mechanical properties of hybrid composites using epoxy resin reinforced with sugarcane bagasse and glass fibres. The natural fibres surface modified before reinforcement, and the hand layup method was employed for composite production. The mechanical properties, specifically flexural and impact strength, were studied for different composite samples with varying percentages of sugar cane fibres. Results indicated that the addition of natural fibres, specifically cane sugar, along with chopped glass fibres led to improved mechanical properties in hybrid composites. Cane sugar fibre composites exhibited higher flexural strength (490.77 MPa) and impact strength (93.92 KJ/m^2) compared to glass fibre composites (flexural strength 93.19 MPa and impact strength 23.92 KJ/m2). Velmurugan *et al*. (2023) also carried out a comparable study with two ecofriendly fibre polymer hybrid systems, one consisting of epoxy, sugarcane bagasse fibre, and wood powder wt./% (50%/30%–45%/5-20%), and the other consisting of epoxy, sugarcane fibre, and rice husk (50%/30%–45%/5%–20%). More so, mechanical properties and SEM analysis were conducted to determine the optimal fibre volume fraction. The study revealed that combining SBF with hybrid materials such as rice husk and wood powder resulted in superior strength and lighter weight. The study also found that when SBF was combined with an epoxy composite matrix, it had a strength of 14 to 18 MPa and weighed 230 to 250 g. However, when SBF was combined with hybrid materials like rice husk and wood powder, it demonstrated superior strength, with an estimated strength of 16 to 20 MPa and a lower weight of 220 to 240 g.

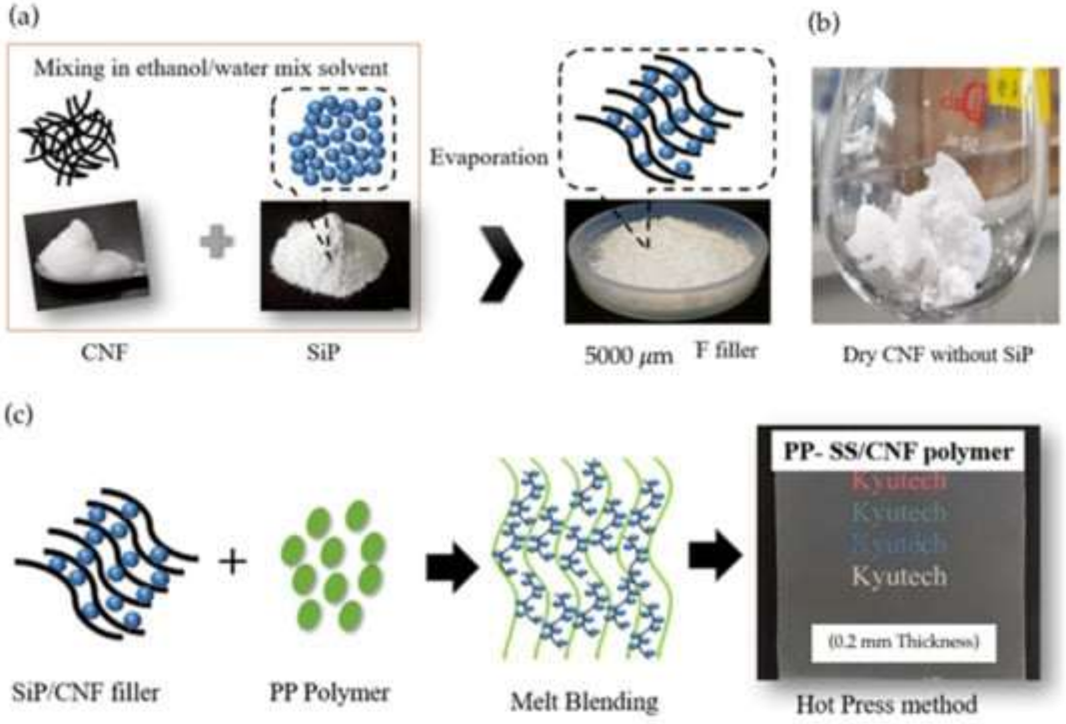


Figure 4.6. Typical process for producing polymer and fibre hybrids (Mustapha *et al*., 2022) Open access

Hybridisation is a great way to improve compatibility between polymer and fibre matrices, and other shortfalls (Mochane *et al*., 2019). Meanwhile, to fully exploit its benefits, it is important to optimise hybridization processes through fibre pre-treatments (Huang *et al*., 2012). Using surface-modified fibres can significantly improve the resulting fibre-polymer hybrid. While the hybridisation of fibre polymer composites aims to enhance the mechanical, thermal, and structural properties of the composites by incorporating a combination of different types of fibres, the treatment of fibres seeks to improve their adhesion and compatibility with the polymer matrix through surface modification of the fibres. By tailoring the surface characteristics of fibres through pre-treatment, strong and durable bonds between fibres and matrix materials are achieved, leading to improved properties in hybrid composites (Rafiqah *et al*., 2023). This optimisation process not only increases the overall strength and stiffness of the hybrid composite but also contributes to better resistance against environmental factors such as moisture absorption. The combined effect of these remediation strategies results in a synergistic enhancement of the overall performance of the composite material. Several methods exist for preparing lignocellulosic fibres, including physical, chemical, and physicochemical pretreatments. Physical methods include comminution and extrusion; chemical methods include acid, alkaline, and organosolv pretreatments; and physicochemical methods include steam explosion, hot-compressed water, ammonia fibre explosion, wet oxidation, and carbon dioxide pretreatments. Depending on the properties of different lignocellulosic materials and their intended uses, a suitable pretreatment technology should be selected with a consideration that each method has its advantages and disadvantages (Huang *et al*., 2012; Pokharel *et al*., 2022; Rafiqah *et al*., 2023; Zafeer-Mohd. *et al*., 2023). **Table 4.4** summarises some of the treatments and their effects.

Table 4.4. Some pre-treaments and their effects on natural fibres (Pokharel *et al*., 2022)

Treatment	**Effect**
Alkaline treatment	Surface roughness increases and hence there is better interlocking between fibre and matrix.
Acetylation treatment	Reduces hygroscopicity of natural fibres and results in more dimensionally stable composites.
Saline treatment	Increases interfacial strength.
Benzoylation treatment	Enhances fibre adhesion and strength, reduces hydrophobicity and improves thermal stability.
Maleated coupling agents	Modifies fibre surface and entanges with the matrix, resulting in adhesion.
Permanganate treatment	Hydrophylicity nature of fibres reduces
Peroxide treatment	Decreases hydrophilicity and increases tensile strength.

4.4. Mechanical properties and the effect of alkali treatment on interfacial bonding

The mechanical properties of hybrid composites made of fibre-reinforced polymers play a vital role in determining their suitability for various applications (Pokharel *et al*., 2022; Rafiqah *et al*., 2023). These composites are essential in modern engineering and manufacturing, ranging from lightweight components to high-performance structures. The mechanical integrity of fibre-reinforced polymer composites is critical across a wide range of sectors since it has a direct impact on their performance and application feasibility. Specific mechanical properties include tensile strength, modulus of elasticity, compressive strength, impact resistance, and fatigue behaviour (Alam *et al*., 2022). For instance, the high tensile strength of fibre-reinforced polymer composites makes them particularly suitable for applications where the strength-to-weight ratio is crucial, such as in the aerospace and automotive industries. These composites can withstand tension without deformation or failure, which is a key factor in their structural integrity (Khan *et al*., 2024). The modulus of elasticity, which indicates the material stiffness is vital for applications where rigidity and minimal deformation under load are required, such as in structural components of buildings or bridges. Composites with high modulus values enable the design of lightweight yet robust structures. Relatedly, compressive strength is critical for load-bearing applications, including those in construction and marine engineering. Furthermore, fibre-reinforced polymers provide high compressive strength, making them suitable for various structural elements (Subramanian, 2021). Impact resistance is critical in applications where materials are subjected to sudden and dynamic loads, such as in sporting equipment, automotive parts, or protective gear. The ability of these composites to absorb and dissipate impact energy enhances their durability and reliability. Fatigue behaviour, which reflects a material's resistance to repeated loading, is equally crucial in applications where cyclic stresses are prevalent, such as aerospace structures and wind turbine blades. Fibre-reinforced polymers with high fatigue resistance ensure the longevity and reliability of the structures they support (Khan *et al*., 2024; Kurzawa *et al*., 2020).

A strong bond between the reinforcement matrix is essential for acceptable load transfer stress across the interface (Rafiqah *et al*., 2023). To enhance the mechanical and other properties of composites, strong fibre-matrix adhesion is essential. The incorporation of high-strength reinforcing fibres is a key factor in producing high-performance plant fibre composites. Tailoring these properties is necessary to optimise materials to meet specific performance requirements, thereby driving innovation and advancement across numerous industries. The mechanical properties of hybrid composites depend on several factors, including the mechanical properties of both the reinforcements and matrix, the dispersion and distribution of reinforcements, their volume fraction and aspect ratio, the interfacial adhesion between polymer and reinforcements, loading and testing conditions, fibres dimension and orientation, and surface modifications. Furthermore, several compounds are known to promote adhesion by chemically coupling the adhesive to the material, such as alkaline, isocyanates, acetic acid, acrylic acid, maleated coupling agents, potassium permanganate, silane, peroxide, *etc*. (Liu *et al*., 2020; Pokharel *et al*., 2022; Rafiqah *et al*., 2023). Alkaline treatment is one of the most often used fibre treatments, and it is regarded as an effective treatment among the other available chemical treatments especially for sugarcane fibre surfaces. The treatment is inexpensive and simple, and the primary goal of employing this method to treat fibres used as reinforcements in polymers is to increase strength. Most studies aim to improve the interlocking between fibre and matrix (Cerqueira *et al*., 2011; Fiore *et al*., 2015; Jalalah *et al*., 2022; Liu *et al*., 2020; Panicker *et al*., 2019). Alkaline treatment is often used interchangeably with mercerisation, which is defined as the process of subjecting plant fibres to the action of a fairly concentrated aqueous solution of strong base to produce great swelling with resultant changes in fine structure, dimension, morphology, and mechanical properties. While KOH, $Ca(OH)_2$, H_2O_2 and other alkaline solutions can be used, treatment with an NaOH solution of 20-27 wt.% is the most preferred for the improvement of strength with fibres applied as reinforcements in polymers. This method is illustrated in **Figure 4.7**. NaOH reacts with the available OH groups in the cellulose and partially removes the lignin, pectin, hemicellulose, and wax and oils from the surface of the sugarcane bagasse molecule and provides enhanced adhesion strength. The treatment of natural fibres with NaOH advances the ionisation of the OH groups to the alkoxide (Liu *et al.*, 2020; Pokharel *et al.*, 2022).

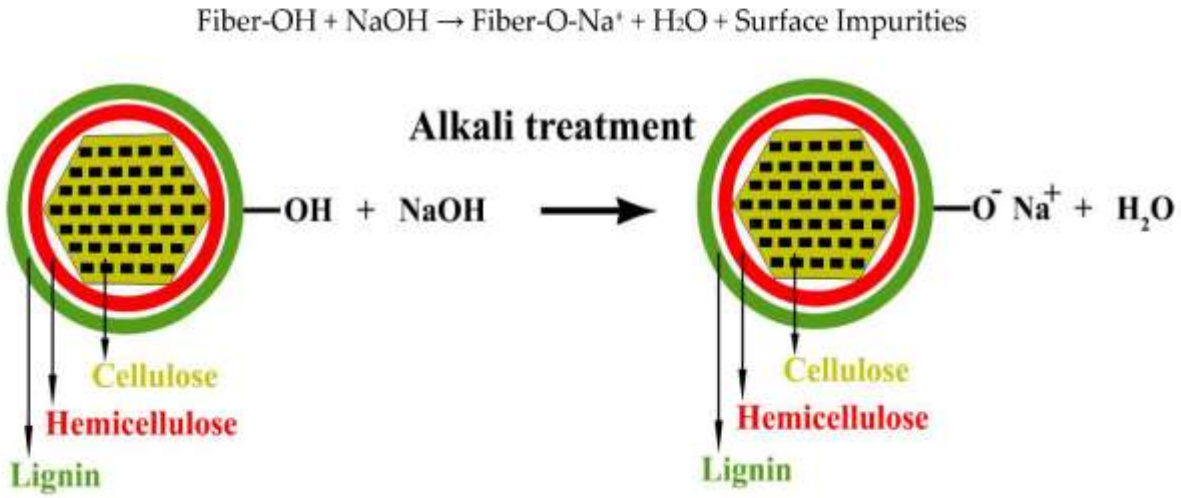


Figure 4.7. Schematic diagram showing the alkaline treatment of raw natural fibres (Pokharel *et al.*, 2022) Open access

The structure and composition of sugarcane bagasse fibres are influenced by the removal of some of the cell wall components and cementing materials. The treatment breaks down the plant fibre bundles, releasing individual fibres as shown in **Figure 4.8** (Cerqueira *et al.*, 2011; Jalalah *et al.*, 2022). The resulting smaller fragments with higher aspect ratios and rough topography enhance the interactions between the fibres and matrix. Additionally, the shorter fibres have a larger surface area, allowing for even distribution with the polymer matrix. The enhanced aspect ratio and surface roughness contribute to superior interfacial bonding between the individual fibres and the matrix material (Cerqueira *et al.*, 2011). The cleavage also exposes the cellulose present in the cell wall and increases its degree of crystallinity (Jalalah *et al.*, 2022). **Figure 4.9** depicts the XRD plot showing sharp peaks at the 30° position, attributed to the high crystalline region in alkali-treated fibre samples (C, D, E, and F). The alkaline treatment not only brings cellulose fibres to the surface but also binds hydroxyl (OH) groups on the fibres, providing a polished effect. These combined effects significantly enhance the potential for intermolecular interactions and bonding between the fibres and matrix. The specific influence of this enhancement on fibre/matrix interactions depends on the nature of the matrix material (Cerqueira *et al*., 2011). Studies by Balaji *et al*. (2018), Bartos *et al*. (2020), Cao *et al*. (2006), Panicker *et al*. (2019), and Vilay *et al*. (2008) have explored these effects. The pre-treatment process of the fibre plays a key role in controlling the overall interfacial bonding, which in turn enhances the mechanical properties of the composite. Effective stress transfer within the composite depends on the quality of this bonding. Alkali treatment, in particular, improves the compatibility of fibres with the matrix, resulting in a reinforced interface that contributes to the overall strength and durability of the composite material.

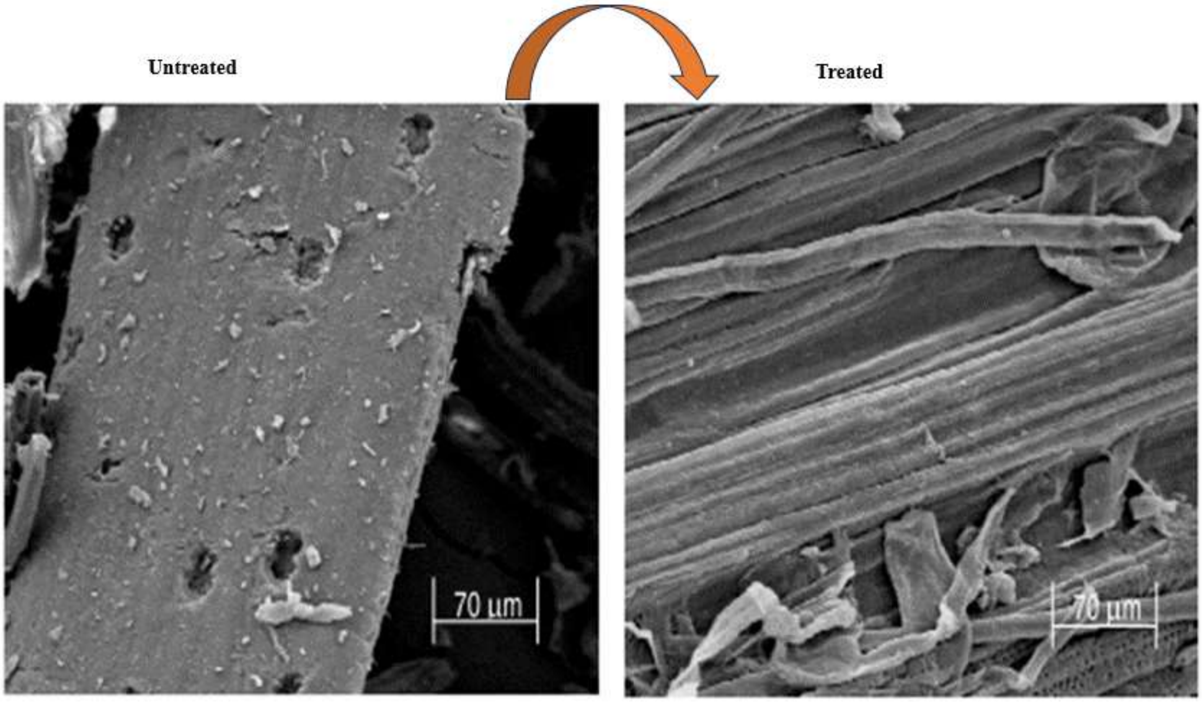


Figure 4.8. Changes in the morphological structure of sugarcane bagasse showing the superficial layer with a high percentage of extractives on the untreated fibres as well as the fibre bundles, releasing individual fibres (Cerqueira *et al*., 2011) Open access

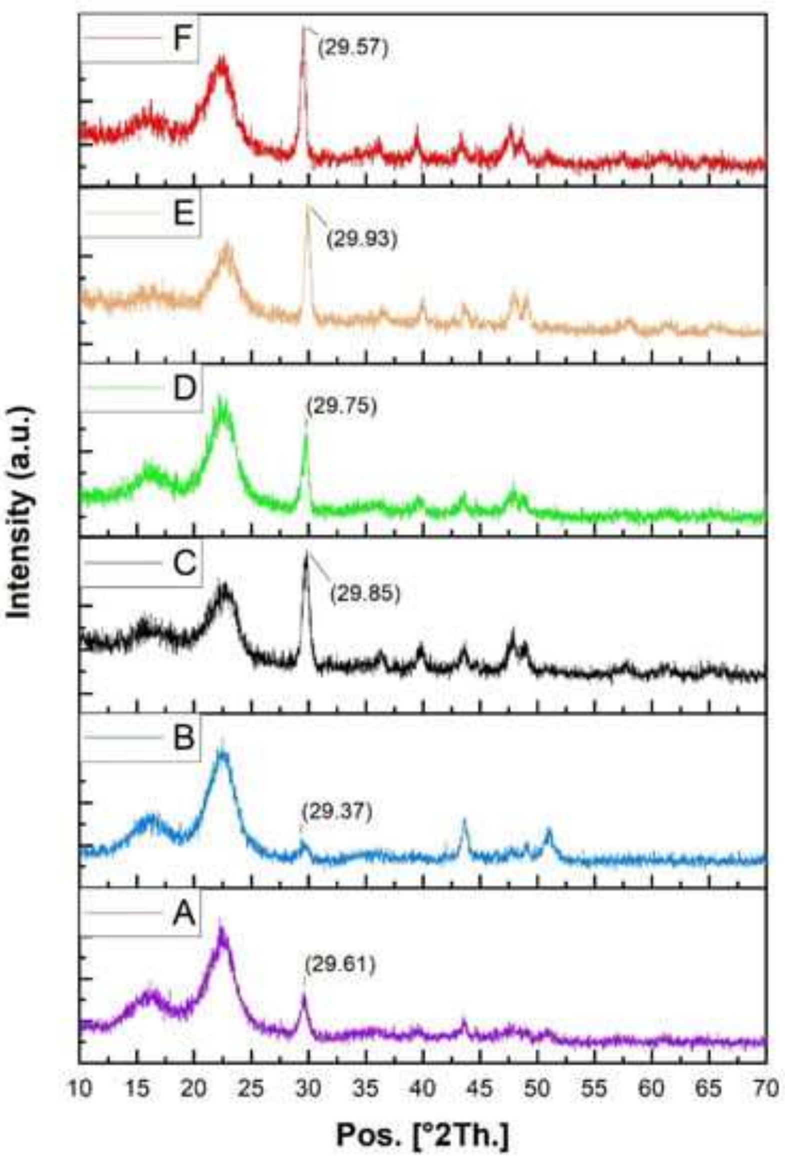


Figure 4.9. XRD showing high crystalline regions @ 30°C after treatment with varying concentrations of NaOH (Jalalah *et al*., 2022) Open access

Alkali treatment is considered the best treatment method for plant fibres, and its effectiveness in property improvement relies on optimal operational parameters (Cordeiro & da Silva, 2024). Researchers can further enhance the ability of sugarcane bagasse fibres to bond with various matrix materials by investigating and controlling the pre-treatment parameters, such as concentration, time, and type of treatment (Prasad *et al*., 2020; Zafeer-Mohd. *et al*., 2023). This systematic approach ensures that hybrid composites exhibit exceptional mechanical, thermal, and durability properties, making them suitable for a wide range of applications (Verma & Goh, 2021). Specifically, composites of alkali-treated sugarcane bagasse with one or more fillers, and with a particular focus on the effect of the varying parameters on the alkali-treated fibres, as well as the resulting product have been explored (Anggono *et al*., 2014; Mulinari *et al*., 2009; Ramesh *et al*., 2017; Sathees-Kumar *et al*., 2021; Vidyashri *et al*., 2019). In a study by Cordeiro and da Silva (2024), the impact of time exposure is examined. The findings, presented in **Table 4.5**, show that the crystallinity index of the resulting composite increases significantly after 3 hours of exposure, while the mechanical properties are at their best after 1 hour of exposure.

Table 4.5. The impact of time exposure on alkali treated sugarcane fibre in composites (Cordeiro & da Silva, 2024)

Sample (fibres)	**Young's Modulus (GPa)**	**Tensile Strength (MPa)**	**Elongation (%)**	**Crystallinity index (%)**
W/O treated_water washed	6,6±5,1	249±123	8,4±5,0	55,8
0,5h Alkali-treated	35±25	586±78	4,20±3,57	66,4
1h Alkali-treated	39±17	582±307	2,83±2,22	66,5
3h Alkali-treated	22±16	468±228	6,58±3,67	69,2

4.5. Flammability

The flammability properties of composite materials are crucial for ensuring their safe use in various applications (Shamsuri *et al*., 2023). Agrowaste fibres and polymers are organic in nature, and they are highly susceptible to catching fire. This feature means that composites made of these materials can easily ignite and burn rapidly when exposed to heat or flames, producing toxic gases, smoke, and heat (**Figure 4.10**). It is believed that the high cellulose content in natural fibres increases flammability, while a higher lignin content increases the chance of char formation during burning, creating a barrier for heat transfer (Renner *et al*., 2021). Flammability properties depend on factors, including chemical structure, molecular weight, composition, and the presence of fillers or additives. Sugarcane bagasse composites — produced by incorporating bagasse fibres into a polymer matrix —exhibit flammability behaviour influenced by various factors, such as fibre orientation, composition, processing techniques, and the type of additives used. Flame properties are often evaluated using standard test methods such as the cone calorimeter test, limiting oxygen index (LOI), and vertical burning tests (UL 94). These tests provide valuable insights into ignition time, heat release rate, flame spread, and self-extinguishing properties (Chukwunwike *et al*., 2019). Reducing the flammability of polymers and polymer composites can be achieved through several methods, such as adding flame retardants, changing the polymer composition, or modifying the processing conditions. Moreover, flame retardants can inhibit the ignition and spread of flames by reducing the number of flammable gases released during combustion or by forming a protective char layer on the surface of polymers or polymer composites, hindering flame propagation (Chukwunwike *et al*., 2019; Gnatowski *et al*., 2022).

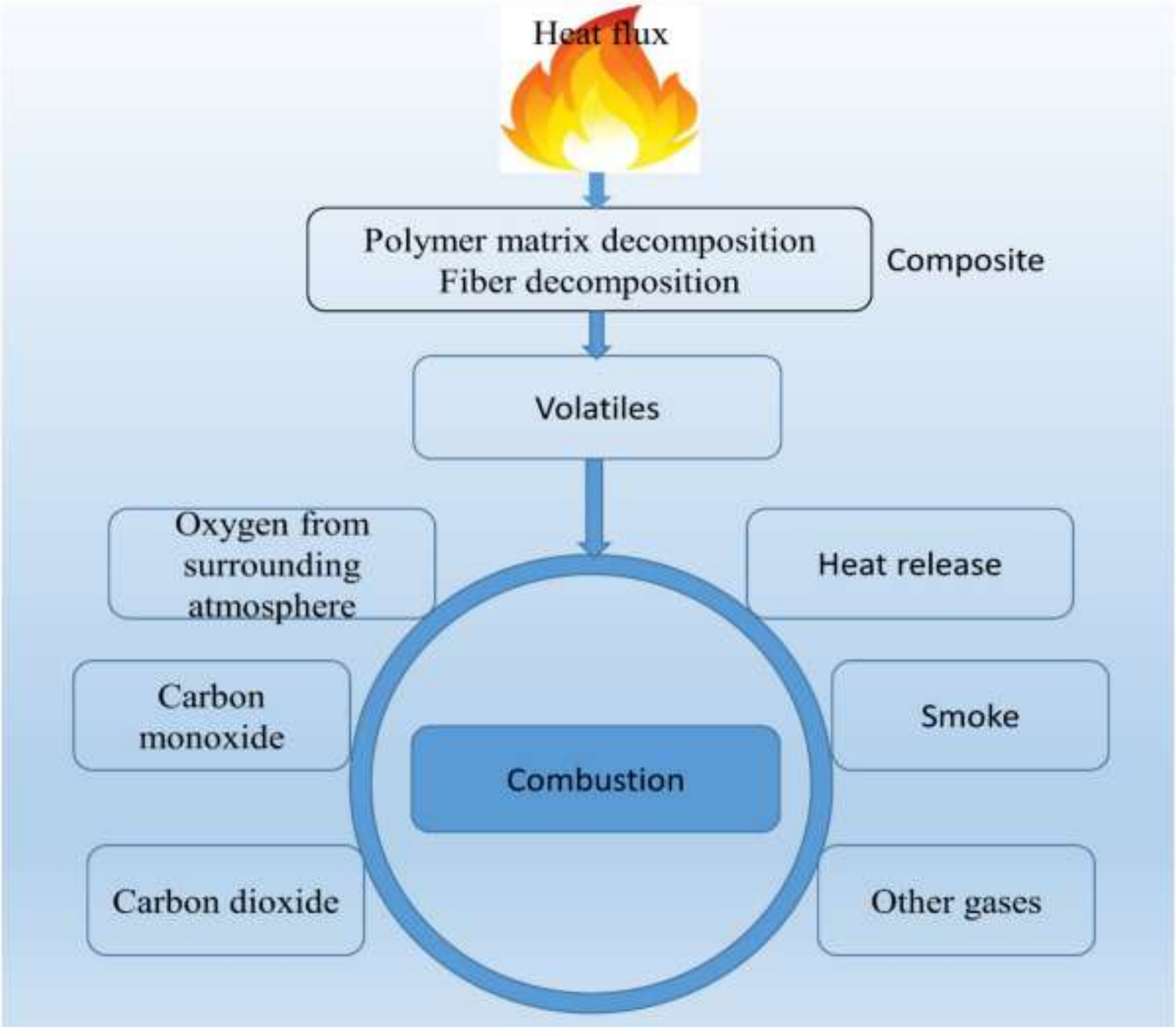


Figure 4.10. Reaction mechanism process in thermal decomposition of a polymer composites (Renner *et al*., 2021) Open access

Incorporating flame retardants into composites serves several purposes, including improving resistance to flammability, delaying and obstructing fire propagation, and inhibiting flaming processes (Shi *et al*., 2022). Many flame-retardant additives have been studied to enhance the fire response qualities of materials, and there are various compounds from which flame-retardant additives can be formulated. Flame retardants —such as phosphorus-based compounds, halogen-containing compounds, and mineral fillers —can be incorporated into the composite formulation to improve fire resistance. They are generally classified according to their mode of action, chemical nature, and protection mechanisms. These additives can interfere with the combustion process, thereby reducing flammability and slowing flame propagation. Depending on their chemistry, flame retardants may act in either the condensed or gas phase through physical or chemical processes. Flame-retardant systems are typically categorised as either additive (active) or reactive. Additive flame retardants are not chemically bonded to the polymers; instead, they are mixed into the formulation during processing. These flame retardants maintain their chemical structure and remain evenly dispersed within the product, but may leach out over time, releasing particles into the air or dust. Oppositely, reactive flame retardants are chemically bonded to the polymers during polymerisation, coupling, or grafting processes and become an integral part of the final material. The primary purpose of incorporating flame retardants is to delay or inhibit combustion. The development of flame-retardant technologies continues to be an active area of research to improve the fire safety of these materials (Chukwunwike *et al.*, 2019; Kim *et al.*, 2021; Shamsuri *et al.*, 2023; Shi *et al.*, 2022).

Noticeably, sugarcane bagasse not only improves the mechanical properties of composites but it may also enhance fire properties through its derivatives (Rafiqah *et al.*, 2023; Shen *et al.*, 2021). The incorporation of modified sugarcane bagasse can enhance mechanical properties, reduce its flammability, and decrease the required amount of other chemical flame retardants. Sugarcane bagasse has been utilised as a template or carrier to create a bio-based reactive flame retardant (Chen *et al.*, 2020). Relatedly, it has been recycled and repurposed to produce a halogen-free bio-based intumescent flame retardant, which was then combined with epoxy resin to create a composite containing polymer with improved thermal properties and flame retardancy of the materials (Shen *et al.*, 2020). Shen *et al.* (2020) created an eco-friendly flame-retardant mixture of bagasse@TGIC@DOPO increase its flame characteristics for flame-retardant applications **Figure 4.11**. The hydroxyl group of bagasse was modified using the epoxy of triglycidyl isocyanurate (TGIC) to produce TGIC-bagasse followed by the addition of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), and the active hydrogen of DOPO reacted with the epoxy group of TGIC to form bagasse@TGIC@DOPO. This flame retardant was then introduced to the epoxy matrix to create a composite material with an interpenetrating network (IPN) structure. The TGA results indicated that the char yield increased from 14.1% to 23.4% after the addition of bagasse@TGIC@DOPO, demonstrating improved thermal stability. The LOI and UL-94 values also showed improvement from 21 (failure) to 29 (V-0) after the addition, indicating a strong flame-retardant effect. Liu *et al*. (2021) conducted a similar study where sugarcane bagasse-ammonium dihydrogen phosphate (ADP) flame retardant was added to an epoxy resin to create epoxy/bagasse-ADP composites. This addition increased the thermal stability and flame retardancy of the composite materials compared to pure epoxy. For the material with 30 wt.% added bagasse-ADP, the char yield was 32.3 wt.%, which was 18.2 wt.% higher than that of pure epoxy (14.1 wt.%). Additionally, the limiting oxygen index increased from 21% to 30%, and the UL-94 classification improved from "Fail" to "V-0." This enhancement was attributed to the nitrogen, phosphorus, and silicon content of the flame retardant.

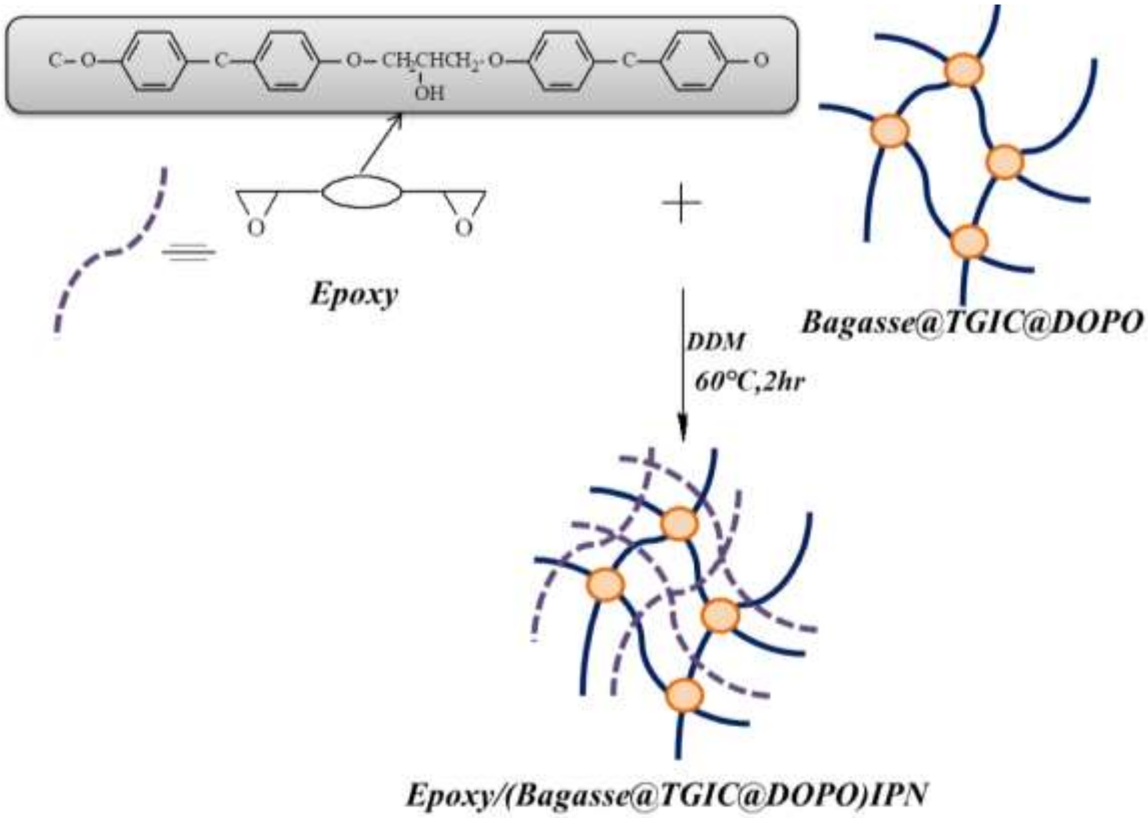


Figure 4.11. Reaction process of epoxy/Bagasse@TGIC@DOPO IPN (Liu *et al*., 2021) Open access

According to literature on biomass ashes, sugarcane bagasse ash contains about 70–90% of inorganic compounds, with silica (SiO2) as the main constituent, see **Table 6 (**Barrera-Torres *et al*., 2021**)**. Its incorporation as a filler has been reported to improve the mechanical properties of various materials including polymers (Iqbal *et al*., 2024), cement (Bahurudeen *et al*., 2015), vulcanized rubber (Barrera-Torres *et al*., 2021) and, most recently, flammability properties of some foams (Capêto *et al*., 2024). A recent study by Capêto *et al*. (2024) explores the potential use of sugarcane bagasse ash and fermentation-derived residues (FDR) in making rigid polyurethane foams. Sugarcane bagasse ash, known for its high silica content, underwent thermal-chemical treatment to reduce particle size and improve uniformity. The treated ash showed a significant reduction in bulk density and contained nearly 60% silica. The FDR (a complex by-product from a fermentation process) was converted into polyol with high viscosity and molecular weight, essential for foam production. The resulting FDR-based polyol, despite its challenging high viscosity, was used to create bio-based polyurethane foams. These foams were reinforced with 4.5% sugarcane, resulting in a denser yet structurally finer material compared to the unfilled foam. FTIR analysis confirmed the expected polyurethane chemical structure, while SEM images revealed that the ash acted as nucleation sites, reducing cell size and foam density. The mechanical properties indicated lower performance, suggesting the need for better viscosity control and particle distribution. Thermal analysis showed a slight decrease in glass transition temperature and improved thermal stability due to the presence of sugarcane bagasse ash. Flammability tests demonstrated enhanced performance, with the ash-filled foam meeting the UL 94 HB standard. The study concludes that SCBA can be an effective, environmentally friendly reinforcement material, improving foam properties and offering a sustainable alternative to conventional fillers.

Table 4.6. Sugarcane bagasse ash mineral composition (Capêto *et al*., 2024)

Chemical compound	Concentration (g/100 g)
SiO_2	59.5±3.1
Fe_2O3	17.8±0.0
K_2O	2.5±0.0
CaO	2.2±0.2
P_2O_5	1.3±0.1
Al_2O_3	0.9±0.1
MgO	0.9±0.00
Na	0.2±0.0
MnO_2	0.1±0.0

4.6. Applications

Sugarcane bagasse hybrid composites are an eco-friendly material blend with diverse applications across multiple industries. These composites offer a sustainable alternative solution with a myriad of advantages in construction, automotive engineering, and other sectors. By combining sugarcane bagasse with other materials like polymers or fibres, versatile composites can be produced that exhibit strength, durability, and environmentally favourable properties. These properties provide a viable substitute for conventional materials such as wood or metal. Owing to their resilience and resistance to moisture and pests, they are suitable for a wide range of applications, from structural components to decorative elements. Moreover, their eco-friendly nature aligns seamlessly with the growing emphasis on sustainable construction practices, making them a sought-after choice for architects and builders aiming to reduce environmental impact without compromising on performance. (Bahrami *et al*., 2020; Marichelvam *et al*., 2020; Zúniga *et al*., 2023).

Humans have been using composite mixtures for centuries to create stronger and more durable construction materials. The earliest recorded use of composites dates back to 1500 BC, when early Egyptians and Mesopotamian settlers used a mixture of mud and straw to build robust structures. In the early 1990s, a new building material was developed by combining hemp particles (the fibrous non-fraction of the hemp stalk known as "hurds") with a lime-based binder. This new material allowed for the construction of sustainable buildings, both for new constructions and renovations. These buildings used biomass as a filler material for a load-bearing structure, which led to the revival of vegetal concrete building materials. Also, vegetal concretes are made up of an organic or inorganic binder and biomass from agroforestry industries. Brick manufacturers are continuously searching for new materials to replace stone, sand, soil, and gravel to produce durable and reliable bricks (Kusuma *et al*., 2023; Ngo, 2020). Sugarcane bagasse is one such material, and it has been researched as a potential supplementary material in asphalt concrete blends (Kusuma *et al*., 2023; Ngo, 2020; Zúniga *et al*., 2023). Moreover, Sugarcrete® (a mixture of clinker, gypsum, and sugarcane bagasse) has been investigated for producing low-cost, lightweight brick with a carbon footprint that is six times less than traditionally made clay bricks. One of the advantages of Sugarcrete® is that it requires significantly less time for curing than conventional concrete blocks and bricks. Normally, the curing time for conventional bricks and concrete blocks is around 28 days. In contrast, Sugarcrete® takes only around 7-10 days to complete the curing process (Zúniga *et al.*, 2023).

In the 1960s, there was a significant increase in research and development efforts focused on hybrid composites, driven by the aerospace and automotive industries. Companies such as Boeing and Airbus were pioneers in using carbon fibre-reinforced polymers (CFRP) in aircraft structures, which significantly reduced weight while maintaining strength and rigidity. This encouraged the advancement of materials by combining different materials in composite materials to produce materials with better properties, typically at a 50/50 ratio within a known resin. Meanwhile, automotive manufacturers started incorporating hybrid composites into vehicle components to improve fuel efficiency and crash resistance. Research on hemp hybrids for lightweight automobile components opened the way for other lignocellulosic commodities, including sugarcane hybrids, as potential substitutes. As a result, researchers have considered the synergies of sugarcane bagasse and other materials (organic and inorganic), such as eggshells and bamboo ash, among others, for car components (Abedom *et al.*, 2023). For example, in 2020, Marichelvam *et al.* developed a novel hybrid composite from sugarcane bagasse and palm sheath embedded in an epoxy resin to evaluate its mechanical properties and potential application using the hand layup method and compression moulding. The best mechanical results were achieved with hybrid palm and bagasse fibre composite samples of proportion 60:40 (S6), which had a tensile strength of 19.80 ± 0.78 MPa, Young's modulus of 0.953 ± 0.076 GPa, flexural strength of 28.79 MPa, impact strength of 2 kJ/m^2, and a hardness value of 38.02 HD. To justify its application, the formulation was developed into an automobile dashboard that would considerably reduce the weight of the automobile, thereby enhancing fuel economy.

Sugarcane bagasse has several functional groups, including hydroxyl (-OH), carboxyl (-COOH), phenolic (C_6H_5OH or C_6H_6O), and ether (RCOOR') groups, which make it suitable for removing contaminants from water. Additionally, other functional groups, such as the amino ($-NH_2$) groups and others, can be introduced into sugarcane bagasse through chemical modification or hybridisation (Juela *et al.*, 2021). The contaminant removal mechanism is based on physical adsorption, chemical reactions, and ion exchange processes. Sugarcane bagasse hybrids are effective in removing various contaminants from water, such as heavy metals, organic pollutants, and dyes (Raj *et al.*, 2022). In 2016, Makhetha *et al.* created hybrid systems using sugarcane bagasse, poly(lactic acid), and ethylene vinyl acetate through melt mixing. These systems were tested for their ability to remove lead from contaminated water. The atomic absorption spectroscopy analysis showed that the composites adsorbed more lead than expected, even considering the partial coverage of the fibre by the polymer. This suggests that some of the lead may have been trapped inside the cavities in the composites and that the polymers may have played a role in the metal complexation process. Both fibre and polymers have functional groups that could interact with the lead ions. The metal impurities underwent monolayer adsorption.

4.7. Conclusions

Repurposing sugarcane bagasse through recycling can significantly increase the value of agricultural waste while supporting the principles of the circular economy. This review addresses a gap in existing research by examining the potential of sugarcane bagasse in advanced applications. Industrial innovations and technologies for utilising agroindustria wastes have promoted resource efficiency, sustainable production, and safer disposal. Modifications are essential for enhancing the properties of sugarcane bagasse hybrids, enabling their application in biofuels, biodegradable packaging, automobiles, and construction materials. Owing to their environmental benefits, cost-effectiveness, and comparable mechanical performance, sugarcane bagasse hybrid composites offer a promising alternative to traditional composites. Their application not only reduces waste but also decreases reliance on non-renewable resources, supporting global environmental conservation efforts. Furthermore, by optimising compatible matrices, pre-treatments, and processing parameters, the limitations of sugarcane bagasse composites can be minimised, resulting in improved mechanical properties and durability. This review concludes that sugarcane bagasse and its derivatives are effective, eco-friendly reinforcement materials, capable of enhancing the properties of polymers and providing a sustainable alternative to conventional fillers. Future research should focus on the use of modified sugarcane bagasse and sugarcane bagasse ash for the development of green flame-retardant fillers.

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CHAPTER 5

The influence of halloysite clay on the properties of polybutylene succinate (PBS)/sawdust, PBS/sugarcane bagasse and PBS/sawdust/sugarcane bagasse hybrid composites

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Abstract

In this study, the influences of natural fibres (sugarcane bagasse (SB) and sawdust (SD)) on the material properties of polybutylene succinate (PBS) prepared through melt compounding were investigated. The study further evaluated the effects of incorporating halloysite nanotubes (HS) and expandable graphite (EG) on the properties of PBS/SD and PBS/SB binary and PBS/SB/SD hybrid composites. The morphological analysis indicated poor interfacial adhesion between PBS and the fibres. The obtained findings indicated enhancements in the complex viscosity of PBS in the presence of natural fibres, and further improvements in the presence of HS and EG. The stiffness of PBS hybrid composites also increased upon the addition of HS and EG. Moreover, the crystallisation temperatures of PBS increased in the presence of fillers, with EG showing better nucleation efficiency. However, the mechanical properties (toughness and impact resilience) decreased due to the increased stiffness of the composites and the poor interfacial adhesion between the matrix and the fillers, indicating the need to pre-treat the fibres to enhance compatibility. Overall, the material properties of PBS/SD/SB hybrid composites were enhanced by incorporating HS and EG at low concentrations.

Keywords: Polybutylene succinate, natural fibres, expandable graphite, hybrid composite, halloysite

5.1. Introduction

In recent years, biodegradable polymers have been regarded as suitable replacements for conventional plastics due to their biodegradability and potential to alleviate plastic pollution caused by conventional polymers such as polyolefins (Nanda *et al*., 2022; Samir *et al*., 2022). Among various existing biodegradable polymers, poly(butylene succinate) (PBS) has received considerable attention due to its appealing properties including, good processability, biodegradability, and thermal and chemical resistance. Nevertheless, PBS has shortcomings, such as softness, a limited Young's modulus, low viscosity and melt strength, and availability at exorbitant prices, and thereby limiting its applications (Aliotta *et al*., 2022; Horiuchi *et al*., 2024; Mochane *et al*., 2021; Platnieks *et al*., 2021). To mitigate these drawbacks, the development of sustainable PBS composites comprising low-cost materials such as natural fibres has emerged due to their unique advantages such as availability at low to zero cost, abundance, high specific modulus, biodegradability, and environmental friendliness (Haris *et al*., 2022; Mochane *et al*., 2021; Nurazzi *et al*., 2021). Natural fibre-reinforced biodegradable polymer composites are an interesting class of materials that are eco-friendly, cost-effective, and biodegradable (Elfaleh *et al*., 2023; Kumarudi *et al*., 2022).

Hybrid composites comprising two or more natural fibres are even more fascinating due to the possibility of obtaining a more diverse range of properties than those that are attained by single-fibre-reinforced composites. Furthermore, hybrid bionanocomposites consisting of natural fibres and nanomaterials have also generated interest due to a combination of properties resulting from the fillers' sizes, ranging from micro- to nano-scale, and the high surface area of nanomaterials (Haris *et al*., 2022; Nurazzi *et al*., 2021). The incorporation of nanomaterials into natural fibre-reinforced composites has proven effective in enhancing the properties of polymer/natural fibre composites. Haris *et al*. (2022), comprehensively reviewed some of the natural fibre/polymer hybrid composites containing at least one type of nanomaterial. Their summarised studies displayed enhancements in the material properties of natural fibre/polymer composites in the presence of nanoparticles. However, it is worth mentioning that there is a lack of studies in the literature on PBS/natural fibre hybrid bionanocomposites. Mochane *et al*. (2021), alluded to the necessity of also diverting research attention to PBS/natural fibre hybrid composites, as a way of widening the applications of PBS/natural fibre composites and addressing the challenges associated with PBS.

A few studies have been reported on PBS/natural fibre hybrid bionanocomposites. The studies attempted to address some of the challenges associated with PBS and PBS/natural fibre composites. Most recently, Theys *et al.* (2025), prepared PBS/maize stalk fibre hybrid bionanocomposites containing modified montmorillonite (MMT) nanoclay and expandable graphite (EG). Their findings indicated a better improvement in the storage modulus and flame retardancy of the PBS/maize stalk fibre in the presence of modified MMT, which acted as a compatibilizer compared to EG. Horiuchi *et al.* (2024), fabricated hybrid bionanocomposites of PBS/canabrava fibres/lignin containing both MMT and sepiolite (SEP) clays. The authors reported enhancements in the crystallization temperature (T_c), thermal stability, and stiffness of the PBS/canabrava fibres/lignin, with SEP showing better improvements compared to MMT. Motloung *et al.* (2023), noticed an increase in the melt viscosity and accelerated degradation of PBS in the presence of chitin fibres and hydroxyapatite nanoparticles. These findings substantiate the need to explore the use of other natural fibres in developing PBS-based hybrid composites with enhanced properties, as these additions would broaden the application scope of PBS and widen the choice of natural fibres for a specific property improvement.

Natural fibres such as sugarcane bagasse (SB) and sawdust (SD) are lignocellulosic waste products with the potential to develop sustainable PBS composites. SD is a natural fibre obtained as a waste product of woodworking and is mostly used for animal bedding, mulch, *etc*. (Allaf *et al*., 2023; Ferede *et al*., 2020). SB is a fibrous lignocellulosic waste material obtained after the crushing and extraction of juice from sugarcane stalks (Mahmud & Anannya, 2021; Motaung *et al*., 2014). Both SD and SB fibres have been employed in the fabrication of PBS composites. Frollini *et al*. (2013) and Feng *et al*. (2013), evaluated the properties of PBS reinforced with SB. On the other hand, a few studies on PBS/SD composites have been reported. Hongsriphan *et al*. (2018), and Petchwattana *et al*. (2017), investigated the influence of accelerated weathering on the properties of PBS/SD composites. In the current study, both SD and SB were used as reinforcing agents in PBS as a viable way to repurpose and add value to them. In addition, these materials are available at low to zero costs. Thus, they can contribute significantly to the reduction of PBS costs, which are usually reflected in the product costs. In South Africa, about 7 million tonnes of SB are produced annually, whereas about 4.7 million m^3 of SD are generated (Mohlala *et al*., 2016; Fahimizadeh *et al*., 2024). This demonstrates the necessity to utilise these abundantly available lignocellulosic waste products in polymer composites.

To our knowledge, PBS-based hybrid composites comprising both SB and SD and/or combining either of these fibres with nanomaterials have not yet been reported. Nanomaterials such as halloysite nanotubes (HS) hold great potential for the enhancement of the properties of polymer–natural fibre-reinforced composites. HS is a naturally occurring nanoclay that exhibits intriguing properties such as a high surface area, biocompatibility, and low toxicity, and it can be integrated with other materials in composites to enhance their properties (Fahimizadeh *et al*., 2024; Krishnaiah *et al*., 2022). Hasan *et al*. (2022) developed jute fibre-reinforced poly (3-hydroxy butyrate-co-3-valerate) (PHBV)-reinforced composites containing HS. A significant increase in the thermal and mechanical properties of PHBV/jute fibre composites was noticed when adding HS. In addition, fillers with layered structures such as Expandable graphite (EG) can be used to further improve the properties of natural fibre-reinforced polymer composites. EG is widely used in polymer composites to impart important properties, including thermal and electrical conductivity, thermal stability, flame retardancy, and improved stiffness (Wu *et al*., 2013, Has *et al*., 2023). Theys *et al*. (2025) incorporated EG into PBS/maize stalk composites and noticed improvements in f lame retardancy and thermal stability compared to PBS/maize stalk composites.

Due to the limited research on PBS-based hybrid composites, it is imperative to investigate the influences of different filler combinations (hybrid systems) on the properties of PBS. This will shed light on the specific types of fillers that can be used to attain certain properties for a specific application. Therefore, in this study, the influences of natural fibres (SD and SB) in combination with HS and EG on the material properties of PBS are investigated. To the best of our knowledge, the effects of the simultaneous incorporation of SB and SD on the properties of PBS are currently uncertain. In addition, hybrid composites based on SD and SB as well as HS and EG have not yet been explored. Therefore, the current study seeks to expand and contribute to the existing knowledge on PBS/natural fibre hybrid composites containing these fillers, with the aim of addressing the challenges associated with PBS, while also beneficiating low-cost and underutilised natural fibres such as SD and SB fibres as reinforcing agents in green PBS composites. The incorporation of both EG and HS can yield a synergistic enhancement of the properties of natural fibre-filled PBS composites containing SD and SB due to their intrinsic properties, such as their high surface area and capacity to act as nucleating and reinforcing agents in polymer composites. Thus, the study intends to develop novel PBS-based hybrid composites based on SD and SB in the presence of HS and EG. The study further explores the influence of HS on the material properties of PBS/SD, PBS/SB, and PBS/SD/SB hybrid composites, and that of EG on the properties of PBS/SD/SB/HS hybrid composites.

5.2. Materials and methods

5.2.1. Materials

The polymer used in this study, polybutylene succinate (PBS), was acquired from 2 MBIO-Engineering Polymers, Ramanathapuram, India, in the form of pellets. It exhibited a melt flow index (MFI) of 2.16 kg/10 min at 190 °C, a heat combustion of 23.6 KJ/g, a melting temperature of about 120 °C, and a density of 1.25 g/cm^3. Ground sawdust (SD) was acquired from a timber processing plant in Bloemfontein, Free State, South Africa. Sugarcane bagasse (SB) was sourced from Tongaat hullet, Tongaat, KwaZulu-Natal, South Africa. Halloysite nanoclay powder (HS), beige-coloured with a formula weight of 294.19 g/mol and a pore size of 1.26–1.34 mL/mol, was purchased from Sigma-Aldrich, Johannesburg, South Africa. Its particles have a diameter of 30–70 nm and a length of 1–3 microns. Another material used is expandable graphite (EG), which was supplied by Qingdao Kropfmuehl Graphite in Hauzenberg, Germany.

5.2.2. Sample preparation

5.2.2.1. Preparation of the sugarcane bagasse (SB) fibres

The crushed sugarcane bagasse waste was washed using a modified version of a method prescribed by Jalalah *et al.* (2022). The bagasse was cleaned with distilled water to remove soil, dirt, and other foreign debris. The fibres were then cut into about 2 cm lengths and underwent boiling water treatment for 60 min to remove colouring matter and sugar traces, and this process was repeated three times. The clean fibres were strained to remove excess water and dried at 20 °C for 72 h. After drying, the fibres were pulverised using a powder pulverising machine and sieved through a 1.0 mm sieve.

5.2.2.2. Fabrication of the composites

Before compounding, PBS, SD, SB, HS, and EG were dried in a vacuum oven at 60 °C for over 12 hours. **Table 5.1** shows the calculated weight percentages of the different components in each of the investigated samples. The neat PBS, binary, and hybrid composites were melt-mixed using a TE-30 co-rotating twin-screw extruder (Nanjing Only Extrusion Machinery Co., Ltd., Nanjing, China) with the temperatures of the heating zones from the hopper to the die set from 120 to 160 °C. The extrusion speed and feed rate were set at 178.8 rpm and 4.4 kg/hr, respectively. The extrudates were then quenched in water, pelletized, and dried in an oven at 60 °C for 24 hours. These dried pellets were injection moulded into various test specimens using an injection moulding machine (ENGEL e-mac50). The injection moulding heating zones were set at 36, 120, 140, 150, and 160 °C. The clamping force, metering, specific back pressure, injection pressure, and injection speed were set at 500 kN, 29 mm, 100 bar, 550 bar, and 100 m/s, respectively. The test specimens were cooled to 22 °C and stored in a Ziplock bag.

Table 5.1. Weight percentages of the components in the composites

Samples	**Percentages (wt.%)**
PBS	100
PBS/HS	97/3
PBS/SD	90/10
PBS/SB	90/10
PBS/SB/SD	90/5/5
PBS/SB/HS	87.3/9.7/3
PBS/SD/HS	87.3/9.7/3
PBS/SB/SD/HS	87.3/4.85/4.85/3
PBS/SB/SD/HS/EG	87.3/4.85/4.85/1.5/1.5

5.2.3. Sample characterisation

5.2.3.1. Microscopic analysis (Scanning electron microscopy—SEM)

Qualitative analysis of the morphological and textural features of the neat polymer, composites and hybrids was determined using scanning electron microscopy (SEM). The specimens were initially fractured using liquid nitrogen and then broken into appropriate sizes to fit the sample chamber in the SEM. Thereafter, they were coated with a thin layer of gold to improve conductivity and imaging quality. These gold-coated samples were then examined using a JSM-7800F Extreme-resolution Analytical Field Emission Scanning Electron Microscope, which was operated at an accelerating voltage of 5.0 kV. To ensure stability and precise imaging, the samples were carefully mounted on 10 mm Cambridge pin-type aluminium stubs using epoxy glue. The high-resolution capabilities of the JSM-7800F allowed for detailed qualitative analysis of the surface morphology and texture of the materials.

5.2.3.2. Chemical Structures (Fourier Transform Infrared Spectroscopy—FTIR)

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy (Perkin-Elmer Spectrum 100, PerkinElmer, Branford, CT, USA) was used to determine the chemical structures of PBS, SD, SB, and hybrid PBS/SD/SB/EG/HS. The samples underwent 32 scans at wavelengths ranging from 500–4000 cm^{-1} at a resolution of 4 cm^{-1}.

5.2.3.3. Flow dynamics (Rheology)

To evaluate the flow and deformation of the fabricated composites under stress, which aids in optimizing manufacturing processes, a modular compact rheometer (Anton Paar) was employed (MCR 301/302). The tests were conducted using a 25 mm diameter parallel-plates configuration at 180°C under atmospheric conditions. Preliminary experiments were executed to establish the linear viscoelastic region of the samples, and a fixed strain amplitude of 1.00% was used. The zero gap was maintained at 1.1 mm for all tests. Replicate experiments were carried out to ensure reproducibility.

5.2.3.4. Thermal stability (Thermo-Gravimetric Analysis—TGA)

TGA analyses were carried out using a TG analyzer (model Q500, TA Instruments) to determine the purity and decomposition temperature of the evaluated samples. Specimens with masses ranging between 8 and 10 mg were heated in triplicate at a heating rate of 10 °C /min from 25 to 800 °C under nitrogen. The resulting measurements from the computer-controlled thermo-gravimetric analyser were presented as a curve in which the mass or mass percentage is plotted against the temperature and/or time. Furthermore, a differential thermogravimetric curve DTG was generated as the first derivative of the weight with respect to temperature.

5.2.3.5. Differential Scanning Calorimetry (DSC)

DSC tests were conducted using a Perkin Elmer DSC7 instrument. Samples with masses ranging between 5 and 6 mg were sealed in aluminium pans. The samples were heated under a nitrogen flow of 20 mL/min from −35 to 160 °C at a heating rate of 10 °C /min and kept at this temperature for 1 min to eliminate the thermal history, then cooled to −35 °C at the same rate and reheated under the same conditions. The melting enthalpies and temperatures were determined from the second heating curves.

5.2.3.6. Impact resilience (A Charpy impact test)

The injection-moulded specimens of the different formulations with dimensions of approximately 80 mm × 10 mm ×4mm (L×W×B) were subjected to a Charpy impact test to evaluate their resistance to breakage by flexural shock. The specimens were notched on one side, with a 0.25 mm notch root radius at a depth of 2 mm, using a CEAST Automatic Notchvis Plus (Instron, Norwood, MA, USA). The notched Charpy impact strength was measured at 25 °C using a fully automated CEAST Pendulum Resil Impactor II (Instron). The drop velocity was 3.7 m/s, resulting in a hammer energy of 14 J. The reported results represent the average of at least six tests per sample.

5.2.3.7. Mechanical: Tensile

Tensile testing was carried out on the injection-moulded, dog-bone-shaped specimens using an Instron 5966 tester (Instron Engineering Corporation, USA, ASTM 638D). The tensile tester is equipped with a 10 kN load cell, and the tests were conducted at a constant strain rate of 50 mm/min and a temperature of 25 °C. The results are based on an average of six tests per sample, along with standard deviations.

5.3. Results

5.3.1. Scanning electron microscopy

Figure 1a–c represents the SEM micrographs of the morphologies of the studied composites. The presence of SD in the smooth PBS matrix is characterized by light, flaky, and smooth-looking structures, while SB fibre is characterised by dark-coloured, coarse and long parallel striped structures (Chimenez *et al*., 2013; Rezende *et al*., 2011). When these individual fibres, SD and SB, are separately added into the PBS matrix, SB and SD show visible agglomerates, voids, and fibre pull-outs in both composites. The voids and fibre pull-outs can be attributed to the fact that there were no fibre pre-treatments prior to processing. Pre-treatments are crucial for improving the morphology and overall performance of fibre-reinforced polymer composites (Pokharel *et al*., 2022). The presence of fibre pull-outs and voids on the surface of the composites is typically a result of inadequate adhesion between the fibres and the polymer matrix. This weak interfacial bonding is often due to the lack of chemical compatibility and mechanical interlocking between the fibres and the matrix. Pre-treatments help improve this adhesion by cleaning the fibre surfaces, introducing functional groups that enhance the chemical compatibility with the matrix in the process (Huang *et al*., 2012; Pokharel *et al*., 2022). The simultaneous incorporation of both SD and SB fibres into the PBS matrix resulted in the separation of the fibres within the matrix, with SD characterized by flaky structures and SB symbolised by dark-coloured, coarse, and long parallel-striped structures, as shown in **Figure 5.2a**. Interestingly, the interaction between the fibres shows SD concealing or encapsulating SB. When mixed into a polymer matrix, the finer SD particles can settle into the interstices of the larger bagasse fibres, effectively "covering" them. This encapsulation might improve the overall distribution and interfacial bonding within the matrix (DeBruijn *et al*., 2021). According to **Figure 5.1c**, the tubular halloysite clay appears to be fairly embedded in the PBS matrix. Furthermore, the absence of obvious cavities suggests good interfacial interaction between the HS and the PBS matrix, although a few visible agglomerates are still visible. It is well known that halloysite clay is capable of dispersing more easily in polymer matrices than platy clay such as montmorillonite and kaolin, without any exfoliation (Fakhruddin *et al*., 2021).

Further improvements in the morphology are observed with the incorporation of HS and EG fillers. Like many mineral clays, HS improves the mechanical interlocking and provides additional surface area for interaction with the polymer matrix, resulting in better dispersion of the fibres and improved adhesion within the matrix. The presence of EG assists in evenly distributing the fibres within the matrix, thereby enhancing the interfacial bonding and reducing the formation of voids and defects. Generally, better dispersion and distribution in the presence of HS and EG can be attributed to the nature of their structures. HS, with its tubular structure, provides a network that supports the distribution of fibres, while EG, due to its layered structure, aids in uniform dispersion and acts as a barrier to fibre agglomeration (Jasinski *et al*., 2024; Martynková *et al*., 2015; Sukur *et al*., 2024). Using polymer composites with better dispersion of filler material(s) usually results in the enhancement of properties such as mechanical performance due to the effective stress transfer provided by the incorporated filler. Thus, in the presence of EG and HS, the PBS/SD/SB hybrid composite could be expected to demonstrate better performance, provided that there is also sufficient interfacial adhesion between PBS and the fillers. The FTIR spectra of PBS, SD, SB, and hybrid composites comprising all the fillers including HS and EG are illustrated in **Figure 5.3**. SD and SB are characterised by a broad hydroxyl group (–OH) between 3600 and 3200 cm^{-1} and-CH_2 stretching at 2950–2800 cm^{-1}. Intense C–O stretching vibrations were noticed at 1200–1000 cm^{-1}. On the other hand, PBS exhibited a strong carbonyl vibration at approximately 1700 cm^{-1}. The hybrid composite demonstrated a structure similar to that of PBS, with the characteristic vibration bands of both SD and SB not being visible. This absence may be attributed to the fine dispersion of the fillers within the continuous PBS matrix.

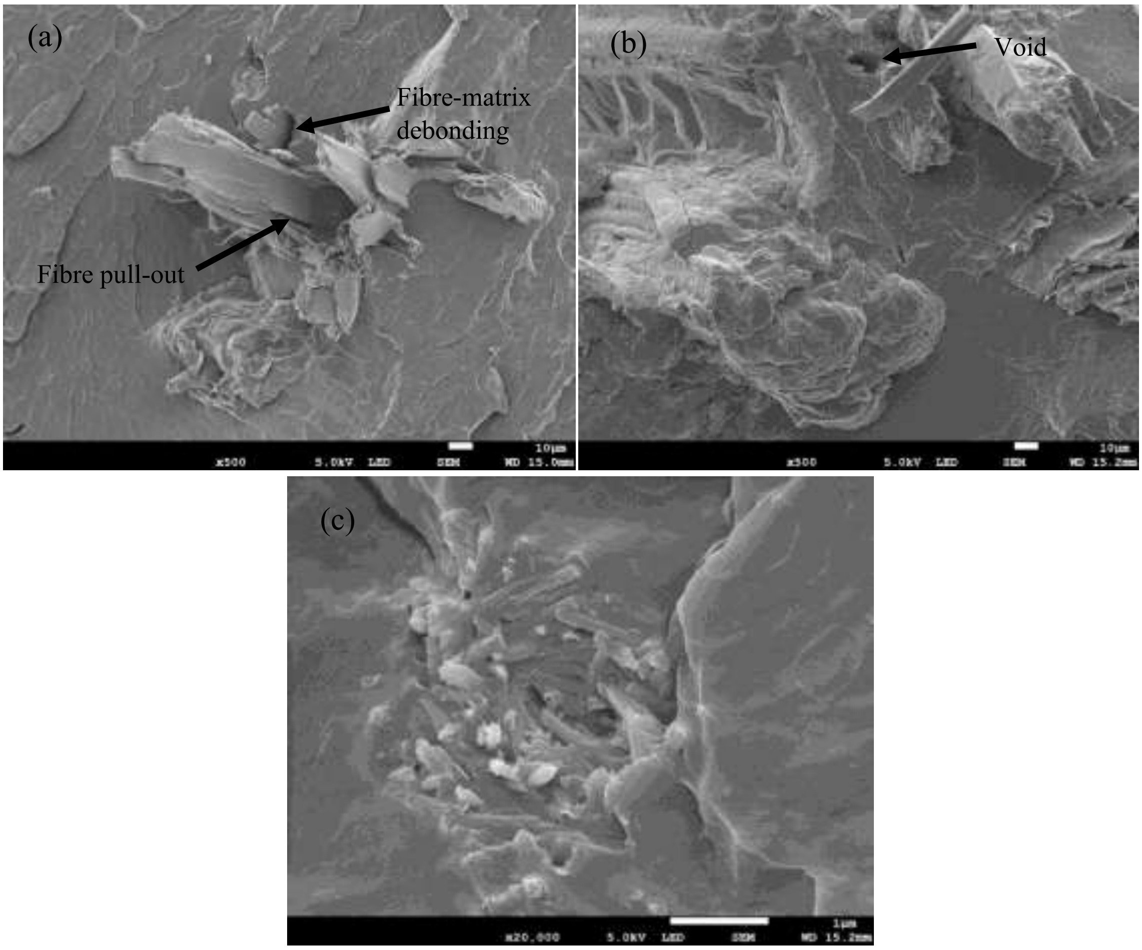

Figure 5.1. SEM Micrographs of the binary composites: (a) sawdust (SD), (b) sugarcane bagasse (SB) and (c) halloysite (HS)

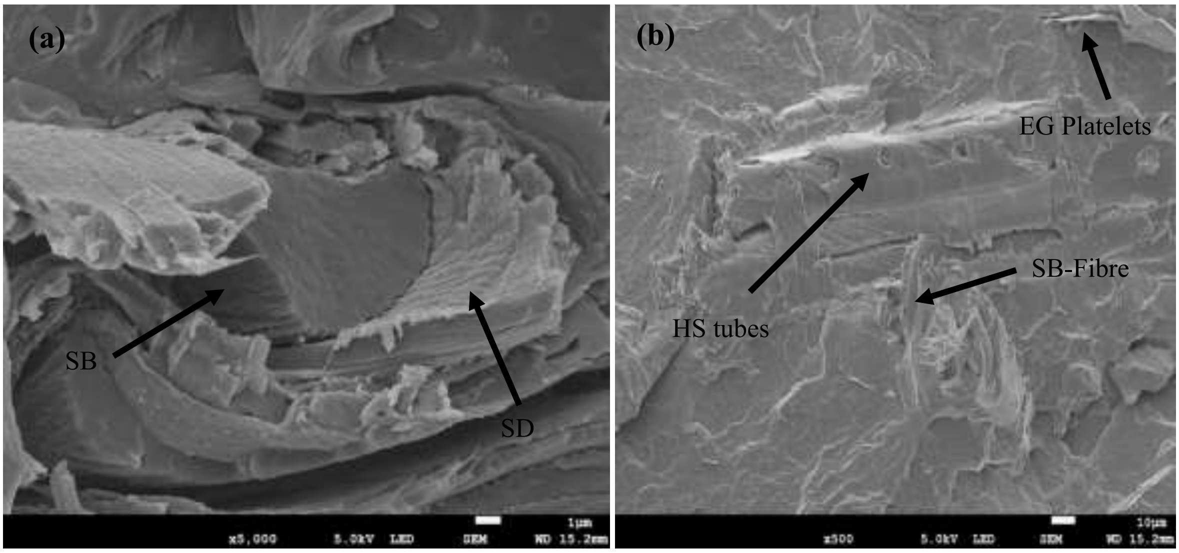

Figure 5.2. SEM Micrographs of the hybrid composites: (a) PBS/SD/SB, and (b) PBS/SD/SB/HS/EG

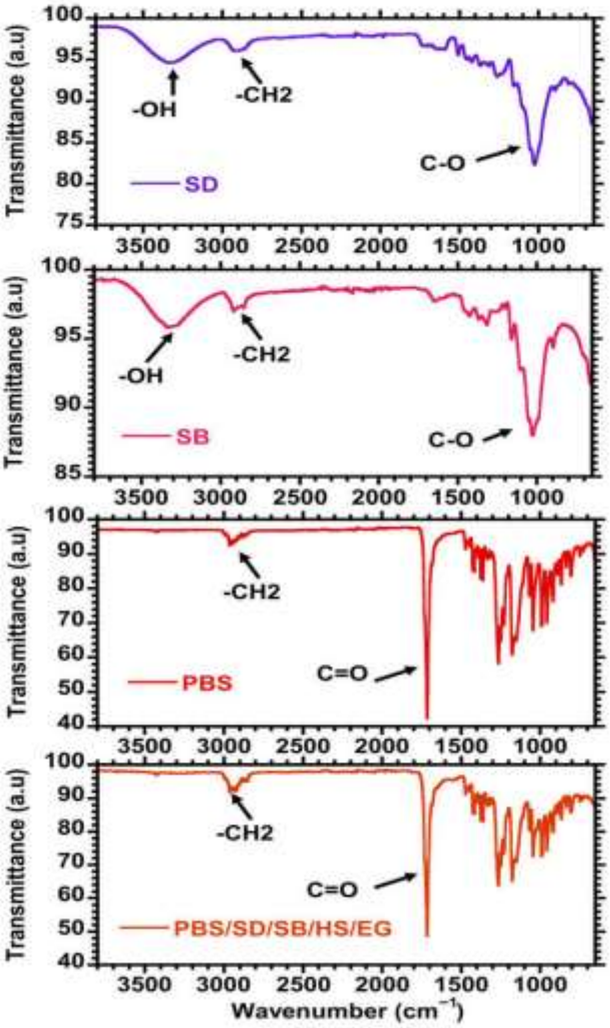

Figure 5.3. FTIR spectra of PBS, SD, SB, and hybrid PBS/SD/SB/HS/EG composites

5.3.2. Rheological properties of the investigated samples

Figure 5.4 illustrates the complex viscosity (η*) of neat PBS, binary composites, and hybrid composites as a function of angular frequency (ω). PBS generally exhibits lower η* due to fewer restrictions on chain mobility, allowing it to flow more easily under shear forces (Choi *et al.*, 2024). A continuous trend emerges with the addition of different fibres and fillers (EG and HS). Natural fibres, in particular, are stiff materials and restrict polymer chain mobility, which increases η* (Guchait *et al.*, 2022). There is, however, a slight difference in the behaviour of the fibres. Composites containing SB display a higher η* than those with SD, due to greater stiffness of SB within the PBS matrix. Compared to SB, SD appears less stiff, which may be attributed to differences in the chemical compositions, sizes, and aspect ratios of the two fibres. The superior stiffness of SB therefore results in a more significant restriction of polymer chain movement, thereby increasing the η* more than SD. Furthermore, the hybrid mixture of PBS, SB, and SD shows a higher η* than the single-fibre composites, as expected. The positive synergy between the fibres leads to the enhanced stiffness of the fibres within the matrix, thus restricting the PBS chains with more than one fibre. Lastly, the formulation with the HS and EG fibres exhibits the highest η* among all the samples, indicating further stiffening and limited movement of the polymer chains.

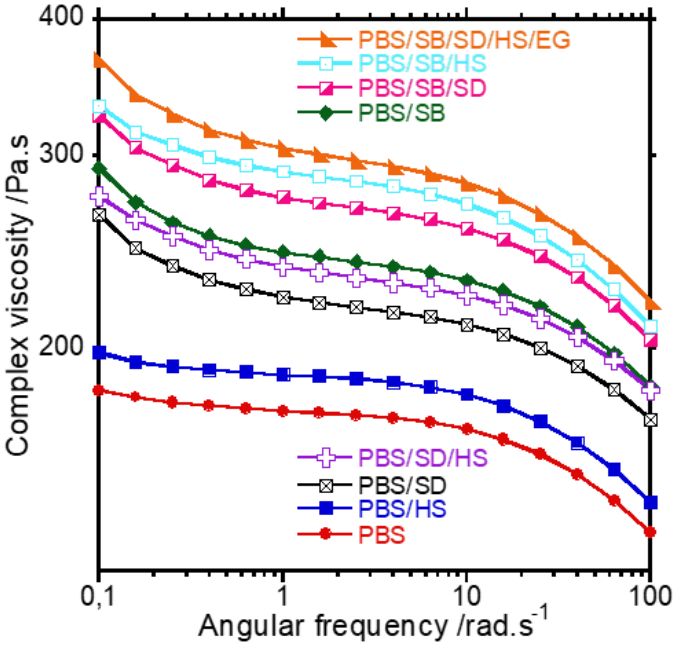

Figure 5.4. Complex viscosity curves as a function of angular frequency of neat PBS, hybrid composites, and ternary composites

5.3.3. Thermal stability of the composites and hybrid composite

Figure 5.5 illustrates typical TGA curves of neat PBS, binary and hybrid composites. The thermal stability of the materials associated with temperatures at 5% ($T_{5\%}$) and 50% ($T_{50\%}$) mass loss is reported in **Table 5.2**. The curves depict weight loss as a function of temperature, offering insights into the thermal stability and degradation behaviour of the samples (Phua *et al.*, 2013). The classic one-step degradation curves were observed for all samples, indicating a single dominant degradation process for each material. Incorporating different fillers for either binary or hybrid components did not seem to alter the primary degradation pathway of PBS, as indicated by the similarity in the curves (Hiller *et al.*, 2023; Xia & Xu, 2020). However, the $T_{5\%}$ and $T_{50\%}$ of the binary and hybrid systems occurred earlier than those of the neat polymer. This early initiation of thermal degradation suggests a potential interaction between the components, which could influence the thermal stability. The shift in onset temperature suggests that the binary and hybrid systems may have different degradation mechanisms or pathways compared to PBS. Additionally, the earlier offset temperature in these systems implies that the degradation process completes more rapidly. This behaviour could be attributed to the presence of additional phases or interfaces in the binary and hybrid systems that catalyse the degradation process at lower temperatures, leading to a reduction in thermal stability. During early decomposition in TGA, test materials tend to release volatile compounds that may affect the degradation mechanism of the materials (Xia & Xu, 2020). For instance, natural fibres release volatiles such as water vapour, acetic acid, and other organic acids (Paolin & Matija, 2024). In the case of halloysite, alkali ammonium compounds, including ammonium hydroxide and alkyl ammonium salts, are released during degradation (Massaro *et al.*, 2022). Expanded graphite, on the other hand, releases volatile acids such as sulphuric acid and phosphoric acid during decomposition (Yeoh *et al.*, 2024). These compounds act as catalysts, accelerating the decomposition process and influencing the formation of the char layer. This, in turn, affects the thermal stability and flammability of the composites. Meanwhile, understanding the role of these volatiles is crucial for designing materials with improved thermal and fire-resistant properties (Massaro *et al.*, 2022; Paolin & Matija, 2024; Xia & Xu, 2020; Yeoh *et al.*, 2024).

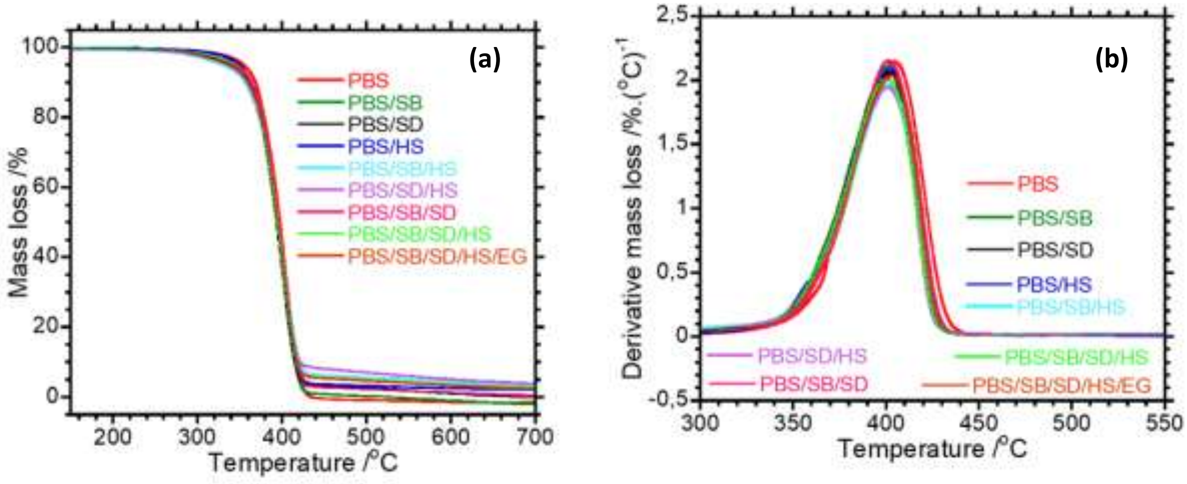

Figure 5.5. (a) TGA curves and (b) derivative curves of neat PBS, hybrid composites, and ternary composites

Table 5.2. Summarised onset ($T_{5\%}$), and offset ($T_{50\%}$) degradation temperatures

Samples	**$T_{5\%}$ /°C**	**$T_{50\%}$ /°C**
PBS	356.7	400
PBS/SB	329.4	395
PBS/SD	338.1	396.1
PBS/HS	348.6	394.4
PBS/SB/HS	336.7	396.7
PBS/SD/HS	337.8	396.7
PBS/SB/SD	337.5	395
PBS/SB/SD/HS	341.1	395.6
PBS/SB/SD/HS/EG	340.0	395.6

5.3.4. Differential Scanning Calorimetry

Table 5.3 summarises the DSC properties obtained during cooling and second heating scans. The corresponding cooling and second heating curves are displayed in **Figure 5.6**. PBS has a T_c at 75.7 °C. Upon adding of either SB or SD, the T_c remained in the same range as PBS. A very slight shift is noticed in PBS/SD/SB hybrid composites (77.6 °C), though this might be statistically insignificant compared to a single-fibre composites. Moreover, a notable shift in T_c (around 78 °C) is observed in PBS/HS and PBS/SD/HS, which implies the nucleation efficacy of HS in accelerating the crystallization rate of PBS. Horiuchi *et al*. (2024), observed increased crystallisation rate of PBS in PBS/Canabarva fibres/lignin hybrid composites in the presence of MMT and SEP clays, and attributed this to induced nucleation caused by the clays. This study indicates the tendency of nanoclays to facilitate heterogeneous nucleation in polymer matrices. The incorporation of EG into PBS/SD/SB/HS composites showed a huge shift in T_c to a higher temperature (~81 °C) insinuating a better heterogeneous nucleation provided by EG particles.

The melting temperatures of the prepared samples are summarised in **Table 5.3**. PBS is a semicrystalline polymer characterised by a melt/recrystallisation/re-melt phenomenon (Righetti *et al*., 2023). Depending on the heating rate and crystallisation temperatures, PBS can display multiple melting peaks resulting from different crystal forms, partial melt/recrystallisation/re-melting, and so forth (Righetti *et al*., 2023). In this case, PBS displayed a small cold-crystallisation peak and a shoulder prior to its main melting temperature (T_m). Modulated DSC studies are important for understanding this complex melting behaviour displayed by PBS. Nevertheless, it is discernible that the T_m of PBS did not practically change when the fillers were incorporated, as observed elsewhere (Horiuchi *et al*., 2024; Motloung *et al*., 2023; They *et al*., 2025). This observation could mean that the fillers did not have a significant influence on the crystal size of PBS (Haris *et al*., 2022). The melting enthalpies decreased with the addition of the fillers, which implied a reduction in the crystallinity of PBS. This change also indicates a disruption to chain folding and stacking in the presence of fillers. A reduction in crystallinity has detrimental effects on the stiffness of polymer materials, which subsequently influences the heat resistance properties, such as heat distortion temperature (HDT). However, in this case, the fibres and other fillers (HS and EG) compensate for the stiffness of PBS despite the reduction in crystallinity.

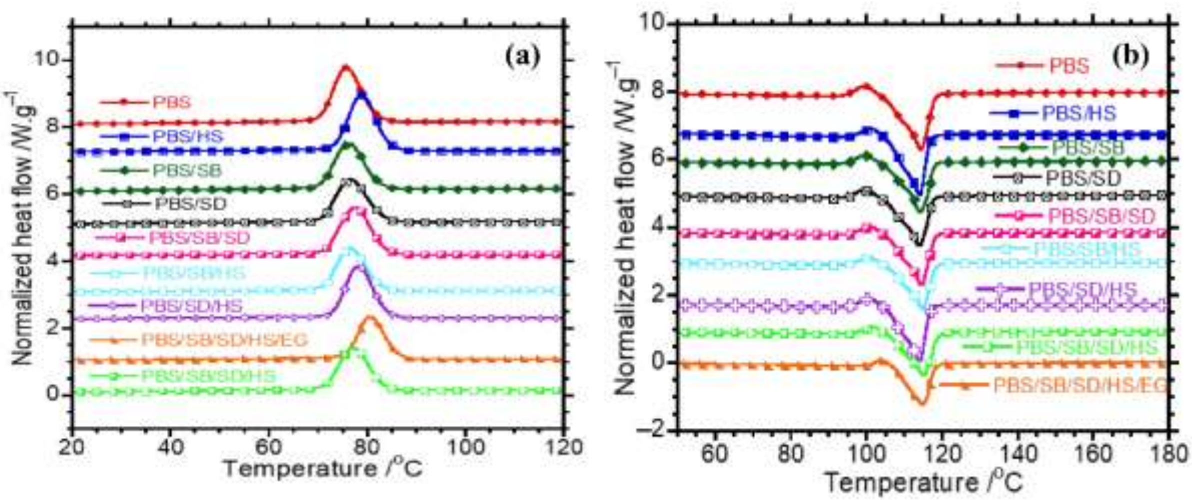

Figure 5.6. DSC thermograms: (a) cooling curves, and (b) second heating curves of neat PBS, binary composites, and hybrid composites

Table 5.3. Summarised DSC properties of the prepared samples

Sample	T_c (°C)	T_m (°C)	ΔH_m (J/g)
PBS	75.7	114.4	71.4
PBS/SB	76.6	114.2	63.5
PBS/SD	76.6	114.0	60.6
PBS/HS	78.9	114.1	65.6
PBS/SB/HS	76.5	115.0	57.2
PBS/SD/HS	78.2	114.0	64.0
PBS/SB/SD	77.6	114.5	63.1
PBS/SB/SD/HS	77.2	115.2	56.6
PBS/SB/SD/HS/EG	80.6	115.0	48.3

5.3.5. Dynamic mechanical analysis of the composites and hybrid composites

The viscoelastic properties of the prepared composites were investigated using DMA, which is an important analytical tool to determine a material's properties, including the stiffness, elasticity, dampening, crosslinking density, *etc*. The influence of natural fibres on the stiffness of the polymer matrix can be determined from the storage modulus curves in DMA. Plots of the storage moduli and tan delta against the temperature are depicted in **Figure 5.7**. In the glassy state, the macromolecular chains are frozen and tightly packed, resulting in the high storage modulus of the polymer. The storage modulus decreases when the temperature is increased due to an increase in chain mobility, making the materials less stiff. It can be observed that PBS exhibited the lowest storage modulus (**Figure 5.7a**). Upon the addition of HS, the storage modulus of PBS increased due to the nano-reinforcement provided by clay nanotubes, which stiffened the macromolecular chains of the matrix. The incorporation of either SD or SB fibres also increased the storage modulus of PBS, implying the reinforcing effect of the fibres. However, there are insignificant differences in the storage moduli of PBS/SD and PBS/SB composites. The hybrid composite (PBS/SD/SB) showed a similar storage modulus to those of PBS/SB and PBS/SD. This contradicts reported studies that demonstrated enhancement of the storage moduli of hybrid composite systems compared to their respective single-fibre composites (Haris *et al*., 2022). Nevertheless, this observation could mean that the effect of a single fibre (either SB or SD) on the storage modulus of PBS can be attained by simultaneous incorporation of SD and SB with 50% loading of each fibre. In terms of product development, this suggests that both SD and SB can be beneficiated as reinforcing fillers by the simultaneous incorporation of them at equal volumes in the PBS matrix to generate hybrid composites, instead of developing single-fibre composites at higher concentrations.

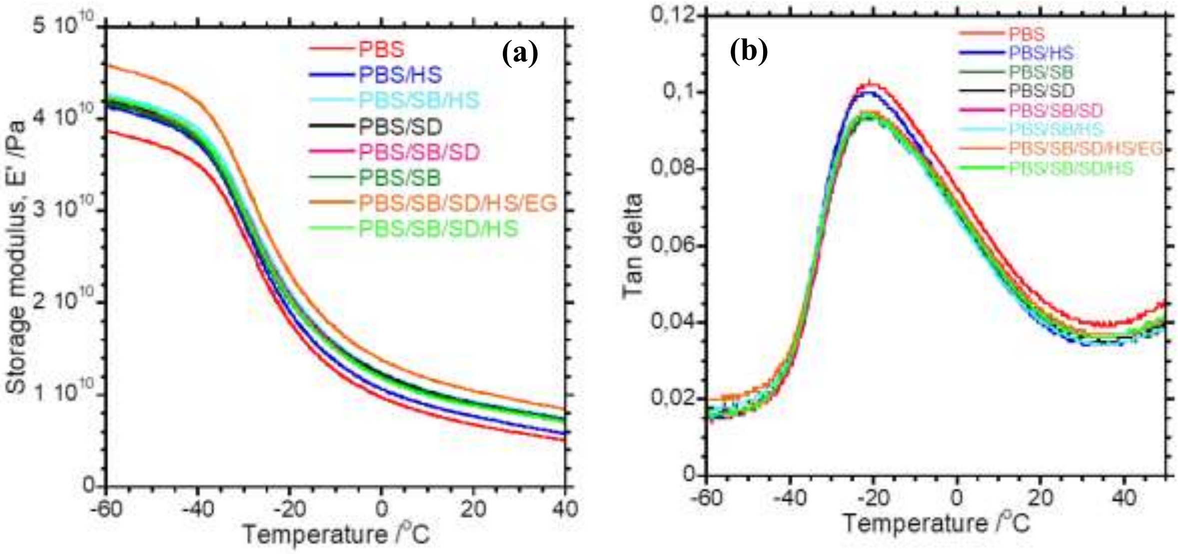

Figure 5.7. DMA: (a) storage modulus, and (b) tan delta

The incorporation of HS in either PBS/SB or PBS/SD/SB did not have a significant influence on the storage moduli of these composites, although there was a slight increase in the storage modulus of PBS/SB. The addition of EG into the PBS/SD/SB/HS hybrid composite system showed a remarkable increase in the storage modulus of PBS over the entire range of temperatures. This insinuates that EG has better reinforcing capacity as it has improved the stiffness of the hybrid PBS/SD/SB/HS composite. EG, as a micro-filler, has a tendency to restrict the mobility of macromolecular chains and increase the stiffness of polymer matrices (Marset *et al*., 2022; Mngomezulu *et al*., 2019). Similar findings have been reported whereby carbon-based materials such as reduced graphene oxide, graphene nanoplatelets, and carbon nanotubes improved the stiffness of hybrid natural fibre/polymer composites (Haris *et al*., 2022). Upon increasing the temperature above the Tg, the storage moduli of the samples decreased dramatically due to increases in the mobility of PBS chains. At ambient temperatures, however, the EG hybrid system showed the highest storage modulus, suggesting enhanced stiffness at normal service temperatures.

Tan delta plots of all the prepared systems are depicted in **Figure 5.7b**. All the samples are characterized by a similar Tg, which indicates a lack of interfacial adhesion between the fibres and the PBS matrix. Usually, a good interfacial adhesion between the polymer matrix and the fibres increases the Tg due to the confinement of the polymer chains by a network of fibres, as observed elsewhere (Haris *et al*., 2022). Meanwhile, a reduction in the tan delta peak is noticed in the composites, implying increased dampening of PBS.

5.3.6. Mechanical properties of the composites and hybrid composites

One of the limiting factors for using PBS is its ductility, which poses a challenge where stiffness is required. Generally, stiff materials such as natural fibres could compensate for low stiffness in soft biopolymers such as PBS. The tensile modulus, which provides information regarding the stiffness of PBS and its respective composites, is shown in **Figure 5.8a**. PBS and PBS/HS are characterised by a low tensile modulus of approximately 380 MPa. The fibre-reinforced composites showed a significant increase in tensile modulus, which is in accordance with the observed increase in storage modulus in DMA (**Figure 5.7a**). The PBS/SB/SD hybrid composite showed a slightly lower tensile modulus compared to the single-fibre composites, while the hybrid composite containing HS and EG showed the highest tensile modulus, reaching above 600 MPa. On the other hand, the elongation at break, which relates to the toughness of a material, confirmed the ductility of PBS, as it showed the highest elongation at break. However, a huge reduction in elongation at break was noticed upon the incorporation of the fibres, as displayed in **Figure 5.8b**. The hybrid composites containing HS and EG showed an elongation at break in a similar range. The elongation at break has a strong dependence on matrix–fibre adhesion for effective stress transfer. In this case, the morphology analysis indicted a lack of compatibility, which explains the reduction in the toughness. Usually, a reduction in elongation at break is accompanied by a decrease in impact resistance.

The impact resilience of the prepared samples is illustrated in **Figure 5.8c**. PBS showed the highest resistance to impact, due to its ductile nature and ability to absorb energy during fracture. A sudden decrease in impact resilience can be noticed in all the composites. The observed decrease could be attributed to the increased rigidity and stiffness of PBS upon the incorporation of the fibres. Usually, stiff polymer materials tend to show low impact resistance. Further, the lack of interfacial adhesion between the fibres and the PBS matrix contributed to insufficient stress transfer from the PBS matrix to the fibres. Better compatibility in polymer-reinforced fibre composites allows efficient stress transfer from the polymer matrix to the fibres, thus increasing the energy required to fracture the material. The impact resilience of all the hybrid composites was below 50% of that of neat PBS. The observed trend indicates the need to functionalise the fibres prior to blending with the polymer matrix to allow efficient stress transfer during impacting while maximising the energy absorption capacity of the material.

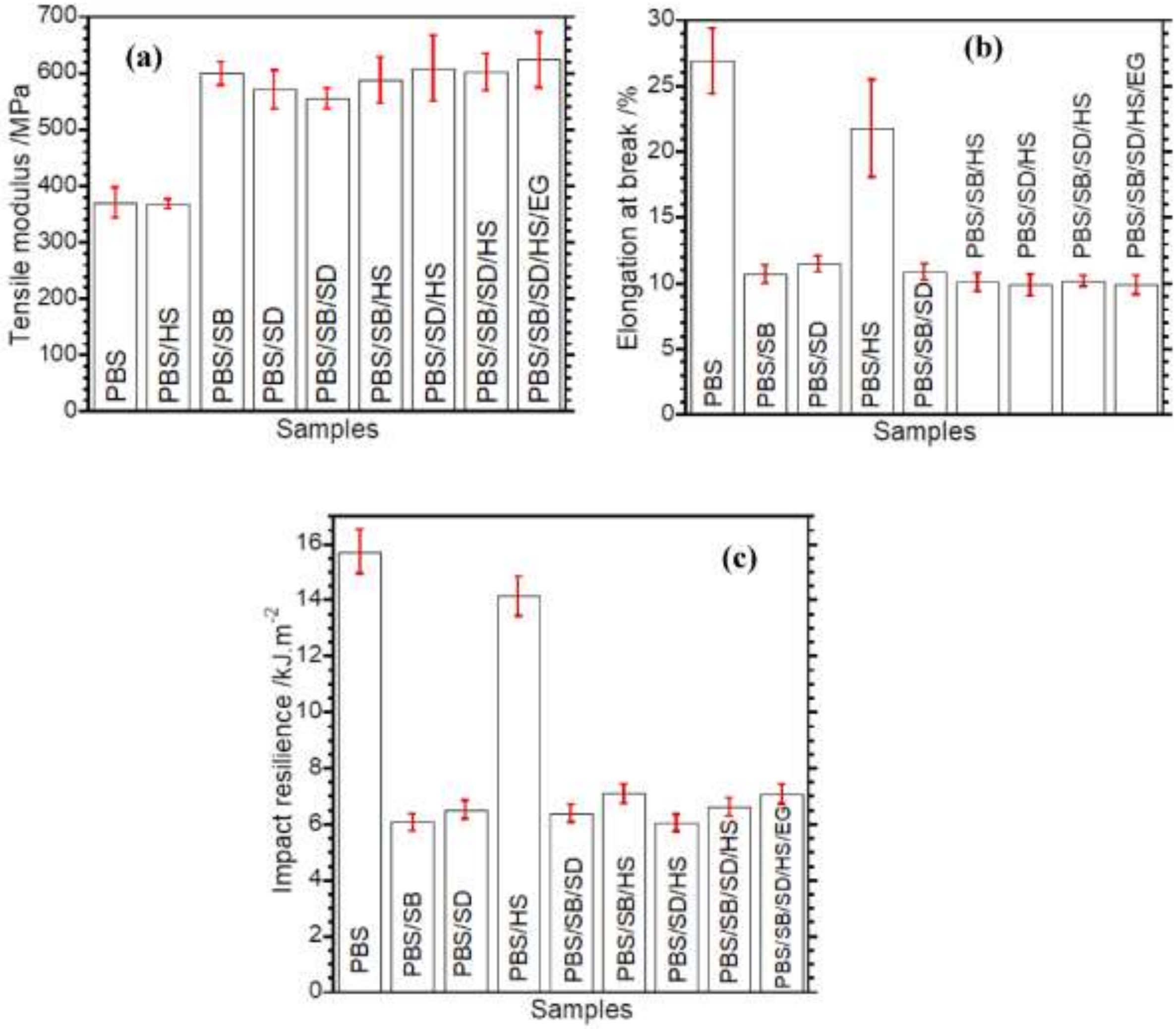

Figure 5.8. (a) Tensile modulus, (b) elongation at break, and (c) impact resilience

5.4. Discussion

In this study, the influences of natural fibres (SB and SD) on the material properties of PBS prepared through the melt compounding technique were investigated. The influences of HS and EG on the properties of the respective PBS/SB/SD hybrids were also evaluated. To elucidate the effects of individual fibres, single-fibre composites of PBS/SD and PBS/SB were also prepared. The morphological analysis showed fibre pull-outs and voids in both PBS/SD and PBS/SB composites. These observations indicated poor interfacial compatibility between the fibres and the PBS matrix, which has a huge amount of potential to adversely impact the mechanical performance. On the other hand, the hybrid PBS/SD/SB composite system demonstrated the encapsulation of SB by flaky SD fibres. The rheological characterisation indicated an increase in the viscosity of PBS/SD/SB compared to PBS/SD and PBS/SB, indicating the synergy of the fibres in improving the flow viscosity of PBS. One of the challenges of using PBS is its low melt viscosity and melt strength. Increasing the viscosity of polymers could indicate, in some instances, the enhancement of melt strength, which is essential for processes such as foaming. In this study, the incorporation of HS also resulted in the enhancement of the melt viscosity of single-fibre composites, with EG-containing hybrid composites showing the greatest improvements. Though the melt viscosity increased with fibre inclusion, all the composites could still be extruded without altering the processing conditions used to prepare neat PBS. The thermal stability of all the composites decreased, and this is attributed to the additional phases released from the fillers that catalysed the degradation process of PBS. Although the onset temperature decreased in PBS/SB compared to that of PBS, the hybridisation with SD (PBS/SD/SB) led to an increase in this temperature, with a further slight increase for the PBS/SD/SB/HS and PBS/SD/SB/HS/EG composites. The DSC analysis confirmed increases in the crystallisation temperatures of PBS and its respective hybrid composites in the presence of HS and EG. The presence of EG showed better heterogeneous nucleation in PBS/SD/SB/HS hybrid composites, indicating that EG promoted chain folding and stacking of PBS chain segments and the formation of crystals at the matrix–filler interfaces. Additionally, faster crystallisation rates are industrially important for processes such as injection moulding, where the parts of items can be manufactured within short cycle times.

The thermomechanical measurements indicated an increased storage modulus of PBS when the fibres were added. The maximum improvement in this property was noticed when EG was included in the PBS/SBS/SD/HS composite. At a normal service temperature (~ 23–25 ◦C) this composite indicated enhanced stiffness, responding to our aim to increase the stiffness of PBS as a viable way to expand its applications. Increasing the stiffness has a direct influence on other properties such as HDT. The tensile modulus also improved after adding the fibres (binary and hybrid composites), insinuating the reinforcing effect of the added fillers on restricting the mobility of PBS chains, as shown in **Figure 5.9**. The reduction in both toughness and impact could be attributed to a lack of interfacial compatibility between the fibres and the PBS matrix, implicating the need to pre-treat the fibres or incorporate compatibilizers such as PBS grafted with moieties like maleic anhydride. These additions will bring a balance in mechanical properties such as stiffness and toughness. Overall, the prepared hybrid composites show great potential in developing green composites for applications such as rigid packaging, cutlery, and many others. Future studies should dwell on improving the interfacial adhesion between the fibres used and PBS and evaluate the environmental impact of the prepared composites at the end-of-life stage.

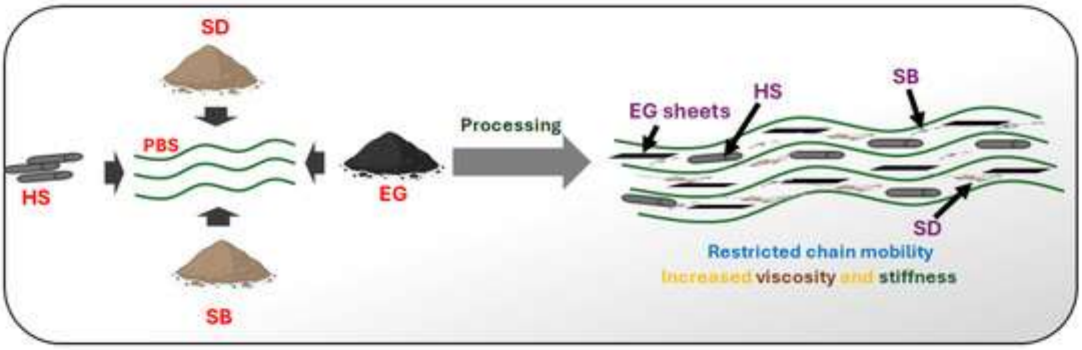

Figure 5.9. Scheme for reinforcing PBS with SB, SD, HS, and EG

5.5. Conclusions

Herein, the effects of the natural fibres SB and SD on the properties of PBS prepared through melt compounding were investigated. The influences of the incorporation of HS and EG on the properties of PBS/SB/SD hybrid composites were also examined. The morphological analysis indicated poor interfacial adhesion between PBS and the fibres. The obtained findings indicated enhancements in the complex viscosity of PBS in the presence of natural fibres, and further improvements in the presence of HS and EG. Moreover, the crystallisation temperatures of PBS increased in the presence of fillers, with EG showing better nucleation efficiency. The stiffness of PBS/SD/SB composites also increased upon the addition of HS and EG. However, the toughness and impact resilience decreased, likely due to the increased stiffness of the composites and possibly poor interfacial adhesion between the matrix and the fillers. This suggests that fibre pre-treatment may be necessary to enhance compatibility. Overall, the prepared hybrid composites show potential for use in the development of rigid materials, such as packaging.

5.6. References

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CHAPTER 6

The influence of sawdust, sugarcane bagasse and their synergy on the properties of PHBH matrix for advanced applications

This chapter will be submitted as:

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Abstract

Accumulation of agricultural waste is a serious concern in the world. The primary goal of this paper is to address the need for sustainable, high-performance polymer composites by examining the microstructure, thermal, mechanical, rheological, and flammability properties of hybrid composites reinforced with sugarcane bagasse and sawdust —aiming to transform agricultural residues into valuable materials. Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) was employed as a polymer matrix phase. The morphological features show poor interfacial adhesion between the polymer matrix and sugarcane bagasse, whereas sawdust exhibits better dispersion within the matrix. The addition of halloysite clay further improved the interfacial adhesion of sawdust to the polymer. The hybrid composite comprising halloysite clay demonstrated higher thermal stability and viscosity compared to all other composites. Moreover, all composites exhibited greater stiffness than the neat matrix, irrespective of the type of reinforcing filler. Overall, the combination of sugarcane bagasse, sawdust, and halloysite clay enhances the thermal stability and stiffness of the polymer matrix, making it suitable for applications in construction and automotive parts.

6.1. Introduction

Selecting appropriate materials for design and manufacturing is an essential component of engineering. This process facilitates the evaluation of the physical and mechanical properties of materials, ultimately leading to improved product performance and enhanced customer satisfaction (Girijappa *et al*., 2019). Natural fibres possess unique characteristics that set them apart from other classes of materials, particularly in terms of their physical, chemical, thermal, mechanical, and electrical properties (Patel *et al*., 2023). These fibres have diameters ranging from a few micrometres to tens of micrometres and lengths ranging from millimetres to centimetres, resulting in moderate to high aspect ratios (Fu *et al*., 2009). They also offer tensile strengths from 80–1500 MPa and Young's moduli in the range of 3–80 GPa, depending on the type of fibre and its treatment (Elfaleh *et al*, 2023; Musthaq *et al*., 2023). Furthermore, natural fibres offer good thermal insulation, biodegradability, and low density (1.2–1.6 g/cm^3), making them attractive for lightweight materials (Girijappa *et al*., 2019). However, factors such as fibre type, fibre-matrix adhesion, surface treatment, fibre content, and processing conditions strongly influence their properties. Moisture sensitivity and thermal stability, which usually is limited to temperatures below 200–250 °C, are significant challenges (Musthaq *et al*., 2023). Nevertheless, these shortfalls can be addressed through various surface treatments (mechanical, physical, chemical, biological, *etc*.), which can be further enhanced via hybridisation with other fibres and/or compatible materials (Mochane *et al*., 2019; Patel *et al*., 2023; Pokharel *et al*., 2022). Furthermore, fibre properties collectively determine their effectiveness as fillers or reinforcements in natural fibre composites (NFCs). These characteristics ultimately shape their performance and define their potential applications across various industries and markets. Thus, their current exploitation in fibre polymer composites, where they are embedded in various polymer matrices for advanced sustainable applications (Mochane *et al*., 2019; Seydibeyoğlu *et al*., 2023; Shamsuyeva *et al*., 2019).

Among the various natural reinforcements studied, sawdust (SD) and sugarcane bagasse (SB) have emerged as promising candidates due to their abundance, renewability, and favourable mechanical and thermal properties (Medina-Martinez *et al*., 2023; Samanth *et al*., 2025). These lignocellulosic fibres primarily consist of cellulose, hemicellulose, and lignin, each contributing to their performance in polymer matrices. Noticeably, cellulose provides structural rigidity and high tensile strength, while lignin offers thermal stability and hydrophobic properties, which improve adhesion in non-polar systems (Shelly *et al*., 2025). The potential of SD and SB to reinforce is closely associated with their physicochemical structure, including a high aspect ratio and surface area. Sawdust with higher lignin content can enhance thermal stability and promote matrix compatibility through lignin–polymer interactions (Mariana *et al*., 2021). Furthermore, SB, rich in cellulose, significantly contributes to mechanical reinforcement and thermal resistance (Samanth *et al*., 2025). Moreover, both fibres possess abundant hydroxyl groups that facilitate interfacial bonding with polar polymer matrices through hydrogen bonding. When modified, these functional groups are capable of covalent interactions, such as esterification. Such interactions promote enhanced stress transfer and reduce fibre-matrix debonding. Additionally, the fibrous morphology of these materials enables effective load distribution within the matrix, thereby improving the mechanical integrity of the composite (Shelly *et al.*, 2025). Their distinct yet complementary properties make them ideal candidates for hybrid composites that deliver enhanced mechanical strength, improved thermal resistance, and overall performance optimisation in sustainable material applications. This study aims to investigate the effects of incorporating sawdust fibres and SB into a polymer matrix, focusing on their influence on the mechanical and thermal properties of the composite. By exploring the interaction mechanisms between these fibres and the polymer phase, the research aims to optimise fibre-reinforced biocomposites for structural and semi-structural applications.

6.2. Materials and methods

6.2.1. Materials

The poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) polymer grade Green Planet™ X131A was purchased from Kaneka Corporation (KITA-KU, Osaka, Japan) in the form of pellets. It exhibited a density of 1.25 g/cm^3. Sugarcane bagasse (SB) was obtained from Tongaat hullet, KwaZulu-Natal (South Africa). Ground sawdust (SD) was sourced from a timber processing plant in Bloemfontein, Free State (South Africa). Halloysite nanoclay powder (HS), beige coloured with a formula weight of 294.19 g/mol and a pore size of 1.26-1.34 ml/mol was purchased from Sigma-Aldrich, South Africa. Its particles have a diameter of 30-70 nm and a length of 1-3 microns.

6.2.2. Preparation of the investigated samples

The SB fibres were prepared following the method reported in our previous research (Sikhosana *et al.*, 2025). Prior to melt extrusion, PHBH, SB, SD and HS were dried at 60 in a vacuum oven for 12 hours. The compositions of the samples are shown in **Table 6.1**. The neat PHBH, binary, and hybrid composites were extruded in a TE-30 co-rotating twin-screw extruder (Nanjing Only Extrusion Machinery Co., Ltd.) with the temperatures of the heating zones from the hopper to the die set from 120 to 160 °C. The extrusion speed and feed rate were set at 178.8 rpm and 4.4 kg/hr, respectively. The extrudates were then quenched in water, pelletized, and dried in an oven at 60 °C for 24 hours. These dried pellets were injection moulded into various test specimens using an injection moulding machine (ENGEL e-mac50). The injection moulding heating zones were set at 36, 120, 140, 150, and 160 °C. The clamping force, metering, specific back pressure, injection pressure, and injection speed were set at 500 kN, 29 mm, 100 bar, 550 bar, and 100 m/s, respectively. The test specimens were cooled to 22 °C and stored in a Ziplock bag.

Table 6.1. Summary of the compositions for all investigated samples

Sample ID	**Compositions (wt.%)**
PHBH	100
PHBH/SB	90/10
PBS/SD	90/10
PHBH/SB/SD	90/5/5
PHBH/SB/SD/HS	87.3/4.85/4.85/3

6.2.3 Characterisations of the investigated samples

6.2.3.1. Scanning electron microscopy (SEM)

The morphology of the cryofractured composite samples was investigated using a JSM-7800F Extreme-resolution Analytical Field Emission Scanning Electron Microscope, which was operated at an accelerating voltage of 5.0 kV. The samples were mounted on 10 mm Cambridge pin-type aluminium stubs using epoxy glue for precise imaging. The high-resolution capabilities of the JSM-7800F allowed for detailed qualitative analysis of the surface morphology and texture of the materials.

6.2.3.2. Differential Scanning Calorimetry (DSC)

DSC tests were performed using a Perkin Elmer DSC7 instrument. Samples weighing ≈ 6 mg were sealed in aluminium pans and heated under a nitrogen flow of 20 mL/min from -35 to 160 °C at a heating rate of 10 °C/min and kept at this temperature for 1 minute to eliminate the thermal history, cooled to -35 °C at the same rate, and reheated under the same conditions. The melting enthalpies and temperatures were determined from the second heating curves.

6.2.3.3. *Thermogravimetric analysis (TGA)*

The thermogravimetric analysis (TGA) was done in a Perkin Elmer Pyris-1 thermogravimetric analyzer. The specimens with a size of ≈ 8 mg were heated from 25 to 800 °C at a heating rate of 10 °C min^{-1} under inert nitrogen.

6.2.3.4. *Dynamic Rheological properties*

The dynamic rheological properties were conducted under the atmospheric conditions with a temperature of 190 °C by utilizing a Physica MCR501 (Anton Paar, Austria) rheometer in a 25 mm diameter parallel plate configuration. The strain amplitude of 1% was determined with preliminary experiments, and the zero gap was set at 1.15 mm for all the tests.

6.2.3.5. *Dynamic mechanical analysis (DMA)*

The dynamic mechanical properties of the neat PHBH and its hybrid composites were analysed by Perkin Elmer Diamond DMA in bending mode. Samples with a thickness of 1 mm were heated from -60 °C to 80 °C at a rate of 5 °C min^{-1} in an oscillating frequency of 1 Hz.

6.2.3.6. *Tensile test*

Tensile testing was carried out on the injection-moulded, dog-bone-shaped specimens using an Instron 5966 tester (Instron Engineering Corporation, USA, ASTM 638D). The tensile tester is equipped with a 10 kN load cell, and the tests were conducted at a constant strain rate of 50 mm/min and a temperature of 25 °C. The results are an average of six tests per sample, along with standard deviations.

6.2.3.7. *Impact resilience (A Charpy impact test)*

The injection-moulded specimens of the different formulations with dimensions of approximately 80 mm × 10 mm × 4 mm (L×W×B) were subjected to a Charpy impact test in accordance with ISO 179 standards to evaluate their resistance to breakage by flexural shock. The specimens were notched on one side with a 0.25 mm notch root radius at a depth of 2 mm using a CEAST Automatic Notchvis Plus. The notched Charpy impact strength (ISO 179) was measured at 25 °C using a fully automated CEAST Pendulum Resil Impactor II. The drop velocity was 3.7 m/s, resulting in a hammer energy of 14 J. The reported results represent the average of at least six tests per sample.

6.3. Results and discussion

Figure 6.1 shows the SEM images of the fractured surfaces of the composites. In **Figure 6.1a**, there are voids due to SB fibre pull-outs and SB gaps in the PHBH matrix. The results indicate poor compatibility between the hydrophobic PHBH matrix and hydrophilic SB. Larger and elongated SB fibres clustered together, creating regions of poor distribution (**Figure 1**). In **Figure 6.1b**, there are vacant spaces of SD that are randomly distributed within the PHBH matrix. Also, voids are also visible, suggesting poor compatibility between SD and the PHBH matrix. The fine SD particles in **Figure 6.1b** show better dispersibility and distribution in PHBH than SB. Moreover, the morphology of the PHBH/SB/SD composite in **Figure 6.1c** is a combination of morphologies in **Figure 6.1(a,b)**, but voids are present indicating poor interfacial adhesion between the fillers and the PHBH matrix. The morphology of the PHBH/SB/SD/HS composite is relatively finer than the morphologies of other composites. This is attributed to HS particles that act as a compatibiliser, and fill the voids around SD locking it within the matrix. Theys *et al*. (2025) reported a similar compatibilising effect of montmorillonite (MMT) in a hybrid polybutylene succinate (PBS)/maize stalk fibre (MSF)/MMT bio-composite. However, there is an interfacial gap between the long SB and PHBH matrix in **Figure 6.1d,** suggesting poor compatibility between SB and the matrix despite the presence of HS. The HS and SD fillers are in powder form and have a higher surface area than the longer SB fibres. Therefore, in the PHBH/SB/SD/HS composite, HS platelets are more likely accessible to SD than SB, thus improving compatibility of SD with PHBH. The surface treatments of the fibres or modifying the halloysite, such as through surface functionalisation or intercalation with specific compounds, could further enhance interfacial adhesion between the constituents of the composite and optimize performance (Empty-Marin *et al*., 2023; Yang *et al*., 2017).

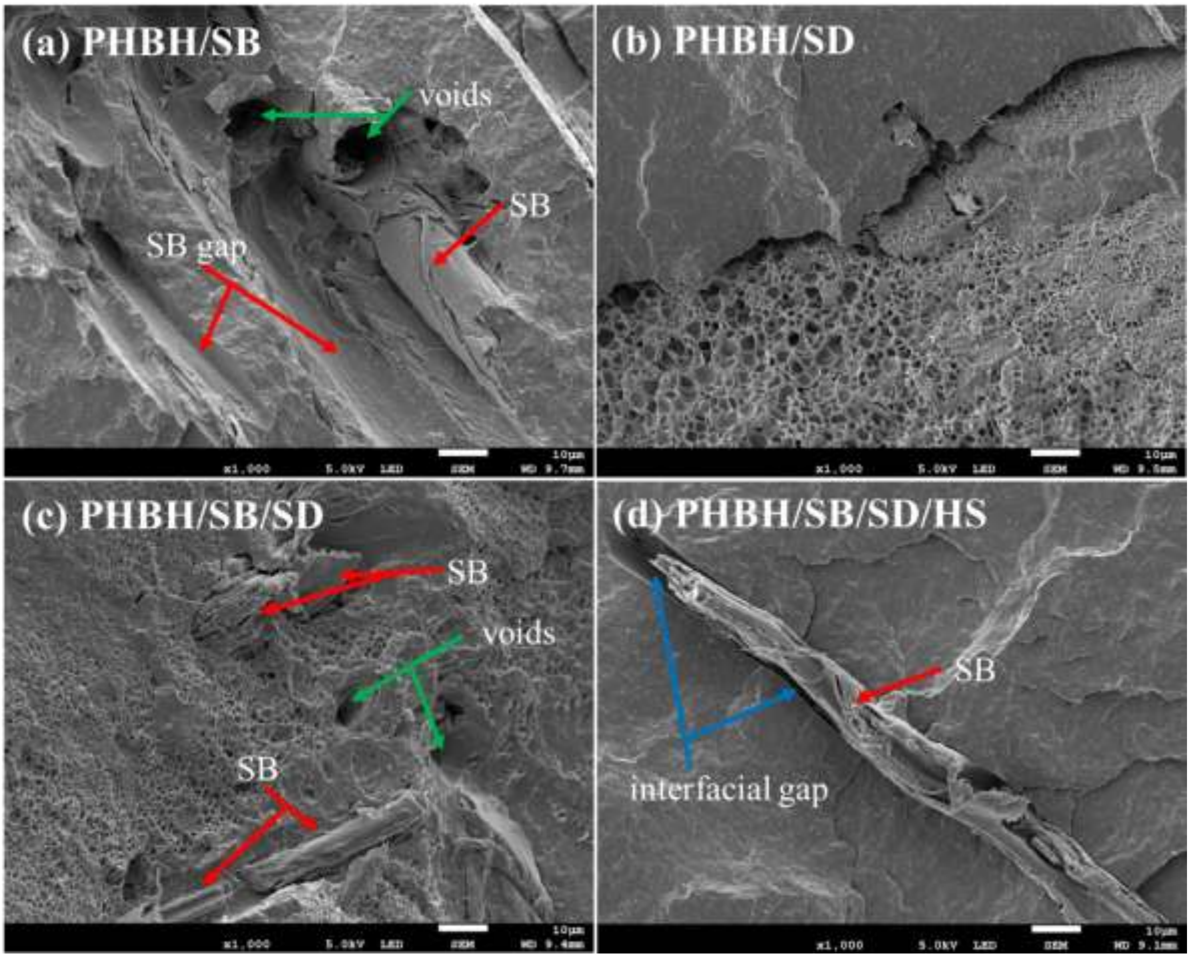

Figure 6.1. SEM micrographs of the fractured surfaces of (a,b) binary composites, and of (c,d) hybrid composites

Figure 6.2 displays the second melting and first cooling curves of neat PHBH, as well as binary and hybrid composites. Neat PHBH in **Figure 6.2a** shows two melting peaks, T_{m1} and T_{m2} at 134 and 146.1 °C, respectively. The T_{m1} has a relatively lower intensity than T_{m2}. The double melting phenomenon for PHBH has been reported in literature (Hu *et al*., 2007). Hu *et.al.* (2007) attributed the lower and higher melting peaks to the melting of crystals formed during the primary crystallisation and the melting of crystals formed by recrystallisation during the heating process, respectively. The lower and higher melting peak positions do not change in the presence of the fillers (SB, SD, HS), suggesting that the lamellae thickness of PHBH crystals is not altered in the binary and hybrid composites. Neat PHBH has a crystallisation temperature (T_c) of 96.7 °C. Meanwhile, the introduction of fillers for binary and hybrid composites lowers the T_c such that the composites have a T_c at about 87 °C. The presence of fillers in the composites disrupts the mobility of PHBH chains, making it difficult for the chains to pack orderly to form crystals; hence, crystallisation is delayed. In the binary composites, the addition of SB slightly reduces normalised melting enthalpy (ΔH^{norm}_{m}) and the crystallinity (X_c) of PHBH, whereas the introduction of SD increases ΔH^{norm}_{m} and the X_c as seen in **Table 6.2**. Earlier, the SEM results in **Figure 6.1** showed poorly distributed clusters of SB in the PHBH matrix due to poor compatibility between the constituents of the composites. The inadequate compatibility promotes the formation of imperfect crystals, hence a slightly lower ΔH^{norm}_{m} and X_c for the PHBH/SB composite. High ΔH^{norm}_{m} and X_c for the PHBH/SD composite are linked to better dispersion of SD particles due to their larger surface area, which promotes better alignment of PHBH chains. The ΔH^{norm}_{m} and X_c of the PHBH/SB/SD composite, despite the presence of fillers, are equal to those of neat PHBH. The fillers in the PHBH/SB/SD composite have two opposing effects on ΔH^{norm}_{m} and X_c. To be precise, SB reduces ΔH^{norm}_{m} and X_c, whereas SD promotes the increase of ΔH^{norm}_{m} and X_c. The net effect is ΔH^{norm}_{m} and X_c that are equal to those of neat PHBH. The PHBH/SB/SD/HS composite has ΔH^{norm}_{m} and X_c that are slightly higher than those of the PHBH/SB/SD composite due to intervention by HS.

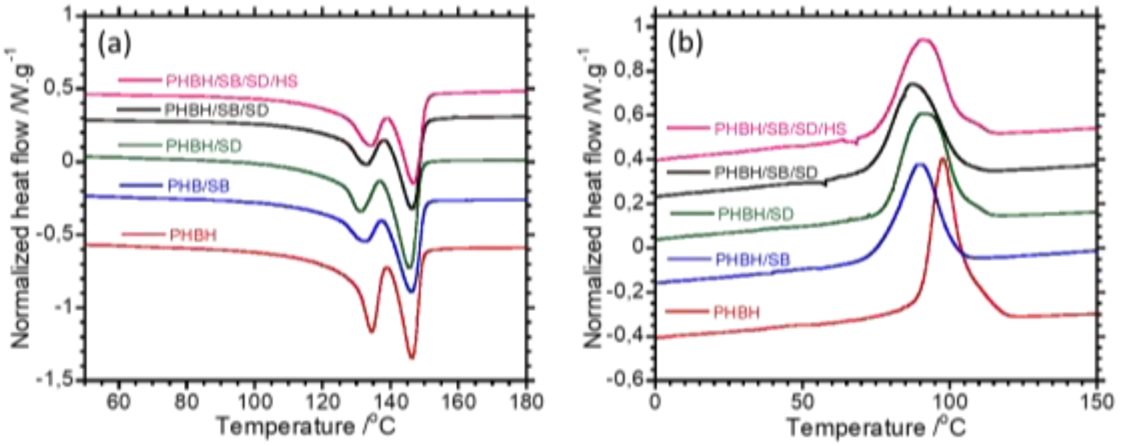

Figure 6.2. DSC: (a) Second heating, and (b) cooling curves of neat PHBH, binary, and hybrid composites

Table 6.2. Melting and crystallisation parameters obtained from DSC

Samples	**T_{m1} /°C**	**T_{m2} /°C**	**T_c /°C**	**ΔH^{norm}_m/J.g.$^{-1}$**	**X_c /%**
PHBH	134.1	146.06	96.7	63.7	43.6
PHBH/SB	131.97	146.06	88.57	59.7	40.9
PHBH/SD	130.89	145.33	87.85	69.5	47.6
PHBH/SB/SD	131.97	145.69	86.11	63.9	43.8
PHBH/SB/SD/HS	133.78	146.42	88.05	66.1	45.3

The TGA curves and $T_{5\%}$, $T_{50\%}$ and T_{max} values of the samples are shown in **Figure 6.3** and **Table 6.3**. The $T_{5\%}$, $T_{50\%}$ and T_{max} values of neat PHBH are lower, indicating that the neat polymer has lower thermal stability than the composites. The thermal stability of PHBH is enhanced by incorporating either SB or SD. SD and SB are lignocellulosic materials comprised of cellulose, hemicellulose, and lignin. The lignin of the fillers acts as a stabiliser, which reduces the degradation rate of PHBH in the composites; hence, high thermal stability is achieved. There are debates/disagreements in literature regarding the influence of cellulose-based materials on the thermal stability of polymer matrices (Masanabo *et.al*., 2024; Valente *et al*., 2021). Masanabo *et al*. (2024), for instance, reported a decrease in the overall thermal stability of poly(butylene succinate-co-adipate)/poly(3-hydroxybutyrate-co-3-hydoxyvalerate) blends when cowpea lignocellulosic side stream/fibres are incorporated. In contrast, Valente *et al*. (2021) reported that the high contents of cellulose fibres (40 wt.%) enhance the maximum thermal degradation temperature of poly(hydroxybutyrate) (PHB) from 236 °C to over 280 °C. The researchers have therefore suggested that the increase in thermal stability proves that there is some degree of interfacial adhesion between PHB and the fibres. The SD shows better improvement of thermal stability for the PHBH/SD composite than PHBH/SB composite. Earlier, the SEM results showed better dispersion of SD than SB in the PHBH matrix for binary composites due to its smaller size. The smaller SD particles interacted better with the PHBH matrix, promoting better heat dissipation and high thermal stability. The simultaneous incorporation of SB and SD to PHBH has a synergistic effect on the thermal stability. The PHBH/SB/SD/HS composite shows the highest thermal stability than other composites as observed from their $T_{5\%}$, $T_{50\%}$ and T_{max} values. The presence of HS in the PHBH/SB/SD/HS composite hinders the diffusion of volatile decomposition products from the composite by stabilising the matrix; hence, a relatively higher thermal stability is achieved.

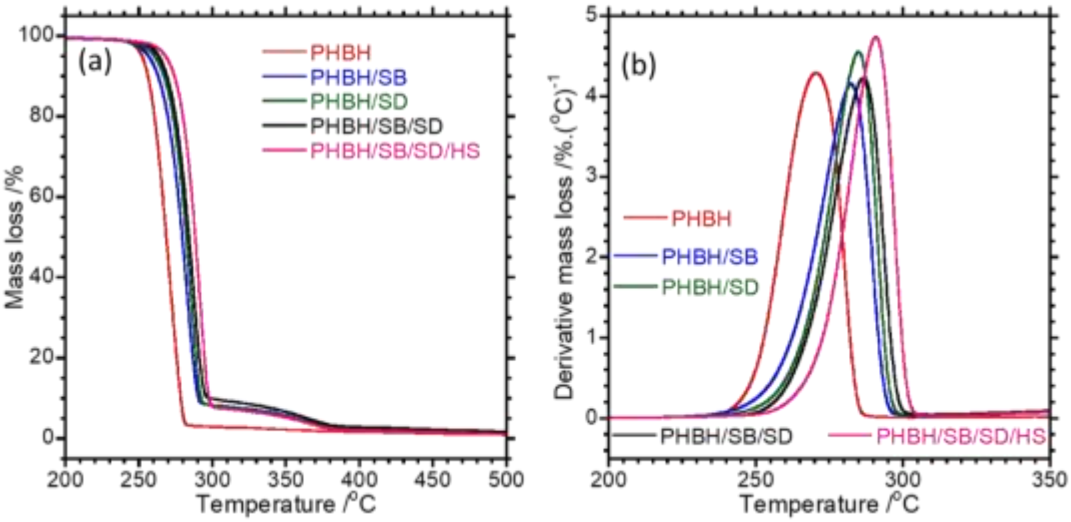

Figure 6.3. (a) Thermogravimetric, and (b) derivative (dTGA) curves of neat PHBH, binary, and hybrid composites

Table 6.3. Degradation parameters obtained from thermogravimetry

Samples	**$T_{5\%}$ /°C**	**$T_{50\%}$ /°C**	**T_{max} /°C**
PHBH	251.8	268.8	270.4
PHBH/SB	256.5	279.6	281.1
PHBH/SD	260.7	282.3	284.6
PHBH/SB/SD	263.5	284.2	286.7
PHBH/SB/SD/HS	268.1	288.4	290.8

Rheological studies are important in polymer processing because they provide insights regarding the processability of the polymer composites. The complex viscosity (η*) curves of neat PHBH, binary, and hybrid composites as a function of angular frequency (ω) are illustrated in **Figure 6.4**. The amplitude was set to 1% following the preliminary amplitude sweep tests conducted to determine the linear viscoelastic region of the samples. Neat PHBH exhibits lower η* and elasticity due to its molecular structure, which lacks significant covalent cross-links, resulting in fewer entanglements and constrictions on the chain movement. The polymer chains are mobile, permitting ease of flow when subjected to shear pressures or elevated temperatures. In **Figure 6.5**, the composites have higher η* and elasticity than that of neat PHBH. The addition of stiff materials into the PHBH matrix hinders the mobility of the polymer chains, thus affecting the viscous behaviour by causing an increase in the η* (Ivorra-Martinez *et al.*, 2020) The η* and elasticity of the composites in **Figure 6.4** increase in the following order:

PHBH/SB<PHBH/SD<PHBH/SB/SD<PHBH/SD/SB/HS. The higher η* and elasticity of the PHBH/SD composite in comparison to the PHBH/SB composite are linked to the different dispersion states of the fillers in the composites, as illustrated in **Figure 6.1**. The fine SD particles dispersed better in the PHBH matrix than the longer SB fibres which formed clusters. The uniformly dispersed SD particles offered a relatively greater restriction on PHBH chain mobility than SB. Consequently, a relatively higher η* and elasticity of PHBH/SD are realised. The viscosity behaviour of a polymer material is not solely dependent on the dispersion state of the filler; it can also be influenced by the shape, size, and interactions of filler particles (Hilliou & Covas, 2020). In hybrid composites, the combination of sugarcane bagasse and sawdust exhibits a higher η* and elasticity than single-fibre composites despite containing equal filler loadings. The combination of 5 wt.% SB and 5 wt.% SD in the PHBH/SB/SD composite forms a percolation network that is better than the individual fillers at 10 wt.% loading. The network contributes to enhanced η* and elasticity. The better η* and elasticity of the PHBH/SD/SB/HS composite is attributed to HS intercalation within SB and SD whilst preventing the agglomeration of sawdust, forming a dense hybrid network in the process. A dense network promotes enhanced η* and elasticity due to entanglements and/or interactions (Pawlak *et al.*, 2024).

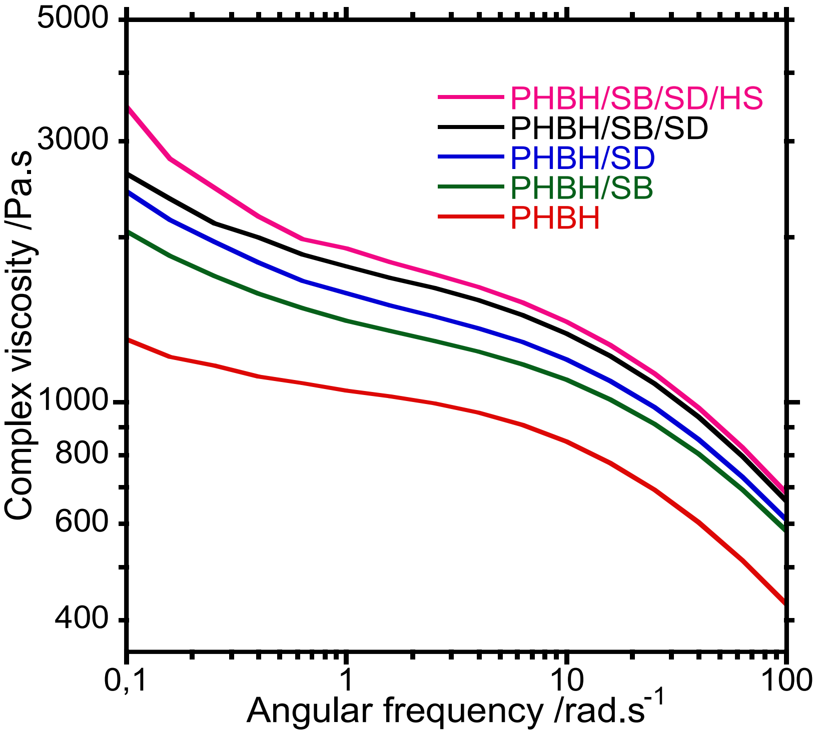

Figure 6.4. Viscosity curves of neat PHBH, binary, and hybrid composites at 190 °C

The storage modulus (E') of neat PHBH and the composites are shown in **Figure 6.5**. Neat PHBH has a lower E' than the composites for the tested temperatures. Overall, the composites have better stiffness than neat PHBH due to the presence of fillers that restrict the mobility of polymer chains. The PHBH/SD composite has higher stiffness than the PHBH/SB composite, and this attribute can be linked to different morphologies of the composites. Earlier, the finer SD particles showed superior distribution in PHBH than the SB fibres that formed clusters in the matrix (**Figure 6.1**). In a relatively better dispersed system such as PHBH/SD, the SD particles promoted effective immobilisation of the polymer chains; hence, better reinforcement is achieved. The higher X_c of the PHBH/SD composite than that of PHBH/SB composite may have also contributed to its relatively higher stiffness. The stiffness of PHBH is enhanced by the addition of the combination of SD and SB due to their synergistic effect. The PHBH/SB/SD/HS composite exhibits better stiffness amongst all the other composites. This behaviour is ascribed to higher stiffness HS nanotubes due to their rigidity and their promotion of better intimate contact between the SD and PHBH. The storage modulus follows a similar trend to the flow curves.

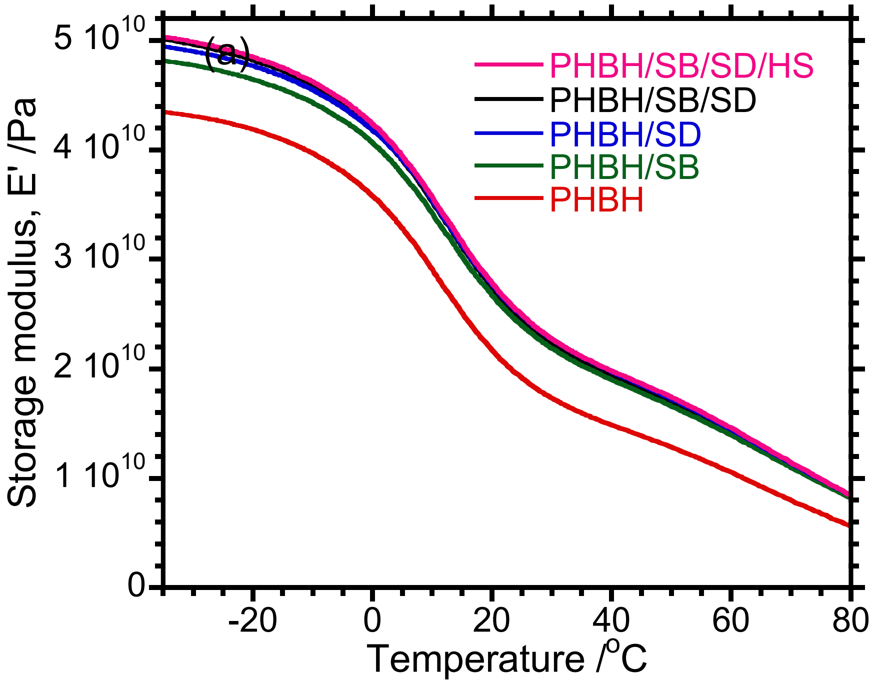

Figure 6.5. Temperature dependence of storage modulus of neat PHBH, binary, and hybrid composites

The mechanical properties of the samples are shown in **Figure 6.6** and **Table 6.4**. The mechanical properties of polymer composites are influenced by several factors, including dispersion, interfacial adhesion, geometry, and the synergistic interactions among the components in the formulation (Kun *et al*., 2021). In this study, two primary contributors to mechanical properties were identified: the degree of dispersion and the stiffness of individual components, with dispersion being the most dominant factor. In the binary systems of **Figure 6.6a**, it was observed that SD composites exhibited a higher tensile modulus compared to SB composites. The SEM analysis confirmed that SD achieved better dispersion within the PHBH matrix than SB. This improved dispersion facilitated more efficient stress transfer between the matrix and the filler, highlighting the importance of uniform distribution. Additionally, the intrinsic stiffness of the individual fillers significantly influenced mechanical properties. In contrast, hybrid systems exhibited poor filler dispersion, resulting in a lack of synergy among the components. Consequently, no enhancement in mechanical properties was observed. The lack of synergy may be due to the orientation and incompatibility of the fillers. In particular, the combination of fine powders and longitudinal fibres appeared to impede effective interaction within the matrix, which is supported by SEM images. This anti synergy led to diminished mechanical performance, contrary to expectations that the hybrid system would yield superior tensile strength through collaborative interactions among the fillers. Furthermore, the anticipated increase in tensile modulus, driven by the addition of high-aspect-ratio fillers like HS, was not achieved. This shortfall was attributed to a lack of affinity between the fillers, which limited stress transfer and reduced the tensile modulus. Furthermore, none of the fillers were effectively adhered to halloysite clay, further diminishing their potential to enhance mechanical properties. In summary, the findings emphasise the critical roles of dispersion and compatibility in influencing the mechanical properties of composite materials. The lack of collaboration among the fillers, combined with poor dispersion in the hybrid systems, negated any potential benefits from their inclusion, highlighting the need for optimized filler selection and dispersion strategies in future studies.

In **Figure 6.6(b,c)**, neat PHBH polymer exhibits higher elongation at break and impact resilience than the binary and hybrid composites. The addition of stiff reinforcements, such as SD, SB, and HS introduces rigidity to the polymer matrix, which restricts chain mobility. This reduction in chain decreases the ductility of the polymer matrix, making it more brittle under mechanical stress. Compatibility between the polymer matrix and the added fillers is a critical factor that influences the mechanical properties of the composites. Poor interfacial adhesion between the hydrophobic PHBH polymer and the hydrophilic fibres as seen in **Figure 6.1** promotes the formation of cracks, voids, and weak interfacial regions within the composite.

These defects act as stress concentrators or crack initiators, significantly diminishing the ability of the material to absorb and dissipate energy upon impact. Consequently, the composites show reduced impact resistance compared to the neat polymer (Ivorra-Martinez *et al*., 2020; Liu *et al*., 2020; Pokharel *et al*., 2022). Incorporating compatibilization strategies could mitigate these defects, improve fibre-matrix bonding, and enhance both tensile and impact performance of the composites.

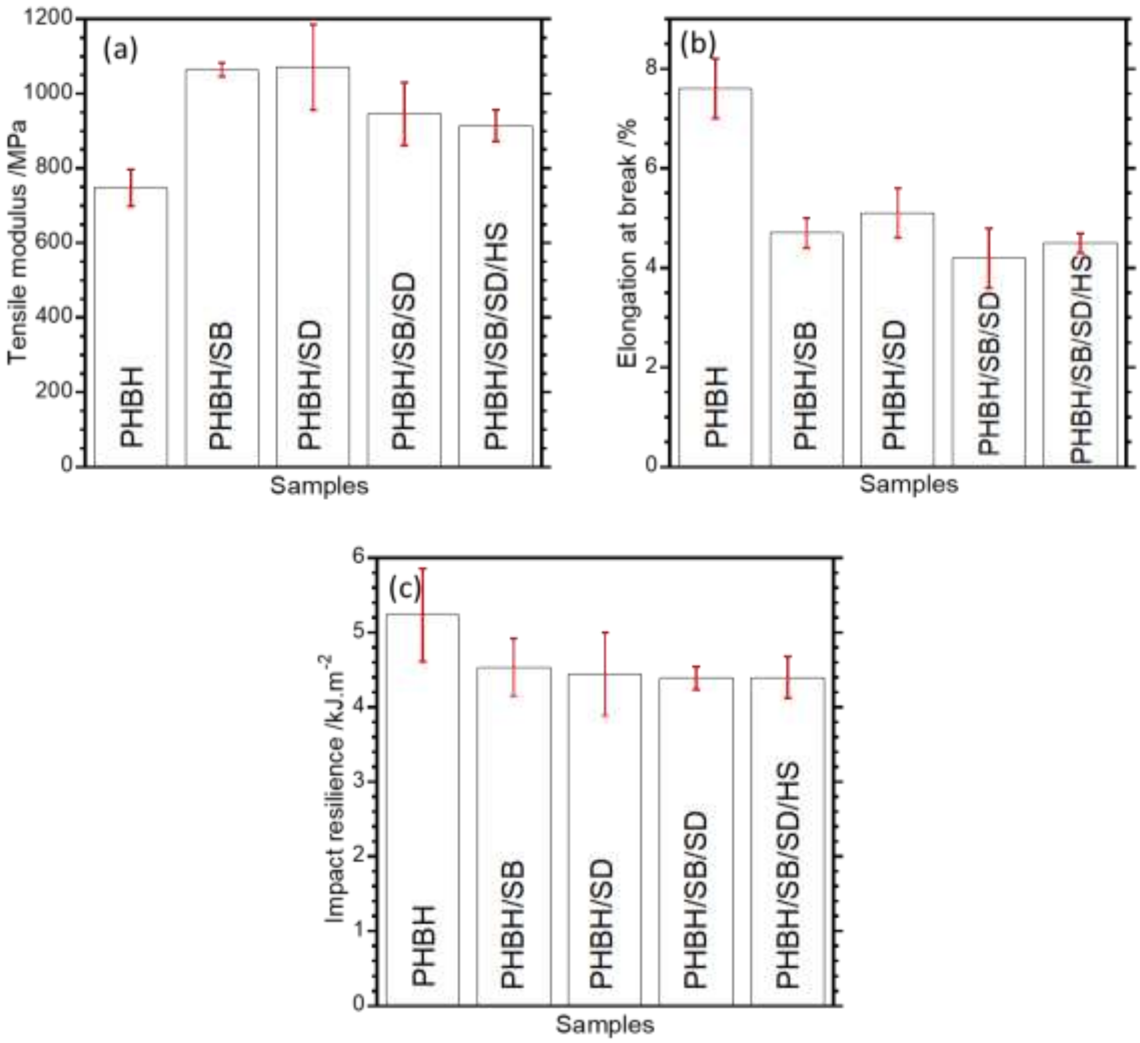

Figure 6.6. (a) Tensile modulus, (b) elongation at break, and (c) impact resilience of neat PHBH, binary and hybrid composites

Table 6.4. Tensile and impact data of neat PHBH, binary and hybrid composites

Sample	Tensile modulus /MPa	Elongation at beak /%	Impact resilience /kJ.m^{-2}
PHBH	748.2 ± 49.4	7.6 ± 0.6	5.2 ± 0.6
PHBH/SB	1063.8 ± 18.5	4.7 ± 0.3	4.5 ± 0.4
PHBH/SD	1071± 113	5.1 ± 0.5	4.5 ± 0.5
PHBH/SB/SD	945 ± 84.5	4.2 ± 0.6	4.4 ± 0.2
PHBH/SB/SD/HS	914.5 ± 42.1	4.5 ± 0.2	4.4 ± 0.3

6.4. Conclusions

The investigation of the morphology showed a high interfacial tension in the hybrid composites due to the hydrophobicity of PHBH and the hydrophilic nature of MSF and SB, but the PHBH/SD composite showed better dispersion of the filler. The differences in morphologies account for the variations in composite performance. The presence of HS in the hybrid composite (PHBH/SB/SD/HS) promoted interfacial adhesion between PHBH and SD. Compared to pristine PHBH, the binary and hybrid composites demonstrated superior stiffness, viscosity and storage modulus. The thermal stability of PHBH was enhanced with the addition of SB and SD, but the mixture of the fillers showed a synergistic effect on thermal stability. Contrarily, the presence of HS in the PHBH/SB/SD/HS achieved higher thermal stability of the composite due to the barrier effect of HS. The addition of fillers resulted in a reduction in elongation at break and impact resilience of PHBH, although the elongation of the composites remained within a similar range. The reduction in mechanical properties provides evidence of high interfacial tension between PHBH and either SB or SD in the hybrid composites. In future work, maleic anhydride grafted poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH-g-MA) will be produced to investigate its effectiveness as a compatibiliser at various loadings for PHBV/SB, PHBH/SD, PHBH/SB/SD, and PHBH/SB/SD/HS composites prepared through melt extrusion.

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CHAPTER 7

Flammability properties of the PHBH and PBS systems

It is well known that fire is a catalyst that thermally oxidises polymer-based materials. Flame-retardant materials are capable of withstanding high temperatures and resist burning. Cone calorimeter is one of the techniques used to analyse the flammability properties of the polymer-based composites. A lower peak heat release rate value is an indication of a flame-retardant system, while a higher peak heat release rate value is an indication of a flammable material (Araby *et al*., 2021). The well-known parameters from the cone calorimeter include heat release rate (HRR), total heat release (THR), mass loss rate (MLR), and smoke production rate (SPR). **Table 1** summarises the cone calorimeter parameters for the PBS based system. Both natural fiber-reinforced composites, specifically sugarcane bagasse (SB) and sawdust (SD), demonstrated higher peak heat release rate values (**Table 1**) when compared to neat poly(butylene succinate) (PBS). This increase is primarily due to the inherent flammability of lignocellulosic materials, which decompose rapidly and act as catalysts during combustion, accelerating the burning process (Mankeed *et al*., 2022). When combined, SB and SD exhibited even greater flammability, likely resulting from the synergistic degradation of their similar organic components (Alias *et al*., 2021; Mankeed *et al*., 2022).

Table 7.1. Selective cone calorimeter parameters for PBS based composites

Samples ID	**pHRR / kW.m^{-2}**	**TTI /s**	**Total heat release /MJ.m^{-2}**	**FPI /m^{2}s.k^{-1}W^{-1}**
PBS	468	64	99.9	0.1368
PBS/SB	578.2	62	111.4	0.1072
PBS/SD	505.8	57	92.8	0.1127
PBS/HS	425.3	95	78.9	0.2234
PBS/SB/SD	576.3	62	111.6	0.1076
PBS/SB/HS	451.9	67	134.2	0.1483
PBS/SD/HS	432.8	65	92.1	0.1438
PBS/SB/SD/HS	436.1	71	90.1	0.1628
PBS/SB/SD/HS/EG	370	89	93.3	0.2405

Nevertheless, the incorporation of halloysite nanotubes (HS) into both binary and hybrid composite systems led to a significant reduction in pHRR, indicating improved flame retardancy. Halloysite nanotubes, in particular, have been shown to enhance the thermal stability of polymer matrices due to their tubular structure and high aspect ratio, which improve heat barrier properties (Kumar *et al*., 2024; Marset *et al*., 2020). Further enhancements in flame retardancy were noted with the incorporation of expandable graphite (EG). The addition of expandable graphite contributes to intumescent action; upon heating, EG expands to form a foamed, carbonaceous char that insulates the underlying polymer (Kmeťová *et al*., 2025). Among all samples examined, the hybrid composite comprising PBS/SB/SD/HS/expandable graphite (EG) showed the lowest pHRR value of approximately 370 $kW \cdot m^{-2}$, highlighting enhanced fire resistance. In addition to the reduced heat release, this hybrid system also demonstrated a relatively high Fire Performance Index (FPI) value of 0.2405 $m^2 \cdot s \cdot kW^{-1}$, which indicates improved flame retardancy. The FPI, defined as the time to ignition divided by the peak heat release rate (pHRR), determines material safety performance. Generally, higher FPI values are associated with delayed ignition and a slower heat release, indicating a lower fire hazard (Murad *et al*., 2025). The exceptional flame retardancy observed in the PBS/SB/SD/HS/EG composite is attributed to the formation of a stable, compact, and continuous carbonised ceramic char layer. This char residue serves as an effective thermal and physical barrier, inhibiting heat and mass transfer between the flame and the underlying material. It also traps volatile degradation products, reducing the availability of flammable gases during combustion. This combined effect yields a significant improvement in flame-retardant performance across multiple key parameters. Another crucial metric alongside the peak heat release rate (pHRR) measurement in the fire performance of composites is the total heat release (THR). In the absence of flame retardants, the composites showed high THR values, with the sugarcane bagasse (SB)-reinforced composites exhibiting notably higher THR compared to those containing sawdust (SD) (**Table 1**). This difference can be attributed to the unique chemical compositions and thermal degradation behaviours of the lignocellulosic fillers (Mankeed *et al*., 2022). Sugarcane bagasse usually contains a higher proportion of hemicellulose, and a lower mineral content compared to sawdust (Murad *et al*., 2025). As a result, it undergoes more extensive thermal degradation and releases more combustible volatiles during combustion (Becker *et al*., 2010). The inclusion of flame retardants significantly reduced the THR values across the composites. Notably, the PBS/SB/SD/HS/EG blend showed the most pronounced reduction in THR. This flame-retardant system enhances thermal stability and reduces heat release through multiple mechanisms. Halloysite nanotubes contribute to thermal stability by reinforcing the char structure and potentially facilitating the formation of a cohesive, ceramic-like residue during combustion (Marset *et al*., 2020). Expandable graphite serves as an intumescent agent, expanding upon heating to create an insulating char layer that shields the underlying material from flames (Kmeťová *et al*., 2024).

Together, these additives inhibit combustion and reduce the production of flammable decomposition products, thereby lowering total heat release (THR) and improving flame resistance. One of the most common hazardous gases released during combustion is carbon monoxide (CO), primarily because it binds to haemoglobin in the blood, reducing oxygen delivery to tissues. Carbon monoxide poisoning can lead to serious consequences, including severe tissue damage, organ failure, and even death, and therefore measurements are necessary (Afzal *et al*., 2025). **Figure 1** depicts carbon monoxide production (COP) curves. The first two peaks correspond to initial pyrolysis and flaming combustion, where incomplete combustion results in high carbon monoxide (CO) levels. The third peak occurs during smouldering, with limited oxygen causing inefficient combustion and a temporary drop in CO as it converts to carbon dioxide (CO_2) (Wyn *et al*., 2020). The PBS/SB/SD/HS/EG composite system produced the least CO due to the formation of a protective, ceramic-like char layer. The addition of expandable graphite (EG) and hybrid synergists further enhances this flame-retardant effect.

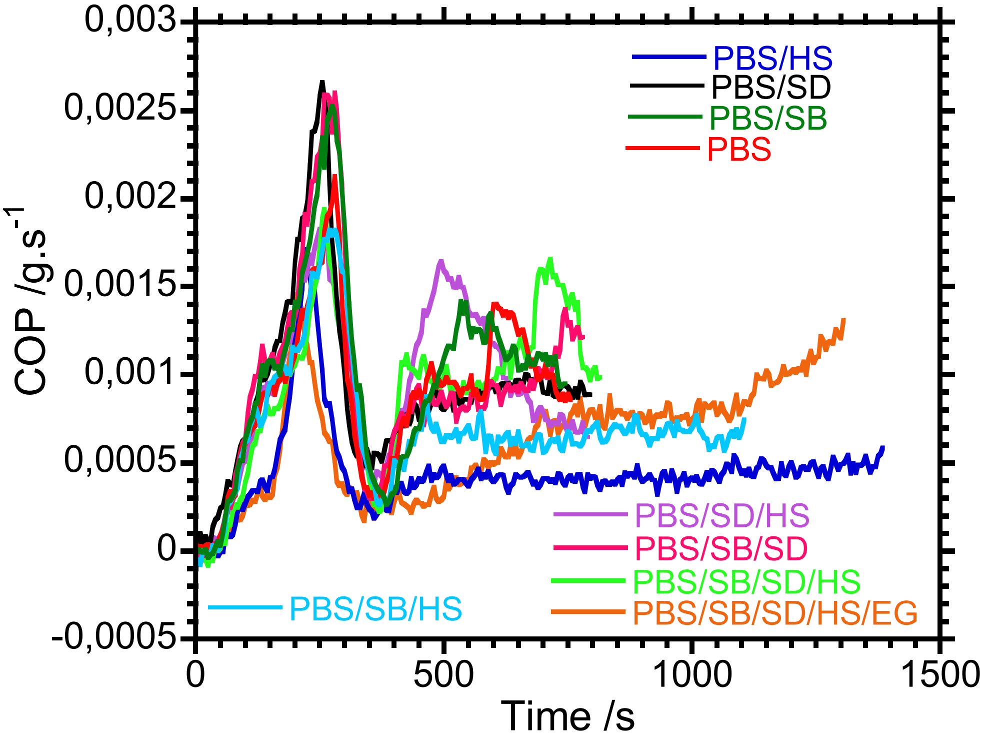

Figure 7.1. Carbon monoxide production of the investigated samples

Table 2 depicts the selective cone calorimeter parameters for PHBH-based system. The addition of single fibres, i.e., sugarcane bagasse (SB) and sawdust (SD), to the poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) matrix, resulted in higher pHHR values compared to the neat polymer, which was similar to the PBS-based system. This increase may be related to the high cellulose and hemicellulose content of lignocellulosic fibres, which readily decompose under heat during pyrolysis, releasing more combustible volatiles and intensifying the combustion process (Mankeed *et al*., 2022; Nurazzi *et al*., 2021), as explained elsewhere in this document.

Table 7.2. Selective cone calorimeter parameters for PHBH based system

Samples ID	**pHRR / kW.m^{-2}**	**TTI /s**	**Total heat release /MJ.m^{-2}**	**FPI /m^{2}s.k^{-1}W^{-1}**
PHBH	508.1	55	85.15	0.108
PHBH/SB	564.1	43	115	0.076
PHBH/SD	571.4	42	116.2	0.073
PHBH/SB/SD	545.1	48	110.9	0.088
PHBH/SB/SD/HS	509.7	46	111.1	0.090

When fibres were combined in the PHBH matrix (PHBH/SB/SD), the peak heat release rate (pHRR) slightly decreased compared to single-fibre composites, which contradicts the findings in the PBS-based system. This phenomenon indicates that the synergistic interactions between the two fibre types could affect the degradation pathway, thereby limiting heat and mass transfer during combustion (Kumar *et al*., 2024). One may suggest that there is a better interaction of fibres in this system, which might have blocked any volatile materials from leaving the system and, in the process, slightly enhanced the flame retardancy. Further improvement in flame retardancy was observed with the addition of halloysite nanotubes (HS) to the fibre-reinforced PHBH system. The PHBH/SB/SD/HS composite exhibited the lowest pHRR among all the composites studied, although its value remained slightly higher than that of the neat PHBH.

This indicates that while halloysite clay contributes to improved thermal stability through its barrier effect, the combined flammability of the natural fibres still plays a significant role in influencing the overall fire behaviour of the composite (Nurazzi *et al*., 2021). Halloysite clay enhances flame retardancy by acting as a heat barrier and promoting char formation, but its effectiveness can be limited by the abundance of easily combustible organic fibre content (Kumar *et al*., 2024; Marset *et al*., 2020). Notably, the Fire Performance Index (FPI) of the PHBH/SB/SD/HS system was lower than that of the neat polymer, indicating a higher fire risk despite the reduced relative risk (RR). FPI is defined as the ratio of time to ignition (TTI) to pHRR and is commonly used to assess the fire growth potential of materials. A lower FPI value indicates faster ignition and/or higher heat release, both of which contribute to rapid fire development (Huang *et al.*, 2023). This observation suggests that although the composite burns with lower intensity (lower pHRR), it ignites more quickly or lacks sufficient delay in ignition, likely due to the volatile degradation products of the fibres. Overall, while the addition of halloysite improves the thermal barrier properties and reduces the pHRR, the reduced FPI implies that additional flame-retardant strategies may be necessary. Combining halloysite with intumescent agents, such as expandable graphite, could be an effective approach to delaying ignition and suppressing the early stages of fire growth.

Conclusions

The flammability analysis revealed significant performance variations between the PBS and PHBH composite systems. In both matrices, the addition of natural fibres increased the peak heat release rate (pHRR) due to the lignocellulosic fillers' combustibility. However, halloysite nanotubes (HS) consistently enhanced flame retardancy by promoting char formation and acting as a thermal barrier. The benefits of flame-retardant synergy were greater for PBS. For instance, HS alone reduced the pHRR by approximately 9%. In the PBS/SB/SD/HS/EG system, there was a 21% reduction in pHRR and a 76% increase in the Fire Performance Index (FPI). Conversely, the PHBH composites (evaluated without EG) exhibited only moderate improvements. In this case, HS provided about a 6% reduction in pHRR compared to the fibre-reinforced control. This comparison highlights that while halloysite alone can enhance thermal stability, its combination with an intumescent additive is crucial for achieving high fire resistance and maintaining balanced flammability performance. These findings have direct implications for fire-sensitive applications. PBS-based hybrids containing HS and EG show promise for use in packaging, construction panels, and automotive components, where reduced heat release and improved char integrity can help slow fire growth and enhance safety in real-world conditions.

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CHAPTER 8

Conclusions and future recommendations

The study investigated the development of sustainable, flame-retardant, natural fibre-reinforced composites using agricultural residues and inorganic flame-retardant additives. The primary objective was to assess the effects of various flame-retardant fillers, expandable graphite (EG), and halloysite nanotubes (HS) on the flammability, structural integrity, and thermal performance of bio-based composites composed of polybutylene succinate (PBS) and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH), which were reinforced with sugarcane bagasse (SB) and sawdust (SD). A range of techniques, including FTIR, SEM, XRD, TGA, rheology, mechanical testing, and cone calorimetry, were employed to assess thermal, structural, and interfacial behaviours. In PBS composites, SD and SB enhanced stiffness and viscosity, with EG and HS contributing to crystallisation and interfacial strength. Hybridising the fibres resulted in improved filler dispersion and melt strength, though weak fibre–matrix adhesion limited toughness. EG increased crystallisation rates, aiding processing, while HS improved structural integrity. Despite slight reductions in thermal stability due to filler degradation, PBS hybrids demonstrated promising properties for rigid applications. In PHBH composites, SD again showed better compatibility than SB, while HS contributed to improved cohesion and thermal stability. Although hybrid systems enhanced stiffness and processing stability, their mechanical performance was limited by brittleness and poor interfacial bonding.

These findings highlight the need for coupling agents, such as PHBH-g-MA, to improve fibre-matrix integration. In conclusion, the analysis revealed that SD exhibited greater compatibility across both matrices, whereas SB contributed to improved mechanical stiffness. Hybrid systems outperformed their single-fibre counterparts, although performance varied according to the matrix utilised. PBS enabled more effective fibre integration, while PHBH necessitated more precise interfacial adjustments. Furthermore, the incorporation of flame retardants into fibre–polymer systems effectively suppressed combustion, as evidenced by the reduced peak heat release rate (pHRR). Although halloysite nanotubes demonstrated heat barrier-forming capabilities, their synergy with intumescent additives, such as expandable graphite, proved to be more effective and promising. This research demonstrates that, with appropriate selection of fillers and processing strategies, agricultural waste can be repurposed into biodegradable, flame-retardant composites that are well-suited for sustainable engineering applications such as packaging, construction, and interior applications.

Future work could further investigate industrial-scale processing, specifically the optimisation of extrusion and injection moulding. This research will help validate reproducibility and cost-effectiveness under real manufacturing conditions. Additionally, long-term durability and environmental ageing studies are essential. These should include hydrothermal, UV, and biodegradation testing to assess material stability and performance throughout its service life. These efforts will aid in transitioning the developed composites from laboratory-scale formulations to commercially viable and sustainable material alternatives.