

THE EFFECT OF GRAPHITE ON THE PROPERTIES OF NATURAL FIBRE HYBRID BIO-COMPOSITE FOR AUTOMOTIVE APPLICATIONS

by

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DECLARATION OF INDEPENDENT WORK

DECLARATION WITH REGARD TO INDEPENDENT WORK

I, **LULAMA THEYS**, identity number _____ and student number _____, do hereby declare that this research project submitted to the Central University of Technology, Free State for the Master of Engineering in Mechanical Engineering, 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 or any other person in fulfilment (or partial fulfilment) of the requirements for the attainment of any qualification.

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DEDICATIONS

I dedicate this thesis to myself and my parents for their love, support, and encouragement throughout my pursuit for education. It is a token of my hard work, dedication to research and developing my skills.

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Firstly and foremostly, I would like to thank our Heavenly Father, God, for walking this journey with me, strengthening, and encouraging me when hope was lost. I would not have been able to do it on my own, and I will say that “The Lord is my Strength and my shield, my heart trusts in him and he helps me.” Psalms 28:7. All Glory and Honour to our King.

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ABSTRACT

A vast amount of waste is produced from the agricultural-based industries, and most of this waste is regarded as unwanted materials. Because the majority of the agrowaste is underutilized, this kind of waste is disposed by dumping in landfill and/or burned. Burning of this waste has serious consequences, such as contributing to greenhouse gas emissions. There is a need to utilize this waste in a positive way in order not to harm the environment. This study reports on the conversion of maize stalks through various physical and chemical methods into a maize stalk fibre (MSF) material that can be used as a reinforcing filler in a biopolymer matrix. Maize stalk with a content of 10 wt% was incorporated into the polybutylene succinate (PBS) matrix for advanced applications. However, both the maize stalk and PBS are known to be flammable; as a result, flame-retardant fillers such as expandable graphite (EG) and montmorillonite (MMT) clay are incorporated into the system at 3 wt% to form hybrid composites. The effect of expandable graphite and its synergy on the morphology, flammability properties, thermal stability, dynamic mechanical analysis, and rheological properties of the PBS/maize stalk fibre are reported in this study. According to the SEM images, PBS/MSF composite shows poor interaction between the fibre and PBS matrix, with clearly observable fibre pull-outs in the system. However, the incorporation of modified MMT improves the interaction between the fibre and PBS matrix, which also has a positive impact in various properties. Even though there seems to be minor interaction between MMT and EG in the PBS/MSF composite according to SEM, because of their rigidity, the fillers still improve the properties of the hybrid composites. The PBS/MSF/MMT shows better flame-resistant properties than PBS/MSF/EG composites; however, the synergy of the two fillers showed better flame-resistant properties than both PBS/MSF/MMT and PBS/MSF/EG composites. The synergy of filler seems to interact better with volatile products of degradation, as the PBS/MSF/MMT/EG reveals higher thermal stability when compared to 90/10 PBS/MSF, PBS/MSF/MMT and PBS/MSF/EG. Because of a slightly better interaction of the components in PBS/MSF/MMT, this particular system shows higher storage modulus when compared to a PBS/MSF/EG composite. The presence fillers reduced the degree of crystallisation of the composites and its hybrid biocomposites when compared to the neat PBS.

Keywords: composites; hybrid; flammability, maize stalk; polybutylene succinate

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LIST OF ABBREVIATIONS

ACF	Alkali-treated corn fibres
APP	Ammonium polyphosphate
BC	Treated biocomposites
BFRs	Brominated flame retardants
BMW	Bayerische Motoren Werke
CA	Citric acid
CBT	Cyclic butylene terephthalate
GO	Reduced by phenylhydrazine
CHL	Chamaerops humilis
CF	Cellulose fibres
CLO	Cloisite
CNC	Cellulose nanocrystal
CNF	Cellulose nanofibrils
CO	Carbon monoxide
CSF	Corn straw fibre
CS	Chitosan
DMA	Dynamic mechanical analysis
DOP	09,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide
DP	Dechlorane plus
DSC	Differential Scanning Calorimetry
DTA	Differential thermal analysis
EDS	Energy Dispersive X-ray Spectroscopy
EG	Expandable graphite
GF	Glass fibre
GO	Graphene oxide
GNPs	Graphene nanoplatelets
HBFR	Halogen-based flame retardants
HFFRs	Halogen-free flame retardants
HNO ₃	Nitric acid
HRR	Heat release rate
IFRs	Intumescent flame retardants

KBF	Kenaf bast fibres
KCF	Kenaf core fibres
LOI	Limiting oxygen index
MCC	Microscale combustion calorimetry
MFI	Melt flow index
Mg (OH) ₂	Magnesium hydroxide
MLR	Mass loss rate
MMT	Montmorillonite
MSF	Maize stalk fibre
MWCNTs	Multiwalled carbon nanotubes
NaOH	Sodium hydroxide
OM	Optical microscopy
Ops	Organophosphate esters
PBBs	Polybrominated biphenyls
PBDEs	Polybrominated diphenyl ethers
PBS	Polybutylene succinate
PDA	Polydopamine
PHB	Polyhydroxybutyrate
PHBV	Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PLA	Poly(lactic acid)
PLA-NF	Ramie fibre-reinforced poly(lactic acid)
POL	Posidonia oceanica
POM	Polarized optical microscopy
PP	Polypropylene
PVA	Poly(vinyl alcohol)
rGO	Reduced graphene oxide
SCB	Sugarcane bagasse
SEM	Scanning electron microscope
TBB or EH-TBB	2-ethylhexyl 2,3,4,5-tetrabromobenzoate
TBE or BTBPE	1,2-bis(2,4,6-tribromophenoxy)ethane
TBPh or BEH-TEBP	Di-2-ethylhexyl tetrabromophthalate
TEC	Triethyl citrate
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis

TiO ₂	Titanium dioxide
THR	Total heat release
UBC	Untreated biocomposites
UCF	Untreated fibre biocomposites
USA	United States of America
XRD	X-ray diffraction
ZnO	Zinc Oxide

CHAPTER 1: GENERAL INTRODUCTION

Due to environmental concerns and sustainability issues, the current generation is facing serious issues in relation to environmental pollution and energy. This has forced scientists and researchers globally to do more work on green technology in the field of materials science through the development of biocomposites (Faruk et al., 2012). In this regard, natural fibres have received a lot of attention as potential reinforcing fillers for polymer matrices. Vegetable, animal, and mineral fibres are all included under the umbrella phrase, “natural fibres” (Figure 1.1). These fibres frequently play a significant role in a plant’s structural performance and, when used in plastic composites, can offer substantial reinforcement. A natural fibre is, by definition, a form of renewable resource and a new generation of reinforcements and supplements for materials based on polymers (Sanjay et al., 2016).

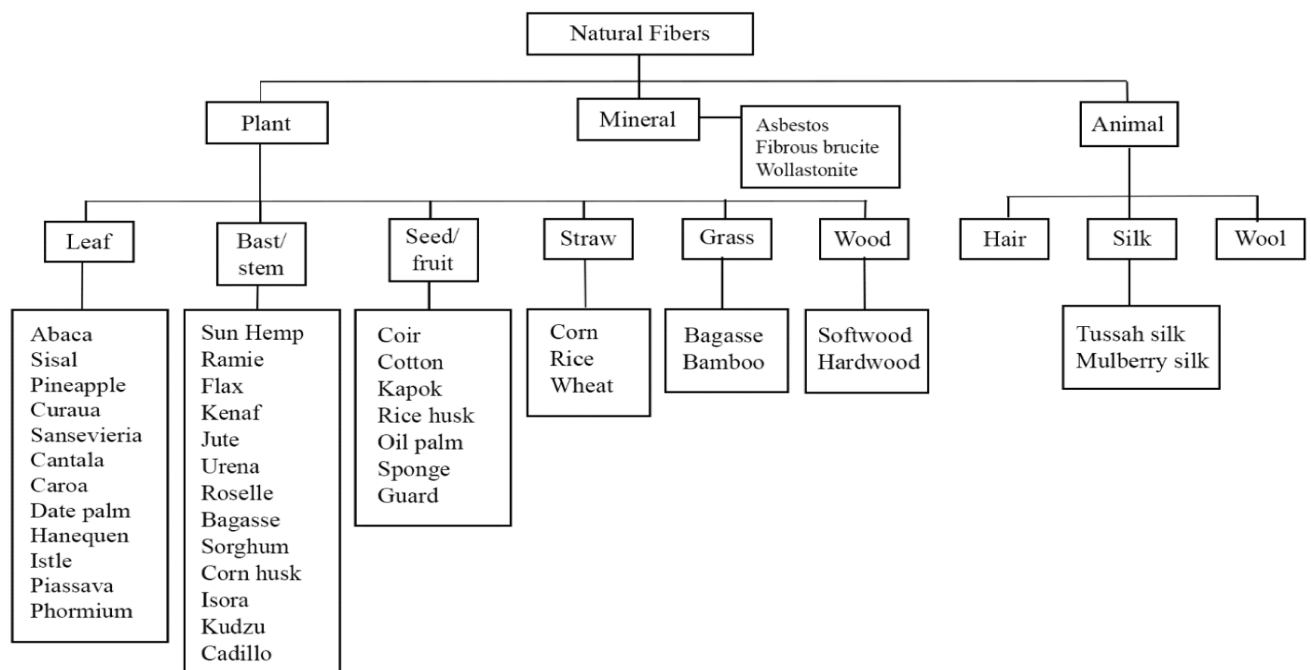


Figure 1.1: Classification of natural fibres (Sanjay et al., 2016).

Natural fibres are used to create environmentally friendly green composites because of their abundant supply, high specific strength, biodegradability, relative cheap, light weight, quick-replenishing ability, and natural abundance (in contrast to non-biodegradable products). Recent environmental awareness has made the development of natural fibre composite materials or ecologically friendly composites a prominent topic. The utilization of natural-fibre-reinforced polymer composites to replace current synthetic polymer or glass fibre-reinforced materials is enormous. For their interior components, the automotive and aerospace industries have been

utilizing a variety of natural fibres actively, focusing mostly on hemp, flax, and sisal, as well as bio-resin systems. Natural fibre composites are appealing for a variety of applications due to their highly specific characteristics and inexpensive cost (Clemons and Caulfield, 2005). In many applications, natural fibres offer a high potential to replace petroleum or non-renewable source materials; natural from the standpoint of economic development and sustainability. Various biopolymers have been used in the fabrication of the natural fibre/biopolymer such as polylactic acid (PLA), polybutylene succinate (PBS), and Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) (Moyo, Kanny and Mohan 2021; Saba et al., 2017; Dangtungee et al., 2016; Al et al., 2018; Wang and Shih, 2016). Amongst the above-mentioned polymers, PBS (polybutylene succinate) has been used as a polymer of choice due its many beneficial characteristics and significant awareness among industry and researchers. PBS is a biopolymer that is environmentally friendly and has several distinctive characteristics such as transparency and ease of fabrication, a shiny appearance, and flexibility (Rafiqah et al., 2021). In this study, a blend of PBS and maize stalk will be fabricated to improve their properties. However, PBS and natural fibres are known to be highly flammable and therefore need flame-retardant fillers. Flame-retardant fillers restrict flame propagation by forming solid residues on the burning material's surface. As a result, by changing the heat transfer pathway to the polymer substrate, they can slow down the rate of heat release during combustion (Mohd Sabee et al., 2022). In the past, halogen flame-retardant fillers were used as flame-retardant fillers of choice in order to improve the flame resistance of the materials. Halogenated flame retardants have been used in many commercial products to prevent them from burning when exposed to heat or fire. In the 1970s, the State of California developed a flammability standard forcing many household products to be flame resistant (Venier, Salamova and Hites, 2015). In many of this applications, brominated flame retardants (BFRs) were added in the furniture found in our homes and offices. Various types of brominated flame-retardant materials have been used in the past, namely polybrominated biphenyls (PBBs), polybrominated diphenyl ethers (PBDEs), 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB or EH-TBB), di-2-ethylhexyl tetra-bromophthalate (TBPh or BEH-TEBP), 1,2-bis (2,4,6-tribromophenoxy) ethane (TBE or BTBPE), dechlorane plus (DP), and organophosphate esters (OPs). Figure 1.2 illustrates the most commonly used brominated flame retardants.

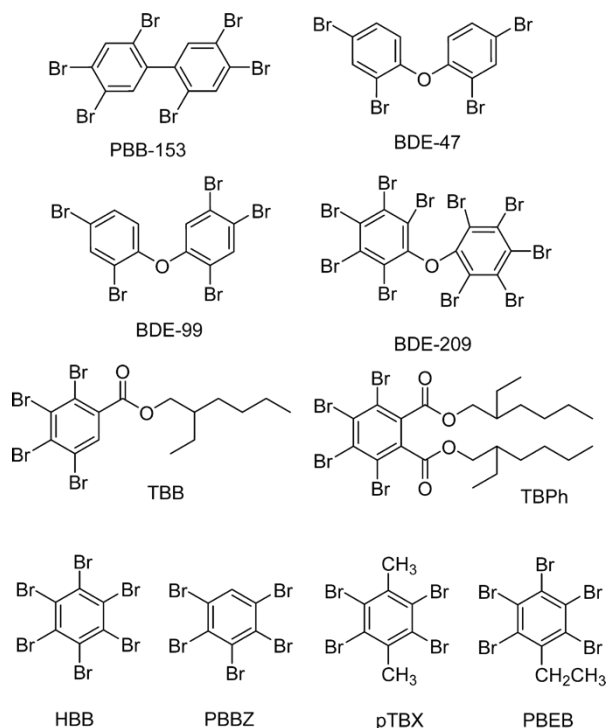


Figure 1.2: Structures of the major Brominated Flame Retardants (BFRs) (Venier, Salamova and Hites, 2015).

It is noted that the BFRs could save a lot of lives by enhancing the flame retardancy; however, it was later discovered that exposure to halogen flame-retardant fillers has been linked with a number of health effects, which include mutagenicity, cancer, or detrimental effects on the reproductive, developmental, endocrine, immune, or nervous systems (Hull, Law and Bergman, 2014). They include diabetes, somatic and neurodevelopmental effects on foetus or child, low birth weight and reduced fertility in women (Shaw, 2010). Alternative fillers were utilized to compensate for the effects of halogen flame retardants. These fillers include clay (MMT) and graphite (EG). The advantage of the above-mentioned fillers is that they are inexpensive, widely available, and they are not harmful to the environment (Mekhemer, Abou El-Ala and El-Rafey, 2000; Andrzejewski, Markowski and Barczewski, 2022; Majeed et al., 2016; Mohammad, Stepashkin and Tcherdyntsev, 2022). The current study investigates the effect of expandable graphite and montmorillonite (MMT) on the properties of PBS/maize stalk fibre composites for advanced applications.

1.1 RESEARCH AIM

The aim of the study is to investigate the effect of expandable graphite (EG) and montmorillonite (MMT) and their synergy on the properties of polybutylene succinate (PBS).

1.2 RESEARCH OBJECTIVES

The objectives of this study are presented:

- (i) To investigate the effect of maize stalk fibre (MSF) on the properties polybutylene succinate (PBS)
- (ii) To investigate the effect montmorillonite (MMT) on the properties of PBS/MSF composites
- (iii) To investigate the effect of the synergy of EG and MMT clay on the properties of the PBS/MSF composites

1.3 THESIS ORGANIZATION

The layout of this thesis is as follows:

Chapter 1: Introduction

Chapter 2: Literature review

Chapter 3: Materials and methods

Chapter 4: Results and discussion

Chapter 5: Conclusion and future remarks

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CHAPTER 2: LITERATURE REVIEW

2.1 AN OVERVIEW OF THE AGRICULTURAL BIOWASTE: FROM WASTE TO NATURAL FIBRE REINFORCEMENT FILLERS

Agriculture waste is regarded as the waste that is produced during cultivating and processing of the products associated with agriculture such as maize, grains, vegetables, and fruits. There are four classifications of agricultural wastes as shown in Figure 2.1.

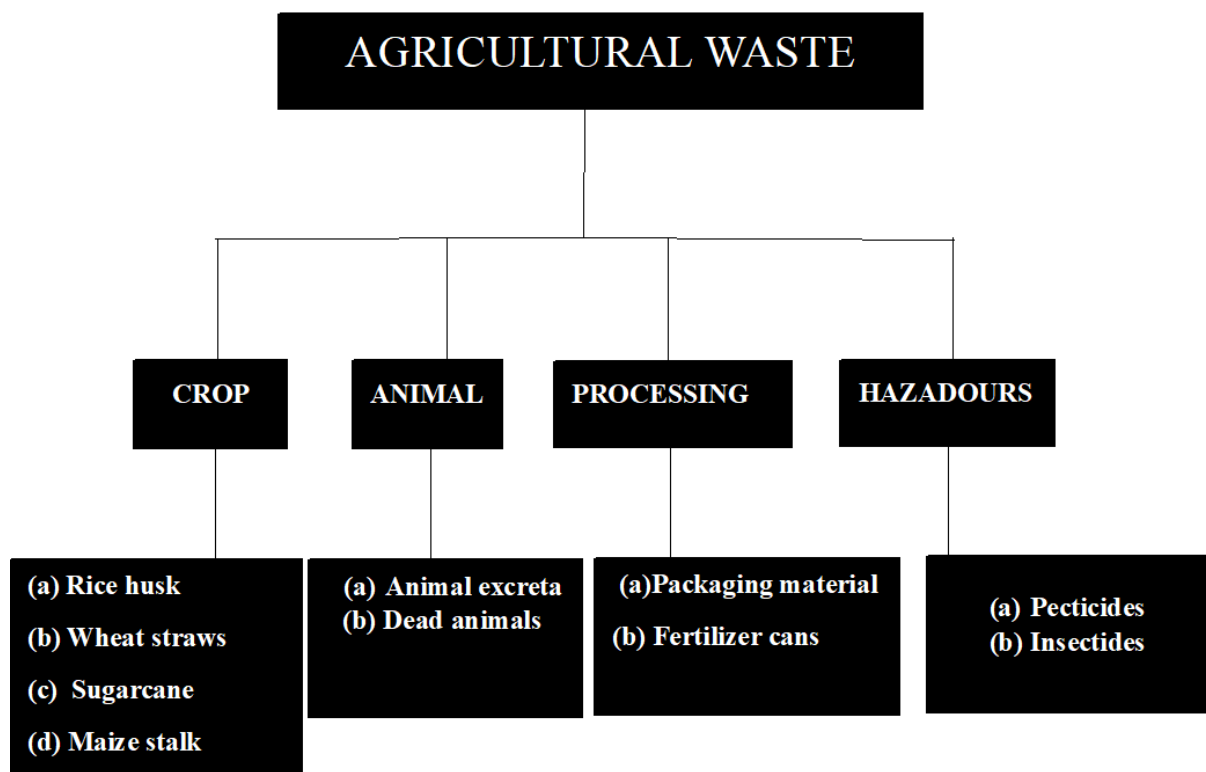


Figure 2.1: Classifications of agricultural wastes (Jena and Singh, 2022.).

There is an estimation of 998 million tons of agricultural waste every year. Most of the waste is used as fodder for animals. Alternatively, in order to free space, farmers normally burn this garbage, which has a negative impact on the environment due to the release of gases. This method contributes negatively to the air pollution we are currently experiencing, which is a serious risk to the health of human beings (Rani et al., 2023). The current trend is that researchers are embarking on converting agro- waste into green products for sustainability and advanced applications. The advantages associated with bio-agrowaste include low cost, easy to produce, and a potential to be the next generation of materials for multifunctional

applications. For example, biowaste can be utilized to produce green energy (Figure 2.2). These typical devices that adopt bio-nanogenerators do not require any external power sources.



Figure 2.2: Agro waste to sustainable energy (Rani et al.,2023).

Amongst the agricultural waste in Figure 2.1, crop waste has been of interest to researchers because of its potential for circular economy. Crop waste consists of rice husk, wheat straws, sugarcane bagasse and corn stalk. Rice husk is produced from milling of rice. For the past five years, the global production of rice annually has been 741 million tons, with 148 million tons of by product in the form of husks produced (Gao et al., 2018). Agricultural waste with high cellulose has been utilized as reinforcing fillers in polymer matrices as well as in the production of nanocellulose. Research has shown that rice husk consists of 15-20% hemicellulose, 20-25% lignin, and 35-40% cellulose (Kumar et al., 2009). Figure 2.3 illustrates a typical example of rice husk. Wheat straw is another byproduct of the agricultural waste. It also has the potential for the production of bioplastics. because of its simplicity in terms of storage and availability in bulk. Wheat straw is produced during the harvesting of wheat grains. The annual production of wheat straw is estimated at 540 million tons. Plastic that may be fabricated from wheat straw has the potential to be eco-friendly. Furthermore, the compositional analysis of the wheat straw reveals 34-40% cellulose, 20% of lignin and 20-25% of hemicellulose. The components of

wheat straw are nodes, internodes, rachis, chaffs, and leaves. Figure 2.4 depicts a typical example of wheat straw (Memon et al., 2018) being burned by farmers.



Figure 2.3: A typical example of rice husk (Ferretti et al., 2022).



Figure 2.4: Typical example of farmers burning wheat straw (Memon et al., 2018).

Sugarcane bagasse is another by product of agriculture cultivation that is found in abundance worldwide. The annual global production of sugarcane bagasse is approximately 1.6 billion tons (Chandel et al., 2012). Statistically, Brazil is the leading producer of sugarcane bagasse, followed by India, and the tenth country being United State of America (USA) (Chandel et al., 2012) as illustrated in Figure 2.5. Furthermore, based on the graph (Figure 2.5), there is a high production of sugarcane bagasse (SCB), which may contribute to a high amount of waste. Sugarcane was found to have a rich content of cellulose (44%), lignin (21%), hemicellulose (28%) and ashes (5%) (Chandel et al., 2012). Figure 2.6 shows a sample of sugarcane bagasse.

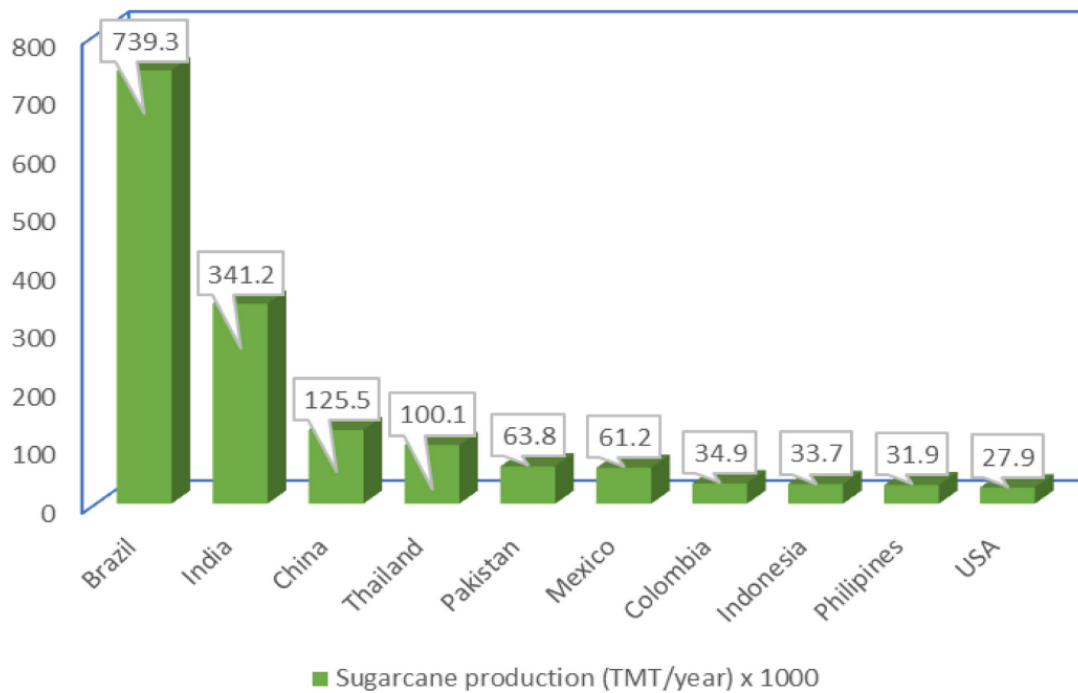


Figure 2.5: The 10 leading countries in the production of sugarcane bagasse (Khoo, Chow and Ismail, 2018).



Figure 2.6: A typical sample of sugarcane bagasse (Ouedraogo et al., 2023).

Maize is one of the highest grain crops produced in South Africa and it is produced in diverse areas in the country. Figure 2.7 illustrates the production of maize.



Crop at initial stage



Crop at 35 DAS



View of JM 218 with N₅



Cob of JM 218

Figure 2.7: An example of the production maize (Aakash et al., 2022).

Maize is produced in various parts of the country (South Africa) and provinces, i.e. KwaZulu-Natal (3%), Mpumalanga Highveld (24%), North-West (32%) and the Free State (34%) (Mtibe, Mokhothu and Linganiso, 2018). Maize stalk is the byproduct produced in the cultivation of the maize and in most cases this stalk is used as a feeder material for animals. Maize stalk is a lignocellulose, which has the potential to be used as biomass to produce bioethanol. Figures 2.8 and 2.9 illustrates the preparation and extraction of maize stalk and its utilization in bioethanol.



Figure 2.8: Preparation and extraction of corn biomass (Ibrahim et al., 2019).

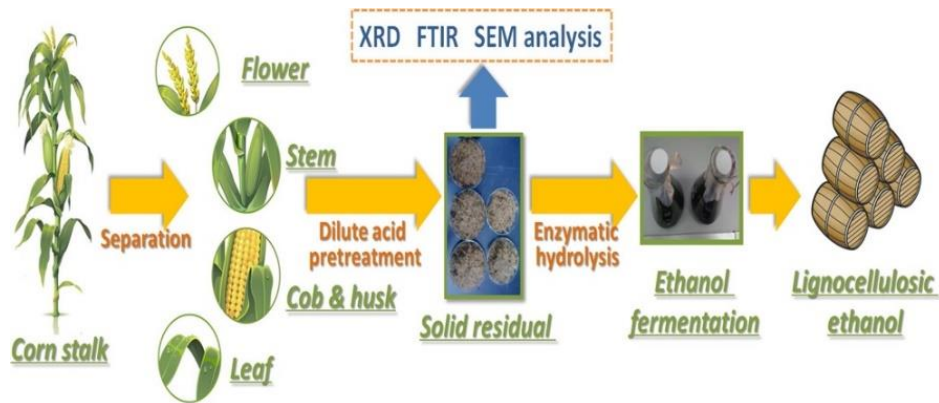


Figure 2.9: Bioethanol production of corn biomass (Li et al., 2016)

Maize is the most significant crop for over 70 million farm households globally and is a staple meal for an estimated 50% of the population in sub-Saharan Africa. Corn, or maize, is an annual agricultural leftover that grows extremely quickly from maize production. Estimates for 2016 and 2017 showed 6.8 million and 6.9 million tons, respectively, from harvested areas of 3.95 million hectares and 3.8 million hectares. Of all the grains, including rice and wheat, it has the biggest potential for output (Kolajo et al., 2019). The world's top providers were the United States, the European Union, China, Brazil, Mexico, and India, with over 750 million metric tons produced in 2008. Its versatility as a food source for both people and animals contribute significantly to its success as a crop. In addition to being eaten straight off the cob, kernels can be dried, boiled, fried, roasted, crushed, and fermented to make cakes, gruel, porridges, breads, and alcoholic drinks. It can further be processed to become oils, non-consumables, thickeners, and sweeteners for food. Approximately 15% of the world's protein and 20% of its calories

come from maize, which is a staple food for over 200 million people (Nuss Tanumihardjo et al 2010). The compositional examination of the pith and rind fractions shows the presence of 36.7% and 46.4% cellulose, 26.3% and 18.2% hemicellulose, and 18.1% and 21.2% lignin, respectively. The maize stalk rind is favoured for biosynthesis due to its increased cellulose content (Kolajo et al., 2018). Due to its higher cellulose content, maize stalk has been utilized as a bio-filler for reinforcing polymers.

2.2 ORIGIN OF NATURAL FIBRES AND THEIR CLASSIFICATIONS

Fibres are a type of substance that resembles hair and can come in single, elongated pieces or continuous filaments, much like thread (Chandramohan and Marimuthu, 2011; Clemons and Caulfield, 2005; Sanjay et al., 2016). Fibres may be spun into rope, thread, or filaments and they can be included into composite materials. It is preferable to organize the fibres according to their lengths when considering composite reinforcement. Short (1mm to 5 mm) fibres are generally utilized to create composites with in-plane isotropic characteristics, or composites with a non-specific (random) fibre orientation. These fibres are typically derived from wood and non-wood species. Long fibres (5mm to 50 mm) having anisotropic characteristics, or composites with a specific fibre orientation, are often made from non-wood annual plant species (Chandramohan and Marimuthu, 2011; Clemons and Caulfield 2005; Sanjay et al., 2016). Fibres are found in a variety of materials, including animals, plants and minerals (Clemons and Caulfield, 2005). Animal fibres generally comprise proteins and can be referred to as protein fibres. Vegetable fibres or cellulose fibres are generally comprised mainly of cellulose. Cellulose fibres serve in the manufacture of paper and cloth. Mineral fibres are naturally occurring fibre or slightly modified fibre procured from minerals. However, mineral fibres as well as animal fibres have several disadvantages; notably, they are highly flammable, absorbs moisture and has poor mechanical properties, which prevent their application in various polymer composites. In contrast, plant fibres are strong, inexpensive, renewable, biodegradable, environmentally friendly and light weight (Madhu et al., 2019; Pandey et al., 2010; Bongarde and Shinde, 2014). For these reasons, the use of plant fibres has been more appealing to researchers and scientists, as there has been an increase in the need to reduce global warming, environmental damage and pollution. Plant fibres can further be categorized as seed, leaf, bast stalk and fruit fibres, as discussed in Chapter 1. Seed fibre is a fibre derived from seeds or seed casings, such as kapok and cotton. Leaf fibres are obtained from well-known plants, such as agave and sisal. Bast fibre or skin fibre are taken from the skin or bast that

covers the plant's stem. In terms of tensile strength, these fibres beat other fibres. As a result, these fibres are used to manufacture robust yarn, textiles, packaging and paper. Flax, jute, kenaf, industrial hemp, ramie, rattan, soybean fibre, and even vine and banana fibres are examples of bast fibres. Fruit fibres are extracted from the plant's fruit, such as coconut (coir) fibre. Stalk fibre is made from the plant's actual stalks. Straws are made from a variety of crops, including grass, maize, and bamboo, as well as wheat, rice and barley. This type of fibre can also be found in tree wood. The most popular natural fibres are cotton, flax, and hemp, but sisal, jute, kenaf and coconut are also widely used. Hemp fibres are typically used for ropes and aerofoils due to their great flexibility and resistance to harsh environments. Hemp fibres, for example, are already used as a seal in the heating and sanitary industries. (Pandey et al., 2010; Prakash et al., 2022; Sanjay et al., 2016, Chandramohan and Marimuthu, 2011; Mueller and Krobjilowski, 2010). An illustration in Figure 2.10 exhibits that plant fibres consist of hemicellulose, cellulose, lignin, waxes, pectin, extractive and trace elements. Cellulose is the most available form of a living terrestrial organism. Cotton and hemp fibres consists of pure forms of cellulose, while in other plants related materials such as stalks, wood, and leaves, cellulose is found in combination with hemicellulose and lignin. Cellulose is found in a secondary wall that comprises of linear homopolysaccharide composed of anhydro-d-glucose ($C_6H_{11}O_5$) (Zwawi, 2021; Li, Tabil and Panigrahi, 2007). When compared with cellulose, hemicellulose differs from cellulose due to various sugar units. Hemicellulose is defined as a branched non-crystalline structure, which differs from a linear cellulosic structure. It has a less degree of polymerization viz 50 and 300, which is considerably less than that of cellulose. Hemicellulose acts as a binder to support microfibrils, cellulose and lignin. It is hydrophilic by nature, soluble in alkaline solution, and easy to hydrolyse in acids. The constituents of hemicellulose may differ from various plants. (Zwawi, 2021; Li et al., 2007).

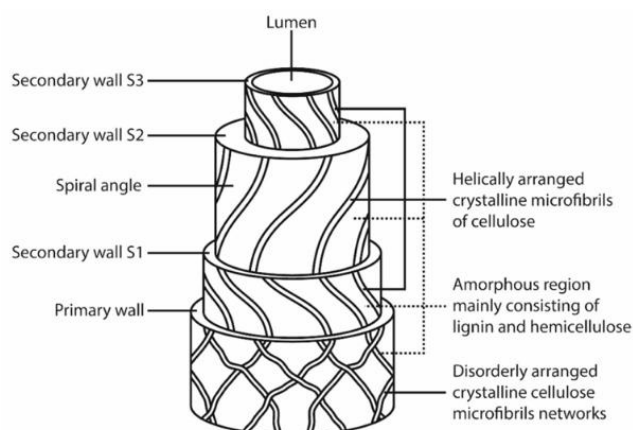


Figure 2.10: Structure of a plant fibre (Li et al., 2007)

2.3 PREPARATION AND MORPHOLOGY OF BIOPOLYMERS/NATURAL FIBRES

The majority of biocomposites fabricated from natural fibres and biopolymers are prepared by a melt-mixing method. The type of method used for preparation of the biocomposite affects their resultant morphology and properties. Different techniques are used to analyse the morphology of the biocomposites, i.e. X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), Transmission Electron Microscopy (TEM), and Polarized Optical Microscopy (POM). There are factors that are found to affect the morphology of the fibre/biopolymer biocomposites, such as treatment of the fibre, content of the fibres and the type of biopolymer. Polylactic acid (PLA), Polypropene (PP) and Kenaf fibre were studied by (Han et al., 2012). The focus in this study was to report on the morphology of PLA. SEM was used to examine the distribution and dispersion of the fibres within the PLA matrix. There was poor interaction between the kenaf fibre and PLA matrix, which is attributed to a lack of fibre treatment. Bleached kenaf fibre is combined in varied weight percentages (10, 20, 30 and 40%) with PLA pellets, using a HAAKE poly-drive internal mixer for 15 minutes at 160 °C and a speed of 50 rpm, was reported by Abdul et al. (2014). The same fibre compositions were used to form PLA/unbleached kenaf fibre biocomposites for comparison. The tensile fracture morphology of both untreated biocomposites (UBC) and treated biocomposites (BC) at 30 weight percent of fibre loading was analysed using Scanning Electron Microscopy (SEM). After bleaching, there was a removal of the waxes stuck into the fibre. The surface morphology of bleached kenaf fibre is also reported to have changed, i.e. becoming more textured and rougher. It is well known that an uneven fibre surface can improve adhesion between the PLA-

kenaf fibre composite. This was demonstrated by the treated composite's (BC) tensile fracture pattern, which reveals small gaps between the PLA matrix and kenaf fibre. The huge bonding gap between the fibre and PLA in the UBC composite resulted in poor interfacial adhesion. It is significant to highlight that compatibility between fibre and polymer can lead to an improvement in the mechanical properties of polymeric composites (Abdul et al., 2014). Jute fibre and poly (butylene succinate) (PBS) was studied (Liu et al., 2009), and the samples were prepared by rheometer at 120 °C. Fibres were treated with the alkali and coupling treatment. The cleaned fibres were subjected to the following processes in the following order: an “alkali treatment” that involved soaking in a solution of 5% sodium hydroxide at room temperature for four hours; and a “coupling agent treatment” that involved soaking in a solution of 1.5% coupling agent KH-570 and 98.5% anhydrous ethanol at room temperature for four hours. Both types of fibres were cleaned and dried in a vacuum oven at 60 °C for 24 hours. Post surface modification, it was observed that jute fibres had some changes in their structure and properties. Leaching of the fibre was observed, leading to the disintegration of hemicellulose, lignin and pectin, destructing of the mesh structure and splitting the fibre into finer filaments. This fibre fibrillation reduces the fibre diameter significantly. The fibre may become cleaner and rougher, once surface contaminants have been removed and it is advantageous in jute/PBS adhesion, since the exposure of the hydroxyl groups to PBS enhances both mechanical interlocking and the bonding reaction (Liu et al., 2009). Kenaf Bast Fibres (KBF) and PBS were maintained in desiccators after being dried at 80 °C in a circulating air oven for 16 hours (Kimble and Bhattacharyya, 2015). A double-winged internal mixer with corotating rotors was used to prepare the composites. Before being introduced into the chamber, the PBS and PBS-g-MA were physically mixed to create the compatibilized composite. The fibre was then gradually fed to the chamber while the rotor was running at a low speed (10 rpm). After all of the fibre had been fed, the process of compounding was continued for 5 minutes at a rotor speed of 50 rpm before it was discharged. The moulded samples were conditioned at room temperature in a desiccator(s) for at least 24 hours. SEM revealed a formation of gaps that surround the fibres, which is evidence of poor fibre–matrix interfacial adhesion between the KBF and the PBS. The poor fibre–matrix adhesion decreased the strength of the composite due an ineffective stress transfer between the fibre and matrix (Kimble and Bhattacharyya, 2015; Thirmizir et al., 2011). There was a report on the recyclability of sisal fibre and Polylactic acid biocomposites. Sodium bicarbonate (NaHCO_3) (Chaitanya, Singh and Song 2019) and distilled water were used to treat the sisal fibres by soaking them in the 10% NaHCO_3 solution. Sisal fibres were immersed in

the NaHCO_3 solution for a maximum of 72 hours while being agitated frequently. The treated fibres were next rinsed in distilled water and dried in an air oven at a temperature of 100 °C for 8 hours. Apart from an increased interfacial adhesion between the sisal fibres and the PLA matrix, the SEM shows an increase in matrix cracking as well as a reduction in fibre visibility at cracked surfaces as the number of recycles increases (Chaitanya, Singh, and Song 2019). Chopped hemp fibre was incorporated into a biopolymer by Wibowo et al. (2004). The preparation of the cellulose acetate plastic and chopped hemp fibre were prepared through two different processing methods. Process I: Powder Impregnation Process Followed by Compression Moulding. A specified composition of liquid plasticizer (triethyl citrate, TEC) was introduced dropwise to pre-dried CA powder and the mixture was stirred mechanically in a kitchen mixer for 30 min. Process II: extrusion Followed by injection moulding. A two-step extrusion method was utilized in fabricating the CAP-hemp biocomposites in comparison to a one-step extrusion step in producing the CABP-hemp bio-composites. The first step was to generate CA plastic granules from CA powder and 30 wt% TEC plasticizers. In the second step, CA plastic granules were fed into a twin-screw extruder (ZSK-30 Werner Pfleiderer, co-rotating, intermeshing, with L/D) 30) while incorporating the chopped hemp ($\sim 1/4$ in.) in the second-to-last port of the extruder. The temperature profiles utilized were ~ 190 °C with a die temperature of ~ 195 °C. The processing speed utilized in this study was 150 rpm with $\sim 40\%$ machine torque reading and a resulting extrudate output of about 65-70 g/minute. Process II shows a smaller amount of fibre pull-out indicating better adhesion between hemp fibre and CA matrix compared to that of Process I. Furthermore, it was difficult for authors to distinguish between fibre and CA matrix in Process II as the fibre is chopped into smaller sizes during pelletizing, which could have enhanced adhesion with CA matrix, and give better fibre dispersion. In contrast, the long fibre in Process I can easily be distinguished from the CA matrix, indicating poor adhesions, as it is not subjected to shear force and chopping during the processing.

2.4 MORPHOLOGY OF THE NATURAL FIBRE HYBRID BIOCOMPOSITES

In general, a hybrid composite is combining two or more fillers into a single matrix. The matrix might be made of polymer, steel, or ceramic (Prakash, Sahu and Johnson Santhosh, 2022). The term “hybrid” in polymeric context can also refer to a mixture of two or more polymers that have been strengthened with one or more fillers. The application of composite materials can be expanded because of hybridization, particularly in high-tech applications. There are three

principal parameters that affect the properties of the resulting hybrid composite product (Mochane et al., 2019). Firstly, materials (i.e. fillers and polymer matrix) are selected based on the intended application. Secondly, the preparation method of the hybrid has an effect on the resultant product. For any intended product, factors such as water absorption, density, weight, mechanical strength, recyclability, disposability, cost of raw materials, production expenses, compatibility with the recycling system currently in place, and experimental procedures must be taken into consideration. The interaction between the fillers and the matrix is the third-most crucial factor. To improve the interfacial adhesion between these components, the fibres may be treated, or a coupling agent may be used, particularly for natural fibres. In most cases, this will enhance the overall qualities of the hybrid product. To mention just a few studies, Gumus et al. (2020) report on the effect of both cellulose nanofibrils (CNF) and titanium dioxide (TiO_2). The hybrid biocomposites were fabricated by step method: firstly, PLA, PHB, TiO_2 and CNFs were blended in a mixer, followed by extrusion with a twin-screw extruder at a temperature of 150-180 °C. The hybrid biocomposite was prepared with 1% of the filler(s). The two nanofillers were found to be well dispersed within the polymer matrices with minimum agglomerations. A better dispersion of the nanofillers, specifically nanocellulose, within the biopolymer matrix may be associated with the ability of biopolymers acting as carriers in the process improving the dispersion of cellulose according to (Kiziltas et al., 2016). Another nanoparticle which has been utilized into the biopolymer/natural fibre biocomposites is zinc oxide (ZnO), because it is a multifunctional nanoparticle. For example, ZnO may be mixed with natural fibre biocomposites to manufacture multifunctional biocomposites with better properties, such as antibacterial protection and ultraviolet absorption. Furthermore, the zinc oxide may be utilized as a nucleating agent to enhance the crystallinity of the biopolymer. Sbardella et al. (2021) report on the surface modification of the basalt fibres with ZnO incorporated into the PLA matrix. The composite laminates were fabricated by compression moulding. The modification of basalt fibres with ZnO was achieved by the hydrothermal process and the resultant product was analysed by scanning electron microscopy (SEM). According to the SEM images, it was observed that the ZnO nanorods have grown homogeneously in both directions within the fibres, i.e. axially and radially. The polarized optical microscopy (POM) revealed a trans crystallization on the surface of the fibres. SEM images showed that the ZnO nanoparticles were wetted by the PLA matrix and were found to be embedded in the biopolymer. Furthermore, it was reported that the ZnO was also found to have adhered to the fibres in the process enhancing the surface roughness. In some cases, within the hybrid system, the fibres may be modified with other chemicals such as alkali, potassium

permanganate, peroxides and salinization. Ramesh et al., 2021 report on the natural fibre/biopolymer/clay hybrid system consisting of kenaf fibre, MMT clay and PLA matrix. In this study, kenaf fibre was treated with 6% sodium hydroxide. The content of the fibre used in this study was 30% and the clay compositions were varied between 1% to 3%. The hybrid biocomposites were prepared by the twin-screw extruder at 185 °C. The effect of modification was proved by better fibre-nano-matrix bonding, which resulted in a better load transfer capacity. There are scenarios whereby there is an addition of flame-retardant fillers within natural fibre/biopolymer composites to form hybrid composites. Lee et al. (2016) report on the use of magnesium hydroxide ($\text{Mg}(\text{OH})_2$) on the properties of kenaf fibre/floreon. Floreon is a plant-based plastic produced from crops such as corn and sugarcane. Kenaf fibre was treated with 6% of sodium hydroxide (NaOH) for a duration of 4 hours. The chemical treatment of the fibre had a positive impact on the interfacial bonding between the fibre and the matrix. The introduction of the magnesium hydroxide showed coarser surface because of severe agglomerations and poor uniform distribution of the flame-retardant filler. Furthermore, Pierkarska et al. (2016) report on the hybrid system based on inorganic nanofillers and cellulose. The hybrid system composed of 3 wt% montmorillonite (MMT), 5wt% of stearic acid-modified calcium carbonate nanoparticles, and 15 wt% of the fibres. The hybrid system was prepared by melt mixer using a Brabender Plasti-Corder at a temperature of 180 °C. The morphology of the system was analysed by SEM, and it was shown that the cellulose fibres (CF) were well dispersed within the biopolymer matrix. Furthermore, there was no aggregation of the MMT within the hybrid composite. The hybrid systems fabricated from natural-natural fibres have been used in various applications such as the automotive, food packaging, and biomedical applications. Natural fibres may be mixed with one another and incorporated into biopolymer matrix. Scaffarro and Gammino (2022) used lignocellulosic leaves of *Chamaerops humilis* (CHL) and *Posidonia oceanica* (POL) as reinforcing fillers for polylactic acid at three-loading concentration, i.e. 5, 10 and 20%. The hybrid composites were prepared by a twin-screw extrusion at a temperature of 190 °C (see Figure 2.11).

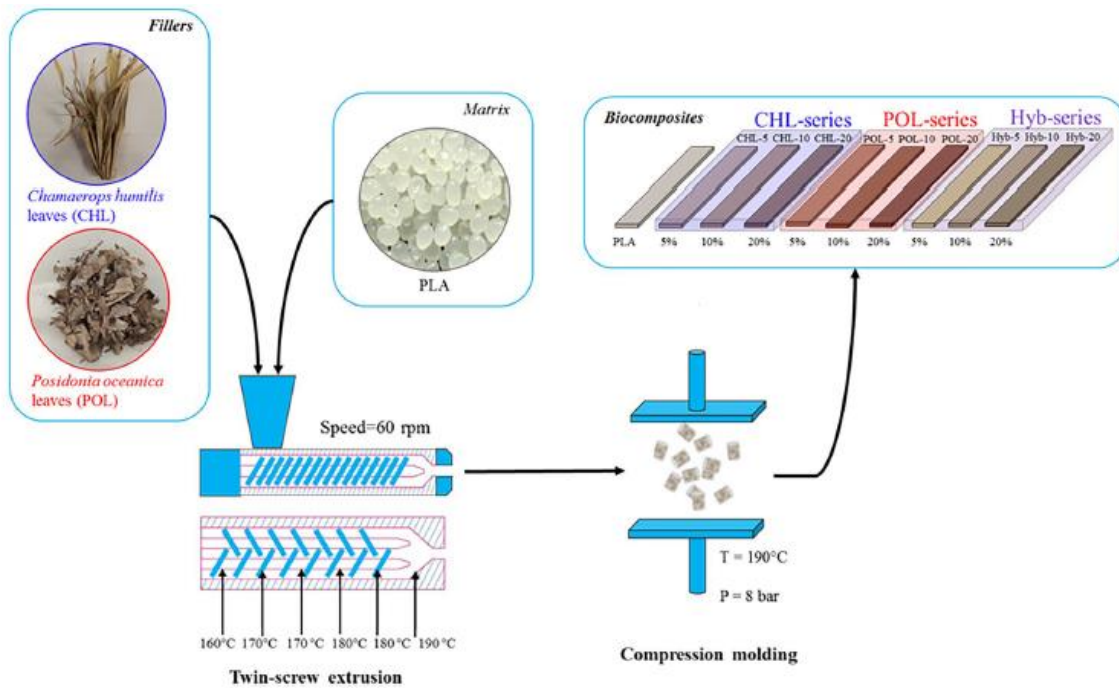


Figure 2.11: Schematic representation of the preparation method (Scaffaro, Maio and Gammino, 2022).

The CHL and POL fibres were found to be fibrous and platelet, respectively with an average length of 2 mm and a diameter of 150 μm . Furthermore, it was revealed from the SEM images that in a high content of the fibre (20%) there was weak interfacial adhesion. However, the hybrid composites showed denser structure with a better adhesion between the fibres and the matrix (Scaffaro and Gammino, 2022). The influence of the kenaf core fibre on the properties of the oil palm fibre/PLA biocomposites was reported by Birnin-Yauri et al. (2016). Oil palm is produced in the rain forest region of West Africa (Figure 2.12), while Figure 2.13 illustrates a typical example of an extraction of kenaf fibre from the plant (Natrayan et al., 2022). The kenaf core fibre/oil palm fibre/PLA hybrid biocomposites were produced by melt mixing followed by compression moulding. According to the SEM images of the kenaf core fibres (KCF-PLA) biocomposites, there was a poor interfacial adhesion between the fibre and biopolymer, which was associated with gaps and fibre clumps. A weak adhesion between the fibre and biopolymer may be associated with the fact that the fibres were treated with distilled water rather than well-known treatments such as silanization and alkalization. However, the hybrid biocomposites at lower KCF content (5%) showed reductions in voids and gaps.



Figure 2.12: Illustration of the a) oil palm tree, b) oil palm bunch and c) cross-section oil palm fruit (Asyraf et al., 2022).



Figure 2.13: On-route extraction of kenaf fibre from plant fibre (Natrayan et al., 2022).

The properties of the green composites depend on the natural fibres, strength, and stiffness of the fibre (Ejaz et al., 2020). Ejaz et al. (2020) report on the jute/flax-reinforced PLA biocomposites. The biocomposites and hybrid composites were prepared by hot press compression moulding. The content of the individual natural fibres was kept at 0-50 wt%, whereas the content of the hybrid system was 40 wt%. The individual fibres were well dispersed in the biopolymer matrix. A careful inspection of the two system revealed a strong interfacial bonding for the PLA/flax, and the PLA/jute biocomposite showed weak adhesion, which was evidenced by fibre pull-outs. There were no fibre pull-outs in the hybrid system, which is an indication of a strong adhesion. (Ejaz et al., 2020). Yusoff et al. (2016) report on a hybrid green composite consisting of three natural fibres, i.e. kenaf, bamboo and coir fibres. For comparison purposes, kenaf-coir/PLA, bamboo-coir/PLA and kenaf-coir/PLA biocomposites were also prepared. The morphological properties of the hybrid biocomposites

were investigated by optical microscopy (OM) and scanning electron microscopy (SEM). The hybrid biocomposites consisting of coir and bamboo fibres revealed poor bonding between the matrix and the filler(s), which is associated with insufficient matrix. Another factor which is associated with poor adhesion is the high impurities of the untreated bamboo fibres, which may have led to less penetration of the fibres and weak interlocking. The hybrid system consisting of kenaf fibres + coir fibres reinforced PLA biocomposites revealed less impurities of the fibres, which enhanced the penetration of the matrix within the fibres. However, for the hybrid system fabricated from bamboo fibres + coir fibres + kenaf fibres/PLA, optical microscopy images showed poor interfacial adhesion associated with the untreated bamboo fibres within the hybrid system.

2.5 MECHANICAL PROPERTIES OF NATURAL FIBRE BIOCOMPOSITES AND THEIR HYBRID BIO-COMPOSITES

Various studies have reported on the mechanical properties of natural fibre/biopolymer composites and their hybrid system. They are assessed using indicators such as flexural, impact and tensile tests. To have information on the composite's suitability for their intended purpose, the composites' mechanical strength must be studied. Various hybrid systems are formed from the biopolymers and natural fibres, i.e. natural fibre-natural fibre, natural fibre inorganic filler(s), and natural fibre, flame-retardant fillers. There are factors which affect the mechanical properties of fibre-reinforced biopolymer hybrid composites. These include the type of filler used, the content of the natural fibre and inorganic filler, the treatment of the natural and inorganic fillers. Gumus et al. (2020) report on the biocomposites composed of cellulose reinforced polyhydroxybutyrate (PHB) and polylactic acid (PLA). The content of cellulose nanofibrils incorporated into the biopolymer matrix was 1%. There was an enhancement in tensile strength with the addition of 1% cellulose nanofibril into the biopolymer matrix. For example, neat PHB and PLA revealed tensile strength values of 11 MPa and 40 MPa, respectively. The addition of 1% of cellulose nanofibril recorded tensile strength values of 13 MPa and 50 MPa for PHB+CNF and PLA+ CNF, respectively. The improvement in tensile strength is associated with a better dispersion of the cellulose nanofibril within the biopolymer matrices, as a result an enhancement in mechanical properties. Well-dispersed fibre(s) with the polymer matrices facilitate better stress transfer between the matrix and the filler; in return an improvement in mechanical properties. Abdul Razak et al. (2013) report on the mechanical properties of the chemically modified kenaf fibre-reinforced poly (lactic acid) biocomposites.

Kenaf fibre in this study was modified with hydrogen peroxide (5% v/v) for 1 hour before incorporation into the biopolymer matrix. All the modified kenaf fibre/PLA biocomposites were compared with the unmodified kenaf fibre/PLA biocomposites. The bleached kenaf fibre/PLA biocomposite showed better mechanical properties when compared to unbleached kenaf fibre/PLA biocomposite. The bleaching of the fibre ensured that the fibre is rough on the surface and as a result it can easily create better interlocking with the biopolymer matrix. An improved fibre-matrix adhesion enhances the stress-transfer between the fibre and biopolymer matrix, which in turn enhances the mechanical properties. Ochi et al. (2008) investigated the mechanical properties of the kenaf fibre-reinforced biopolymer composites. The volume fraction of the natural fibres was 30%, 50%, and 70% within the biopolymer matrix. The tensile and flexural strength was found to enhance with an increase in fibre content. However, inasmuch as the mechanical properties of the biocomposites was increasing with an increase in fibre content, at 70% of the fibre, there were voids and an incompatibility between the fibre and the polymer matrix. The orientation and size of the fibre were found to play a key role in the mechanical properties of the natural fibre-reinforced biopolymer composites. For example, Liang et al. (2021) report on the mechanical properties of the long sisal fibre/polylactic acid composites. Furthermore, the long sisal fibres were categorized into the continuous and unidirectional continuous long sisal fibres. The fibres were treated with sodium hydroxide (NaOH), which in the process removed pectin, wax, part of lignin and hemicellulose. The content of the fibres was varied between 0-40%, irrespective of the size and orientation of the fibres. The incorporation of the long sisal fibres in the biopolymer matrix enhanced the tensile and flexural strength of the biopolymer with an increase in fibre content. However, there was a decrease in the mechanical properties of the biopolymer with the incorporation of the short sisal fibre, due to poor compatibility between the fibre and the biopolymer matrix. Luo et al. (2014) report on the mechanical properties of the corn fibre-reinforced PLA biocomposites. In this study, the corn fibre was treated with alkali and sizing treatment. The content of the fibre was kept at 20 wt%, while the one for the sizing agent (γ -aminopropyl triethoxysilane) was varied between 8-12 wt% and sodium hydroxide was kept at 8 wt%. Figure 2.14 illustrates a chemical interaction between the fibre and biopolymer matrices.

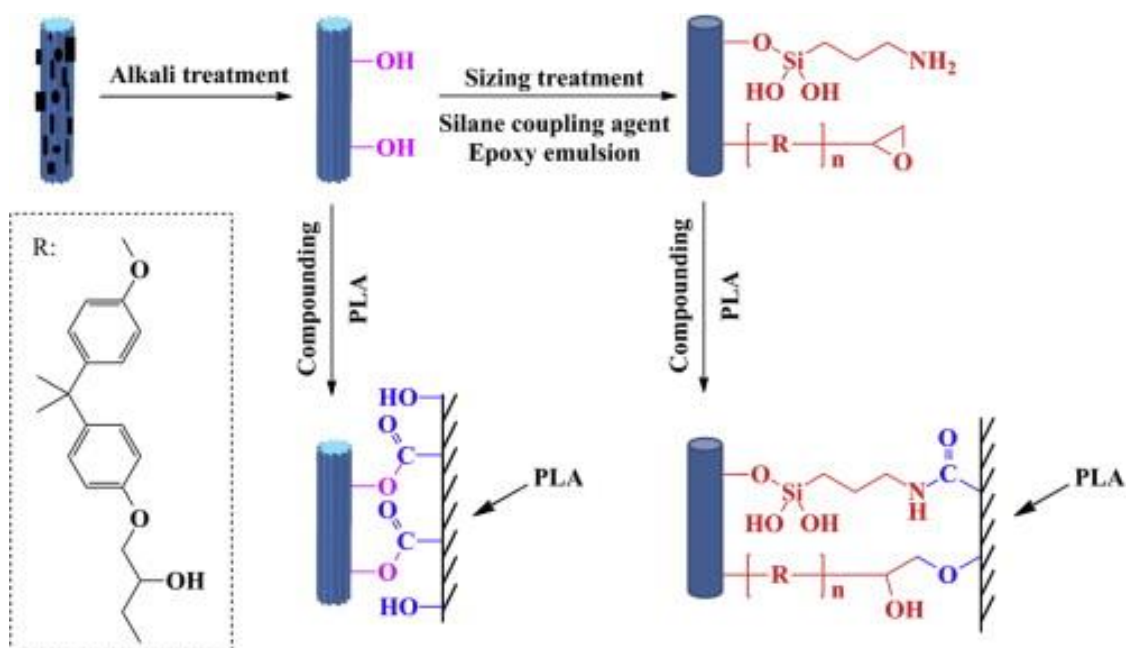


Figure 2.14: An illustration of the chemical interaction between the fibre and biopolymer (Luo et al., 2014). Copyright Elsevier.

The untreated fibre biocomposites (UCF/PLA) recorded a tensile strength and tensile modulus values of 39.8 ± 1.4 MPa and 4.97 ± 0.34 GPa, respectively. Alkali-treated corn fibre-reinforced PLA (ACF/PLA) improved the tensile strength by 18.1%, while the tensile modulus was enhanced by 9.5% when compared with UCF/PLA. The composites treated with 12% (SCF12) of the sizing agent revealed a tensile strength value of 49.5 ± 2.0 MPa and a tensile modulus of 6.63 ± 0.07 GPa. The enhancements in tensile strength and tensile modulus are 34.7% and 33.4%, respectively when compared with UCF/PLA. Poor mechanical properties in case of the UCF/PLA are attributed to poor interfacial adhesion between the fibre and biopolymer matrix due to inadequate stress transfer from the biopolymer to the fibre. The ACF/PLA biocomposites showed better mechanical properties when compared with the UCF/PLA, due to a better interfacial bonding between the two components of the composite. The impact of alkali treatment is to bring surface roughness, which catalyses interlocking between the fibre and the biopolymer matrix, which in turn enhances the stress transfer from the PLA to the corn fibres. Furthermore, it is well known that the hydroxyl groups of the fibre may interact with the carboxyl groups of the biopolymer matrix and improve the interfacial adhesion, which in turn provides better mechanical properties. The presence of the sizing treatment enhanced the mechanical properties due to the introduction of chemical reactions between the corn fibre and polymer matrix. The presence of the fibre enhanced the mechanical

properties of the biopolymer, as evidenced by the discussions above. However, an improvement in mechanical properties is not sufficient for advanced applications. To improve the mechanical properties of biopolymer, hybrid systems are fabricated. Pal et al. (2017) fabricated the hybrid composites based on PLA, cellulose nanocrystal (CNC), and reduced graphene oxide (rGO). The content of cellulose nanocrystals was 1-3 wt% and graphene oxide was utilized as lower content, i.e. 0.5-0.7 wt%. The hybrid biocomposites were prepared at a PLA/CNC/rGO ratio of 99.3/1/0.5 ratio. The aim of the study was to optimize the ratio of the CNC and rGO within the biopolymer matrix. The incorporation of the CNC and rGO increased the mechanical properties parameters such as the tensile strength, with a reduction in elongation at break. The reduction in elongation at break is a common trend, since reinforcing fillers tends to immobilize the movement of the polymer chains. The combined effect of the CNC and rGO enhanced the tensile strength and Young's modulus by 23.35% and 58.71%, respectively. The observation was attributed to a better dispersion of the fillers into the polymer matrix. A hybrid natural fibre formed from poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV), sisal with fibre length of 0.25 and 5 mm, and clay nanoparticles were investigated and reported by Dangtungee et al. (2014). The sisal fibre was treated with a 3 vol% of silane coupling agent and the composite was prepared by hot-press technique. The content of the fibre was varied between 5-30 wt%. The incorporation of clay nanoparticles decreased the tensile strength and stiffness of the PHBV/20 wt% with short and long sisal fibres. The reduction in mechanical properties is associated with poor dispersion of the clay with the matrix. Silane-treated hybrid composites revealed a slight enhancement in tensile modulus of the hybrid composites. Silane can enhance an interfacial interaction between the fibre and polymer matrix. In some cases, flame-retardant fillers such as magnesium hydroxide $Mg(OH)_2$, and ammonium polyphosphate (APP) are normally added to the biopolymer/natural fibres to improve the flame retardancy and in the process affects the mechanical properties. Mechanical properties of the alkali treated kenaf fibre-reinforced PLA composites were reported by Shukor et al., 2014. Kenaf fibre in this study was treated with 3%, 6% and 9% of sodium hydroxide before incorporation into the PLA matrix. The incorporation of the APP into the PLA/kenaf fibre biocomposite decreased the flexural properties. This was attributed to a poor compatibility between the PLA and APP, which further influenced the kenaf fibres, as a result decreasing the flexural properties of the system. Poor interaction between the fibre and PLA acts as a stress concentration, which decreases the impact properties. Inorganic fillers were reported to be very effective in improving the natural fibre-reinforced biopolymer biocomposites. Furthermore, other factors such as the annealing of the samples played a key role in the mechanical properties of the

hybrid composites. Chen et al. (2017) studied the effect of surface modification of kenaf fibre, its content and annealing on the mechanical properties of the hybrid composite. Kenaf fibre was modified with 4% of sodium hydroxide to eliminate impurities, lignin and hemicellulose. Furthermore, kenaf fibre was treated with OX-silane and multiwalled carbon nanotubes (MWCNTs) were modified with nitric acid (HNO_3). Before annealing, there was an enhancement of 57% in tensile strength of the hybrid composite consisting of PLA 69%, modified kenaf fibre 30% and MWCNTs 1% (termed PC1F30-OX) when compared to neat PLA. An improvement in tensile strength was associated with chemical reaction between modified kenaf fibre and PLA. Annealing of the PC1F30-OX improved the tensile strength more than unannealed samples. PLA is a semicrystalline polymer; as a result, it can recrystallize into spherical microdomains. Similar results were reported in impact strength, whereby there was a 76% increase in impact strength of the PC1F40-OX (PLA 59%, MWCNTs 1%, modified kenaf fibre 40%) when compared to PLA before annealing.

2.6 THERMAL STABILITY OF THE NATURAL FIBRE BIOCOMPOSITES AND THEIR HYBRID BIOCOMPOSITES

Thermal stability of various natural fibres/biopolymer composites have been reported in the literature (Johari et al., 2016; Li et al., 2011; Nor et al., 2022; Santillo et al., 2022; Shumao et al., 2009; Woo et al., 2020; Yu et al., 2014; Qi et al., 2022). The thermal stability of such biocomposites has been investigated by thermogravimetric analysis (TGA) in order to assess the chemical degradation. Generally, the content of the natural fibres and the coupling agent played a significant role in the thermal stability of the natural fibres' biocomposites. Johari et al. (2016) report on the thermal stability of the cellulose-reinforced polylactic acid. Cellulose in this study was extracted from sisal fibres. The extracted cellulose was further modified with silane and alkali treatments. The thermal stability of neat PLA and cellulose/PLA biocomposites revealed a single-step degradation. The biocomposites revealed a weight loss in the temperature range between 100-110 °C, which is associated with moisture in the fibres. The incorporation of 5 wt% of cellulose microfibrils improved the thermal stability of the biocomposites when compared with neat PLA. For an example, the T_{10} , T_{50} and T_f were reported as 311 °C, 339 °C and 359 °C, respectively. The biocomposites with 5 wt% revealed T_{10} , T_{50} and T_f at temperature values of 319 °C, 349 °C and 368 °C, respectively. The silane-treated cellulose microcrystalline fibres revealed the following values, i.e. T_{10} , T_{50} and T_f , 318 °C, 354 °C and 375 °C, which are higher than the untreated samples. This is attributed to

the reactive compatibilization that was promoted by silane agent. Nor et al. (2022) report on the properties of the woven kenaf fibre-reinforced polylactic acid (PLA). One of the properties reported by the authors is the thermal stability of the biocomposites. Unlike in the study conducted by Johari et al. (2016), Nor et al. (2022) report a single thermal degradation step for neat PLA, while there were multiple degradation steps for kenaf fibre/PLA biocomposites. Furthermore, it was observed that the thermal degradation of the neat PLA was higher than kenaf fibre-reinforced PLA biocomposites. The three degradation steps in the composites were explained as follows: the weight loss in the temperature range between 57 °C to 129 °C is attributed to moisture, while the second degradation step above 300 °C is attributed to the decomposition of the three major component of the fibres, i.e. cellulose, hemicellulose and lignin. The last degradation step was associated with the decomposition of the PLA matrix. The thermal stability of the woven kenaf fibre-reinforced PLA showed lower thermal stability at higher fibre content. However, the highest fibre content in the biocomposites revealed the highest char residues because of high lignin content. The properties of the corn stalk microcrystalline cellulose/PLA composites were investigated by Li et al. (2011). In this study, the incorporation of corn stalk microcrystalline cellulose enhanced the thermal stability of the PLA composite. Fibres produced from straw have been utilized to reinforce biopolymers because of being biodegradable, renewable, and low cost (Qi et al., 2022). The chosen ratio of the corn straw fibre (CSF) to the PLA matrix was kept at 3:7 ratio (CSF: PLA). The corn straw fibre (CSF) was subjected to various sieves of different sizes. The TGA curve of PLA showed its degradation in temperatures between 300 °C and 370 °C. At this temperature PLA is broken down into lactide, which is partnered by a small quantity of carbon monoxide (CO), carbon dioxide and acetaldehyde. Furthermore, it was reported that all the samples revealed a single-step degradation. In temperatures around 250 °C, the CSF/PLA composites showed no changes except for evaporation of the water and impurities in the system. At higher temperatures, i.e. 500 °C, there was a carbonization of the CSF reported by the authors. Thermal stability of natural fibre hybrid composites was reported by various authors (Woo and Cho, 2021; Santillo et al., 2022). The hybrid's composites in this case are formed from natural fibres, flame-retardant fillers and biopolymer matrices. Santillo et al. (2022) report on the properties of the chitosan hybrid composites consisting of components such graphene oxide (GO), cellulose nanocrystals (CNCs) and borate by solution mixing. According to the TGA curves, neat chitosan (CS) showed two degradation steps, i.e. the first one in the region of 60-150 °C, which was attributed to the evaporation of moisture in the samples. The second degradation step is associated with the pyrolysis of the polysaccharides, which might be due to the breaking down

of glycosidic bonds. The composites also revealed a two-step degradation. It was noticed that the evaporation of water occurred at higher temperatures in the composites when compared to neat PLA, and the composites showed lower thermal stability than neat PLA. The difference in evaporation temperatures of water in neat CS and CS-based composites is that in CS alone, water may be attached to the amine groups and the water that is attached to the amine functional group is normally removed at lower temperatures. In case of the composites, water evaporates at higher temperatures when compared to neat chitosan because of the presence of the cellulose, graphene oxide and borax, which might have interacted with the functional groups of water to form a strong polymer-water bond. The reduction in thermal stability of the composites when compared to neat CS matrix was attributed to a lack of functional groups that may assist in the formation of hydrogen bonds between the CS matrix and the filler components. Multi-walled carbon nanotubes (MWCNTs) functionalized with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) were investigated by Yu et al. (2014). Figure 2.15 illustrates the mechanism behind the functionalization of the MWCNTs by the DOPO.

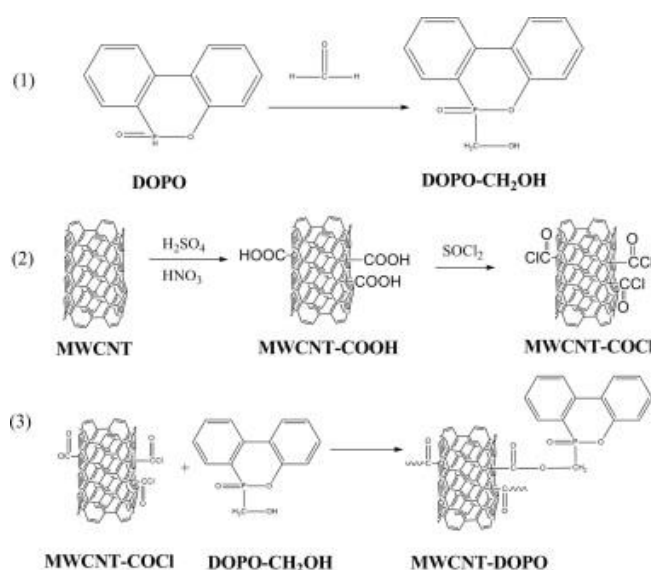


Figure 2.15: Illustration of the surface modification of MWCNTs by DOPO (Yu et al., 2014).

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Ramie/PLA biocomposites degraded at temperatures around 318 °C. The incorporation of unfunctionalized MWCNTs improved the thermal stability from 318 °C to 335 °C. Functionalized MWCNTs showed a decrease in thermal stability when compared with non-functionalized MWCNTs, which is associated with the degradation of DOPO. Other materials that were observed to influence the thermal stability of the natural fibres/biopolymer composites are the flame-retardant fillers, with their addition leading to hybrid composites. The

effect of ammonium polyphosphate (APP) on the properties of PLA was reported by Shumao et al. (2010). The thermal stability of the silane-treated, ramie fibre-reinforced polylactic acid (PLA-NF) showed decomposition of the gases and moisture in the range of 50-150 °C, with major degradation occurring around 280–390 °C. The incorporation of ammonium polyphosphate (APP) reduced the starting decomposition of the ramie-reinforced PLA biocomposites. When compared to PLA-NF, in the presence of APP, the two degradation steps were observed between 240-280 °C, as well as 300-385 °C, which is a clear reduction when compared with PLA-NF biocomposite. The first weight loss is attributed to the pyrolysis of the APP, while the advanced decomposition of the ramie fibres is due to the acid release by the APP during its decomposition.

2.7 FLAMMABILITY PROPERTIES OF NATURAL FIBRES HYBRID COMPOSITES

It is well known that the polymers and fibres consist of organic components and as a result they can easily burn. To utilize natural fibre biocomposites in advanced applications and to ensure safety of the society, flame-retardant materials are added into the natural fibre/biopolymer composites. There are various types of flame-retardant fillers such as the (i) halogen-based flame retardants (HBFR); (ii) halogen free-flame retardants (HFFRs); (iii) intumescent flame retardants (IFRs); and (iv) biobased flame retardants (Chukwunwike et al., 2019). There are four classes of the HBFRs, i.e. iodine, bromine, fluorine, and chlorine. The effectiveness of this halogenated flame retardant is in an increasing order of: Fluorine < Chlorine < Bromine < Iodine. Amongst the above-mentioned HBFRs flame-retardant fillers, chlorine and bromine were the HBFRs flame-retardant fillers utilized the most. However, the HBFRs flame-retardant fillers are no longer utilized to improve the flame-resistant properties of the polymers and/or natural fibre/polymer composites due to the release of smoke and toxic gases that are very dangerous to the human health and the environment at large. The HFFRs are nontoxic, low cost, and easy to handle; as a result they are favourable flame-retardant fillers. The intumescent flame-retardant fillers are those materials that swell when the material is exposed to heat. In the process they increase in volume and reduce in density. The mechanism of action for intumescent flame retardants is based on the production of voluminous structure, forming a heat-protective barrier through carbonization (Lu and Wilkie, 2010). The biobased, flame-retardant fillers are known to be the ones attained by from biological matter found on earth. The improvement in flame-resistant properties of the biobased flame-retardant fillers is

achieved by a charring effect, which is produced on the surface of the sample. Figure 2.16 illustrates the fire triangle model.

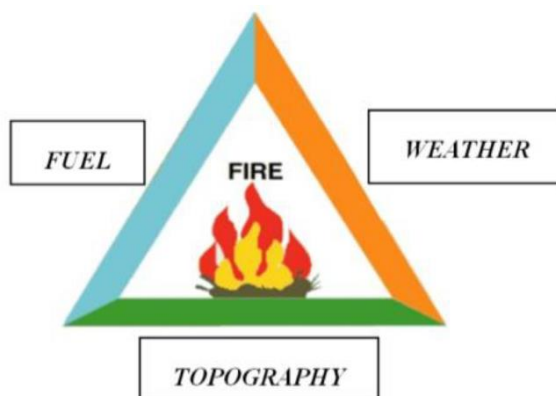


Figure 2.16: Fire triangle model (Mangiameli, Mussumeci and Cappello, 2021). MDPI Open access.

The flammability properties of the flame-retardant filler(s)/natural fibre(s)/biopolymer hybrid composites were affected by the type of flame-retardant filler, synergy of flame-retardant fillers and the type of biopolymer/natural fibre(s) composites. In the majority of the studies, techniques such as cone calorimeter, limiting oxygen index (LOI) and UL 94 were used for analysing the flammability properties of the polymer-based composites. Woo and Cho (2021) report on the effect of ammonium polyphosphate on the flammability properties of kenaf fibre/polylactic acid (PLA). The flammability properties of the hybrid system were investigated by the limiting oxygen index (LOI). The basic principle of the LOI test is that the more oxygen is required in a specific sample, the higher the flame retardancy of a particular sample. PLA/Kenaf fibre recorded an LOI value of 23.9; the incorporation of 10, 20, 30 and 50 wt% of APP revealed LOI values of 32.1, 35.2, 38.4 and 45.3, respectively. During the process of burning, APP undergoes a transformation into polyphosphoric acid and further converts into a char by esterification and dehydrogenation. The formed char is able to act as a heat barrier against the entering of oxygen into the samples, and as a result enhances the flammability resistance of the system. Similarly, Shumao et al. (2010) report on the flammability of ramie fibre-reinforced PLA matrix in the presence of APP as a flame-retardant filler. The flammability properties of the samples in this study were evaluated by limiting oxygen index (LOI) and UL 94. The silane-treated ramie-fibre/PLA composite revealed the lowest LOI value, i.e. 19.1, with dripping according to the UL 94. The incorporation of APP was found to enhance the LOI values when compared with ramie-fibre/PLA composite. The ramie/PLA system had no char that is able to protect the PLA matrix, while the presence of APP promotes

the formation of carbonaceous char, which can act as a heat barrier and enhances the flame retardancy of such systems. The flammability properties of the system composed of starch, flax fabric and APP are reported by Prabhakar and Song (2017). Ammonium polyphosphate was incorporated into the flax and starch composite in varying percentages, i.e. 3%, 6%, and 9%. The hybrid composites showed a significant flame self-extinguishment, as it was supported by LOI and HBT results. The improvement in flame resistance was associated with a stable char, which in this study was recorded to be in the range of 30-40%, and it was stable enough to protect the underlying substrate from combustion. In some other cases, the improvement in flame retardancy was achieved through coating of the fibre with a flame-retardant filler upon its incorporation into the biopolymer matrix. Zhang et al. (2018) coated flax fibre with polydopamine (PDA) in a dopamine solution, which was further modified with iron phosphate on a fiber surface. Cone calorimeter was utilized to evaluate the flammability properties of the hybrid composite. PLA was found to have burned very quickly and recorded a peak heat release rate of $396 \pm 12 \text{ kW/m}^2$. It was further reported that the incorporation of the flax fibre without a flame-retardant filler slightly increased the pHRR value to $407 \pm 17 \text{ kW/m}^2$. The fibre-treated biocomposites showed a 16% reduction in the pHRR value when compared with the flax/PLA composites. Furthermore, the treated flax fibre showed a reduction in total smoke production when compared with flax/PLA composites. The flame-retardant filler in the treated system produced a layer that protected the combustion products, thus reducing the HRR and the release of smoke. Kovacevic, Bischof and Fan (2015) report on the thermal properties of the Spartium junceum L. fibre-reinforced PLA composites. In this study, the fibres were treated with montmorillonite nanoclay (MMT) in order to improve the flame resistance of the biocomposites. The flammability properties of the fibre-reinforced composites was investigated by microscale combustion calorimetry (MCC). A low heat-release rate (HRR) was reported for MMT-reinforced fibre biocomposites. The MMT include two samples, i.e. (i) biocomposite reinforced with fibres treated with MMT; and (ii) biocomposites reinforced with fibre-treated MMT and citric acid (CA). It is well known that MMT has a tendency of forming a strong, protective barrier and such barrier can protect the volatiles from leaving the substrates, as a result enhancing the flammability resistance of the biocomposites. The synergistic effect of the fillers was also reported to have a significant impact on the flammability properties of the natural fibre-reinforced polylactic acid. Hapuarachchi and Peijs (2010) report on the synergistic effect of carbon nanotubes and sepiolite nanoclays on the flammability of natural fibre/polylactide. Figure 2.17 shows the flow diagram of in the development of flame-retardant, natural-fibre biocomposite.

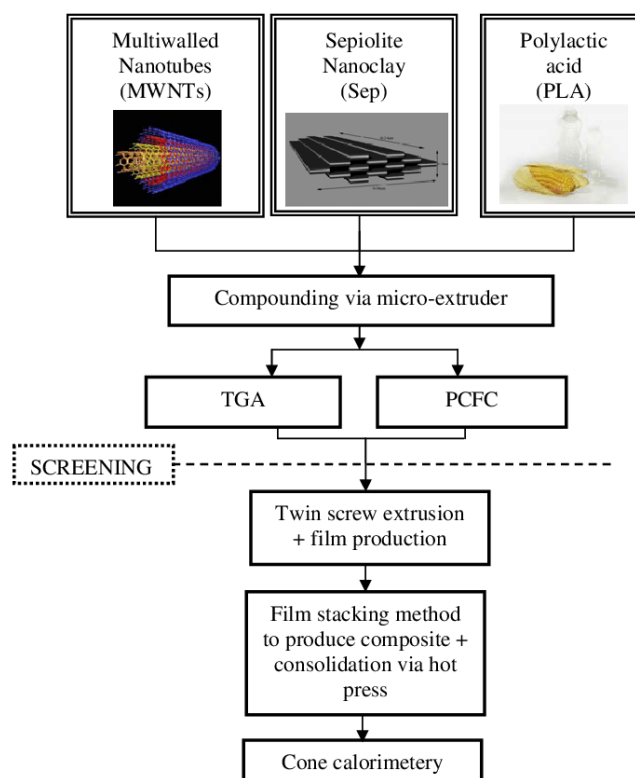


Figure 2.17: Flow diagram of the natural fibre biocomposites (Hapuarachchi and Peijs, 2010).

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In this study, a system consisting of 10 wt% + 2 wt% MWCNT was chosen as the optimum formulation for the composite. The main reason for such a selection is the fact that 10 wt% sepiolite is sufficient to form a protective barrier layer and 2 wt% of MWCNTs is good enough to create networks within the system. The synergistic effect of sepiolite and MWCNTs in the absence of natural fibre resulted in the best performance with a 58% drop. The introduction of the non-woven hemp fibre resulted in a 45% decrease. From the studies it transpires that the flame-retardant fillers are capable of blocking heat from entering the natural fibre(s)/biopolymer biocomposites due to their ability to form char layers.

2.8 APPLICATION OF NATURAL FIBRES AND THEIR POLYMER BIOCOMPOSITES

To lessen environmental pollution, totally biodegradable alternatives have been developed in response to the unfavourable rise in the usage of traditional plastics. Over decades, the superiority of natural fibres over costly carbon and glass fibres has been demonstrated. Natural fibres have less density than these synthetic fibres, making them lighter and contributing to

increased fuel economy. The practical uses of biopolymer composites began in the late 20th century. Natural fibres are widely utilized in many different industries worldwide, including sports, automobiles, aircraft, medicine, textiles, packaging, infrastructure and construction, upholstery and furniture, and several home goods (Aaliya, Sunooi and Lackner, 2021). Biopolymer composites are expected to see much more widespread use in industrial sectors in the near future. Natural fibre-reinforced biopolymer composites have a number of benefits over conventional composites in the automotive industry, including greater stability, lighter weight, better acoustic insulation, improved mechanical properties, less wear on tools and machinery, less or no release of toxic or noxious gases, and the ability to be recycled, renewed and environmentally friendly. In interior car parts, where strength of composite is a need for performances, biopolymer composites made from PLA reinforced with natural fibres like kenaf and jute are proven to be an effective use. The use of kenaf fibres to enhance the mechanical characteristics of automotive structural components has also been investigated. In the automobile industry, insulating materials are made from cotton and coconut fibres. Coconut fibres were employed in the body components of Daimler-Benz, while a hemp fibre-reinforced composite was used in the side panels of the Audi A3. In their first commercial car, Toyota, a multinational automobile company based in Japan, they used composites made by reinforcing kenaf fibres in PLA matrix made from sugar cane and sweet potatoes in the spare-tire cover of the RAUM 2003 model. Natural-fibre-reinforced polymer composites are used in various external and interior applications by big German automakers such as Ford, Daimler Chrysler, Mercedes, Volkswagen, Audi, Opel, and Bayerische Motoren Werke AG (BMW). Components like as door panels, headliners, dash boards, package trays, and cushioned seats are made of natural fibre-reinforced composites. Wood-flour-filled door panels were used by Italian automaker FIAT in its Brava, Punto, Marea, and Alfa Romeo cars. Additional uses of biopolymer composites in the automotive industry include the reinforcement of bamboo and kenaf fibres in PLA composites used in the translucent roof of the Toyota 1/X plug-in hybrid concept car, the headliner/ceiling material made of bamboo fibre-reinforced PBS composites, and the preparation of car floor mats made of PLA and PBS composites in Mitsubishi Motors Corporation's Lexus models (Thyavihalli Girijappa et al., 2019; Yaashikaa, Kumar and Karishma, 2022).

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CHAPTER 3: MATERIALS AND METHODOLOGY

3.1 MATERIALS

3.1.1 Polybutylene succinate (PBS)

Polybutylene succinate (PBS) was supplied by 2 MBIO- Engineering Polymers, India in a pellet form. PBS has a Melt flow index (MFI) of 190 °C 2.16kg/10min.), heat combustion of 23.6 KJ/g and it has a melting temperature of approximately 120 °C, and a density of 1.25 g/cm³.

3.1.2 Montmorillonite Clay (MMT)

Montmorillonite (MMT) clay, in the form of powder was supplied by Sigma Aldrich, South Africa. Montmorillonite was modified with 15-35 wt% octadecylamine and 0.5-5 wt% aminopropyltriethoxysilane, to enhance its compatibility with polymer matrix. The nano clay has a density of 2 g/cm³.

3.1.3 Expandable Graphite (EG)

Expandable graphite (EG) was supplied by Qingdao Kropfmuehl Graphite in Hauzenberg, Germany.

3.1.4 Maize Stalk fibre (MSF)

Maize stalk Fibre (MSF) was acquired from a farm in Cofimvaba in the Eastern Cape, South Africa.

3.2 METHODS

3.2.1 Washing of maize stalk fibre

The rind and the pith are the two main parts of the maize stalk fibre. Cellulose and lignin make up the rind. Sugar, protein, fat, and hemicellulose make up the pith. The rind is extremely strong and resilient. As a result, it is utilized to create composite materials made from maize stalk fibre. Since the pith is weak, it is normally removed when fabricating the composites (Chen et al., 2019; Zhang et al., 2016; Subramani and Vishnupriya, 2014). A sharp object such

as a microtome knife was used to split the rind and the pith, by sliding the knife between rind and the pith. Maize stalk fibre rind and pith were separated using an 18-mesh wire sieve. The rind was soaked in water for an hour following the recording of the weight. The rind was removed from the water and weighed once more to determine whether it had absorbed any moisture. The weight was then noted. After being weighed, the wet rind was dried for 24 hours in a vacuum oven pre-heated at 70 °C. It was taken out of the oven after 24 hours, weighed, and checked to determine if any moisture remained. The rind was ground into a fine powder using a coffee grinder once it had dried completely.

3.2.2 Preparation of PBS/EG/MMT/MSF hybrid composites

Before preparation, PBS, MMT, MSF and EG were dried at 50 °C in a vacuum oven for a period of 24 hours. To prepare the polymer composites and hybrid composites, PBS, MMT, MSF and EG were physically mixed in a beaker, and then the mixture was extruded using a co-rotating twin-screw extruder with an L/D ratio of 40 (L = 720 mm) and extrusion speed of 202 rpm. The extruder was operated at various temperature profiles set at 135 °C, 140 °C, 145 °C, 150 °C, 155 °C (i.e. for different zones from hopper to die). The extrudates were cooled in a water bath as they exited the die, and then dried in an oven at 50 degrees for 24 hours. Table 3.1 shows the sample ratios of all the investigated samples. Figure 3.1 illustrates the type of extruder utilized in this study.

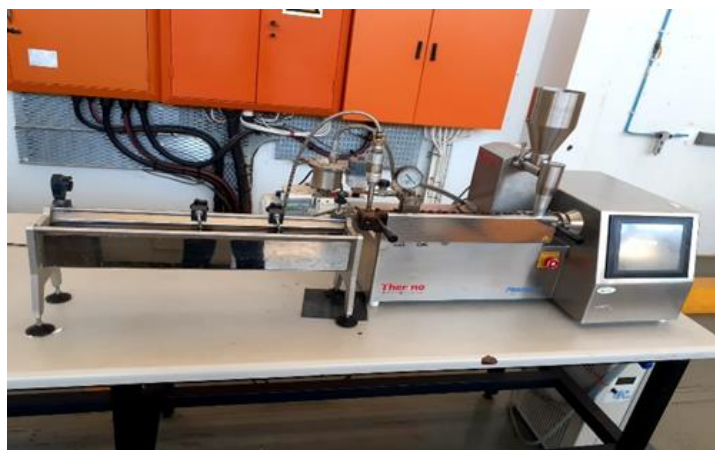


Figure 3.1: A co-rotating twin-screw extruder utilized for the fabrication of PBS/MMT/MSF/EG composites.

Table 3.1: Compositions of the samples

Sample	Weight Percentage%
PBS	100
PBS/EG	97/3
PBS/MMT	97/3
PBS/MMT/EG	94/3/3
PBS/MSF	90/10
PBS/MSF/EG	87/10/3
PBS/MSF/MMT	87/10/3
PBS/MSF/MMT/EG	84/10/3/3

3.3 CHARACTERIZATION AND SAMPLE ANALYSIS

3.3.1 Scanning Electron Microscopy (SEM)

The concept of SEM dates back to the nineteenth century, when a first electron microscope was built in 1933 by using the work of two physicists named Ruska and Knoll. SEM, often known as SEM analysis or SEM technique, is a tool that has been employed across a wide range of fields (Bogner, 2007). On a nanoscale to micrometre (nm–m) scale, it can be regarded as an efficient approach for the analysis of organic and inorganic materials. With a high magnification that can reach 300,000x and even 1000x (in some recent models), SEM creates extremely exact images of a variety of materials. Together with SEM, Energy Dispersive X-ray Spectroscopy (EDS) produces qualitative and semi-quantitative data (Inkson, 2016). Together, the two techniques have the ability to offer essential details on the material composition of scanned specimens that are not possible to obtain by standard laboratory assays. Organic and solid inorganic materials, such as metals and polymers, are among the materials which SEM has been used to analyse their morphology. The morphological analysis of the samples was done by Shimadzu ZU SSX-550 Superscan scanning electron microscope (Figure 3.2). The samples were fractured by liquid nitrogen, and they were broken into proper size to fit the sample chamber in the SEM. The samples were encapsulated with gold in order to produce conductive coatings within the samples (Mohammed and Abdullah, 2018).



Figure 3.2: A SEM used to analyse the surface morphology of the samples.

3.3.2 Thermogravimetric analysis (TGA)

The total mass of a sample can be determined using the TGA method as a temperature-dependent property (Bottom, 2008). Polymeric materials degrade and lose volatile components during deterioration. As a result, a key characteristic of many materials is the mass change caused by temperature. During TGA, a sample is purposefully exposed to a certain temperature program while being subjected to strict environmental restrictions, and weight changes are simultaneously monitored (Menczel and Prime, 2009). All of the studied samples' thermal stability was assessed using a thermogravimetric analyser, or TGA5500 (TA Instruments, USA) (Figure 3.3). The samples, which weighed 7-8 mg, were heated at a rate of 10 °C/min under air from 25 °C to 800 °C.

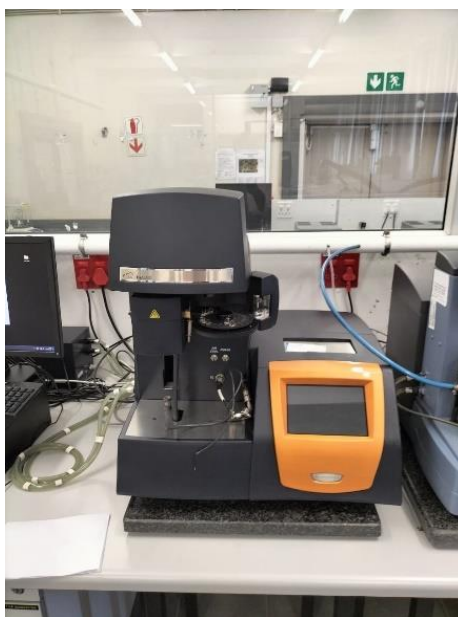


Figure 3.3: A TGA analyzer used to assess thermal stability of the samples.

3.3.3 Dynamic mechanical analysis (DMA)

In the DMA approach, a sample is either subjected to a circular strain and the stress response that results is measured, or a cyclic stress is applied and the strain response that results is measured. The bulk of commercial DMA equipment regulates the input as strain while monitoring the stress that results from it. Molecular relaxation processes in polymers are investigated using DMA, and the relationship between inherent mechanical or flow properties and temperature and time is established (Chartoff, Menczel and Dillman, 2009). Using a (Perkin Elmer DMA 8000, USA) analyser, DMA testing of the materials were carried out in the dual cantilever bending mode at temperatures ranging from -50 °C to 90 °C (Figure 3.4). 1 Hz and 0.05% were used as the frequency and strain amplitude, respectively.



Figure 3.4: Perkin-Elmer DMA utilized to determine dynamic mechanical properties of samples.

3.3.4 Cone calorimetry

The notion of oxygen consumption during burning serves as the foundation for the cone calorimeter, and parameters such as mass loss rate (MLR), heat release rate (HRR) and total heat release (THR) are commonly used in cone calorimetry test (see Figure 3.5). The HRR, which is what ignites a fire, is the most crucial variable. A substance's flammability increases with its HRR, and as a result, such a substance is regarded as highly flammable (Dewaghe et al., 2011). Dual Cone calorimetry with an incident heat flux of 35 kW/m^2 was used for analysing the samples. The samples with dimensions of $100 \times 100 \times 6 \text{ mm}^3$ were fabricated by compression moulding.



Figure 3.5: A cone calorimeter used to analysis the flammability of the samples.

3.3.5 Rheology

Rheology is a method for calculating a material's viscoelastic qualities. The viscoelastic characteristics of a material are explained using the ideas of a complex modulus and a phase angle. The complex modulus represents how a material will behave under dynamic loading at a specific strain level. The phase angle is the difference in time between the responses of the elastic (storage) and viscous (loss) moduli (Widyatmoko, 2016). Additionally, the viscosity of the flow can have an impact on the effectiveness of particle dispersion. In determining the degree of filler dispersion in a polymer composite, rheological characteristics of a material are also helpful (Abraham et al., 2017). By using a Physica MCR501 (Anton Paar, Austria) rheometer in a 25 mm diameter parallel plate setup, the dynamic rheological properties were tested at 190 °C under air circumstances. The zero gap was fixed at 1.15 mm for all tests, and preliminary experiments were used to calculate the strain amplitude of 1%. Figure 3.6 illustrates the type of rheology used in this study.



Figure 3.6: The rheological properties of the samples were studied using a rheometer.

3.3.6 Differential scanning calorimetry (DSC)

DSC is an evolution of the differential thermal analysis (DTA), and the two techniques have a common parameter, which is temperature. The main concept of both techniques is to measure the thermal changes of a specimen in relation to the thermal inert reference since both are exposed to a controlled temperature system. The differential scanning calorimetry (DSC) were analysed using Perkin Elmer Pyris-1 differential scanning calorimeter under nitrogen at the flow rate 20 mL/min. Samples of mass in the range of 5-10 mg were wrapped in aluminium

pans and heated from room temperature to 140 °C at the heating rate of 10 °C/min and were cooled under the same conditions. The peak temperature of melting and crystallization as well as the melting enthalpies were recorded.

3.3.7 X-Ray diffraction analysis (XRD)

X-ray diffraction analysis (XRD) is a technique utilized when one wants to understand crystallographic structure, physical properties, dispersion of fillers within polymer matrices, and chemical composition. The samples were analysed by A D8 Advance diffractometer (BRUKER AXS, Germany) with PSD Vantec1 detectors and Cu K α radiation ($\lambda = 1.5406$), and under the following conditions: a tube voltage of 40 kV, a current of 40 mA and V20 slit. The 2θ angle were chosen in the angle range of 5 to 90° with an increment of 0.5.

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CHAPTER 4: RESULTS AND DISCUSSION

4.1 SCANNING ELECTRON MICROSCOPY (SEM)

Figure 4.1 (a and b) depicts the SEM images of PBS/EG and PBS/MSF composites, respectively. According to Figure 4.1(a), there is a clear indication for graphite stalks within the PBS matrix and the graphite agglomerates are well dispersed in the biopolymer matrix as indicated by symbol A and B, and the arrows. The presence of agglomerates may suggest poor interfacial adhesion between the EG and PBS matrix. It is well known that particles tend to agglomerate because of particles' adhesion to one another by weak forces. To avoid or minimize agglomeration of particles, graphite is normally modified to improve its adhesion with polymer matrices. However, in our study, graphite was not functionalized or modified. Noh et al. (2015) investigated the fracture surfaces of the graphene-polymer composites. Various graphene fillers such as graphene nanoplatelets (GNPs), graphene oxide (GO) and GO reduced by phenyl hydrazine (CCG-P) were well dispersed within the cyclic butylene terephthalate (CBT), even at higher filler content (20 wt%). Furthermore, the GO and CCG-P were found to show superior dispersion when compared with the GNP-based composites. The presence of oxygenated functional groups in the GO facilitated a better dispersion of GO within the matrix, while the presence of phenyl groups in CCG-P enhanced its dispersion in the polymer matrix. In Figure 4.1(b) it can be observed that there is a fibre pull-out (see symbol C) which is an indication of poor interfacial adhesion between fibre and the matrix. This behaviour is associated with an incomplete wettability or bonding between the polymer and fibre during the preparation. It is well known that the fibre-matrix interfacial bond plays a critical part in load transfers emerging from the polymer matrix to the fibre. Contrary to our observation, Wang et al. (2019) report on few agglomerations and uniform fibre dispersion within the PLA matrix, even at higher glass fibre (GF) content.

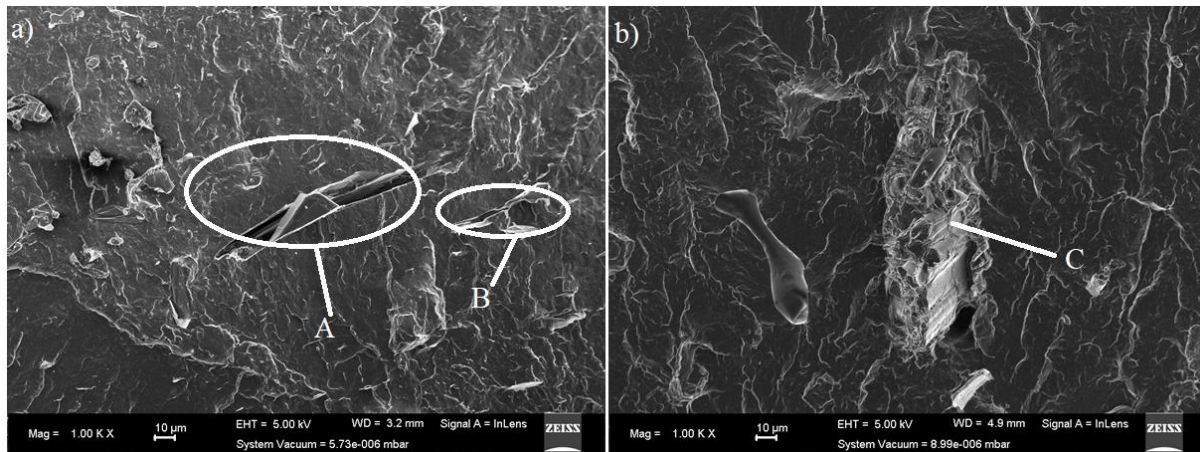


Figure 4.1: SEM images of (a) PBS/EG 97/3 and (b) PBS/MSF 90/10.

Figures 4.2(a) and (b) illustrate the SEM images of the PBS/MSF/EG 87/10/3 and (b) PBS/MSF/MMT 87/10/3, respectively. There are clear fibre pull-outs (symbol E) (Figure 4.2(a)) and debonding of the fibre from the PBS matrix in the presence of the graphite, with minimum fibres being well dispersed in the presence of graphite. This may be due to a minimum affinity between unmodified or unfunctionalized graphite and PBS matrix. Similar results were reported by Kumar et al. (2018), whereby the authors observed some broken fibres and pull-outs for a graphene-modified kenaf fibre system. However, with the addition of Montmorillonite clay (MMT) in the PBS/MSF system (Figure 4.2b), there is a good dispersion of the fibre with fewer fibre pullouts when compared with SEM image in Figure 4.2(a). The presence of MMT improved the interfacial adhesion between the PBS matrix and maize fibre (MSF) which may have restricted the fibre-PBS pullouts and debonding. Montmorillonite (MMT) is organically modified; as a result, it can ensure that there is an improvement interfacial adhesion between the fibre and PBS matrix. Similar results were reported by Ramesh et al. (2021), whereby there was a good dispersion of the kenaf fibre within the PLA, with the clay (MMT) acting as the modifier in the system (Ramesh, Prasad and Narayana, 2021).

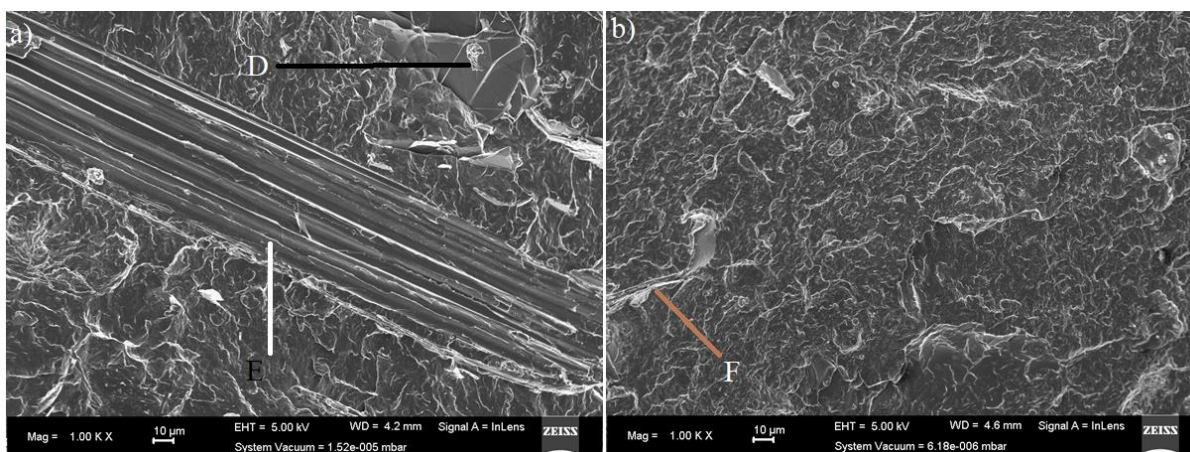


Figure 4.2: SEM images of: (a) PBS/MSF/EG 87/10/3 and (b) PBS/MSF/MMT 87/10/3.

Figure 4.3 shows the SEM images of the PBS/EG/MMT 94/3/3 and PBS/MSF//MMT/EG 84/10/3/3. There seems to be a fair dispersion of the MMT clay within the PBS matrix; however, there is a clear graphite debonding from the composite (symbol G). The debonding of EG is expected since expanding into graphite layers occurs temperatures around 250 °C. It is well known that expanded graphite distributes better within polymer matrices when compared with expandable graphite. It is known that expanded graphite is a multi-pores structure which can host/ intercalate polymers within a graphite sheet, while expandable graphite is designed from a natural mineral graphite. Another factor that might have contributed to the agglomeration of the EG is their fragility of the graphite, which happens to break easily during processing with the various polymer matrices. It is noted in the majority of the polymer-graphite composites that it is not easy to delaminate the graphite completely, as it still exists in the dense stacking of the graphite layers. A fairly good dispersion of the MMT into the PBS may be attributed to two factors; firstly, a low MMT content (3%) and secondly, an organically modified MMT accelerated a sufficient entering of the PBS molecules into the MMT layers. As reported in the literature (Fukushima et al., 2010), the incorporation of the CLO clay revealed a good interaction with the PLA. A hybrid system consisting of the PBS/MSF/MMT/EG hybrid composites revealed a fibre pull-out (symbol H) and an expandable graphite agglomerate (symbol I). A combination of both MMT and EG had minimum effect in terms of improving the dispersion of the maize stalk within the PBS matrix. Similar results were observed by Fukushima et al. (2010), whereby the authors assumed that Cloisite 30 B (CLO) clay interacted and dispersed better in the PLA matrix when compared to the binary composites (EG+CLO+PLA). This was attributed to a high affinity between the clay and the biopolymer matrix. The hydroxyl groups of the clay and the carbonyl groups of the

biopolymer matrix form a very strong hydrogen bond, and which result in a better dispersion of the clay within the biopolymer matrix.

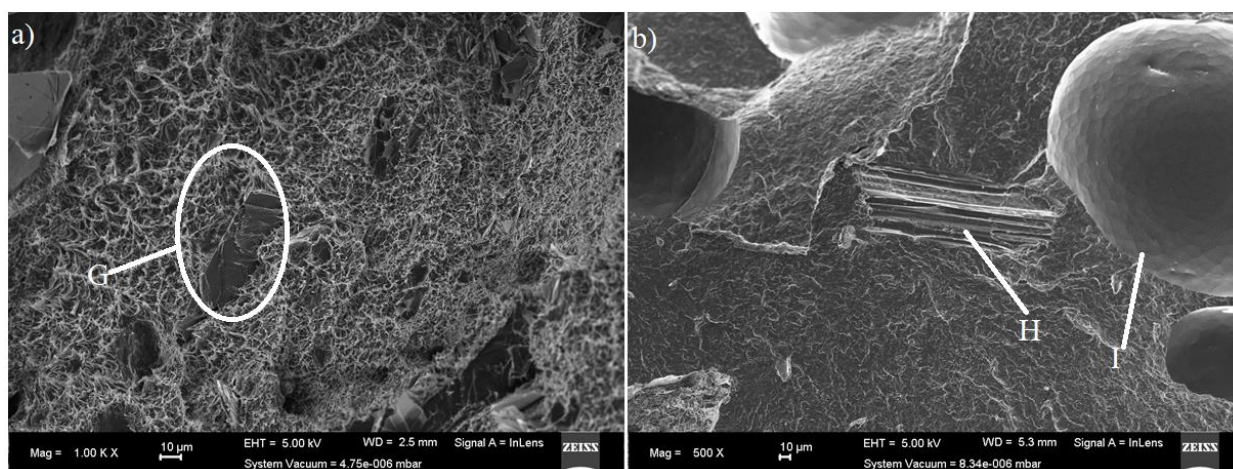


Figure 4.3: SEM images of the (a) PBS/EG/MMT 94/3/3 and (b) PBS/MSF/MMT/EG 84/10/3/3.

4.2 X-RAY DIFFRACTOMETER (XRD) OF SELECTIVE SAMPLES

In this study, selective samples were chosen for the analysis of XRD. Figure 4.4 illustrates the XRD pattern of neat samples i.e. MMT and PBS. Table 4.1 depict the Compositions of the clay containing chemicals. According to Figure 4.4 (a) neat PBS showed an overlapping crystalline XRD diffraction peak at 2θ values of 19.2° , 21.7° , 26.8° and 29.0° corresponding to the (002), (021), $(12\bar{1})$, and (111) planes of the neat polymer (Puchalski et al., 2018; Karakehya, 2021; Phiri, 2023;). The peaks at 2θ values of 36° and approximately 45° are assigned to the amorphous part of the PBS matrix due to an extended side chains present in the backbone of the polymer chains (Phiri, 2023). Figure 4.4 (b) depicts various XRD diffraction peaks for MMT, with the characteristics peak of MMT between 5° to 10° with a (001) reflection. Furthermore, other characteristics reflections at 2θ values of 22.1° , 23.3° , 29.95° , 37.8° , and 62.5° are assigned to the crystalline lattice Structure.

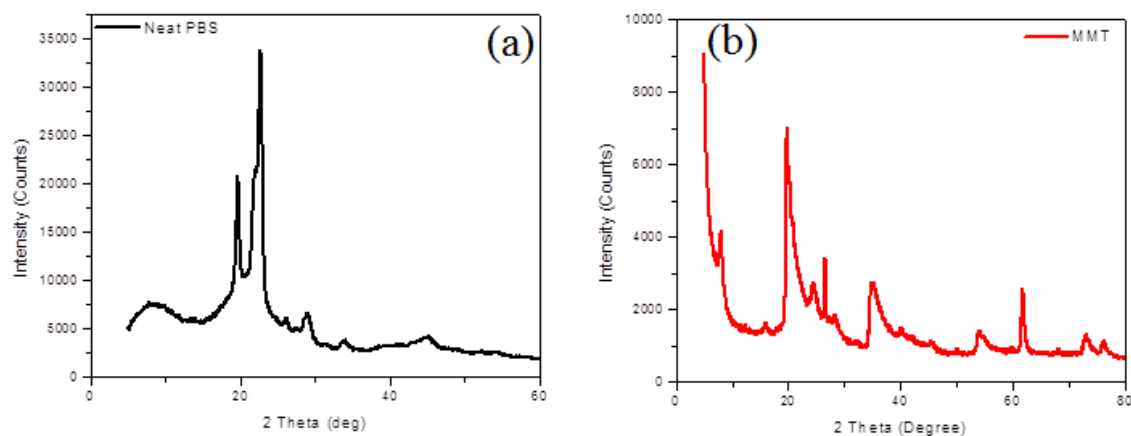


Figure 4.4 XRD patterns of neat PBS and MMT.

Table 4.1 Compositions of the MMT clay (adapted from Alias et al., 2021)

Component(s)	Content
SiO ₂	73.0
Al ₂ O ₃	14.0
Fe ₂ O ₃	2.7
K ₂ O	1.9
MgO	1.1
Na ₂ O	0.6
CaO	0.2

Table 4.1 shows the percentage of elements present in clay and it is evident that silica (SiO₂), Al₂O₃, and Fe₂O₃ appear in high concentrations in the clay. The high concentration of silica is due to the chemical elements emanating from the sand sludge (Katte, 2017). Figure 4.5 shows the schematic representation of the MMT clay showing chemical orientation within the MMT.

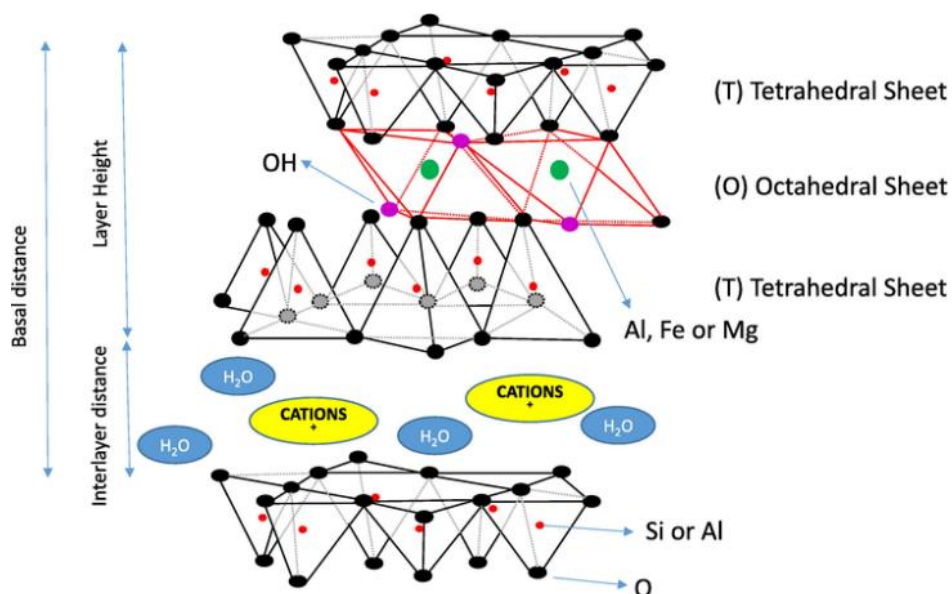


Figure 4.5 Schematic illustration of the MMT clay (Nascimento, 2021).

It is well known that the properties of the clay containing polymer composites depends on the dispersion of the clay within the polymer matrix. In most cases, if the clay is not modified it is very hard to obtain a good dispersion since the clay are mixed with non-polar polymer matrices. Various factors are known to affect the dispersion of the clay within the polymer matrix, i.e., modification of the clay, and preparation method. There are various types of clay dispersion within the polymer materials as shown in Figure 4.6

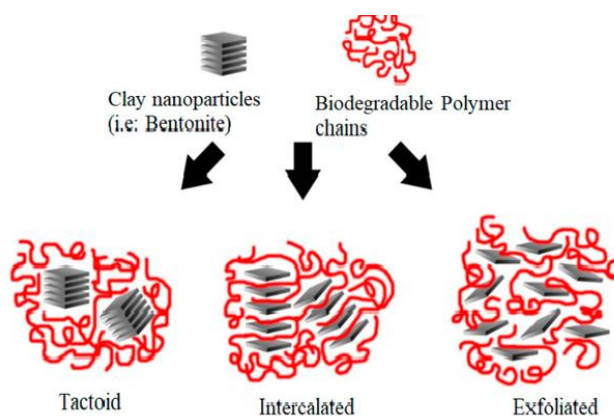


Figure 4.6 Schematic illustration of the clay dispersion/nanocomposite's structure (Mapossa, 2023).

The idea is such that, when the polymer matrix cannot be intercalated into the clay galleries, then there is a possibility of an aggregated composite. However, in an intercalated system, the polymer chains intercalate easily into the clay layers, and such system shows improvement in

properties of the composite when compared with neat polymer matrix. The exfoliated system represents a system whereby the clay layers are uniformly dispersed in the polymer matrix. Figure 4.7 illustrates the XRD patterns of neat PBS, PBS/MSF and PBS/MSF/MMT composites. It is fundamental to understand the peak intensity in order to understand the interaction between the MMT and PBS matrix. There is a reduction in the peak height intensities (viz at $2\theta = 19.7^\circ$ and 21.7° as evident by symbol A) of the composites when compared to neat PBS. The 87/10/3 PBS/MSF/MMT composite showed the lowest peak intensity when compared to both the neat PBS and PBS/MMT composite. According to the (Alsewailem and Tannoglu, 2014), the suppression of the peak intensities is associated with the interaction between the clay and polymer matrix. It seems as if the presence of silane was able to form a chemical link between the maize stalk fiber and the PBS matrix through the siloxane bridge. A possible dispersion taking place in this system in the presence of silane, is either exfoliated or intercalated. One may also add that the presence of EG not analysed herein in the XRD, may have promoted tactoid type of clay dispersion while modified MMT strive to promote either exfoliated or intercalated. Perera et al., 2020 reported similar observation, whereby an increase in silanized organoclay (OMMT-S) at 5phr resulted in less peak intensity compared to the C-5 nanocomposites (natural rubber/ 5 phr of OMMT) and the observation was attributed to a better dispersion of the OMMT-S.

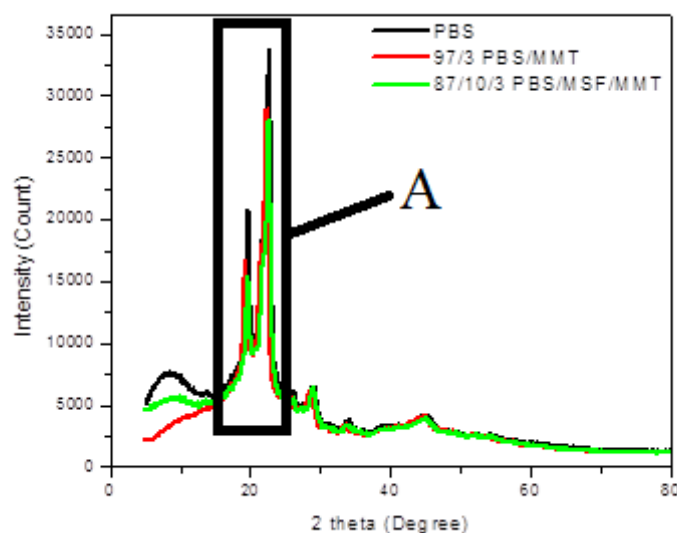


Figure 4.7 XRD graphs for PBS, 97/3 PBS/MMT and 87/10/3 PBS/MSF/MMT.

4.3 FLAMMABILITY PROPERTIES OF THE PBS/MSF AND THEIR HYBRID BIO COMPOSITES

Cone calorimeter is the technique that is used for physical modelling of the combustion of polymeric systems. Fire reaction parameters such heat release rate (HRR), total heat release (THR) and time to ignition (TTi) are reported to evaluate the flammability properties of the biocomposites. Figure 4.8 illustrates the HRR peaks of the 90/10 PBS/MSF and 97/3 PBS/EG biocomposites, with the 97/3 PBS/EG biocomposite showing a lower HRR when compared with the 90/10 PBS/MSF. It is well-known that a reduction in HRR peaks symbolizes a highly flame-retardant system (Hirschler, 2015). The digital images in Figure 4.9 and SEM images in Figure 4.10 provide a clear understanding about the flammability mechanism of these systems, which is based on the strength of the char residues against heat. Lower HRR peak (*viz* 681.8 kW/m²) is attributed to a better char layer, as seen in Figure 4.9(a) and Figure 4.9(b) of PBS/EG due to the presence of the expandable graphite as an intumescent flame-retardant filler. However, as much as the PBS/EG showed a better char layer when compared to PBS/MSF composites, there are still some cracks in this system, as shown by symbol A in Figure 4.10 (a). A high HRR peak (approximately 845.2 kW/m²) for the 90/10 PBS/MSF composites is associated with the high flammability of the maize stalk. This is also associated with a weak char layer as illustrated by Figure 4.9(b) and Figure 4.10 (b). According to Figure 4.10 (b), the char residues of the 90/10 PBS/maize stalk look porous and discontinuous, with such char allowing ease of heat penetration into the system, as a result proving to provide a negative impact on the flammability of the maize stalk/PBS biocomposites. Similar results were reported by Chai et al., 2012, who investigated the flammability properties of the biocomposites systems. In their study, flax fibre revealed a very high peak heat release rate due to fibre being combustible themselves. As for low HRR peaks for graphite composites in this study, similar results were reported by Tomiak et al. (2021), whereby the addition of graphite into the PA6 matrix reduced the burning rate of the composites significantly. The authors reported HRR peaks of: PA6 (899 kW/m²), PA 6 + 10 wt% EG (706 kW/m²) and PA6 + 25 wt% (716 kW/m²) for dry samples in the heat flux of 50 kW/m². This behaviour is associated with the formation of a voluminous, compact, and thermally stable char.

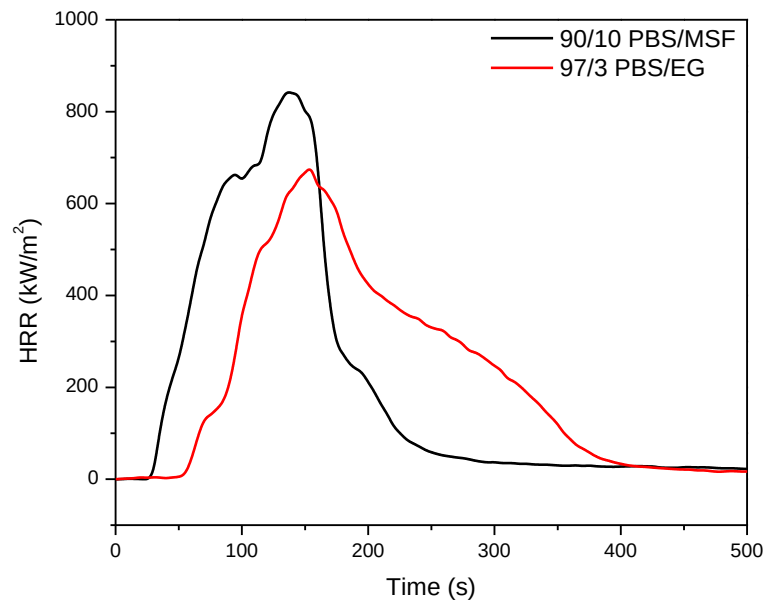


Figure 4.8: Heat release rate (HRR) of 90/10 PBS/MSF and 97/3 PBS/EG composites.

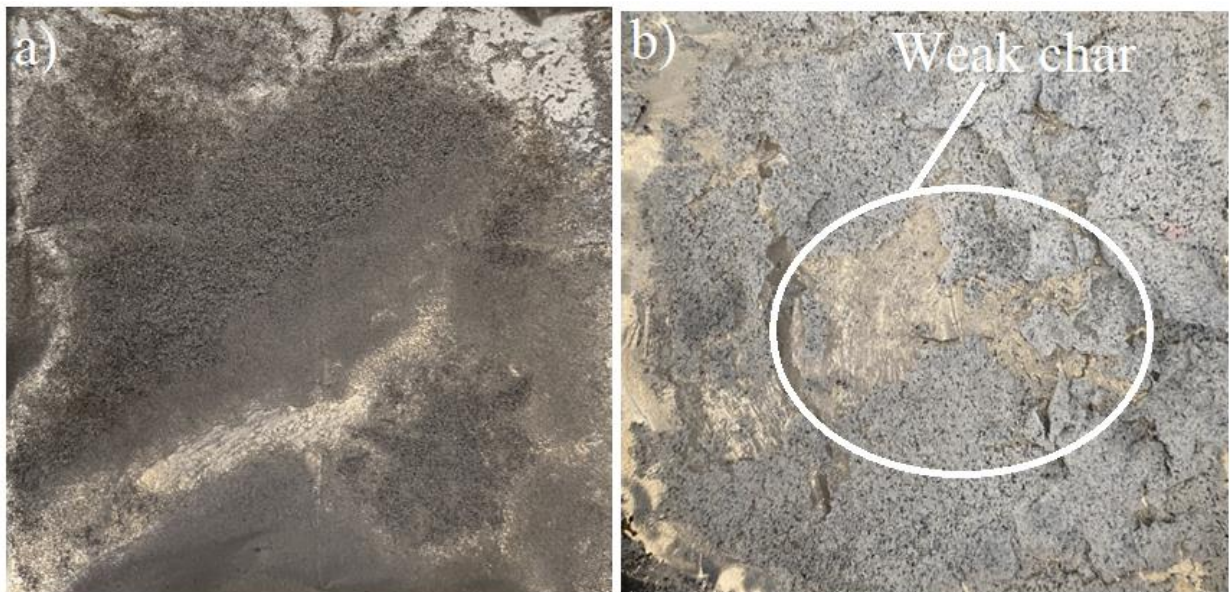


Figure 4.9: Digital images of: (a) 97/3 PBS/EG and (b) 90/10 PBS/MSF.

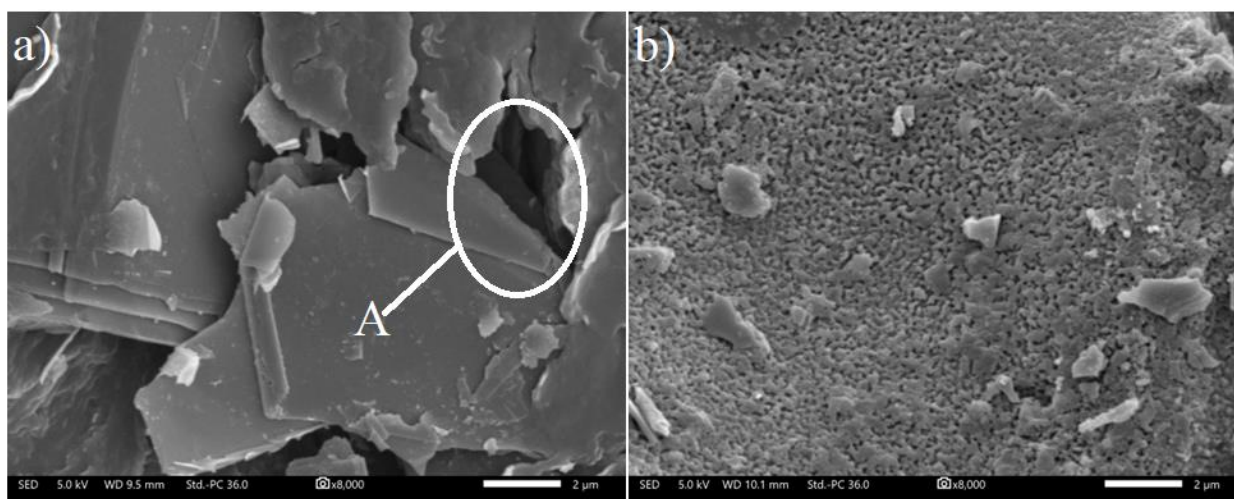


Figure 4.10: SEM images of the char residues of the 97/3 PBS/EG and 90/10 PBS/MSF.

Table 4.2 illustrates a fire performance index (FPI) as a ratio of TTI to PHRR. The higher the FPI value, the less flammable that material is (Nemati et al., 2016). The 97/3 PBS/EG composite showed a higher FPI value ($0.094 \text{ m}^2 \text{ s/kW}$) in comparison to the PBS/MSF biocomposite ($0.045 \text{ m}^2 \text{ s/kW}$) (Table 4.2). The results are in support with the PHRR results that the graphite composite is more flame retardant than the maize stalk biocomposite.

Table 4.2: Parameters from the cone calorimeter analysis of the investigated samples.

Sample ID	PHHR (kW/m^2)	TTI (s)	Time to PHRR (s)	FPI ($\text{m}^2 \text{ s/kW}$)	FIGRA
90/10 PBS/MSF	845.2	38	135	0.045	6.2
97/3 PBS/EG	681.8	64	155	0.094	4.4
94/3/3 PBS/MMT/EG	666.2	45	85	0.068	7.7
87/10/3 PBS/MSF/EG	697.6	95	215	0.14	3.2
87/10/3 PBS/MSF/MMT	682.9	22	75	0.032	9.1
84/10/3/3 PBS/MSF/EG/MMT	589.2	73	90	0.12	6.6

The synergy of the graphite and MMT clay showed a slight improvement in the flammability resistance (Figure 4.11) when compared with the PBS/EG composites as denoted by HRR values of 681.8 kW/m^2 and 666.2 kW/m^2 , respectively. The slight differences in their HRR peaks are also associated with their similar char structures, with the synergy of the graphite and MMT clay showing a slightly better strength than the PBS/EG composite (Figure 4.12 (a) and (b)), accompanied by slightly better flame-resistant property.

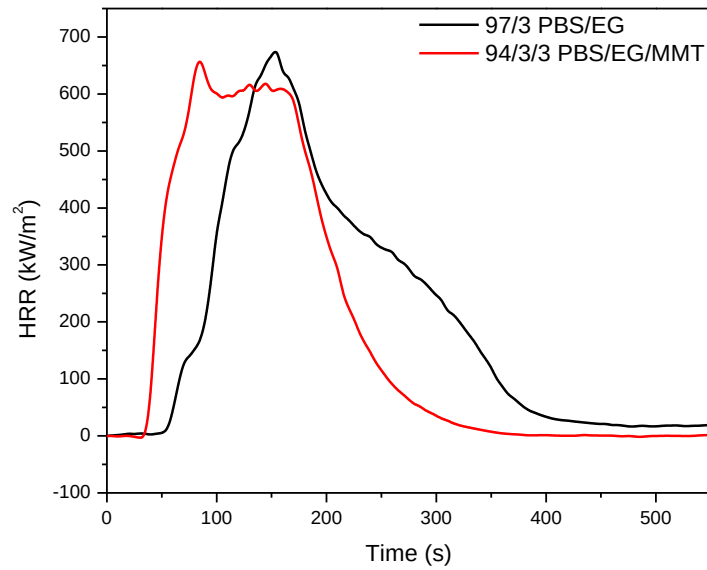


Figure 4.11: Heat release rate (HRR) of the 97/3 PBS/EG and 94/3/3 PBS/EG/MMT.

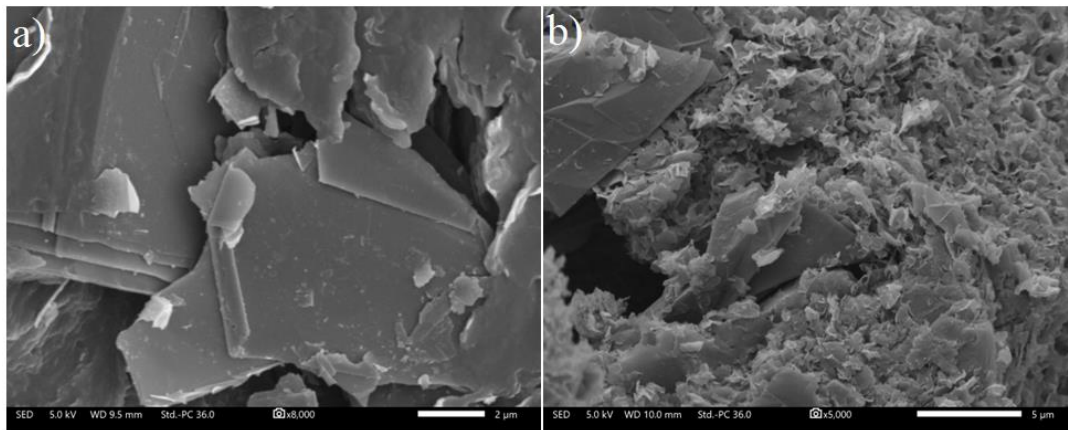


Figure 4.12: SEM char residues of the: (a) 97/3 PBS/EG and (b) 94/3/3 PBS/EG/MMT.

It is noted that the addition of the EG and MMT reduced the HRR of the PBS/MSF composite (Figure 4.13), as a result enhancing the flame resistance of the hybrid biocomposites better than the PBS/MSF. It seems as if the two flame-retardant fillers interacted with MSF to a certain extent whereby their interaction blocks the volatiles from leaving the system and less heat entering the system. A careful inspection of the HRR peaks shows a lower peak for the PBS/MSF/MMT (682.9 kW/m^2) when compared to the PBS/MSF/EG (697.6 kW/m^2). This is associated with two key factors; (i) firstly there is a better interaction between the clay nanoplatelets and PBS/MSF composites when compared to EG. Secondly, there is an enhanced charring effect in the system consisting of PBS/MSF/MMT when compared with the

PBS/MSF/EG hybrid composites (Figures 4.14(a) and 4.14(b)). A compact and continuous char can block volatiles from leaving the system and act as a barrier against heat, as result reducing the HRR thereby enhancing the flame retardancy of the system. According to Figure 4.14(a), the PBS/MSF/EG hybrid composites show some micro-cracks (symbol B), which might have allowed the penetration of heat into the system, as result higher HRR peak when compared to PBS/MSF/MMT.

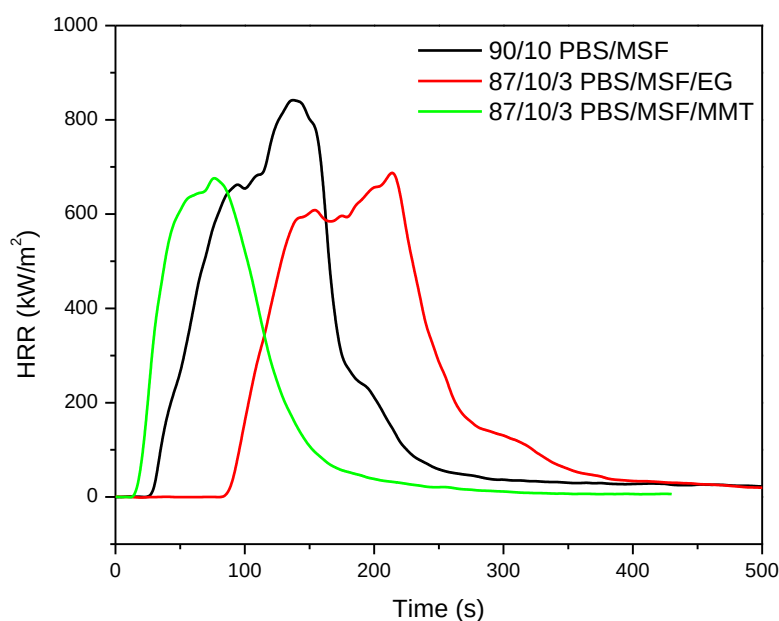


Figure 4.13: Heat release rate of the 90/10 PBS/MSF, 87/10/3 PBS/MSF/EG and 87/10/3 MSF hybrid composites.

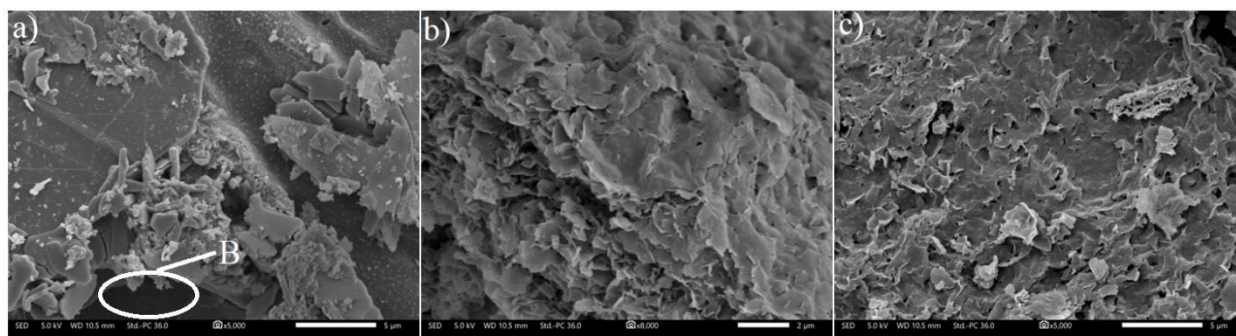


Figure 4.14: SEM char residues of the: (a) 87/10/3 PBS/MSF/EG and (b) 87/10/3 PBS/MSF/MMT and 84/10/3/3 PBS/MSF/MMT/EG.

According to Figure 4.15 and Table 4.2, the hybrid system consisting of PBS/MSF/EG/MMT showed a lower HRR peak of approximately 589.2 kW/m², which was the lowest amongst all

the investigated samples. Furthermore, the very same composite system showed a relatively high FPI value, namely 0.12. A combination of the two parameters indicates that the PBS/MSF/EG/MMT hybrid has better flame retardancy properties amongst all the investigated samples. The flame retardancy of the PBS/MSF/EG/MMT is attributed to the carbonized-ceramic char layer, which happens to be more stable, compact, and continuous (Figure 4.14 c). This type of char residue is resistant to heat and can trap the volatiles from leaving the composite system, thereby enhancing the flame resistance of the composites. Similar results were reported by Nemati et al. (2016), whereby the introduction of the nanoclay prevented the release of volatiles and flammable gases from the wood flour/polystyrene composites. Generally, it is believed that the nanoclay acted as a heat barrier which prevented the penetration of oxygen (O_2) into the composite(s) and as a result reduces the HRR peak, which correlates with the flame retardancy of the composite system. Similar effects of flame retardancy was reported by Liew et al. (2018), where expandable graphite was used as an intumescent filler for palm empty fruit bunch fibre/polymer composite. In this study the flammability of the composites was analysed by the Bunsen burner test. The burning of the composites depended on the concentration of the expandable graphite, with 1% of EG showing the longest flame time, while 5% of expandable graphite revealed shorter burning length which is an indication of the less flame spread. Weak flame resistance at 1% of EG content is associated with insufficient content of the EG, which was not sufficient to protect the overall composite. However, the 3 wt% and 5 wt% contents of EG had better char residues, which resulted in a better flame retardancy.

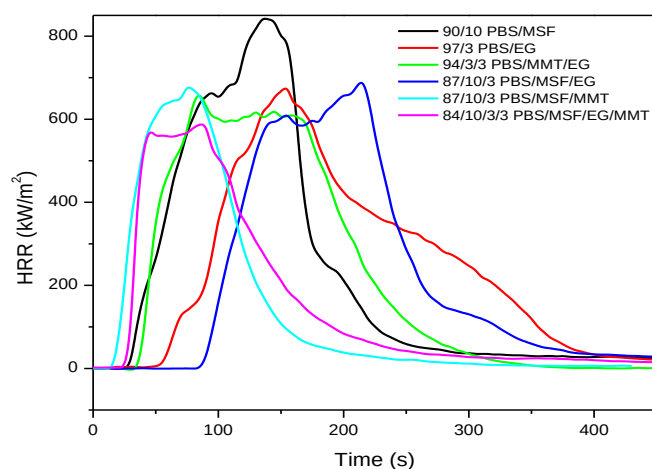


Figure 4.15: HRR peaks of all the investigated samples.

Another parameter of importance in the flammability properties of the analysis by the cone calorimeter is the total heat release (THR). Total heat release (THR) is regarded as the measure of the heat energy during process of burning samples. Figure 4.16 illustrates the THR vs time curves of the PBS/MSF and their hybrid biocomposites systems. The PBS/MSF and PBS/EG composites release high THR values when compared with PBS/MSF/MMT and PBS/MSF/MMT/EG hybrid composites. According to the SEM chars, the PBS/MSF/MMT and 84/10/3/3 PBS/MSF/MMT/EG hybrid composites (Figure 4.14) show more compact, homogenous, and stable chars when compared to other investigated samples, and this type of chars are known to block volatile products catalysing the flame effectively or acting as fuel into the gas phase. As a result, there is a decrease in THR values (Subasinghe and Bhattacharyya, 2014). However, in other composites there seems to be few cracks within the composites, even though the flammability properties depended on the type of composites. Because of the presence of cracks within the char residues in these composites, there is a high penetration of the heat within the composites, which allows the volatiles gases to act as fuel in the system, as a result higher THR values.

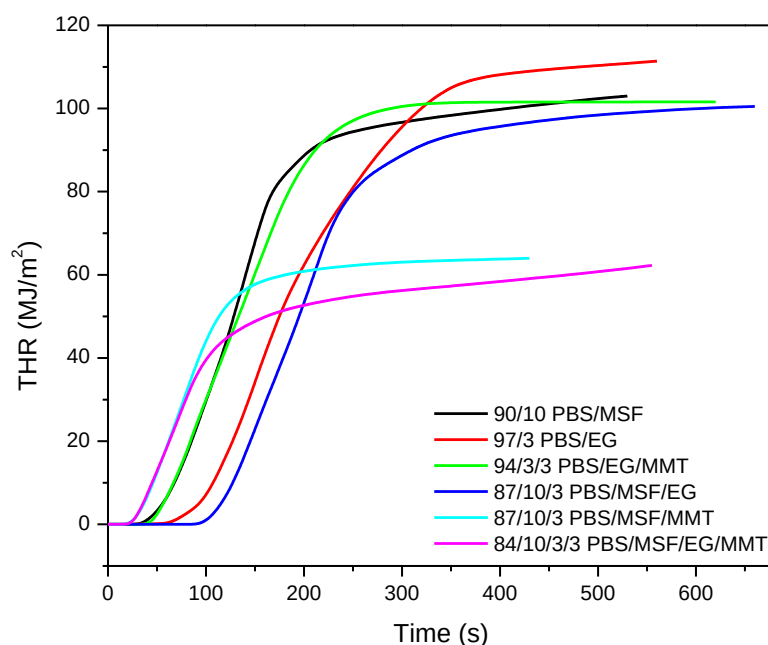


Figure 4.16: Total heat release (THR) of the PBS/MSF composite and their hybrid systems.

One of the toxic gases that are released during burning of polymeric composites is carbon monoxide (CO). If one inhales as low as 200 parts per million in a period of 2-3 hours it may

cause serious health problems such as dizziness, fatigue, and headache. However, a higher exposure of the carbon monoxide may lead to death, memory loss and mental confusion. As a result, there is a need to ensure that there a reduction in the carbon monoxide production. Figure 4.17 depicts the COP vs time for PBS/MSF and their hybrid composites. PBS/MSF seems to show higher production in terms of carbon monoxide (CO), while other composites showed a reduction in the carbon monoxide (CO) production. This may be attributed to the presence of the flame-retardant filler(s) within these composites, even though their performance differs from one system to another. For example, the PBS/MSF/MMT and PBS/MSF/EG/MMT hybrid composites show lower production of carbon monoxide. Due to their compactness and homogenous chars, this type of chars can resist the release of CO and as a result less CO is being released. In all curves, there are two types of peaks that are observed from the graphs. The second peak is related to the reduction in CO production during the acceleration of the flame during an oxidation reaction which in the process, enhances the production of CO₂.

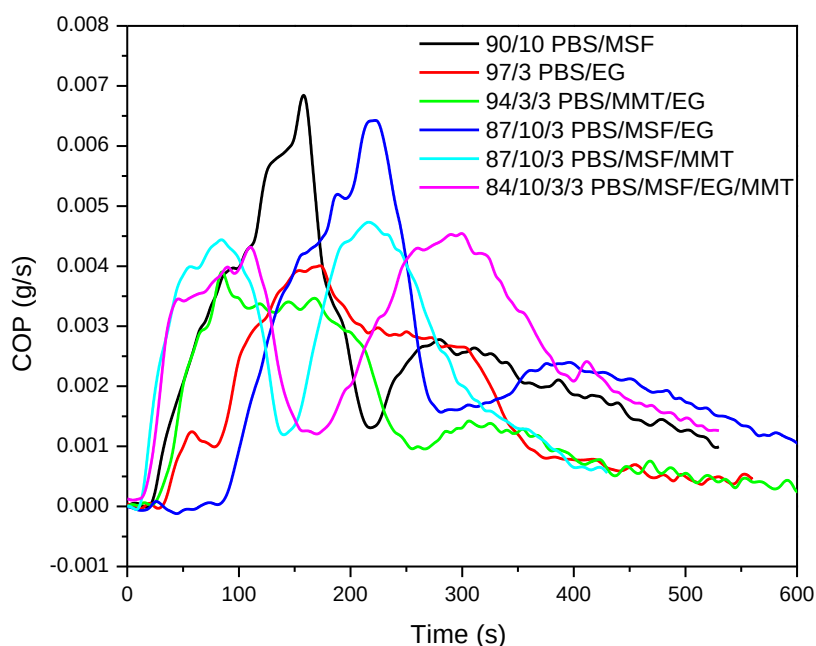


Figure 4.17: Carbon monoxide production of the PBS/MSF composite and their hybrid systems.

4.4 DYNAMIC MECHANICAL ANALYSIS (DMA)

Figure 4.18 depicts the storage modulus vs temperature curves of the neat PBS and 90/10 PBS/MSF composite. The MSF-reinforced PBS bio composite showed a higher storage modulus value(s) when compared with neat PBS (Figure 4.18). Various factors affect the storage modulus of the fibre-reinforced polymer composites, i.e. stiffness of the fillers, crystallinity, dispersion of the fibre, modification of the fibre and the fibre-polymer interaction. The bonding between the fibre and polymer is reported in the literature as the main factor in case of obtaining superior properties (Mohammed et al., 2015). However, in this study SEM images of the 90/10 PBS/MSF bio composites showed poor interaction between the fibre and the biopolymer. Based on the above observation, the main factor playing a role in this case in terms of enhancing the storage modulus and loss modulus (Figure 4.19) of the composites is the stiffness of the maize stalk fibre (MSF).

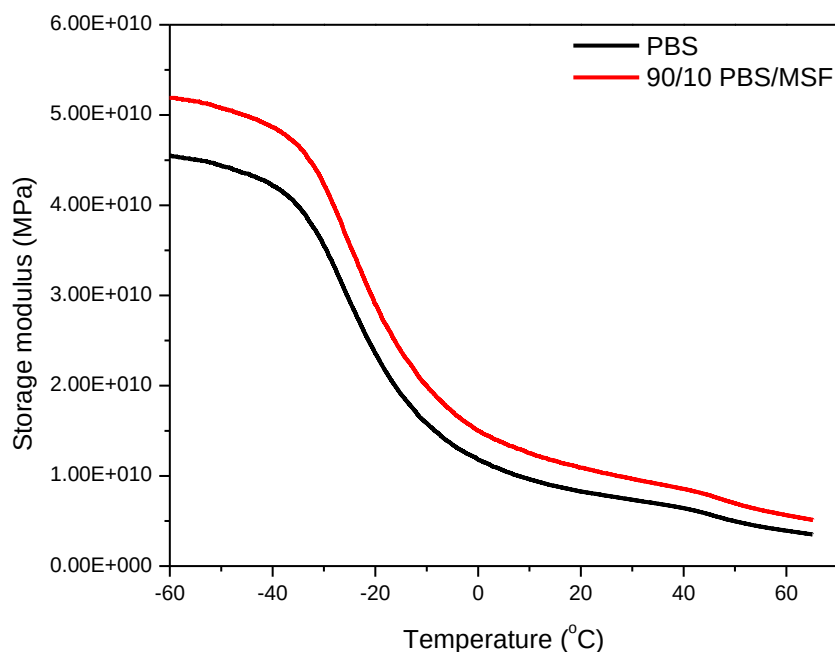


Figure 4.18: Storage modulus of the neat PBS and 90/10 PBS/MSF composite.

The glass transition of PBS and its composite (90/10 PBS/MSF) are observed at a temperature of approximately -30 °C (Figure 4.19). Similar glass transition value is reported by Motlounge et al. (2023), who investigated the properties of the poly (butylene succinate)/hydroxyapatite composites reinforced with chitin. In the glassy region between -60 °C and -20 °C, the polymer chains are frozen. As the temperature increases there is more mobility hence the storage modulus decreases.

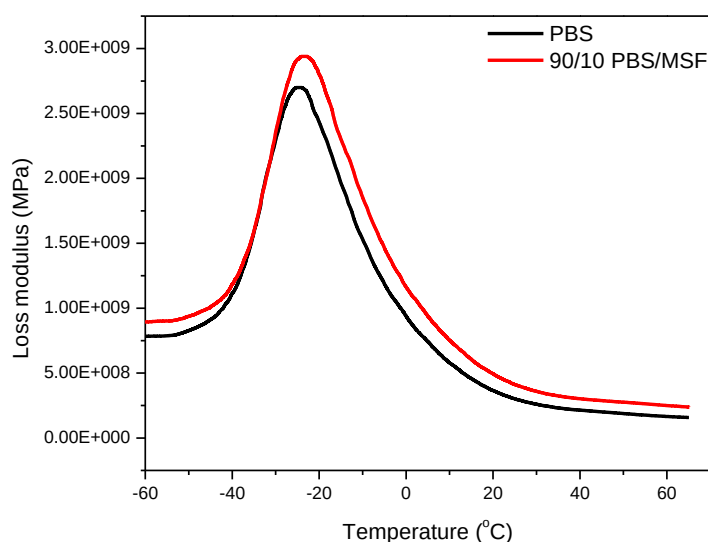


Figure 4.19: Loss modulus of the PBS and PBS/MSF composite.

The addition of montmorillonite clay and EG enhanced the storage modulus and loss modulus of neat PBS (Figure 4.20). The improvement is associated with the immobilization of the polymer chains by MMT and EG. There seems to be a slight difference between the systems, whereby the MMT showed slight improvement in the storage modulus of PBS in the temperature range of -10 °C and 60 °C. This may be attributed to a better dispersion of MMT within the PBS matrix when compared with the EG filler. Another factor which might contribute to an enhancement of the storage modulus is the high aspect ratio of the fillers. Properties of polylactic acid/polycaprolactone /hydrophilic nano clay were investigated. An improvement in storage modulus with the addition of clay is attributed to high dispersion and an improvement in compatibility between the filler and the polymer matrix (Eng et al., 2013) Furthermore, Koosha et al., 2015, report on the storage modulus of the electro-spun chitosan/PVA nanocomposite reinforced with clay. Clay nanoparticles were incorporated into the system with 1% and 3% content. The addition of 1% and 3% showed higher storage modulus when compared with the CS/PVA throughout the temperature range. Furthermore, 3% of clay showed higher values when compared with 1% of the clay-based nanocomposite.

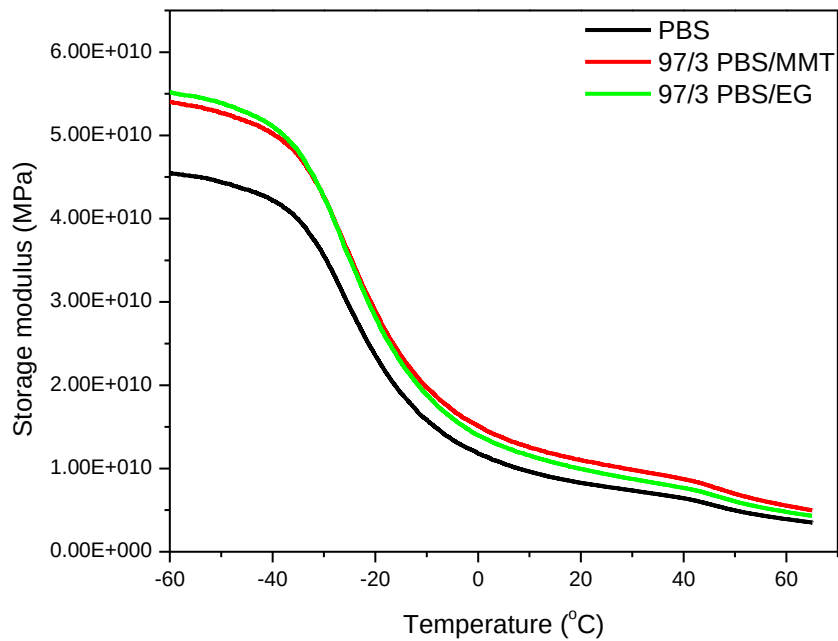


Figure 4.20: Storage modulus of PBS, 97/3 PBS/MMT and 97/3 PBS/EG.

There seems to be less or no shifting in terms of the glass transition (T_g) of the PBS with the addition of clay nanoparticles. The observation is attributed to a smaller amount of clay and expandable graphite in the PBS matrix. A similar observation is reported by Robledo-Ortiz et al. (2019), with the addition of nano clay showing no shift due to a smaller amount of clay utilized in their study. The DMA analysis is also considered when it comes to verifying the interfacial adhesion between the polymer matrix and clay nanoparticles. The PBS/MMT nanocomposite shows a lower T_g peak when compared to the PBS/EG composite. It well known that a good dispersion of the filler within the matrix is assumed to have higher chain segments when compared with poor dispersion of the filler within the matrix. The higher chain segment movement may increase the internal friction and as a result increases the loss modulus. Furthermore, a strong interfacial interaction between the filler and matrix results in lower peak value.

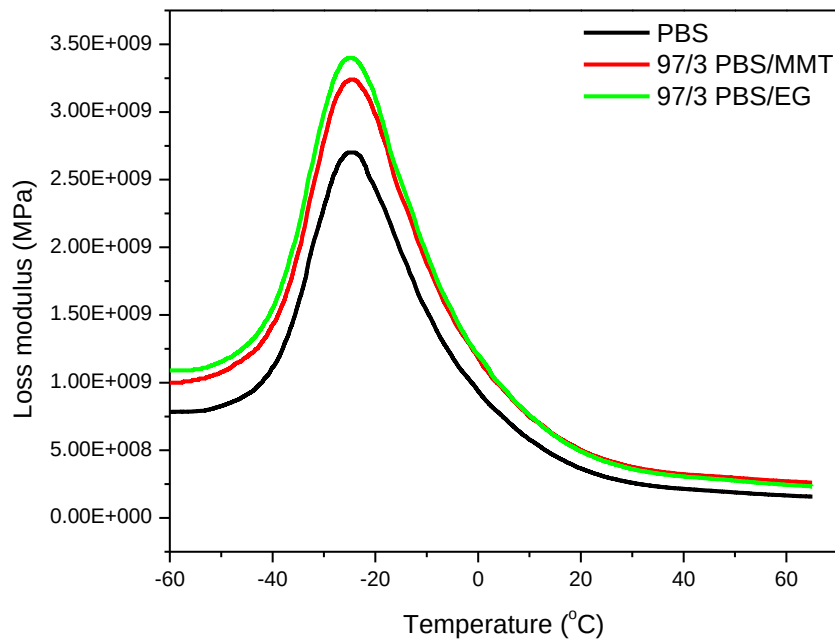


Figure 4.21: Loss modulus of the PBS, 97/3 PBS/MMT and 97/3 PBS/EG.

The incorporation of MMT into PBS/MSF enhanced the storage modulus of the fibre biocomposite (Figure 4.22). The incorporation of EG seems to have little effect on the storage modulus of the PBS/MSF biocomposite. The dispersion of MSF and EG within the PBS matrix were found to be not strong when compared to the PBS/MSF/MMT composite. The incorporation of the 3 wt% of MMT appeared as a fine bonding agent in facilitating the bond between the fibres and matrix by process of the fibre-nano-matrix. The formation of the bond between the filler and polymer matrix in the presence of clay reduces the motion of the polymer chains, thereby enhancing the storage modulus. The storage modulus of the composites system designed from 5 wt% of the nanoclay with untreated and sodium hydroxide (NaOH)-treated jute fibre was fabricated by the hand layup method (Arulmurugan and Venkateshwaran, 2020). The incorporation of the nanoclay is reported to have improved the storage modulus due to an enhanced interaction between the three components, i.e. nanoclay, polyester and fibre. Furthermore, another possible explanation for better enhancement is the presence of the clay nanoparticles, which happen to stiffen the movement of polymer chains and in the process improving the storage modulus. There seems to be little or no difference in terms of the shifting of the glass transition temperature (Figure 4.22b).

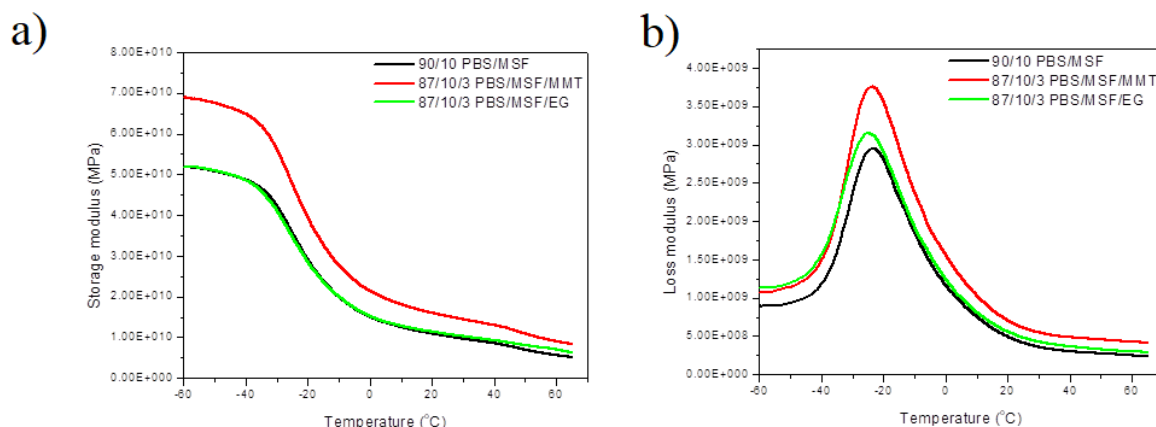


Figure 4.22: Storage modulus (a) and (b) loss modulus of the MSF biocomposite and their hybrid system with EG and MMT.

The impact of EG and MMT on the storage modulus and loss modulus of the PBS/MSF biocomposites is depicted in Figures 4.23(a) and 4.23(b), respectively. The incorporation of EG into the PBS/MSF/MMT reduced the storage modulus of the PBS/MSF/MMT/EG hybrid composites. According to the morphology section, there was a poor fibre dispersion and agglomerates of the EG in the PBS/MSF/MMT/EG hybrid composites, which is the main factor in reduction of storage modulus. It is well reported in the literature that the bonding between the fibre and polymer is the main factor in case of obtaining superior properties (Mohammed et al., 2015). Due to a better stress transfer between the MSF and PBS matrix because of a better dispersion, the storage modulus of the PBS/MSF/MMT is higher than the PBS/MSF/MMT/EG hybrid composites. There is a slight shift in glass temperature of PBS in the PBS/MSF/MMT when compared to PBS/MSF/EG and PBS/MSF/MMT/EG composites (Figure 4.23b). A slight rise in glass transition temperature was ascribed to a strong interfacial interaction between the MSF and PBS matrix in the presence of MMT.

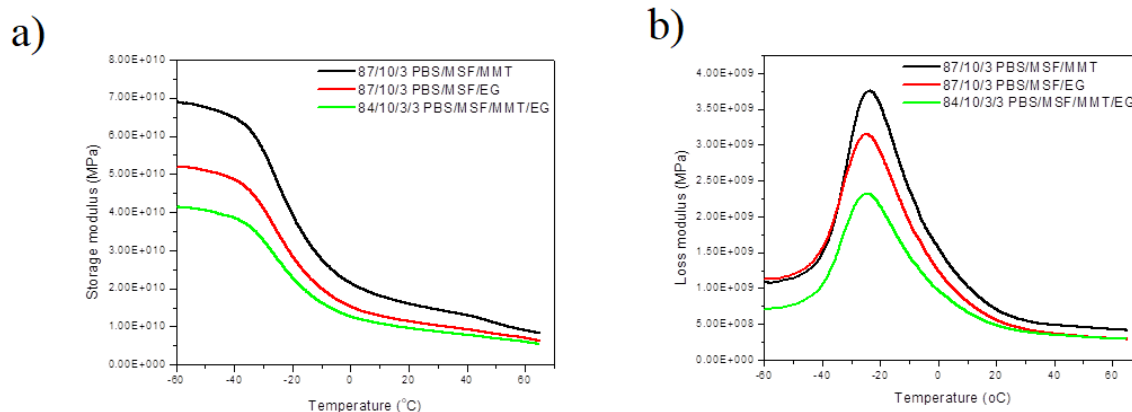


Figure 4.23: Storage modulus of the: (a)PBS/MSF/MMT, PBS/MSF/EG,PBS/MSF/MMT/EG and (b) their loss modulus graphs.

4.5 RHEOLOGICAL PROPERTIES OF PBS AND ITS HYBRID BIO-COMPOSITES

Rheological analysis provides information about the flow, dispersion and distribution state of the fillers, and the interaction between the components of the polymer composites. The evolution of the flow properties as a function of the angular frequency for the neat PBS, binary and hybrid polymer composites is shown in Figures 1(a,b). At lower frequencies, neat PBS shows Newtonian behaviour, whereas shear thinning is observed at higher frequencies. Generally, at lower frequencies ($< 1 \text{ s}^{-1}$), the complex viscosities and storage modulus (G') for the binary polymer composites are higher than those of neat PBS. To be precise, the complex viscosity and G' of PBS in binary composites are enhanced in the following order, 97/3 PBS/EG < 97/3 PBS/MMT < 90/10 PBS/MSF. The higher complex viscosity and G' in the 90/10 PBS/MSF composite than in both the 97/3 PBS/EG and 97/3 PBS/MMT composites are attributed to its higher filler (10 wt.% MSF) loading which offered better restriction in the molecular chain motion of PBS. The differences in complex viscosity and G' of MMT and EG containing binary composites at equal filler loadings are attributed to the characteristics of MMT and EG. MMT is organically modified and has a relatively larger interlayer spacing than EG. This allows for better intercalation of PBS chains, hence better restriction in the molecular chain motion of PBS in the 97/3 PBS/MMT composite than in the 97/3 PBS/EG composite. Introducing a combination of EG and MMT to PBS has a synergistic influence on the complex viscosity and G' of PBS, such that the 94/3/3 PBS/MMT/EG composite has higher complex viscosity and G' than both the 97/3 PBS/EG and 97/3 PBS/MMT. Similar findings were reported by (Mokhena et al.,2021), who attributed their results to the rigidity of both MMT and

expanded graphite in 94/3/3 PBS/MMT/expanded graphite composite, and their enhanced dispersion which imposed better restriction on the molecular motions of PBS chains. Moreover, the enhanced dispersion of expanded graphite was attributed to the nanosized clay, which penetrated between the expanded graphite layers and promoted their separation under shearing during melt processing. In the current study, expandable graphite was used. Therefore, a combination of MMT and expandable graphite achieves a Synergistics effect on flow properties as in the case of expanded graphite. The 87/10/3 PBS/MSF/MMT is Newtonian at lower frequencies and has a higher complex viscosity than the 87/10/3 PBS/MSF/EG composite which is non-Newtonian over the entire frequency and has a larger complex viscosity than neat PBS at lower frequencies. This suggests that there are relatively more entanglements in the 87/10/3 PBS/MSF/MMT composite than in the 87/10/3 PBS/MSF/EG composite. The 84/10/3/3 PBS/MSF/EG/MMT composite shows a very strong shear thinning effect, better complex viscosity and G' than all the other composites. However, the effects in the 84/10/3/3 PBS/MSF/EG/MMT composite are more pronounced at lower frequencies. This suggests formation of a network (solid-like) structure in combination with a better distribution of the fillers in the PBS matrix for the 80/10/3/3 PBS/MSF/EG/MMT composite.

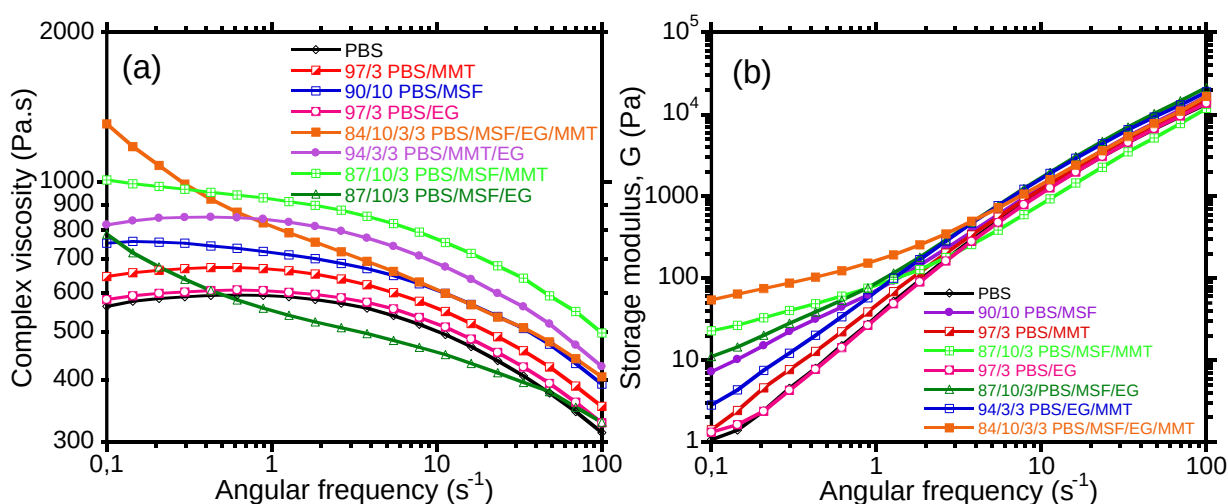


Figure 4.24 Melt rheological properties as a function of frequency: (a) complex viscosity, and (b) storage modulus.

4.6 THERMAL STABILITY OF THE NEAT PBS AND ITS HYBRID BIOCOMPOSITES

Figure 4.25 depicts the TGA curves of neat PBS and PBS/MSF composite. The addition of maize stalk reduced the thermal stability of the PBS in the composite. This may be associated with a poor interaction between the fibre and the PBS, as a result there is free mobility of the free radicals and volatile products, which initiate the degradation of the polymer chains and in the process reduce the thermal stability. Contrary to our results, Mofokeng et al. (2012) report higher degradation temperatures in a case of sisal/PLA composites when compared to pristine PLA matrix. The behaviour is attributed to the ability of the polymer matrix in protecting the fibre from degrading at lower temperatures and the interaction between the two components, i.e. fibre and PLA retarding the degradation process and as such immobilize the diffusion of the volatile products from the composites.

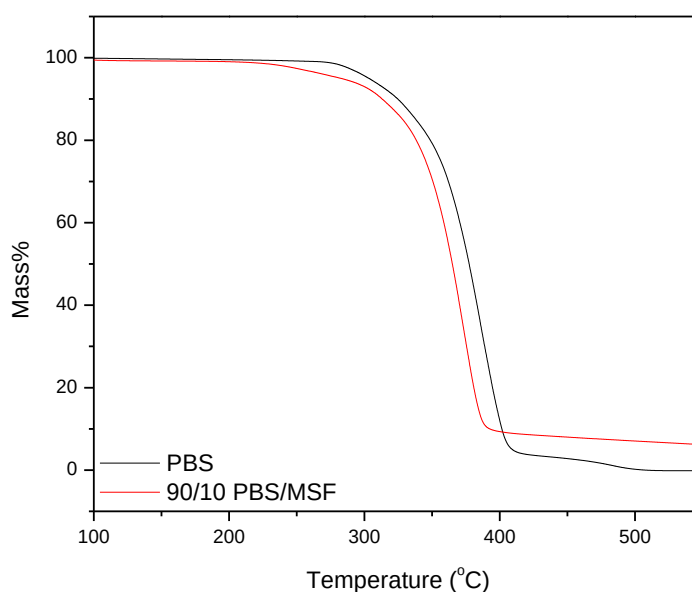


Figure 4.25: TGA curves of neat PBS and 90/10 PBS/MSF.

Figure 4.26 shows the TGA curves neat PBS, PBS/MMT, PBS/EG and PBS/MMT/EG composites. The composites show higher thermal stability than PBS matrix in the temperature range between 300 °C to 350 °C. This may be attributed to the temporary immobilizing of the volatile components by the polymer matrix. However, above these temperatures, the composites show lower degradation temperatures when compared to neat PBS. As the

temperature increases the organic modified clay and the acids entrapped in EG start to diffuse out of the samples and as a result accelerate the degradation of the PBS matrix.

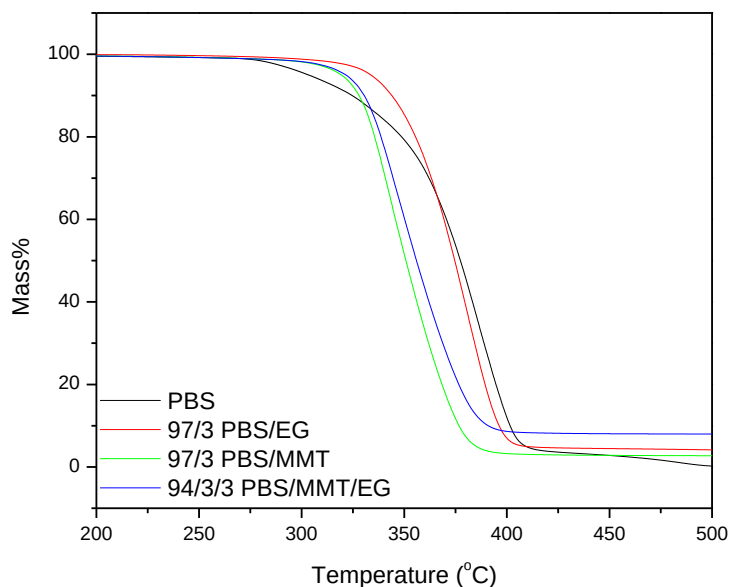


Figure 4.26: TGA curves of neat PBS, PBS/EG, PBS/MMT and PBS/MMT/EG.

Figure 4.27 illustrates the thermal stability of the 90/10 PBS/MSF and their hybrid composites with MMT and EG. The PBS/MSF/EG, PBS/MSF/MMT and their synergy show a higher thermal stability when compared to a 90/10 PBS/MSF composite. This behaviour may be attributed to a strong heat protective layer, which inhibits heat from entering the system and restrain chain unzipping during the propagation activity. The synergy of EG and MMT in the PBS/MSF composites show a slight enhancement in thermal stability when compared to all the investigated samples in Figure 4.27. The two fillers form a strong carbonized-ceramic char layer which retard the degradation process and inhibit the diffusion of the volatile products out of the hybrid composites and in the process enhance the thermal stability of the hybrid composite. A similar observation was reported by Mochane and Luyt (2015), whereby a combination of fillers (expanded graphite, Cloisite 15A, and diammonium phosphate (DAP)) showed higher degradation temperatures at 10% mass loss than a EVA/wax blend and EVA/wax/EG composite. Because of the early evaporation of wax in the absence of combined fillers, their thermal stability was found to be low. However, combined fillers are reported to have interacted with wax and decrease the rate of its diffusion and in the process show improved thermal stabilities.

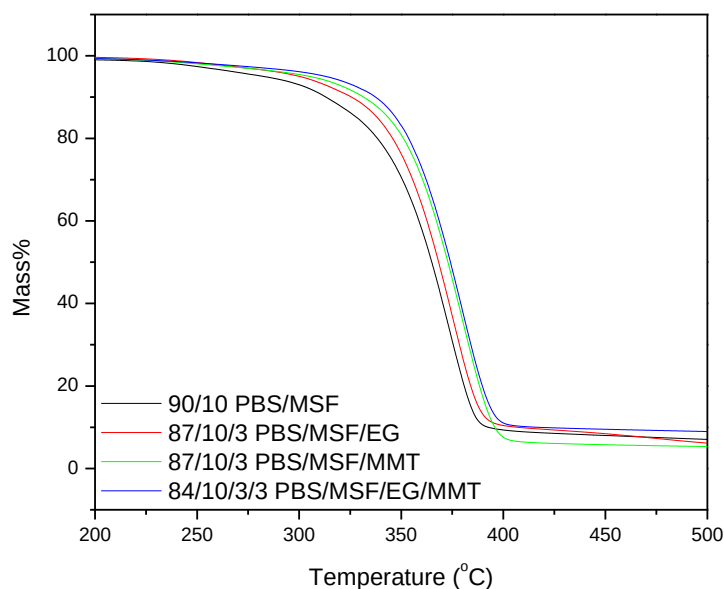


Figure 4.27: TGA curves of neat PBS, PBS/MSF/EG, PBS/MSF/MMT and their synergy.

4.7. Thermal properties of the neat PBS, PBS composite and its hybrid biocomposites

Figures 4.28-4.30 and Table 4.3 depict the DSC data obtained for all investigated samples. It is observed in Figure 4.28 that neat PBS and its MSF composite revealed two endothermic peaks. The two peaks are due to various mechanisms taking place into the PBS, such as the melting re-crystallization, incomplete crystals, and complete crystals (Mokhena et al., 2021). There seems to be no significant changes in the melting temperature of PBS with the addition of MSF. This might be an indication that the MSF had minimum effect in relation to the size of large crystalline domains.

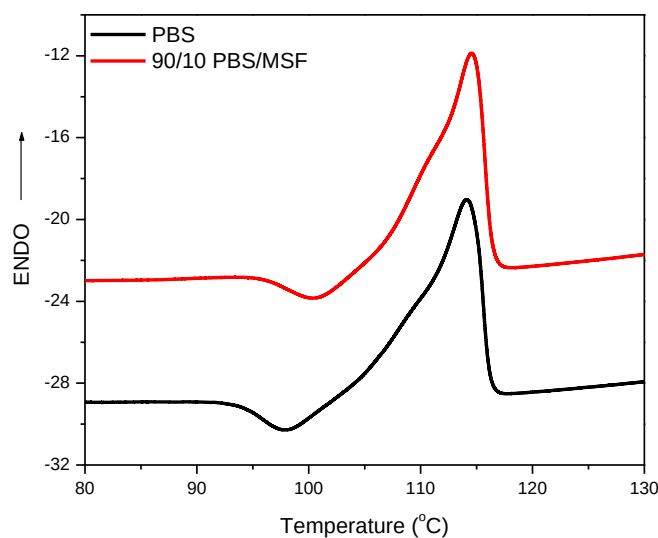


Figure 4.28 The DSC heating curves of PBS and 90/10 PBS/MSF composite.

Similarly with the incorporation of the EG and MMT, there seems to be less change in terms of the melting point of the PBS with the presence of EG and MMT (**Figure 4.29 and Table 4.3**). Furthermore, the synergy of the two fillers also had a minimum effect on the melting temperature of neat PBS and PBS/MSF composite (**Figure 4.30 and Table 4.3**). However, there is a decrease in the melting enthalpies of the composites and hybrid composites when compared to neat PBS. This is obvious since the melting enthalpies are associated with the amount of polymer in the composites and/or hybrid composites (Dikobe et al., 2009). The addition of the MMT, MSF, and EG decreases the amount of the polymer in the sample, as a result the melting sizes with their corresponding enthalpies are also expected to decrease correspondingly.

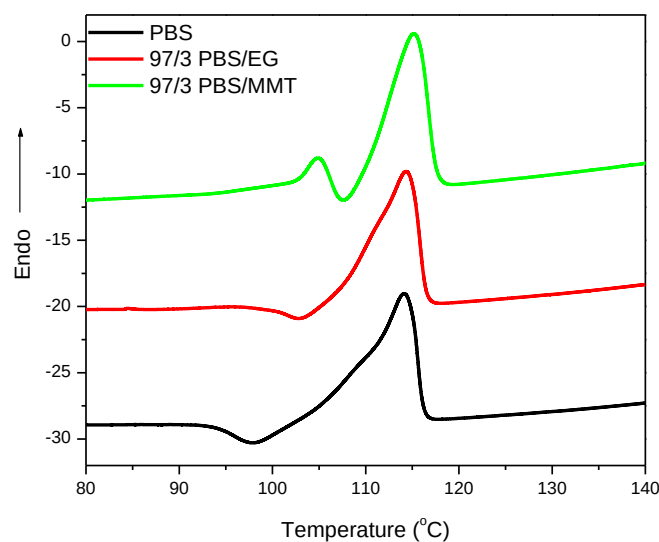


Figure 4.29 The DSC heating curves of PBS, 97/3 PBS/EG and 97/3 PBS/MMT composite.

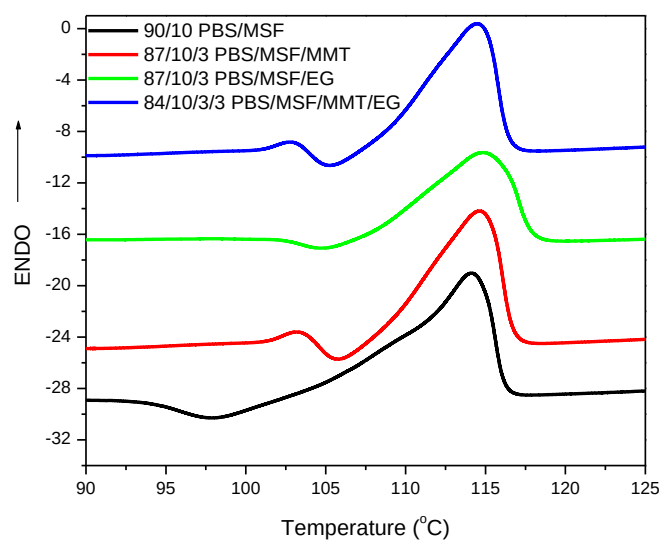


Figure 4.30 The DSC heating curves of 90/10 PBS/MSF, PBS/MSF/MMT, PBS/MSF/EG and PBS/MSF/MMT/EG

The normalized of melting enthalpies recorded in Table 4.3 were calculated according to equation 4.1 below:

$$\Delta H_m^{Norm} = \frac{\Delta H_m}{w} \quad (4.1)$$

Whereby, the ΔH_m is represented as the experimentally observed melting enthalpies of the neat PBS, while w is the weight fraction of PBS in the composite(s). An assumption in this calculation is based on the fact that the MSF, MMT, and EG does not influence crystallization of PBS. According to Table 4.3, the observed melting enthalpies were lower than the normalized or calculated melting enthalpies. The observation may be due to the ability of the fillers in reducing the chain mobility of the PBS as a result decreasing the crystallinity of the composites and hybrid composites. The degree of crystallinity was calculated by the following equation:

$$X_c = \frac{\Delta H_m^{Norm}}{\Delta H_m^o} \times 100 \quad (4.2)$$

The 100%-degree crystallinity of PBS used in this study for calculation of the X_c is 110.3 J/g. According to Table 4.3, there is a reduction in the degree of crystallinity with the addition of fiber and flame-retardant fillers (*viz* EG and MMT). The reduction in crystallinity is related to the immobilization of the polymer chains during the crystallization process and the crystal growth of PBS matrix. It is noticed that the degree of crystallization of the MMT contained samples shows lower values when compared with EG containing and neat PBS samples (Table 4.3). A better interaction between PBS and MMT, in its composites and its hybrid systems immobilized the PBS chains in the process impeding the crystallization of the PBS. This is very interesting since majority of the studies showed that the clay nanoplatelets acted as a nucleating agent. However, researchers reported on the antinucleating behaviour at low content of the clay, i.e., 1, 2 and 3%, which is similar to the observation reported in the current study. This behaviour was associated with better dispersion and inhibition of the polymer chain mobility Raghavendra et al., 2012.

Table 4.3 Summary of the thermal properties of the investigated samples.

Sample ID	T_m (°C)	ΔH_m (J/g)	ΔH_m^{Norm}	X_c
PBS	114.12	68.68	68.68	62.27
90/10 PBS/MSF	114.56	61.47	68.30	61.92
97/3 PBS/EG	114.34	61.43	63.33	57.42
97/3 PBS/MMT	115.50	56.09	57.83	52.43
94/3/3 PBS/MMT/EG	115.48	55.17	58.69	53.20
87/10/3 PBS/MSF/MMT	114.63	50.31	57.83	52.43
87/10/3 PBS/MSF/EG	114.83	48.86	56.16	50.92
84/10/3/3 PBS/MSF/EG/MMT	114.47	50.84	60.52	54.87

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CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

The idea of the study was to produce a hybrid biocomposite system that has a higher performance than the PBS/MSF composites for automobile applications. The high-performance hybrid biocomposite is expected to replace non-biodegradable/natural fibre composites in advanced applications. Furthermore, the purpose of selecting maize stalk was also to reduce the agro-waste. This is to avoid the burning of the stalks, which might lead to a decrease in soil fertility that has a negative impact on the growth of the crops. It can be concluded that the utilization of maize stalk as a reinforcing natural fibre within the biopolymer matrix improved the dynamic mechanical properties of the PBS matrix, irrespective of its dispersion in the biopolymer matrix. This is an indication that the stiffness of the fibre played a key role in improving the storage modulus of the PBS. However, the flammability of the PLA was found to increase with the addition of the fibre, which one may conclude that it is associated with a high flammability of the fibres. The incorporation of the MMT and expandable graphite improved the flame resistance of 90/10 PBS /MSF composite, even though the MMT composites seem to show better flame-resistant properties. This behaviour is associated with better dispersion of the MMT within the system due to hydroxyl groups of the clay and the carbonyl groups of the biopolymer matrix forms a very strong hydrogen bond. A similar observation can be concluded in terms of the dynamic mechanical properties of the PBS/MSF/EG and PBS/MSF/MMT, whereby the MMT showed superior properties. It is realized that the flammability properties of this system are based on the compactness and continuous chars. Irrespective of the dispersion of the fillers within the PBS matrix, the 84/10/3/3 PBS/MSF/EG/MMT showed a stronger, compact, and continuous char layer when compared to all the investigated samples. Similarly, this particular hybrid system (PBS/MSF/EG/MMT) showed better thermal stability when it was compared to 87/10//3 PBS/MSF/MMT, PBS/MSF/EG and 90/10 PBS/MSF composite. In conclusion, one can state that when EG-based composites are compared with clay-based composites, the clay composites show better properties. However, a synergy of the EG and MMT into the PBS/MSF seems to have shown better overall properties. For future purposes, there is a need to study the synergy of the various clays with the maize stalk fibre, since there seems to be a good affinity between the clay, MSF, and PBS matrix. Furthermore, it could be interesting to investigate the hybrid system consisting of natural fibres, i.e. maize stalk, and another fibre-reinforced biopolymer matrix in the presence of a green flame-retardant filler(s). The hybrid systems that contain

MMT show superior properties compared to the systems that contain EG. As result the hybrid system with MMT can be suggested for use in automotive applications. For future recommendations, in order to verify the results that are obtained in cone calorimetry, techniques such as limiting oxygen index and vertical burning test UL94 might be used for flame resistance properties