PREPARATION AND CHARACTERIZATON OF MAIZE STALK FIBER/CALCIUM CARBONATE/POLYLACTIC ACID HYBRID BIOCOMPOSITES FOR ADVANCED APPLICATIONS

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BLOEMFONTEIN

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DECLARATION OF INDEPENDENT WORK

DECLARATION WITH REGARD TO INDEPENDENT WORK

I, **Lwazi Glen Magunga**, student number _____, do hereby declare that this research project submitted to the Central University of Technology, Free State for the Master of Health Sciences in Environment, 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 it 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.

_____ 08/12/2023

SIGNATURE DATE

DEDICATIONS

I would like to express my heartfelt gratitude to YAHWEH for the wisdom, provision, and purpose bestowed upon me throughout my life, thus shaping me into the person I am today.

This thesis is dedicated to my wife, Andiswa; and our daughter, Milani Magunga; and my parents: Julias and Joana Magunga.

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ABSTRACT

Maize holds a crucial position as a vital food crop, playing a significant role in both the economy and food security of South Africa. Given its status as a stable food, the production of maize is notably high, resulting in a substantial amount of maize stalk waste. Effectively addressing this waste has become a pressing concern, sparking the development of various solutions. One particularly promising approach involves the integration of maize stalk waste with polymers to bolster the mechanical properties of polymers. Among the plethora of polymers available, PLA stands out as one of the most widely utilized polymers, renowned for its biodegradability, and low toxicity. Its inherent limitations however include: restricted heat resistance, brittleness, and susceptibility to moisture absorption, and thereby present an opportune scenario for reinforcement to enhance its overall properties. This study investigates the potential of using maize stalk fiber (MSF) and Calcium carbonate ($CaCO_3$) as a reinforcing filler in a PLA matrix. The properties of interest in this study were morphology, flammability properties, dynamic mechanical analysis, rheological properties, and thermal stability. 5%, 10%, 15% and 20% of the fiber dosages were incorporated into the in the PLA matrix. Higher filler dosages (i.e 20%) resulted in high fiber pullouts in the PLA matrix. The incorporation of $CaCO_3$ further improved dispersion and enhanced fiber-polymer interactions. Incorporation of 20% MSF increased the peak heat release rate (pHRR) of PLA from 554.5 kW/m^2 to 697.4 kW/m^2 whilst the incorporation of calcium carbonate reduced the pHRR to 483.3 kW/m^2. Increasing $CaCO_3$ dosage improved the thermal stability of PLA. Higher storage modulus was observed for hybrid composites containing 15 and 20% MSF. The results of the study showed that the $CaCO_3$ and MSF fillers have the potential to be used as reinforcing agents in PLA biocomposites for various applications.

Keywords: Maize stalk; polylactic acid; calcium carbonate; flammability properties; degradation

Research outputs

Published journal articles and chapters:

1. **L Magunga**, M Mohapi, A Kaleni, S Magagula, M.J. Mochane, MT Motloung. Bioplastics and biocomposites in flame-retardant applications. In Book: Handbook of Bioplastics and Biocomposites Engineering Applications. John Wiley & Sons, Inc. 2023 (Scrivener Publishing LLC), 573-593. https://doi.org/10.1002/9781119160182.ch25

Manuscripts under review:

1. **L. Magunga**, S.I. Magagula, M.T. Motloung, K. Lebelo and M.J. Mochane. Cellulose reinforced polyamide composites: effect of preparation method on composite properties. Cellulose Chemistry and Technology 2023 (Accepted).
2. **L. Magunga**, S.I. Magagula and M.J. Mochane. Recent progress on the development and applications of maize stalk fiber reinforced polymer composites. (In progress).

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LIST OF ABBREVIATIONS

$CaCO_3$	Calcium carbonate
CO_2	Carbon dioxide
DMA	Dynamic mechanical analyses
FAO	Food and Agriculture Organisation
HDPE	High density polyethylene
HRR	Heat release rate
LDPE	Low density polyethylene
µm	micron meter
MAH	Maleic anhydride
MLR	Mass loss rate
MSF	Maize stalk fiber
Mpa	MegaPascal
nm	nanometers
NaOH	Sodium hydroxide
OMMTs	Organic modified montmorillonites
PCL	Polycaprolactone
PGA	Polyglycolic acid
PHA	Polyhydroxyalkaonates
PHBV	Poly -hydroxybutyrate – co-hydroxy valerate
PHR	Peak heat release

PDLA	Poly-D-lactic acid
PDLLA	Poly-DL-lactic acid
PLA	Polylactic acid
PLLA	Poly-L-lactic acid
POSS	Polyhedral oligomeric silsequixonane
PP	Polypropylene
PVC	Polyvinyl chloride
RFI	Resin film infusion
RTM	Resin transfer moulding
SEM	Scanning electron microscopy
Si	Silica
SiO_2	Silica oxide
TiO_2	Titanium dioxide
THR	Total heat release
TGA	Thermogravemetric analysis
VaRTM	Vacuum assisted resin transfer moulding
ZnO	Zinc Oxide

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Chapter 1: Introduction

1.1 General Background

The principles of sustainability, industrial ecology, eco-efficiency, green chemistry, and engineering are being incorporated into the development of the next generation of materials, products, and processes as a result of a growing understanding of the interconnectivity of global environmental factors [1]. The need for innovative materials and products that are environmentally friendly and independent of fossil fuels is being driven by the depletion of petroleum supplies as well as the expansion of environmental legislation. This new shift in thinking fits composite materials, especially "green composites,"[2]. Natural fibers are superior since they are easily accessible, flammable, biodegradable, and non-toxic. Natural fibers' high moisture absorption and low processing temperature have a negative impact on how they are used [3]. Natural fibers do not produce any toxic fumes when they're processed, and they do not wear down the machinery either. Additionally, natural fibers' primary drawbacks are their natural hydrophilicity, and high flammability, which hinder their use as reinforcement in polymers. Due to their hydrophilic nature, they absorb a lot of moisture which leads to weak matrix-fiber interface adhesion and fiber dispersion [4]. The incorporation of natural fibers with other materials to form polymer composites is not only done to improve the polymer properties, but as a solution to a growing agricultural waste management issue.

In 2017 the food and agriculture organization of the United Nations (FAO) reported that the agricultural sector is accountable for 21% of greenhouse gases emitted globally [5]. The World Commission on Environment and Development's Report warned of the severe environmental catastrophe brought on by the population growth's acceleration, which has raised demand for natural resources needed for economic development [5, 6, 7]. With the demand or population growing exponentially each year the supply also increases which means that waste also increase massively every year. In 2017, the FAO reported that due to the development of agricultural soils, the green revolution's technical impact on productivity, and the rapid population growth, agricultural food production grew more than 3 times in the last 50 years [5]. The concept of a new model of sustainable development, which entails the integration of economic, social, and environmental variables to guarantee the welfare and improvement in the quality of life of all people, was established by the Rio Declaration on Environment and Development [5-8]. The establishment of these guidelines and their thematic issues related to science and technology,

climate, energy, water etc. meant that much efforts need to be put into the utilization of agricultural residues with other materials to form quality end products that can be utilized by people and the formation of these products should include innovation from science and technology and also solve issues related to climate, water etc. Utilizing bio-based materials is an alternate strategy for creating ecologically friendly products.

For the development of natural fiber-reinforced composites, a deeper insight of the chemical nature and surface adhesive bonding of natural fibers is required. Natural fibers' constituents include waxes, lignin, pectin, cellulose, hemicellulose, and water soluble compounds. Even for the same type of fiber, composition might vary depending on growth conditions and fiber extraction procedures [9]. Natural fibers are usually utilized with thermosets and thermoplastics. Thermoset and thermoplastic polymers are non-biodegradable. Natural fibers used in combination with both thermoset and thermoplastics do not produce entirely biodegradable composites; however, natural fibers combined with biodegradable matrix such as Polylactic acid (PLA), Polyglycolic acid (PGA), Poly-b hydroxyalkanoates (PHA), and Polycaprolactone (PCL), PHBV do produce biodegradable composites. Natural fibers improve the elastic modulus and tensile strength of polymer composites compared to virgin polymers [10-12]. Researchers and various industries have recently become more interested in biopolymer-based composites because of their renewability and sustainability as well as their versatility for a variety of applications [13]. Although they have serious limitations such as brittleness, and a high rate of crystallization; biocomposites made of natural fibers and biopolymers are the safest alternative to synthetic polymers [14].

Among various biopolymers, Polylactic acid (PLA) is one of the most studied due to its exceptional physical and mechanical characteristics, renewability, and biodegradability. PLA has gained significant attention for conventional uses including packaging materials, fiber production, and most recently; composites are used for a range of practical and mechanical applications. Among the most potential candidates for future improvements, PLA holds a prominent place on the market for eco-friendly polymers [15]. PLA is a thermoplastic aliphatic polyester that is produced from non-fossil renewable natural resources by fermentation of polysaccharides or sugar, such as those extracted from corn, potato, cane molasses, and sugar-beet. This enables the biological cycle to come to full circle (**Figure 1.1**) which starts with the photosynthesis process right through to the biodegradation of PLA [16]. PLA is considered as one of the most prevalent and commercial bioplastics worldwide, which had an estimated production of 800,000 tons in 2020 [17]. PLA is used in various industries such as healthcare, textile, packaging, and so on [18, 19]. Due to its biodegradability, PLA provides several End-

of-Life options, including mechanical recycling, chemical recycling, landfilling, and industrially composting [20-21]. Relatedly, PLA can be categorized into: (i) Racemic PLLA (Poly-L-lactic Acid), (ii) Regular PLLA (Poly-L-lactic Acid), (iii) Poly-D-lactic Acid (PDLA), and (iv) (Poly (DL-lactide acid) (PDLLA) [22]. The D- or L- enantiomers of PLA are comparable as they are made from the same renewable resource (lactic acid: $C_3H_6O_3$) [22, 23]. The idea of producing PLA is well-liked since it accomplishes the aim of producing inexpensive, and non-petroleum plastic. Notably, the adaptability of PLA as a bioplastic, and the fact that it breaks down spontaneously when exposed to the environment are two of its major advantages. For instance, a PLA bottle dumped in the ocean would normally break down after six to twenty-four months [24]. Table 1.1 shows the advantages and disadvantages of PLA, while Table 1.2 illustrates the properties of the PLA.

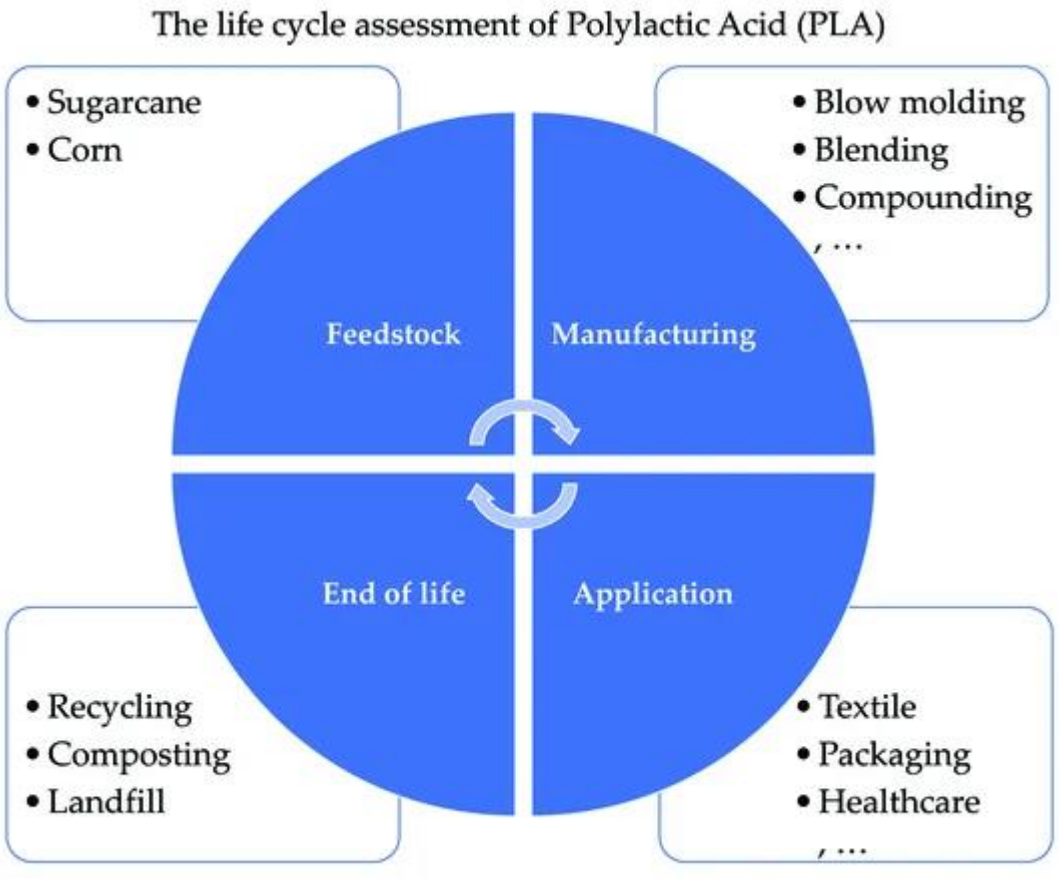

Figure 1.1 Life cycle of PLA. Adapted from MDPI open access [24].

Table 1.1 Advantages and disadvantages of PLA [25-27].

Advantages	***Disadvantages***
Made from renewable resources	Low thermal stability
Compostable	Higher permeability
Recyclable	Low to average impact strength
Low cost	Poor toughness
Good compatibility	Hydrophobic
Good tensile strength and ductility	Slow degradation rate (low crystallinity)

Table 1.2 Properties of PLA. Content summarized from the following references [15] [28] [29].

Density	1.24 g/cm^{-3}
Melting point	170 to 180 degrees Celsius
Glass transition temperature	50 to 80 degrees Celsius
Heat deflection temperature	52 degrees Celsius
Tensile strength	50 Mpa
Flexural strength	80 Mpa
Shrink rate	0.37-0.41%
Impact strength	96.1J/m

1.2 Natural fiber reinforced composites vs natural fiber reinforced hybrid biocomposites

Composites comprising of natural fibers and polymers have certain limits, and they are difficult to process [30, 31]. Additionally, composites that incorporate both the matrix and reinforcement from renewable resources have also been produced, thus making the composites totally degradable [32]. Nonetheless, under high humidity or in aquatic conditions, these totally

biodegradable bio-composites lack the desired mechanical characteristics and durability, thus restricting their usage in advanced applications. Hybrid composites with multiple reinforcements or matrices have been developed. These hybrid composites are made by combining two or more fibers or other reinforcing elements [32]. Similarly, hybrid bio-composites can be viewed as a proportionate total of the separate constituents within a matrix that achieves a balance of the constituent's strengths and limitations [33]. The disadvantages of one reinforcement could be compensated with the advantages of another reinforcement through hybridization. As a result of a suitable material selection, cost- effective hybrid composites with the essential qualities might be obtained. In addition to the aforementioned benefits, hybrid composites are lighter than non-hybrid synthetic fiber-reinforced composites due to the lower density of natural fibers [34]. According to literature, a hybrid composites is influenced by variables such as the fiber-matrix interface, fiber length, chemical composition of reinforcing agent, nature of the polymer matrix, and hybrid design [35, 36]. Different hybrid composites that have unique properties have been developed and used by researchers since they have the potential to provide better properties than single filler polymer composites. These hybrid composites were grouped into: i. Synthetic-natural fiber hybrids; ii. Natural-natural fiber hybrids; and iii. Inorganic fillers /fiber Hybrid nanocomposites [4]. The inorganic filler/natural fiber/polymer hybrid system are preferred because they have the tendency to enhance the properties more than their counterpart's hybrid systems. Different inorganic fillers have been incorporated into the polymer/fiber systems in order to improve the properties. The inorganic fillers included talc, graphite, carbon nanotubes, clays, and calcium carbonate [37-39]. Amongst the above-mentioned inorganic fillers, calcium carbonate is preferred due to its ability to increase the tensile modulus, impact strength, impact energy and surface gloss of polymers [40, 41]. In this study, a hybrid system consisting of PLA/Maize stalk/calcium carbonate was fabricated in order to overcome the limitations of the PLA/Maize stalk fiber composites.

1.3 Research aim

The aim of this study is to prepare maize stalk fiber/calcium carbonate/Polylactic acid hybrid biocomposite for advanced applications.

1.4 Research objectives

The objective is:

- To investigate the effect of maize stalk on the properties (viz. morphology, flammability, rheological properties and dynamic mechanical analysis) of the PLA matrix.
- To investigate the effect of calcium carbonate on the properties of PLA/MSF composites.
- To find the optimum ratio between the three components of the hybrid system i.e. PLA: MSF:$CaCO_3$.

1.5 Thesis outline

The outline of this thesis is as follows

Chapter 1: General introduction

Chapter 2: Literature review

Chapter 3: Materials and methods

Chapter 4: Results and discussion

Chapter 5: Conclusion and future recommendations

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Chapter 2: Literature review

Recent progress on the development and applications of maize stalk fiber reinforced polymer composites

This chapter has been submitted for publication as:

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2.1 Abstract

In many countries, such as South Africa where maize is the stable food for most communities, an increase in population results in higher maize production, and consequently, more maize stalk waste. In order to control the accumulation of the maize stalk waste, the maize stalk was fed to livestock as animal fodder, disposed-off in landfills and incinerated. However, nowadays, the amount of maize stalk waste in the environment can be attributed to inability to feed them all to livestock, or be disposed-off in landfills. Meanwhile, incineration is a health hazard because it causes air pollution which may cause serious lung diseases for human beings, acid rain, and global warming in the long run. As a result, researchers have come up with a more environmentally friendly way of managing maize stalk. That is, using maize stalk fiber as a reinforcement in polymer composites, which can be used in various other industrial applications such as automotive parts for the automotive industry, packaging, building, and construction materials. This does not only manage the accumulation of maize stalk waste in the environment, but it also improves the agricultural economy since maize stalk is an agricultural by-product. The main aim of this chapter is to review the latest literature on maize stalk fiber reinforced polymer composites and improvements that have been done on these composites for specific applications.

Keywords: Maize stalk; reinforcement; landfill; agro waste; polymer

2.2 General overview: Introduction

Due to the increasing population in many parts of the world, waste management is increasingly becoming a serious issue. This is because an increase in population results in more waste generated. The accumulation of waste in the environment poses serious environmental risks. Therefore, the amount of waste disposed-off in landfills needs to be reduced urgently. Interestingly, agricultural waste (or agro-waste) takes up a huge chunk of the waste generated. This means that farms have become huge contributors to the waste problem. Once the harvesting season is over, farmers either leave some of the crop residues on the land as waste or use them as energy sources. Notably, one of the most abundantly available and underutilized agro-wastes is maize or corn stalk. In most parts of the world, only 40% of the maize stalk is used as animal fodder whilst the rest is discarded as waste [1]. Maize stalk is also classified as a natural fiber. Like most natural fibers, maize stalk is composed of 38-40% cellulose, 28% hemicellulose, 7-21% lignin and 3-7% ash content. Maize stalk also consists of extractable components such as pectin waxes and oils. These extractable components are usually present in small quantities [2, 3]. Nowadays, research and development has been focused on using agro-waste materials like maize stalk as reinforcement materials in high performance polymer composites. This is due to their abundant availability and eco-friendliness [4]. Over the last few years, maize stalk has become the most popular agro waste material for the development of high-performance polymer composites. This is because maize stalk has a high specific strength and modulus, low density, renewable and no health risks [3]. Due to properties such as lightweight, high specific weight, high durability, high stiffness and strength, maize stalk-based polymer composites may be used in a wide range of structural applications especially in the aerospace and construction industries [4].

Chicongo *et al*. [3] investigated the effectiveness of using maize stalk as reinforcement in natural rubber. In that study, the curing and physic-mechanical properties of the composite were determined as a function of filler loading. The results were compared with the results obtained from using commercial grade hydrated silica as reinforcement. Based on torque and scorch results, maize stalk reinforced natural rubber composites exhibited a good processing safety. Moreover, based on mechanical properties and statistical treatment of data, maize stalk reinforced composites consisting of 20 phr treated maize stalk exhibited optimum mechanical properties. Moreover, the tensile strength of the composites was 22.4 MPa, and the elongation

at break was 404% and the hardness was 55%. These results were closely comparable with those of composites reinforced with commercial hydrated silica. This proved that maize stalk has the potential to be used as reinforcement in natural rubber. The results also proved that the chemical modification of the maize stalk resulted in the enhancement of interfacial adhesion between the fiber and the natural rubber matrix. The poor compatibility between hydrophilic fibers and a hydrophobic polymer matrix results into a weak interface. A weak interface may lead to poor mechanical properties, high moisture sensitivity, swelling and dimensional instability. In order to improve the interfacial bonding strength between a fiber and matrix, the fiber surface needs to be chemically modified. Additionally, chemical treatment imparts a hydrophobic nature to the fiber and therefore enhances its compatibility with the polymer matrix. Furthermore, chemical modification has a direct influence on the fiber's structure and it also changes the fiber's composition. The chemical modification may also reduce the water absorption tendencies of the fibers which in turn improves the fiber's bonding capability with polymer matrices. Various methods of fiber modification such as acetylation, alkaline treatment, and silane hydrolysis have been extensively investigated [1].

Over the past few years, there has been a growing interest towards improving the performance of composites. The idea of hybridizing materials in composites in a common matrix has been under development since 2013. Hybridization has the potential to strike a balance between more attractive characteristics and cost for a composite structure, which is challenging to achieve with a single kind of reinforcement [5]. Currently, nanofiller particles are rated as high-potential filler materials for improving mechanical and physical properties of polymer composites [6]. Moreover, the homogenous dispersion of nanofiller particles increases the matrix-filler interfacial area in the composites. This high matrix-filler interfacial area is responsible for improving properties such as relaxation behaviour, mechanical, molecular mobility and thermal properties of the composites [7, 8]. Furthermore, nanofillers with larger aspect ratios (ratio of largest to smallest dimension) are of considerable interest and are a better reinforcement in the production of nanocomposites [7]. During the preparation of nanocomposites, nanofillers are generally incorporated on a weight basis [9]. The properties of the resultant composite are greatly influenced by the specific surface area of the nanofillers which shows uninterrupted influence. Nanofillers are classified as either organic or inorganic in nature. Examples of inorganic nanofillers are silica (SiO_2), titanium dioxide (TiO_2), calcium carbonate ($CaCO_3$) and polyhedral oligomeric silsequixonane (POSS). Contrastingly, nanofillers such as coir nanofiller, carbon black and cellulosic nanofillers are classified as

organic nanofillers because they are organically derived and are naturally present. Hybridization based on the combination of natural fibers and nanofillers in the matrix results in the reduction of water absorption properties and improved mechanical properties [10]. This review is aimed at covering the latest developments on the utilization of maize stalk waste in polymer composites as a means of agro-waste management. Emphasis will be placed on the preparation, and applications of maize stalk fiber-based composites.

2.3 Maize stalk or corn stover: Origin and properties

Maize stalk or corn stover is a by-product of maize. After maize has been harvested for economic purposes, its by-products such as maize stalk are left as waste in the field **(Figure 2.1**). This is because maize stalk has no direct use. In South Africa, a small portion of the maize stalk is fed to livestock, whilst the majority of it is either left in the field or dumped into landfills as explained in this document. This shows that the maize stalk is somehow underutilized. In order to ease up space in the landfills, the maize stalk ends up being incinerated. Incineration is very harmful to the environment as it produces poisonous and harmful greenhouse gases, which cause global warming and acid rain in the long run. Maize stalk has a high carbon to nitrogen ratio, which makes it to be resistant to soil microbial degradation, and therefore prolonging its degradation in the soil [1].

Figure 2.1 A picture showing maize stalk lying as waste in a maize field [11], obtained with permission from Elsevier.

Maize itself is an important source of carbohydrates, and it serves as a stable food for at least most of the southern African population. Therefore, an increase in population means an increase in maize production and hence an increase in maize stalk waste as explained elsewhere in this document. Since the growth in population cannot be easily controlled, more knowledge is needed about possible value addition strategies to agricultural wastes like maize stalk. Maize stalk consists of 38-40% cellulose, 28% hemicellulose, 7-21% lignin and 3-7% ash content as the main components of the plant cell wall. It is also composed of other components such as pectin, waxes, and oils in small quantities just like any other natural fiber. Maize also has excellent properties such as a high specific strength and modulus, low density, renewable and has no health risks [3]. All these properties qualify maize stalk to be used as a reinforcement material in polymer composites. Furthermore, in order for the maize stalk to be used as a reinforcement, it needs to be reduced into nanomaterials or nanofibers. For this, various methods such as alkaline treatment, physic-chemical treatment and enzyme treatment just mention a few have been used to isolate the different components of maize stalk [1]. The research focus nowadays is to use green methods to utilize maize by-product constituents.

2.4 Physical processing of maize stalk

Maize or corn stalk is made up of stalk rind or shell and stalk pith as illustrated by **Figure 2.2** below. The stalk pith is mainly composed of proteins, fat, hemicellulose, and sugar [12]. Contrastingly, the stalk rind or shell is mainly composed of cellulose and lignin, which are highly admired for their excellent strength and toughness properties. Due to its excellent strength and toughness properties, the stalk rind or shell is mainly used in the preparation of maize stalk fiber-based composite materials. Furthermore, the stalk pith is loose and has poor strength. As a result, it is removed when preparing maize stalk fiber reinforced composites or otherwise it will be difficult to achieve good mechanical properties [13].

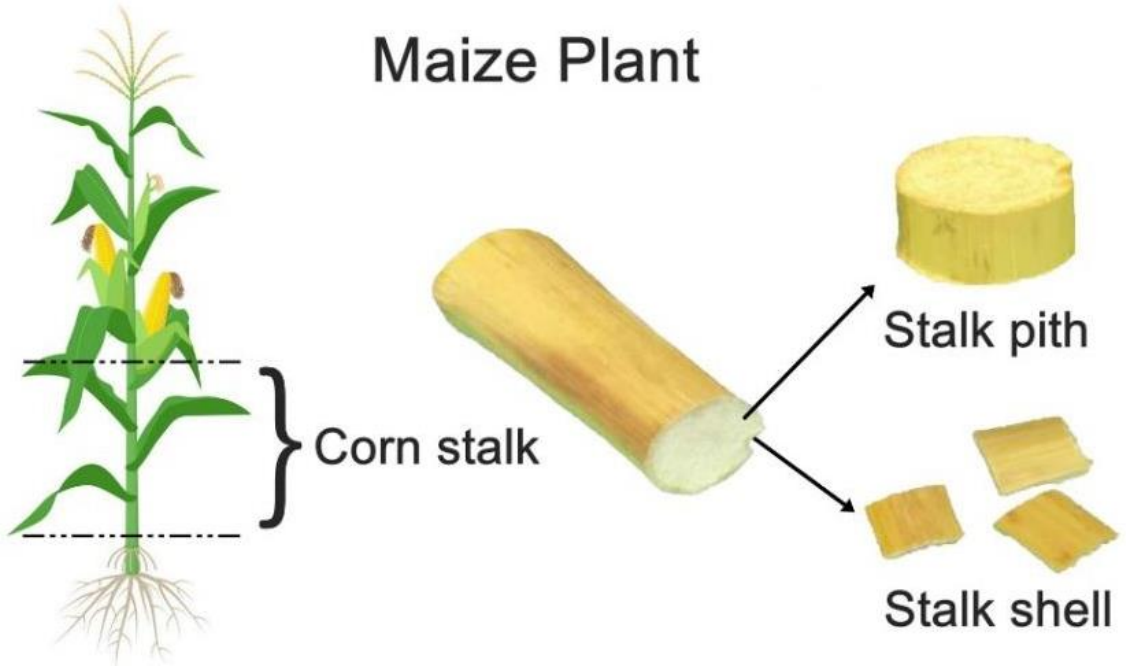

Figure 1.2 An illustration of the maize stalk rind or shell and maize stalk pith [14] (from MDPI open access).

During the preparation of the maize stalk fiber reinforcing materials, the maize stalks are firstly selected and then subjected to a rind-pith separation process. During the rind-pith separation process, the rind is separated from the pith. The separated maize stalk rind or shell is then washed with water. Next, the washed maize stalk rind is dried in an oven to a constant temperature of 70 °C. **Figure 2.3** shows a clear picture of the separated maize stalk rind or shell. Next, the dried maize stalk rind is cut into strips of approximately 0.5 – 1.5 x 3 – 5 cm and then crushed into a powder using a crusher. Finally, the comminuted maize stalk strips are then poured into a high speed mixer and further comminuted for a fixed amount of time [13].

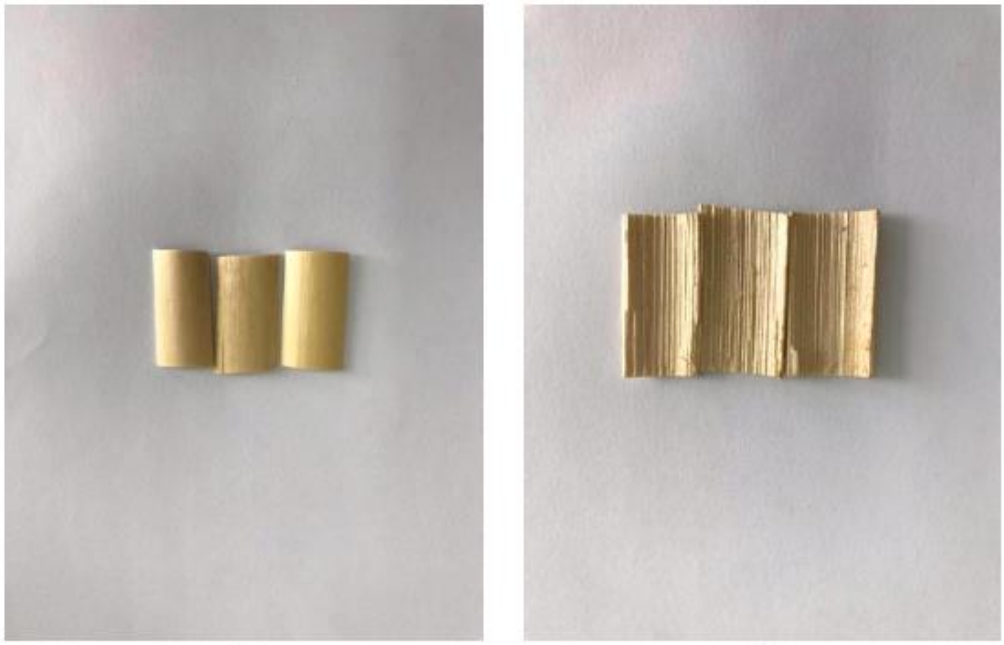

Figure 2.2 A picture showing the (a) exterior and (b) interior of maize stalk rind or shell separated from the maize stalk pith [13] (from MDPI open access).

2.5 Chemical modification of maize stalk fiber

Maize stalk is one of the agricultural waste materials that is getting the most attention from researchers nowadays. However, the major drawback of using maize stalk fiber is its extremely low compatibility with polymer matrices [15]. This is caused by the barriers created by the complex cell wall of the maize stalk fiber [15]. In order to improve its compatibility with polymer matrices therefore, the fiber surface is pretreated using various surface modification methods before preparation [15]. There are many surface modification methods that have been used to modify the physical or chemical structure of natural fibers like maize stalk fiber. These modification methods include isocyanate treatment, acrylation, latex coating, permanganate treatment, acetylation, silane treatment, and peroxide treatment just to mention a few. These methods have achieved various levels of success in improving fiber strength, fiber fitness, and fiber-matrix adhesion in natural fiber composites. However, some of them are not feasible to use because they require advanced and expensive technology. Based on that factor, chemically treating natural fibers is one of the most commonly used methods to modify their physical and chemical nature. Chemical treatment basically involves immersing the natural fiber in a medium at a specific concentration for a specific amount of time. **Figure 2.4** shows the steps involved during the chemical treatment of maize stalk fiber. The chemical treatment of the

maize stalk fiber involves a physical and chemical process as shown by **Figure 2.5.** From **Figure 2.5,** it is clearly visible that the physical and chemical processing affect the chemical composition and physical appearance of the maize stalk fiber. Chemical treatment depolymerizes the lignin and hemicellulose fractions of the maize stalk fiber which increases the accessibility of cellulose [15]. Just like lignocellulosic fiber, maize stalk fiber consists of cellulose, hemicellulose, and lignin. These fractions are connected together by hydrogen bonds. The hydrophobic – hydrophilic interactions between the natural fiber and polymer matrices are critical to the composite's properties, which are mostly dependent on the ratio between cellulose and hemicellulose in the fiber. **Table 2.1** below shows a summary of the various chemical modification methods used during the preparation of maize stalk fiber reinforced polymer composites.

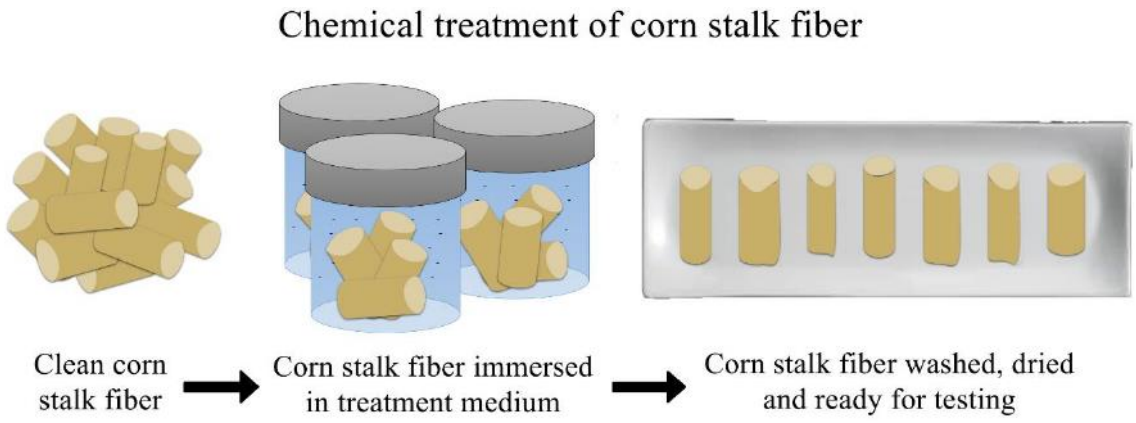

Figure 2.3 Steps involved during the chemical treatment process of maize stalk fiber [16] (from IOP open access).

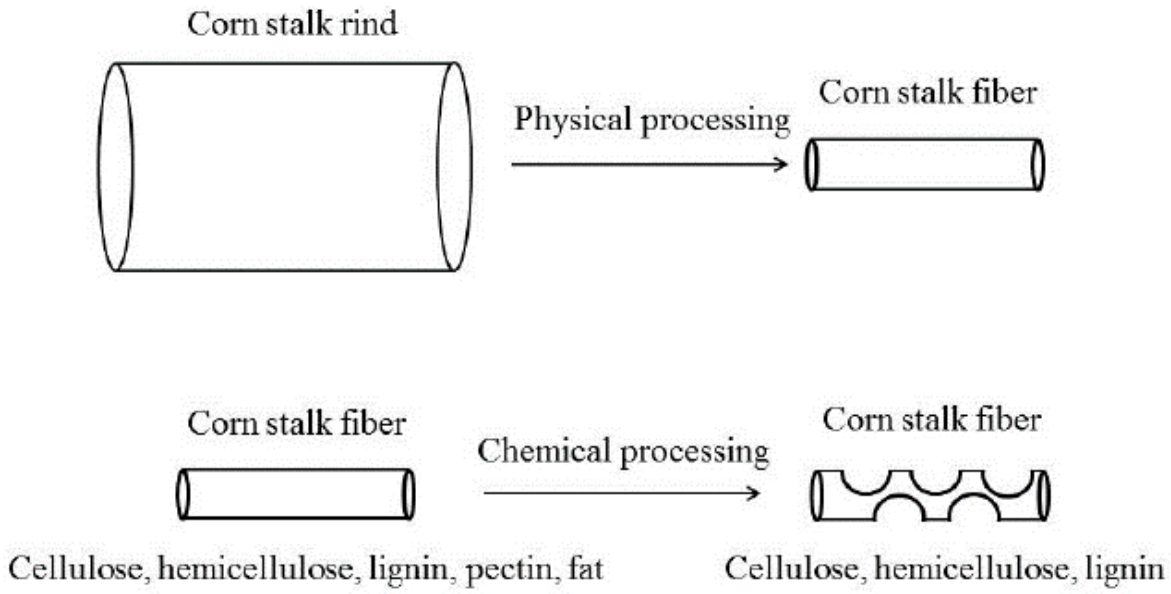

Figure 2.4 Physical and chemical processing of maize stalk fiber [13]. MDPI Open access.

Table 2.1 A summary of the various chemical treatment methods used during the preparation of maize stalk fiber reinforced polymer composites.

Maize fiber/polymer composite	**Preparation**	**Chemical modification**	**Properties**	**Ref**
Maize fiber/Epoxy	Compression molding	15+ sodium hydroxide	• The lignin content of alkali-treated maize fibers was lower than that of raw maize fibers. • The water retention capacity of alkali-treated maize fibers was more than twice that of raw fibers. As a result, alkali-treated maize fibers can be used for water-absorbing purposes.	[17]
Maize stalk cellulose fiber/ clay geopolymer	Injection molding Dry mixing	98% purity sodium hydroxide,	• For a sole maize stalk cellulose fiber, tensile strength of 1184 MPa and young modulus of 16 GPa were attained. • The Pure geopolymer had a compression strength of 16 MPa and a compression strength of 27 MPa for 1 weight percent fiber loading, which was close to the 28 MPa compression strength of geopolymer made from fly ash and 1 weight percent cotton fiber loading that cured for 28 days.	[18]

Maize fiber/ high density polyethylene	Drying, cutting, mixing, compounding, pelletizing, and injection molding were the six stages used to create the composites.	0.9% Maleic anhydride	• The results revealed that as the temperature was raised, both thermal effusivity and the factor rose dramatically. Maize fiber dispersion and adhesion in a high-density polyethylene matrix were found to be of high quality.	[19]
Maize hull fiber/ Poly ethylene	Injection molding	5% Maleic anhydride	• Tensile studies found that if no modifier was applied, the tensile parameters (strength and modulus) of composite materials dropped, but the strength of modified composite materials nearly equaled that of the matrix, and therefore the modulus was improved.	[20]
Maize straw fiber/Polypropylene carbonate	Hot pressing	2.5 mol/L sodium hydroxide and 0.4 mol/L sodium sulfite	• When compared to the untreated maize straws, the granular maize straws had significantly higher tensile strength (598.6 MPa), elongation at break (6.2 percent), Young's modulus (16.6 GPa), and specific strength (434 MPa).	[21]
Long maize stalk fiber/Polylactic acid	Injection molding	None	• The resulting composites have lower mechanical properties than Polylactic acid due to poor interfacial interaction between the fiber and the polymer matrix. Tensile strength was reduced by 29 to 40%, strain at break was reduced by 47 to 73 percent, stress at break	[22]

			was reduced by 23 to 57 percent, and impact strength was reduced by 14 to 42 percent as a result of the untreated maize fiber	
Al-Si-Mg/Maize stalk particulate fiber	• Injection molding • Melt blending	• Carbonization of maize stalk	• At 8 and 10 wt. percent carbonized maize stalk, the tensile strength and hardness values increased to 85.60 N/mm^2 and 24HRB, respectively, however the impact energy values, percentage elongation values, and percentage reduction in area dropped slightly as the reinforcement increased.	[23]
Maize stalk fiber/polymeric resin	• Hand layup method	• 5% sodium hydroxide treatment • Acetic anhydride and 1-2 drops of concentrated hydrochloric acid	• The diameter of the natural fibers was shortened, and the hemicellulose and lignin elements were partly eliminated in the chemical treatment, resulting in a good surface area and greater adhesion between fibers and the matrix.	[24]
Corn stem fiber/ wood plastic composite	• Co-rotating twin screw extruder • Injection molding	• 3% Maleic anhydride • 4% stearic acid	• The highest flexural strength (46.10 MPa) and tensile break strength (26.58 MPa) were reached when the maize stem with the highest cellulose content was used as the reinforcement.	[25]

		• 3% polyethylene wax		
Corn cob fiber/ polyamide 4,10	• Melt processing • Injection molding	• Corn cob pyrolysis with bio carbon	• Improvements in tensile modulus and heat deflection temperature were achieved by preventing fracture propagation and increasing the stiffness of the filler particles by 6 and 12 percent, respectively.	[26]
Corn cob fiber/ starch acetate composites	• Twin screw extruder	• 5% talc • Ethanol	• Increased corncob content resulted in increased compression strength. • Despite the fact that ethanol penetration aided in the establishment of a starch acetate–fiber matrix, corncob blends produced poorer interconnections and cell growth in the foams than cellulose blends.	[27]

2.6 Preparation of maize stalk fiber/polymer composites

The preparation of maize stalk fiber/polymer composites is a waste management strategy that is used to reduce the amount of maize stalk accumulating in the environment. The maize stalk fiber/polymer composites are prepared in such a way that the properties of the composites are good enough for further applications. Generally, there are a wide range of preparation methods that are used to prepare composite materials. Each preparation method has processing conditions that are dependent on the type of reinforcing material and polymer matrix. Based on their processing conditions, the preparation methods can be broadly classified into open moulding or closed moulding techniques [28-33]. Open moulding techniques include: hand layup, spray-up and filament winding; whilst closed moulding techniques include: vacuum bag moulding, resin transfer moulding (RTM), vacuum-assisted resin transfer moulding (VaRTM), resin film infusion (RFI), injection moulding, and pultrusion moulding [34]. Both the open and closed moulding techniques have benefits and drawbacks. The open moulding techniques are the most common types of techniques for preparing composites. They have been utilized because of advantages such as simplicity, and cheap processing costs [35]. The major drawback of open moulding techniques is that they require well-trained and highly skilled operators to ensure laminate quality, especially the void and fiber volume fraction of composite laminates [36]. Closed moulding techniques are preferred for making 3-dimensional composite [29, 37, 38]. Additionally, closed moulding is mostly an automated moulding technique with reduced material, labour and waste disposal costs and greater productivity. The most commonly used open moulding techniques for thermoplastic composites are compression moulding [39], extrusion moulding [40, 41], and injection moulding [42-44]. Hand layup [45, 46], resin transfer moulding (RTM) [47], vacuum-assisted resin transfer moulding (VaRTM) [48], and resin film infusion [49] are used for the production of thermosetting composites [35]. Meanwhile, the fabrication method of a composite material is selected based on the constituent materials of the particular composite, the availability of the required tools and the properties required for the ultimate composite structures [35]. **Table 2.2** shows a summary of the different methods used to prepare maize stalk fiber reinforced polymer composites.

Table 2.2 A summary of the various preparation methods used in the preparation of maize stalk fiber reinforced polymer composites.

Maize fiber polymer composites	**Preparation method**	**Properties**	**Ref**
Maize straw slagging/ high density polyethylene composites	Extrusion method	Tensile strength of the composites reached its maximum at 34.3 MPa when maize straw slagging was incorporated at 30 wt%. Increase of maize straw slagging content to 40 wt% resulted in decrease in tensile strength properties to 29.45 MPa	[50]
Maize pith fiber/ polylactic acid	Melt mixing method	When maize pith fiber was incorporated with PLA, the biocomposites had a reduction in tensile properties	[51]
Corn cob/ polypropylene / wood ash	Injection molding	Incorporation of wood ash increased the tensile and flexural modulus of the composites with 10 wt% wood ash achieving highest values of 2550 and 324 Mpa.	[52]
Corn cob/ polylactic acid	Compression molding	Treated Corn cob/PLA composites showed better mechanical properties than untreated corn cob/PLA composite.	[53]
Corn cob / polyethylene composites	Injection molding	When the Polyethylene coupled with maleic anhydride loading rate was increased from 4 wt% to 5 wt%, the tensile and flexural moduli increased by 51.9 MPa and 81.9 MPa, respectively.	[54]

Corn cob/chitosan	Solvent casting	Incorporation of corn cob in chitosan negatively affected the tensile strength and elongation at break of the bio-composite film but improved the modulus of elasticity and thermal properties.	[55]
Corn stalk/ low density polyethylene composite	Compression molding	CS/LDPE composite without incorporation of eco-degradant (made from fatty acid, metal salt and lubricant) resulted in reduced tensile strength. Incorporation of the eco-degradant resulted in increase in tensile strength with highest value obtained at 10 wt% filler loading	[56]
Corn husk fiber/ recycled polystyrene foam	Melt compounding and compression molding	Addition of 60 wt% corn husk fiber content resulted in tensile strength, tensile modulus of 17 MPa and 2390 MPa respectively.	[57]

2.7 Development of maize stalk fiber reinforced hybrid composites

A hybrid composite is a system which consists of two or more reinforcing materials incorporated into a single matrix [58, 59] or consisting of a combination of the two scenarios. Furthermore, the combination of a variety of fibers in a single matrix may result in the development of a hybrid biocomposite. Various methods have been used to integrate reinforcing materials in a matrix; and these methods include: (i) intermingling of two types of short fibers thoroughly before incorporating them into a polymer in a mixer, or added alternately into the polymer with or without modification [60-62]; (ii) sandwiching of fibers [62, 63]; or (iii) using non-woven or woven fabrics of both types reinforcements [62-64]. Furthermore, the design and processing of hybrid biocomposites usually involves combining a synthetic fiber and natural fiber (biofiber) and then incorporating them into a matrix or combining two natural fibers (biofibers) and incorporating them into a matrix [65]. The overall behaviour of a hybrid composite is dependent upon its individual constituents. The properties of hybrid composite materials are exclusively controlled by factors such as the length of the individual fibers, fiber orientation, fiber to fiber matrix bonding, fiber content, extent of intermingling of fibers and arrangement of both fibers in the matrix. Hybridization offers new opportunities to broaden the function of composite materials, particularly in advanced applications by improving the toughness of impact resistance [66]. Hybrid composites also provide more design freedom as compared to non-hybrid composites and this leads to a synergestic effect, which is not possessed by any one material alone [66]. The synergestic effect can be achieved via several ways which include the selection of suitable fibers, suitable fiber combinations and their interaction in the hybrid system [66]. It is worth mentioning that the development of maize stalk fiber-based hybrid composites is still at its infant stages. Not much has been done as of yet. **Table 2.3** below is a summary of the work that has been done to develop maize stalk fiber-based hybrid composites.

Table 2.3 A summary of the preparation methods and properties of maize stalk hybrid polymer composites

Hybrid composites	**Preparation**	**Properties**	**Refs**
Areca fiber/maize powder/ phenolic formaldehyde		The final findings revealed that the hybrid composite has good mechanical characteristics.	[67]
Bagasse fiber/ corn stalk fiber/ E-glass fiber / polypropylene hybrid composite	Injection molding	Corn Stalk Fiber/glass hybrid composites had significantly better mechanical characteristics than Bagasse Fiber/glass composites.	[68]
Corn husk fiber/ sugar palm fiber/ corn starch	Solution casting	When compared to the neat CS-film (corn starch), the water vapor permeability of the hybrid composites fell by 96.55 percent, indicating enhanced water barrier qualities.	[69]
Corn stalk flour/ polyvinyl based wood plastic composite/ Sisal fiber	Hot press molding method and Compression molding	Corn stalk fiber reinforced sisal fiber and polyvinyl based wood plastic exhibited high flexural strength, tensile strength, tensile modulus and flexural modulus with 20%, 49.5%, 60,5% and 22.9% increase, respectively.	[70]

Areca fiber / maize powder / epoxy resin	Hand layup method	Addition of areca fiber and maize in epoxy resin resulted in improvement in tensile strength with highest tensile strength value recorded at approx. 55 MPa at weight fractions of 80 wt% areca fiber: 10 wt% maize powder: 10 wt% epoxy resin.	[71]
Unsaturated polyester/ jute fiber/ maize cob	Mechanical mixing	The weight percentage of 5% jute fiber, 5% maize cob and 90% unsaturated polyester resin produced greater mechanical performance compared to the controls.	[72]
Areca fiber/ maize powder / urea formaldehyde	Hot pressing method	The findings revealed that moisture absorption decreases as the fiber to maize powder ratio declines.	[73]
Maize fiber/ jute fiber/ epoxy resin soya bean oil	Compression molding	Raw fibers had higher initial and final degradation temperature when compared hybrid bio composite material.	[74]
Corn cob / E- glass fiber/ epoxy	Hand layup method	The sample with Corn Cob particles, E-Glass Fibers, and Epoxy in the ratio of 25:5:70 had the highest Modulus of Rigidity, impact strength, and Modulus of Elasticity. The sample with the ratio of	[75]

		27.5:2.5:70, on the other hand, had the highest tensile strength and modulus.	

2.8 Applications of maize stalk fiber/polymer composites

The incorporation of natural fibers like maize stalk fiber into polymer matrices leads to the production of materials that are both eco-friendly and sustainable. As a result, natural fiber composites like maize stalk fiber reinforced polymer composites have attracted a lot of uses in several industrial's applications such as in the health sector, military, building and construction, automotive, aerospace, railway coaches, manufacturing and packaging [76-77] (see **Table 2.4**). In applications such as automotive, aerospace, marine, sporting equipment and electronic devices, natural fiber composites have become a potential substitute to metal or ceramic based materials [76]. A lot of the natural fiber composites used in automotive components are still based on polyester or polypropylene polymers and flax, hemp or sisal fibers [77]. The use of natural fiber composites in the automotive industry is motivated by price, weight reduction and marketing rather than technical demands [78]. Germany is one of the leading users of natural fiber composites for automotive parts. The German auto-manufacturers like Mercedes, BMW, Audi, and Volkswagen use natural fiber composites for making the interior and exterior parts of their automobiles [77]

Table 2.4 A summary of the applications of maize fiber reinforced polymer composites.

Maize fiber polymer composites	**Preparation method**	**Surface modification**	**Mechanical properties**	**Applications**	**Refs**
Maize fiber/ epoxy poly matrix composites	Compression molding	Alkaline treatment	Alkaline treated maize fiber composites exhibited high tensile properties and high-water holding capacity	Packaging materials	[17]
Maize fiber/ poly ε- caprolactone	Sequential molding and forming process	Alkaline treatment	At fiber area fraction of 55% the tensile strength and elongation at break increased to 114.5 MPa and 13.0%, respectively.	Composite structures, bioanalysis and diagnostics, therapeutics	[79]
Carbonized maize stalk/polyesters	Compression molding	Cobalt octoate, Ethyl ketone peroxide and polyvinyl alcohol coating	Tensile modulus increased from 159.55 N/mm^2 to 824.62 N/mm^2. Tensile strength increased from 35.0 N/mm^2 to 53.60 N/mm^2 and compressive strength of 30.32 MPa. Impact strength decreased as maize stalk ash increased.	Automobile and building	[80]
Corn fiber/ polypropylene	Injection molding	Maleic anhydride grafting	Tensile strength, flexural strength and impact strength increased to 94.42 MPa, 237.23 MPa and 475.67 MPa respectively	Packaging materials	[81]

Corn fiber/ Wood-polymer composites	Hot pressing molding	Silane treatment	Friction coefficient improved from 100 to 150 degrees Celsius.	Automotive and aircraft industry	[82]
Corn fiber/ PLA	Mechanical mixing and injection molding	Alkali and Sizing treatment	Optimal sizing concentration was found to be 12 wt% with a maximum tensile strength and tensile modulus of 49.5 ± 2.0 MPa and 6.63 ± 0.07 GPa, respectively.	Packaging materials	[83]
Corn fiber/ polypropylene	Hand layup method	Methyl ethyl ketene peroxide, Cobalt naphthenate and sizing treatment	Length, width and thickness of fiber influenced the tensile properties of the CF/PP composite. Maximum tensile strength and impact value was found to be 21.24 MPa and 14.05 KJ/m^2 with length fiber, thickness and width of fiber at 120mm, 6mm and 10mm, respectively.	Packaging materials	[84]
Corn fiber/ high density polyethylene	Injection molding and Co-rotating twin screw extrusion	Stearic acid	The maximum properties obtained was, tensile strength of 26.6 ± 1.6 MPa, flexural strength of 46.1 ± 2.1 MPa, tensile modulus of 2397.1 ± 225 MPa and flexural modulus of 3456.8 ± 283 MPa	Commercial building materials	[85]
Corn stalk flour/ polyvinyl based wood plastic composite/ Sisal fiber	Hot press molding method and Compression molding	Polyvinyl chloride	Corn stalk fiber reinforced sisal fiber and polyvinyl based wood plastic exhibited high flexural strength, tensile strength, tensile modulus, and flexural modulus with 20%, 49.5%, 60,5% and 22.9% increase, respectively.	Building materials and automotive industry	[70]
Corn husk fibers/ low density	Melt compounding	none	At 5% fiber loading of corn husk, the composite exhibited a maximum tensile strength of 24. 7 ± 0.98 MPa and hardness of 4.54 ± 0.60 KP/mm^2	Packaging applications	[86]

polyethylene composites	and compression molding		and achieved its maximum young's modulus of 456 ± 0.42 MPa at 10% fiber loading.		

2.9 Mechanical properties

Mechanical properties of maize fiber reinforced polymer composites are reliant on the type of chemical treatment used, concentration of maize fiber used, interfacial adhesion, preparation method, extraction technique, isolation and growing period of the fibers [87]. Research by Workiye and Woldsenbet [18] studied the effects of maize stalk fiber Reinforced with calcined kaolinite clay geopolymer composite, the researchers used 15% diluted sodium hydroxide solutions at room temperature for 72 hours to treat the maize stalk fiber for 30 minutes and the results showed that compression strength of the composite increased from 16 MPa to 27 MPa, also confirming the researcher's hypothesis that the compression strength of a calcined kaolinite based geopolymer can be improved by incorporating maize stalk fiber.

A study by Agunsoye *et al*. [88] focused on the mechanical properties of maize fiber reinforced epoxy composites, the study used 2–12wt% carbonized and 2, 4, 6, 8, 10 and 12 wt% uncarbonized maize stalk Nano-particle fibers to evaluate its effects on properties of epoxy composites. The results showed that addition of 2wt% carbonized maize fiber increased the hardness value from 2.2 HV to 17.83 HV and addition of 2wt% uncarbonized maize fiber increased hardness value from 2.2 HV to 10.35 HV and the tensile properties per percent filler addition of carbonized maize fiber were greater compared to those of uncarbonized maize fiber.

Chen *et al*. [89] studied the effects of maize straw fiber, polyvinyl chloride and glass fiber in wood plastic composite and their findings demonstrate that the glass fiber, maize straw fiber, and poly (vinyl chloride) (PVC) in wood polymer composites had a good physical interlocking structure which enhanced the tensile strength and the flexural strength of the wood polymer composites by an increase of 31% and 23%, respectively.

Maslowski *et al*. [90] explored the use of maize straw, wheat straw and barley straw on the mechanical properties of natural rubber biocomposites, and their results showed that the maize, barley, and wheat straw enhanced the mechanical properties of natural rubber by improving its tensile properties with the highest values being at 20 phr filler content, thus obtaining a tensile strength of maize straw (16.4 ± 0.8 Mpa), barley straw (15.5 ± 0.8 Mpa), wheat straw (18.6 ± 1.0 Mpa); and the hardness of the natural rubber composite increased with increasing filler content with highest values obtained at 50 phr filler content. Table 2.5 shows the

Table 2.5 Effects of chemical treatment on mechanical properties of Maize fiber polymer composites

Maize fiber reinforced polymer composites	**Purpose/treatment**	**Fabrication technique**	**Results**	**Ref**
Maize cob/ unsaturated polyester resin	To determine physico-mechanical properties of maize cob fiber and jute fiber reinforced unsaturated polyester resin	Hand layup technique	Due to the good dispersion of maize cob fiber, increased surface area, and intermolecular interactions between the particulate MC filler/matrix; the Maize Cob/Unsaturated Polyester Resin had better flexural resistance of 31.41 Mpa to 28.88 Mpa against 25.72 Mpa to 22.14 Mpa for jute fiber/unsaturated polyester resin.	**[91]**
Maize chuff fiber/ Polypropylene	To determine the tensile modulus of maize chaff fiber reinforced polypropylene composites using	melt-blending using twin screw extruder	The optimal value for the composites in terms of tensile strength and modulus was found to be 5wt% MAPP.	**[92]**
Maize husk/ polyester	To determine the amount or content of maize husk fiber required and effect of water immersion on mechanical properties. The liquor ratio for the alkaline treatment was 1:2	Hot compression	With increasing fiber content, tensile strength improved initially, then declines. The specimen with the highest tensile strength had a value of 29 MPa after being soaked in water for 6 days. The increased fiber-matrix interaction in SRC is credited with the increase in tensile strength.	**[93]**

Corn Cob particles/E-Glass Fiber/Epoxy	To determine effect and properties of maize cob/E-Glass fiber/epoxy hybrid composite using 5% sodium hydroxide as chemical treatment	Hand layup	Maize cob with fiber content of 25% and glass fiber of 5% had a higher tensile modulus and tensile strength of 926.78 Mpa and a 18.04 Mpa, respectively; and maize fiber content and glass fiber content of (27.5%; 2.5%), (25%;5%), and (22.5%;7.5%); had good flexural strength properties with (22.5%;7.5%); and having maximum flexural strength of 37.14 MPa.	**[75]**
HDPE/ HD-g-MAH / Maize-cobs Nanocomposites	3% maleic anhydride was used to determine the effects of organic montmorillonite on properties of HDPE/ HD-g-MAH / Maize-cobs Nanocomposites	Injection molding	Results indicated that maize comb Nano cellulose fiber improved the mechanical properties up by 3%, and the addition of 2% Org-MMT to the matrix was enough to increase the exfoliation and dispersion of the filler. 3% high density polyethylene grafted maleic anhydride improved the adhesion, and enhanced the interfacial adhesion of the whole composite. The tensile strength and modulus increased from 19.18 MPa for high density polyethylene to 20.24 Mpa at 5%; and maize cob filler loading and modulus of elasticity increased up 52%. Flexural strength and modulus increased from 15.57Mpa for high density polyethylene to 17.99 MPa at 5% filler loading; and Flexural modulus also increased from 1.99MPa to 2.27Mpa.	**[94]**

2.10 Thermal properties

Thermal properties are an important indicator that a polymer composite can or cannot withstand heat. Thermal properties are best for directing the applications of a specific material based on its ability to absorb heat [95]. Thermal properties can be affected by fiber content, chain structures, interfaces, fabrication methods, extraction methods, and functionalization [96]. One study by Trigui *et al*. [19] analysed the thermal properties of maize fiber reinforced high density polyethylene bio-composite. The researchers used 10-40wt% fiber content, and different preparation methods were employed, namely injection molding, drying, cutting, mixing, compounding and pelletizing method, and the temperature ranged from -20^{o}C to 120^{o}C. The results of the experiment indicated that increase in temperature resulted in an increase in thermal effusivity, and thermal factor; and increase in fiber loading resulted in decrease in thermal conductivity, and thermal diffusivity of the maize fiber reinforced high density polyethylene composite. Furthermore, Bavan *et al*. [97] studied the thermal properties of maize fiber composites using 5% sodium hydroxide chemical treatment for 6-8 hours, and the temperature was heated at 10^{o}C per minute. The thermogravimetric analysis and differential scanning calorimeter results showed that alkali treated fibers exhibited a maximum weight loss temperature of 284^{o}C compared to 278^{o}C for raw maize fiber and the highest decomposition temperature of 340-444^{o}C compared to raw fiber with 334-434^{o}C.

Luo *et al.* [98] evaluated the thermal properties of Maize fiber reinforced polylactic acid using alkali and silane as chemical treatment. The researchers used alkaline and alkaline/silane treatment to evaluate its effects of thermal properties. 5, 10, and 15% Sodium hydroxide was used for the alkaline treatment, and 10wt% sodium hydroxide treatment with 1, 2, 3, and 4 wt% silane treatment was used. The results of the experiment showed that the use of alkaline/silane treatment produced better mechanical properties for the composites compared to alkaline treatment and the thermal properties of the alkaline/silane coupled composites were also better than alkaline treated composites. Another study was conducted by Fuqua and Ulven. [99] with the focus on the mechanical properties of maize fiber reinforced polypropylene composites. The maize fiber loadings used were 3, 5, 7, and 9wt%, respectively; and the maize fiber was treated, and polypropylene was treated with Maleic anhydride to improve its properties. The thermogravimetric analysis and differential scanning calorimetry results showed that the addition of fiber loading to the matrix system aided the crystallization process, resulting in higher peak crystallinity temperatures but further addition of fibers resulted in a decline in

crystallization and thermal stability. Higher peak temperatures of crystallization were obtained with addition of 5 and 10wt% polypropylene grafted with maleic anhydride.

2.11 Flammability properties

Natural fibers are generally highly flammable materials, and one of the most used unorthodox methods of eradicating these highly flammable natural materials by farmers is outdoor burning, which is detrimental to the environment. Using natural fibers reinforced with polymer composites safely removes these natural fibers from the environment preventing the consequences caused by burning these materials, and it also provides fire retardant treatment for composite materials which is very critical for their application [100].

When exposed to extreme heat, polymers typically underperform, and can also become dangerous but integrating natural fibers with polymers can play a significant role in improving this problem. The flame retardancy properties of natural fibers is dependent on the composition of the natural fiber e.g. higher mechanical properties are dependent on higher cellulose composition and higher flame retardancy is dependent on higher lignin composition. In addition, maize fiber typical has good lignin content making it useful as a flame retardant [101].

The development of fire-retardant techniques has lowered the flammability of polymer composites. The main fire retardant techniques used are surface coatings, chemical treatments, and flame retardants (phosphorus, nitrogen, halogen, silicon, Nano-metric particles and mineral based flame retardants etc.) [102]. Zhang *et al*. [50] investigated the flammability of maize straw slagging reinforced high density polyethylene composites. The results showed that addition of maize straw slagging at 40wt% improved the flame-retardant properties of maize straw slagging reinforced high density polyethylene composite. The limited oxygen index of the composites was improved to 31.26% showing excellent flame-retardant properties. Maize fiber unlike most natural fibers is a natural flame retardant and has an estimated melting point of 170^{o}C. Yang *et al*. [51] studied the use of maize pith fiber as a flame retardant to polylactic acid, and the results of the study confirmed maize fiber as a flame retardant with the results showing that maize fiber coated with 3% PA-THAM, and chemically treated with sodium hydroxide improved the limited oxygen index value; and there was improved char residue production, the heat release rate and total heat release of maize fiber reinforced PLA with PA-THAM had good flame retardant properties . Kaya *et al*. [103] studied silica xerogel extracted from maize stalk ash and its effects on epoxy composites. The researchers found that the silica

xerogel synthesized from maize stalk ash was responsible for improvement in thermal properties of the epoxy composite and at 600^{o}C produced high char residues.

2.12 Conclusion

Maize stalk fiber is a type of natural fiber. When it is used as a reinforcement in polymer composites, similar preparation and chemical surface treatment methods as the ones used in natural fiber-based polymer composites are used. The applications of maize stalk fiber reinforced polymer composites are also similar to those of natural fiber reinforced polymer composites. In conclusion, the use of maize stalk fiber as a reinforcement in polymer composites is an excellent way of controlling the accumulation of maize stalk waste in the environment. Since maize stalk is an agricultural waste, this does not only solve the environmental pollution issue, but it also improves the agricultural economy. In spite of the work that has been done so far, there is still more work to be done on the development of maize stalk fiber-based polymer composites, especially on maize stalk fiber-based hybrid composites. This will not only solve the environmental pollution issue, but it will open up new applications for the maize stalk fiber reinforced polymer composites.

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Chapter 3: Experimental section

3.1 Materials

3.1.1 Polylactic acid

PLA used in this study was supplied in pellets form by 2MBio- Engineering Polymers, India. It has a density of 1.24 g/cm^3, melt flow index of 3g/10 min, and a melting point of 155℃.

3.1.2 Sodium hydroxide

Sodium hydroxide was supplied in pellet form by Merck (pty) Ltd. The Sodium hydroxide contains an Assay percent range of ≥98%, and has a melting point and boiling point of 318℃ and 1390℃, respectively.

3.1.3 Calcium Carbonate

Calcium carbonate ($CaCO_3$) was supplied in powder form by Envoi de Solvay specialites France, and it has a density of 0.9 g/cm^3.

3.1.4 Maize stalk fiber

Maize stalk fiber (MSF) was obtained from a farm in Cofimvaba, Eastern Cape, South Africa.

3.2 Methods

3.2.1 Washing, and chemical treatment of Maize stalk fiber

The maize stalk fiber contains two major components, namely, the rind and the pith. The rind consists of lignin and cellulose. The pith consists of sugar, protein, fat, and hemicellulose. The rind has high strength and toughness. Therefore, it is used to prepare maize stalk fiber-based polymer composites. The pith has poor strength; hence, it must be removed when preparing maize stalk fiber containing composites to achieve high strength. A sharp object was used to separate the rind from the pith in the maize stalk fiber. Once the weight was recorded, the rind

was soaked in water for an hour. After an hour, the rind was washed, removed from water, and weighed again to see if it had absorbed any moisture, and then the weight was recorded. Once weighed, the wet rind was dried in a vacuum oven pre-set at 70°C for 24 hours. After 24 hours, it was removed from the oven and weighed again to see if the moisture had been removed. Once the rind was completely dry, it was crushed into fine powder using a coffee grinder.

3.2.2 Preparation of PLA/Calcium carbonate/Maize fiber hybrid biocomposite

Calcium carbonate and pulverized PLA were thoroughly dried in a vacuum oven for 12 hours at 30 and 40°C, respectively. Neat PLA, binary composites, and PLA/maize stalk/calcium carbonate hybrid composites were melt processed in co-rotating twin-screw extruder (Thermo Scientific, Waltham, MA, USA) with L/D of 40 shown in Figure 3.1. The barrel temperatures from the hopper to the die were set at 140, 160, 180, 180, 180, 180, 180, 180, and 190 °C. A feeding rate of 5.6 g/min and screw speed of 202 rpm were used. The extruded polymer samples were cooled in water bath, pelletised, followed by drying at 60 ℃ for 24h. The composition of the calcium carbonate was varied from 5 to 10%, while the maize stalk was varied from 5 to 20%. The designations and compositions of the samples are listed in **Table 3.1**.

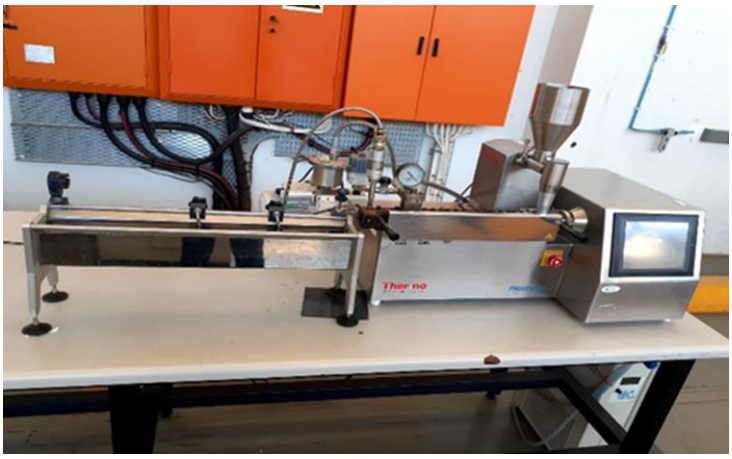

Figure 3.1 A co-rotating twin-screw extruder for the preparation of maize stalk fiber/calcium carbonate/PLA hybrid biocomposite.

Table 3.1 Compositions of the Samples

Sample	PLA (wt.%)	$CaCO_3$ (wt.%)	MSF (wt.%)
PLA	100	-	-
95/5 PLA/$CaCO_3$	95	5	-
95/5 PLA/MSF	95	-	5
90/10 PLA/MSF	90	-	10
85/15 PLA/MSF	85	-	15
80/20 PLA/MSF	80	-	20
90/5/5 PLA/$CaCO_3$/MSF	90	5	5
85/5/10 PLA/$CaCO_3$/MSF	85	5	10
80/5/15 PLA/$CaCO_3$/MSF	80	5	15
75/5/20 PLA/$CaCO_3$/MSF	75	5	20
85/10/5 PLA/$CaCO_3$/MSF	85	10	5
80/10/10 PLA/$CaCO_3$/MSF	80	10	10
75/10/15 PLA/$CaCO_3$/MSF	75	10	15
70/10/20 PLA/$CaCO_3$/MSF	70	10	20

3.3 Characterization of samples

3.3.1 Scanning Electron Microscopy (SEM)

A highly focused electron beam is used to scan a sample's surface in SEM, which creates images of the sample. Furthermore, the sample's surface topography and chemical composition are revealed by the signals that are created when the electrons interact with the sample's atoms. A faster scan pattern is used to scan the electron beam, and an image is created by combining the strength of the detected signal with the position of the beam [1]. Moreover, samples are examined in a variety of cryogenic or high temperatures using specialist instruments, as well as in high vacuum in a standard SEM or low vacuum or wet conditions in a variable pressure or environmental SEM [2]. A SEM (ZEISS-Auriga Cobra, Germany) shown in **Figure 3.2** was used to obtain the SEM images for the samples. The samples were fractured after immersion in liquid nitrogen for 2 minutes. The fractured surfaces were sputter-coated with carbon to prevent charging followed by imaging at accelerating voltages of 2 and 3 kV.

Figure 3.2 A scanning electron microscope (ZEISS-Auriga Cobra, Germany) used for observing the surface morphology of the samples**.**

3.3.2 Thermogravimetric analysis (TGA)

TGA is a technique used for calculating a sample's total mass as a temperature-dependent attribute. During degradation, polymeric materials deteriorate, and lose volatile components. Therefore, mass change due to temperature is a fundamental feature of many materials. This behaviour can reveal extensive information about the test materials [3]. Thermo gravimetric analysis can also give crucial information for a variety of materials characterization goals. During TGA, a sample is intentionally exposed to a specific temperature programme under stringent ambient constraints, and thereby concurrently monitoring changes in weight [4]. A thermogravimetric analyzer (TGA5500, TA Instruments, USA) shown in **Figure 3.3** was used to evaluate the thermal stability of all the investigated samples. The samples weighing 7–8 mg were heated from 25℃ to 800℃ under air, and at a heating rate of 10℃/min.

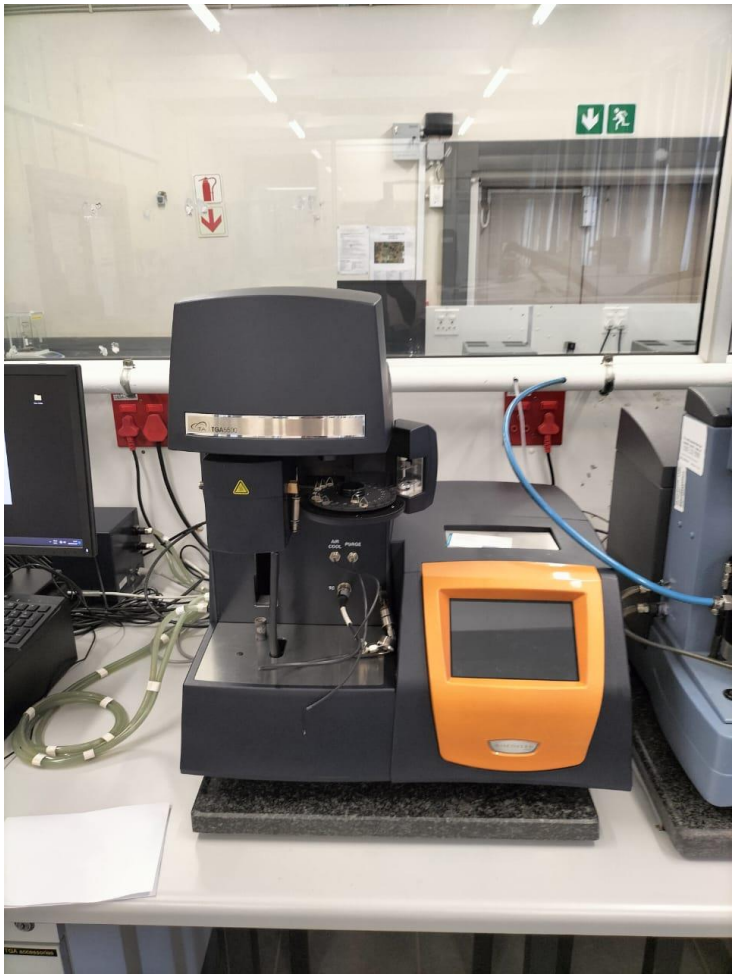

Figure 3.3 A thermogravimetric analyzer (TGA5500) used for evaluating thermal stability of the samples.

3.3.3 Rheology

Rheology is a technique used for measuring the viscoelastic properties of materials. A rheological test is usually performed either by applying a fixed amount of strain and measuring the stress that is developed or by applying a small stress to the sample and measuring the developed strain. The dynamic rheological properties were conducted under the atmospheric conditions with a temperature of 190°C by utilizing a Physica MCR501 (Anton Paar, Austria) rheometer shown in **Figure 3.4,** and in a 25 mm diameter parallel plate configuration. The strain amplitude of 1% was determined with preliminary experiments and the zero gap was set at 1.15 mm for all the tests.

Figure 3.4 A rheometer used for measuring rheological properties of the samples.

3.3.4 Dynamic mechanical analysis (DMA)

DMA is a technique, which involves either applying a circular strain to a sample and measuring the stress response that occurs or applying a cyclic stress and measuring the strain response that follows. Strain is the regulated input while the resulting stress is monitored in the majority of commercial DMA equipment. Molecular relaxation processes in polymers are studied using DMA, and inherent mechanical or flow properties are determined as a function of temperature and time [5]. Moreover, DMA tests of the samples were performed in the temperature of -50 to 90 ℃ in the dual cantilever bending mode using a Perkin Elmer DMA 8000, analyser from USA, and shown in **Figure 3.5**. The frequency and strain amplitude were set at 1 Hz and 0.05%, respectively.

Figure 3.5 Perkin-Elmer DMA used to analyse dynamic mechanical properties of samples.

3.3.5 Cone calorimetry

The cone calorimeter is a fire testing technique, which is based on the principle of oxygen consumption during combustion. The well-known parameters for cone calorimetry include mass loss rate (MLR), heat release rate (HRR), and total heat release (THR). The most important parameter is the HRR, which is the driving force of a fire. The higher the HRR of a material, the higher the flammability and as a result such a material is considered highly flammable [6]. Cone calorimetry measurements were performed using cone calorimetry (i-cone Fire Testing Technology, East Grinstead, UK) shown in **(Figure 3.6**), in accordance with ISO 5660. The prepared test samples (dimensions of 100 × 100 × 3 mm^3) were wrapped in aluminium foil with the top surface open and exposed to a radiant cone at a heat flux of 25 kW m^{-2}. The parameters such as peak heat release rate, time to ignition, carbon monoxide, carbon dioxide and mass loss rate were measured and recorded.

Figure 3.6 A cone calorimeter used for investigating the flammability properties of the samples.

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Chapter 4: Results and discussion

4.1 Scanning electron microscopy (SEM)

Figure 4.1 illustrates the SEM images of the 90/10 PLA/MSF and 80/20 PLA/MSF composites. A careful inspection of the images revealed that both the 10 and 20wt% of the MSF showed a fairly good dispersion within the PLA matrix. The 90/10 PLA/MSF nevertheless revealed less pullouts (Symbol A) when compared with the 80/20 PLA/MSF composite (symbol B). This behaviour suggests an improper fiber/matrix interaction due to higher fiber incorporation i.e., 20wt% of the fiber. It is possible that at higher fiber content, there is an insufficient wetting of the fiber by the polymer matrix, which may result in fiber pullouts. Bax and Mussig [1] investigated the surface morphology of PLA reinforced cordenka and PLA reinforced flax composites. Similarly, with our observation, SEM images of the fracture surface of PLA/cordenka and PLA/flax showed fibre pullouts, thus suggesting a poor adhesion between fibre and matrix. The surface morphology also showed voids between the PLA and the fibres, which could be the result of debonding during mechanical testing or inadequate approximation during the creation of composite materials. This behaviour was further emphasized by Siakeng *et al* [2], who evaluated the surface morphology of coir/pineapple leaf fibres reinforced PLA hybrid composite. Their SEM analysis revealed that fibre pullouts indicated a weak bond between the fibre, and matrix; and fractures on the matrix surface indicated either insufficient or uneven fibre loading in the matrix.

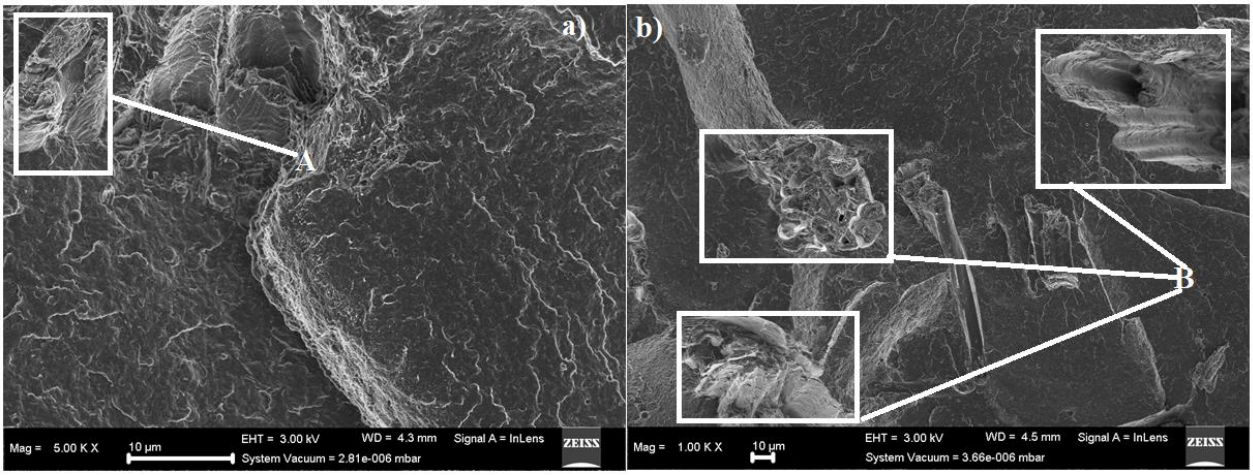

Figure 4.1 SEM images of a) 90/10 PLA/MSF and 80/20 PLA/MSF composites.

The incorporation of calcium carbonate into the PLA improves the dispersion of fibre within the PLA matrix **(Figure 4.2 c** and **d)**. There is better dispersion of the fiber at 5wt% in the presence of calcium carbonate for 80/15/5 PLA/$CaCO_3$/MSF, while the 75/5/20 PLA/$CaCO_3$/MSF composite showed minor fiber pull outs (Symbol C). Because of lesser fiber content in the composites, calcium carbonate was able to encapsulate most of the fiber and in the process, it enhances adhesion between the fiber and the polymer matrix. In case of the 20wt% of the fiber, there was an encapsulation of the fiber by calcium carbonate; however, there are clear visible fiber pull-outs that might be associated with higher fiber content, which was not completely encapsulated by calcium carbonate. Notably, separation of the fibre in some cases from the polymer is well documented in the literature, as it was proven by the study conducted by Oksman *et al.* [3]. Fibre pullouts, which were observed in the form of single fibre were reported to be caused by separation during the extrusion process. The addition of ZnO into the oil palm empty fruit bunches fibre (OPEFB) into polyurethane foamed polymer composites was reported in the literature [4]. The incorporation of ZnO into the composites was expected to play a key role in terms of filling in the voids and cavities. At low ZnO content(s) i.e., 5% and 10%, it was discovered that the ZnO was not dispersed thoroughly in the composites. The addition of 20% ZnO into the fibre composites resulted in agglomerations within the composites with a lot of voids.

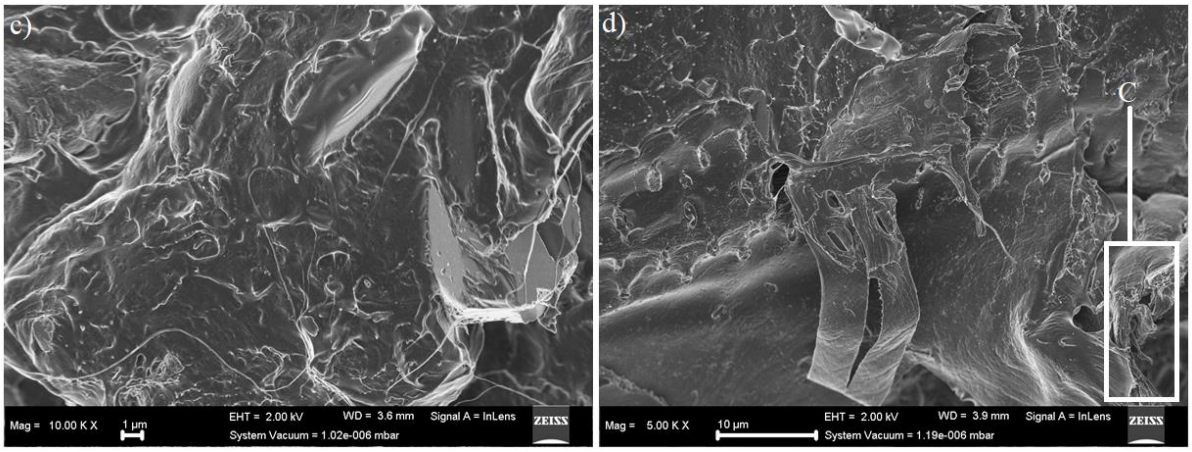

Figure 4.2 SEM images of a) 85/5/10 PLA/$CaCO_3$/MSF and 75/5/20 PLA/$CaCO_3$/MSF composites.

The wettability of the fibre by the PLA matrix was more enhanced in the PLA/$CaCO_3$/MSF 75/5/20 when compared with the PLA/$CaCO_3$/MSF 70/10/20 system **(Figure 4.3)**. This was revealed by few cavities in the 70/10/20 PLA/$CaCO_3$/MSF (see symbol D), even though there was a better embedding of the MSF in the PLA matrix. However, the PLA/$CaCO_3$/MSF 75/5/20 hybrid system showed a complete covering of the fiber by calcium carbonate (symbol E). This is an indication that the optimum composition of calcium carbonate required for enhanced wettability might be at 5%. Similar results were observed by Srinivasan *et al* [5], who investigated the morphology of banana fibre reinforced epoxy composite. The authors used calcium carbonate as a particulate to increase interfacial adhesion. Surface fracture images from the study showed that because there were no voids in the composite, sufficient stress flow existed inside the matrix allowing the calcium carbonate particulate to entirely infuse into the matrix and fill the voids in the composite. SEM results from the study also showed that the calcium carbonate particulate was completely embedded in the banana fibre.

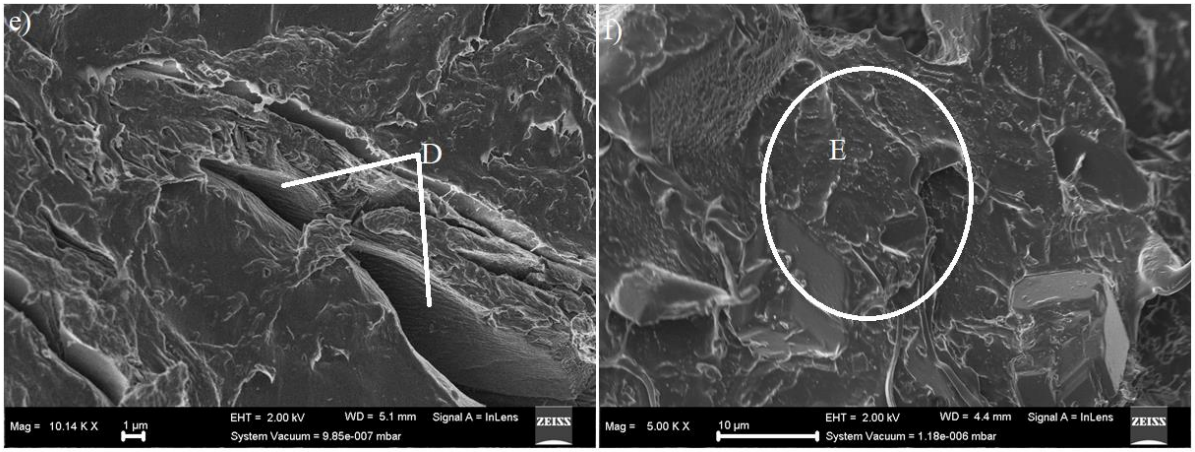

Figure 4.3: SEM images of: (a) PLA/$CaCO_3$/MSF 70/10/20 and (b) PLA/$CaCO_3$/MSF 75/5/20.

4.2 Flammability properties of the Maize stalk reinforced PLA composites

Cone calorimeter is the bench scale device to measure the fire behaviour of solid materials. Parameters such as heat release rate (HRR), ignition time, mass loss rate (MLR), total smoke release (TSR), and total smoke production (TSP) are measured and reported. **Table 4.1** illustrates summary of the cone calorimetry results. **Figure 4.4** illustrates the heat release rate (HRR) of PLA, PLA/MSF and PLA/$CaCO_3$. The HRR symbolizes the intensity of fire within a system, and the higher the HRR peak, the more flammable the material. PLA revealed a very high HHR peak approximately around 554.5 kW/m^2, which explains that the PLA matrix burned out completely with little or no char. **Figure 4.5** illustrates the digital images of the char residues of the PLA, PLA/MSF and PLA/$CaCO_3$. The results are well supported by the digital image in **Figure 4.5(a),** which shows little or no char layer at all for neat PLA. The high peak heat release rate (PHRR) value of neat PLA was expected since the PLA is known for its high flammability, and its behaviour to flow in fire. The results are well supported by study conducted by Reti *et al.* [6], who investigated the flammability properties of intumescent PLA. In their study, the HRR peak of the PLA was found to be higher than the intumescent PLA composites, with a peak value (PHHR) of 320 Kw/m^2 [6]. The flammability of PLA was further verified by Zhang *et al.* [7] in the study based on the flammability properties of PLA modified with different Organic Modified Montmorillonites (OMMTs). Their results showed that PLA had a pHRR value of 416KW/$m^{2,}$ which was the highest HRR value out of all the specimens tested [7].

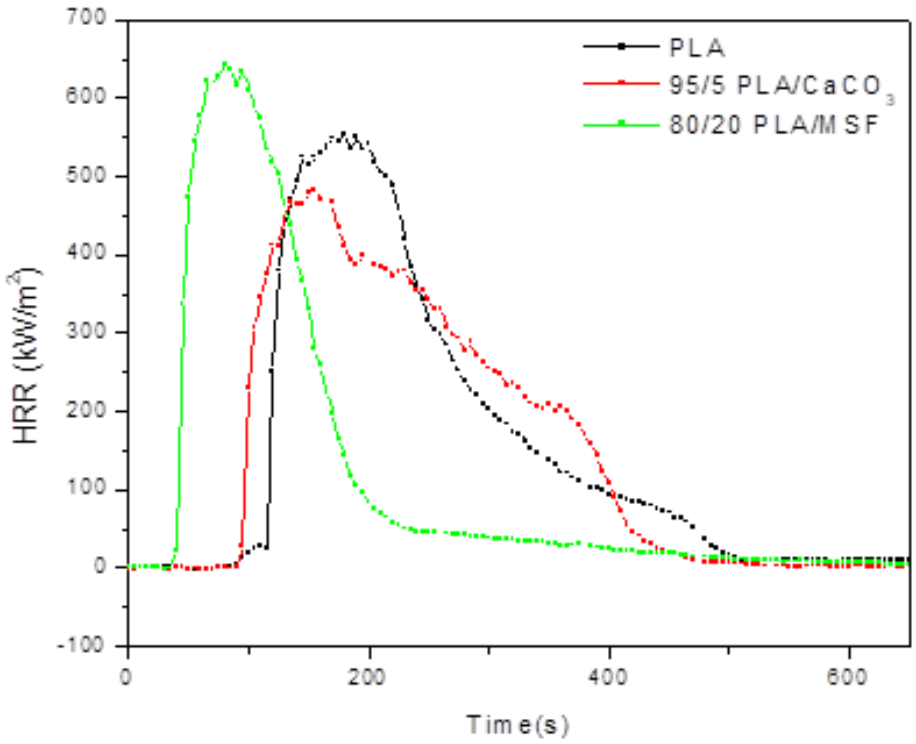

Figure 4.4 Heat Release rate curves versus time of PLA, 95/5 PLA/$CaCO_3$ and 80/20 PLA/MSF.

Table 4.1: Summary of the cone calorimeter data for all investigated samples.

Sample ID	pHRR (kW/m^2)	TTi (s)	FPI (m^2s/kW)	FIGRA ($kW\ m^{-2}s^{-1}$)
Neat PLA	554.5	125	0.23	4.41
PLA/$CaCO_3$ 95/5	483.3	98	0.21	4.93

PLA/MSF 80/20	697.4	29	0.042	24.1
PLA/$CaCO_3$/MSF 95/5/5	139.9	157	1.12	0.9
PLA/$CaCO_3$/MSF 85/5/10	130.0	30	0.23	4.3
PLA/$CaCO_3$/MSF 75/5/20	148.2	72	2.1	2.1

Table 4.1 shows that the incorporation of 20wt% maize stalk fibre into the PLA produced the highest HRR peak value at 697 kW/m^2 which was the highest amongst the three specimens (PLA, 95/5 PLA/$CaCO_3$, and 80/20 PLA/MSF). The results are well supported by the digital images, and a careful inspection of **Figure 4.5 (b)** shows a very weak char formation, which is an indication of a flammable material. In addition, various factors such as chemical composition, crystallinity, fibrillar orientation were found to affect the flammability of fibres [8] [9], lignin, and cellulose content. In this study, an increase in flammability **(Fig 4.5 (b))** (High HRR peak values) for PLA/MSF is mainly attributed to high cellulose content, and the presence of weak char **(Figure 4.5 (b))** is attributed to the lignin content in the maize stalk fibre. Pornwannachai *et al.* [10] investigated the effects of various water-soluble flame-retardants on flammability properties of the flax fibre/PLA and flax fibre/PP composites. The incorporation of flame-retardants to either flax fibre/PP or flax fibre/PLA composites reduced their flammability, as it was evident by reduced HRR upon introduction of flame-retardants.

Similarly, Dorez *et al.* [11] assessed the flammability behaviour of flax fibre reinforced PBS composites. Results showed that addition of flax fibre into the PBS increased the flammability of the PBS/flax composite as it was the case in this study as well. One may conclude that the addition of the fibre into the polymer matrices reduces the flammability resistance of the polymer matrix.

Dorez *et al.* [11] assessed the flammability behaviour of flax fibre reinforced PBS composites. In contrast to our study, their results showed that addition of flax fibre alone into the PBS

decreased the flammability as seen on their reduced pHRR of the 70/30 PBS/flax fibre composite in comparison to neat PBS. Furthermore, incorporation of ammonium polyphosphate (APP) led to earlier PBS degradation, promoted matrix charring, and caused phosphorylation of flax fibres. Those combined effects were beneficial to the attained strong char barrier and significantly reduced pHRR for the 65/30/5 PBS/flax fibre/APP composite. One may conclude that the formation of hybrid composites comprised of dual fillers such as APP and flax fibre in PBS to develop ternary composites is an effective strategy of overcoming the limitations associated with incorporating single filler to form binary composites. Hence, in this study, hybrid composite systems comprised of PLA/Maize stalk/calcium carbonate were fabricated in order to overcome the limitations of the PLA/Maize stalk fiber composites.

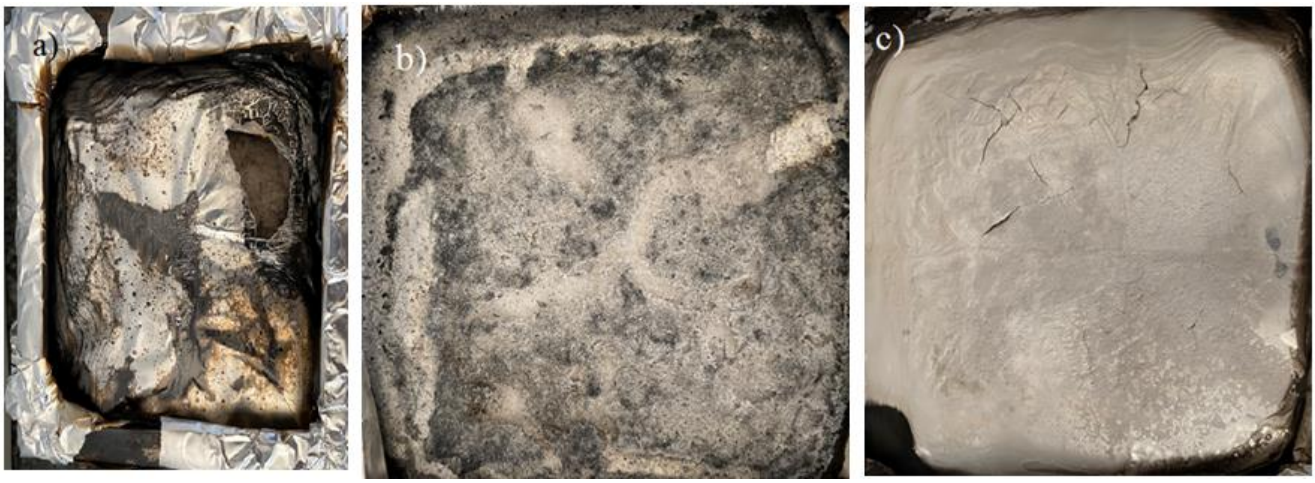

Figure 4.5 Digital images of: (a) PLA, (b) 80/20 PLA/MSF, and (c) PLA/$CaCO_3$.

The incorporation of calcium carbonate could be said to have improved the flame resistance of the PLA, which is symbolized by a low HHR peak when compared with PLA and PLA/Maize stalk fibre composites **(Figure 4.4** and **Table 4.1)**. This may be ascribed to the ability of calcium carbonate nanoparticles to form an insulating barrier, which reduces and stops the flame from spreading while improving the thermal stability of the polymer matrix, which in turn enhances the flame resistance. Furthermore, one possible reason for an enhancement in flame resistance of the PLA/$CaCO_3$ composites may be ascribed to the release carbon dioxide upon the endothermic decomposition of calcium carbonate, which probably dilutes and cools the volatile flammable products. The digital image in **Figure 4.5(c)** illustrates a compact and thick char, and such chars are well-known to prevent heat from entering the system, and also preventing volatile products from leaving the system, thereby enhancing the flammability

resistance of the system. Furthermore, **Figure 4.6** illustrates the heat release rate (HRR) of PLA, PLA/$CaCO_3$ (95/5), and PLA/$CaCO_3$/MSF (90/5/5, 85/5/10 and 75/5/20) hybrid composites. Generally, the addition of calcium carbonate at 5wt% resulted in a reduction of the HRR peaks. Low peak HRR values are often associated with systems that are flame resistance i.e. as seen in **figure 4.5 (C).** Flame resistance system are ascribed by system that are able to form effective char residues. The effectively protective char normally suppresses the HRR, and the protective barrier restricts the substrate's ability to absorb oxygen and delays the combustible breakdown of the products' volatilization. The pHRR results suggest that incorporating calcium carbonate in the matrix enhanced the flame retardancy of the hybrid biocomposite mainly because calcium has high thermal insulation properties which decreases thermal conductivity, which in turn decreases the release of combustible gases during combustion and lessens the "wick effect of maize stalk fiber "which is responsible for speeding up the flow of polymer melt along the surface of maize stalk fibre to the flame zone. Tang *et al.* [12] found similar results after they incorporated $CaCO_3$ into a polypropylene matrix. The pHRR of the PP/$CaCO_3$ system was reduced dramatically by 40.1% when compared to pure Polypropylene.

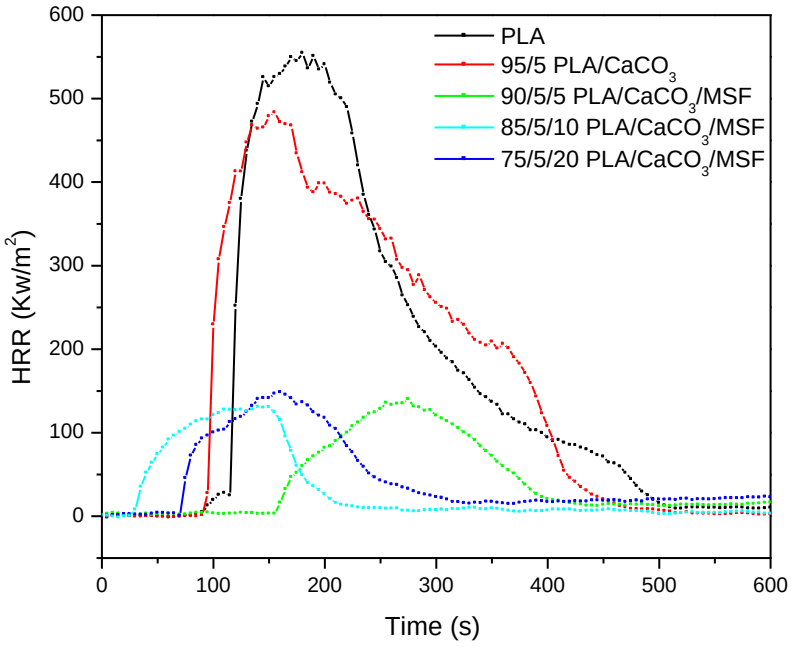

Figure 4.6 Heat Release rate curves versus time of PLA, 95/5 PLA/$CaCO_3$, 90/5/5 PLA/$CaCO_3$/MSF, 85/5/10 PLA/$CaCO_3$ and 75/5/20 PLA/$CaCO_3$.

PLA matrix consisting of both calcium carbonate and maize stalk fibre obtained the lowest PHRR when compared with samples of neat PLA and PLA/$CaCO_3$ composite. PLA/$CaCO_3$/MSF with ratios of 90/5/5 and 75/5/20 showed little or no difference in PHRR values, while PLA/$CaCO_3$/MSF with a ratio of 85/5/10 had a PHRR value of approximately 130 kW/m^2. The difference in PHRR values between PLA, PLA/$CaCO_3$ and PLA/$CaCO_3$/MSF may be attributed to the interaction between calcium carbonate and maize stalk fibre in the PLA matrix as shown in the SEM image in **Figure 4.3** (a, and b). In addition, calcium carbonate acts as compatibilizer, which is responsible for an increase in interfacial adhesion and dispersion between maize stalk fiber and PLA that is characterized by the encapsulation effect of calcium carbonate on the maize stalk fibre, and in turn results in a decrease in flammability. Cheng *et al.* [13] found that calcium carbonate increases the compatibility between bamboo fibres and polypropylene that in turn increased the overall properties of composite. Similarly, AG de Oliveira *et al.* [14] observed a network-type surface and co-continuous phase morphology after the addition of calcium carbonate, indicating that calcium carbonate improved the dispersion/ interaction between the HDPE and PLA phases. **Figure 4.7** (a), (b) and (c) shows the digital images of PLA/$CaCO_3$/MSF with ratios of: (85/5/15), (90/5/5) and (75/5/20).

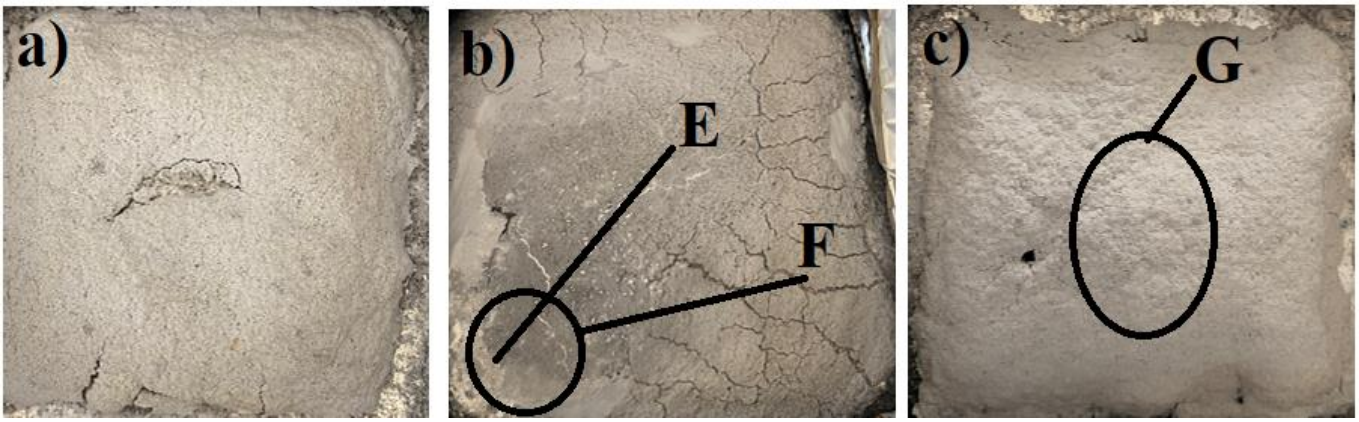

Figure 4.7 Digital images of: (a) 85/5/10 PLA/$CaCO_3$/MSF, (b) 90/5/ 5 PLA/$CaCO_3$/MSF, and (c) 75/5/20 PLA/$CaCO_3$/MSF.

PLA/$CaCO_3$ /MSF sample with a ratio of 85/5/10 showed the best flame-retardant properties as shown in **Figure 4.7** (a). A compact and continuous char formation prevents oxygen and heat from entering the polymer thus reducing the PHRR of the polymer matrix. A compact char layer inhibits the release of combustible gases, the production of a thicker and more compact

residue layer functioning as an insulating barrier is crucial to achieve low heat release rate (HRR) values during burning therefore the creation of this kind of residue layer is essential in order to improve flame retardant properties. This is well supported by cone calorimetry results from Maqsood and Seide [15], which showed that a compact char layer produced from PLA/Ammonium polyphosphate (APP)/starch composites was responsible for restricting heat and mass passage, therefore suppressing combustion and inhibiting the underlying polymeric substrate from burning any further. The authors also found that the compact char layer was formed by the cohesive agglomerates which allowed the char to be more solid and homogenous. **Figure 4.7** (b) shows PLA/$CaCO_3$/MSF with loading ratio of 90/5/5. The digital image shows that maize stalk fibre loading of 5 wt% has a fairly compact char, but with little cracks and voids (symbol E and F). In addition, the presence of cracks impacts this particular char layer negatively, as evident by less flame retardancy of the PLA/$CaCO_3$/MSF 90/5/5 when compared with PLA/$CaCO_3$/MSF 85/5/10 with less or no cracks. However, the PLA/$CaCO_3$/MSF (90/5/5) composite had a better char layer in comparison to neat PLA (**Figure 4.3 (a)** and **Figure 4.5(b))** as evident by low HRR peak for PLA/$CaCO_3$/MSF (90/5/5). The image shown in Figure 4.5 (c) is similar to **Figure 4.7(a)**. **Figure 4.8** shows the carbon dioxide production of neat PLA, PLA/$CaCO_3$ and PLA/MSF. It can be noticed from Figure 4.6 that the incorporation of maize stalk fibre with PLA continues to show poor flame-retardant properties after achieving the highest CO_2 production amongst all the specimens tested. However, the incorporation of PLA with calcium carbonate showed the lowest carbon dioxide production rate. Similar observations were found by Zhou *et al.* [16], the authors utilized calcium carbonate with octaphenylsilsequioxane to enhance the flame retardancy of PEEK composites. The results showed that after nano calcium carbonate and octaphenylsilsequioxane were introduced in the PEEK matrix, a decrease in concentration of flammable gas was observed. Another interesting observation by Qong *et al.* [17] assessed the impact of calcium carbonate on flammability properties of alginate fibres. The results showed that calcium carbonate was effective in improving the flame retardancy of alginate fibres.

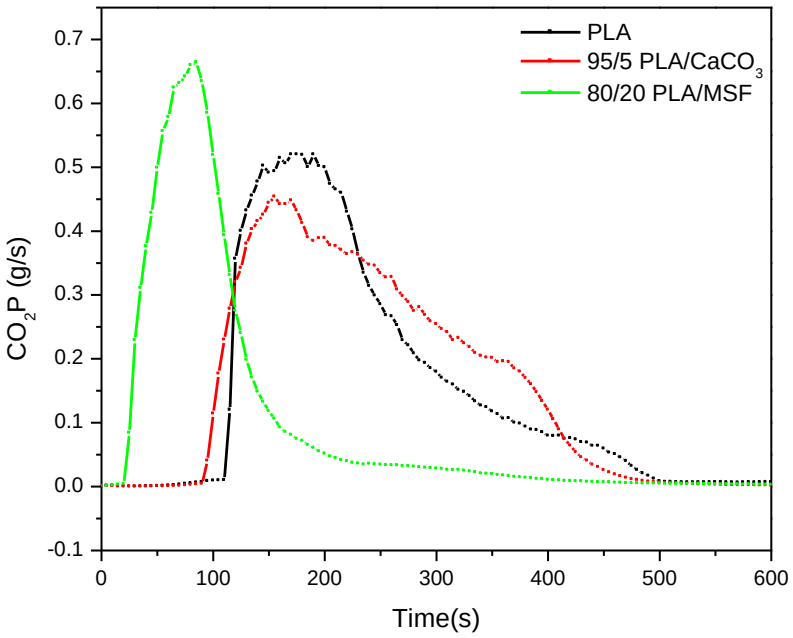

Figure 4.8 Carbon dioxide production of the: PLA, 95/5 PLA/$CaCO_3$ and 80/20 PLA/MSF.

Figure 4.9 illustrates the carbon dioxide production of PLA, PLA/$CaCO_3$, PLA/$CaCO_3$/MSF with sample ratios of 90/5/5, 85/5/10, 75/5/20. The interaction between maize stalk fibre, and calcium carbonate is important for low carbon dioxide production that can be seen in the differences between samples containing PLA/$CaCO_3$/MSF and PLA/$CaCO_3$. Moreover, calcium carbonate continues to act as a compatibilizer by encapsulating maize stalk fibre . It can be said that calcium carbonate improves the composites properties while boosting phase adhesion, lowering interfacial tension, and stabilizing the surface morphology. All PLA/$CaCO_3$/MSF samples seemed to exhibit the lowest overall carbon dioxide, which can be attributed to the excellent dispersion between maize stalk fibre and calcium carbonate. Meanwhile, PLA/$CaCO_3$/MSF with sample ratio of 85/5/10 showed the least carbon dioxide production, which is correspondent to its pHRR value of 130 $kW/m^{2,}$ (i.e., the lowest out of all the samples).

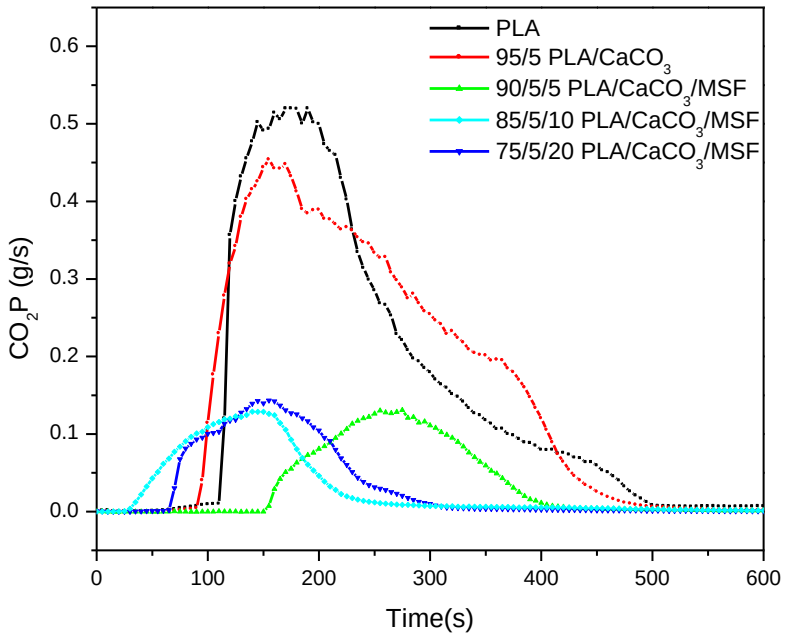

Figure 4.9 Carbon dioxide production of the: PLA, 95/5 PLA/$CaCO_3$, 80/20 PLA/MSF, 90/5/5 PLA/$CaCO_3$/MSF.

Carbon monoxide is emitted by all polymer materials, and therefore it poses a big risk when exposed to people. As carbon monoxide is fatal at relatively low concentrations, human death occurs in about an hour at a concentration of about 1500 ppm [18]. **Figure 4.10** illustrates the carbon monoxide production of PLA and PLA/$CaCO_3$ composite. The data for PLA/MSF is not discussed since the carbon dioxide production (CO_2P) data did not show any peak. The incorporation of 5wt% of calcium carbonate reduced the CO_2P peak of the PLA/$CaCO_3$ when compared to neat PLA. This is due to the ability of $CaCO_3$ in trapping carbon monoxide from leaving the system , and in the process reducing the carbon monoxide when compared to neat PLA.

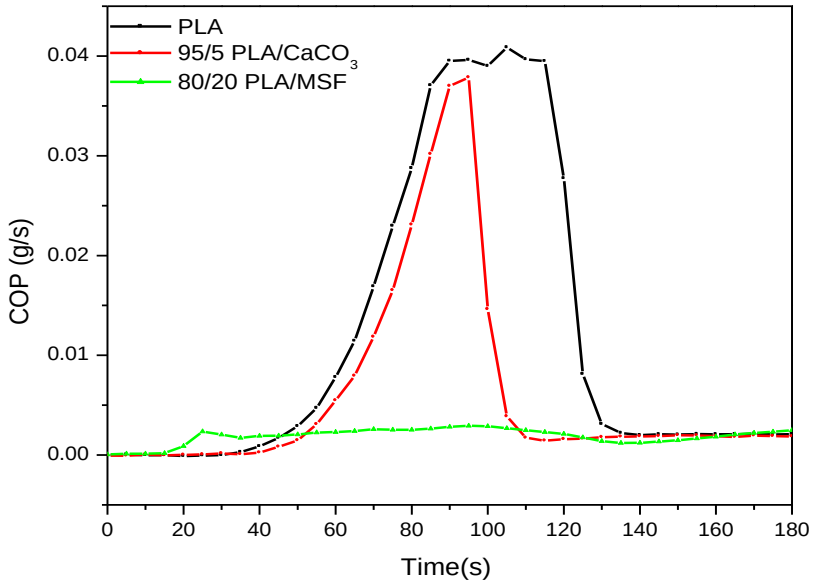

Figure 4.10 Carbon monoxide production of the: PLA, and 95/5 PLA/$CaCO_3$.

Figure 4.11 depicts the carbon monoxide production (COP) of PLA, 95/5 PLA/$CaCO_3$, and 85/5/10 PLA/$CaCO_3$/MSF hybrid composite. Carbon monoxide production of 90/5/5 PLA/$CaCO_3$/MSF, and 75/5/20 PLA/$CaCO_3$/MSF are not reported because there were no peaks for the two samples. The 85/5/10 PLA/$CaCO_3$/MSF hybrid composite showed a lower peak when compared to PLA and 95/5 PLA/$CaCO_3$. The presence of calcium carbonate in the PLA/MSF composite formed an effective char layer which allowed a release of smaller amount of carbon monoxide. The formation of a compact char usually delays the penetration of heat into the composite, and the release of volatile materials from the composite[15]. In case of PLA and PLA/$CaCO_3$ composite, a high carbon monoxide production may be associated with ineffective char residues. Such chars thereby allow ease of penetration for oxygen and heat into the system, which can easily burn the sample and release high amounts of carbon monoxide. It was reported in the literature by Ogabi *et al.* [19] that rigid poly(urethane-isocyanurate) released higher emission of carbon monoxide (CO). Furthermore, it was observed that the amount of CO produced during the thermal degradation of the composite system consisting of carbon/epoxy as well as carbon /phenolic resins became higher with the increase in fiber layers.

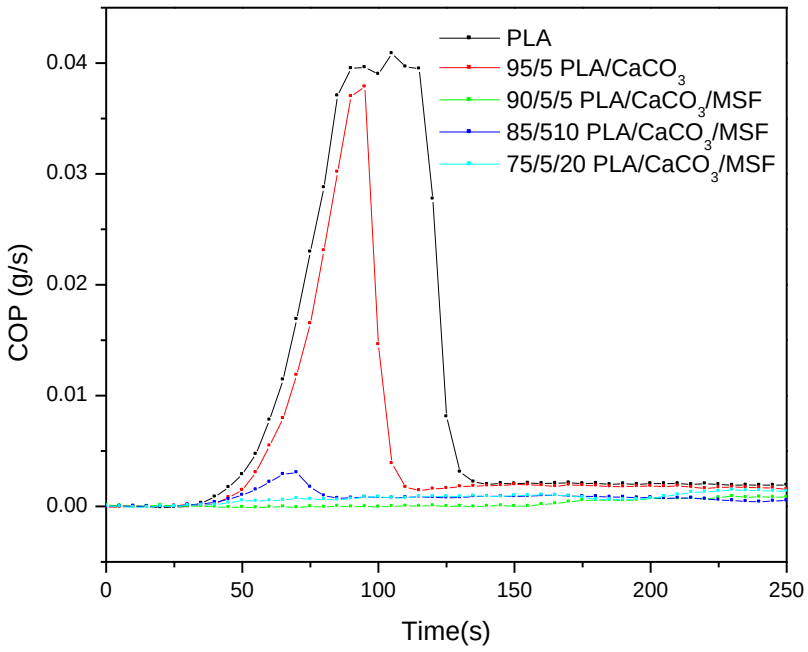

Figure 4.11 Carbon monoxide production of: PLA, 95/5 PLA/$CaCO_3$, and 85/5/10 PLA/$CaCO_3$.

Figure 4.12 shows the total heat release (THR) of: PLA, 95/5 PLA/$CaCO_3$, 80/20 PLA/MSF, 90/5/5 PLA/$CaCO_3$/MSF, 85/5/10 PLA/$CaCO_3$/MSF, and 75/5/20 PLA/$CaCO_3$/MSF. Total heat release (THR) of a polymer is the amount of heat produced when a polymer burns or is exposed to heat. In many applications, especially those involving high fire risk sectors like aerospace and transportation; total heat release is an important feature to be measured [20, 21]. PLA generally has a high THR, and the addition of 5% calcium carbonate only had minimal effect in lowering the THR of PLA. No specific reason was found for lower THR value for 20/80 MSF/PLA composite when compared with neat PLA and PLA/$CaCO_3$. PLA/$CaCO_3$/MSF samples therefore showed lower THR values when compared to neat PLA, PLA/$CaCO_3$, and PLA/MSF composites, which emphasized that the flame retardancy of the PLA/$CaCO_3$/MSF samples due to an effective and compact char.

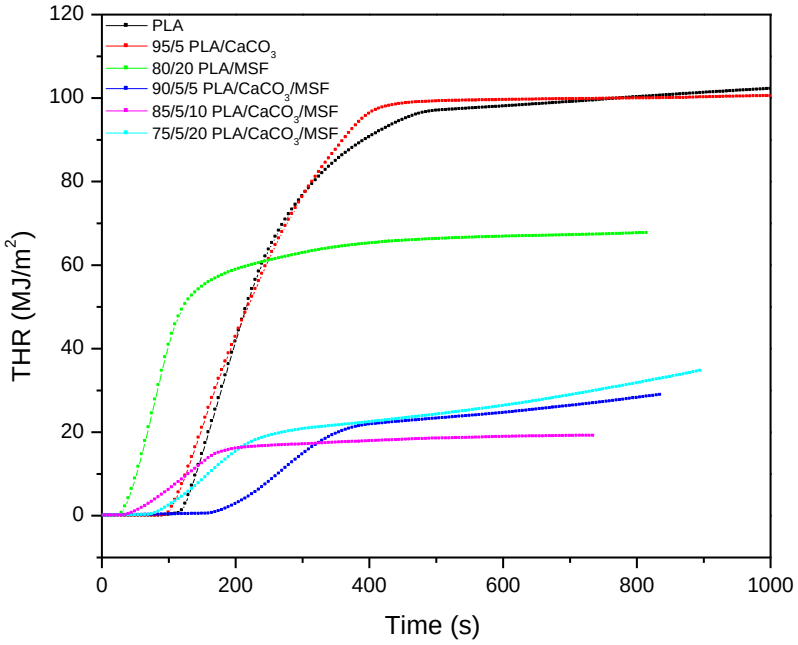

Figure 4.12 Total heat release (THR) of the: PLA, 95/5 PLA/$CaCO_3$, 80/20 PLA/MSF, 90/5/5 PLA/$CaCO_3$/MSF, 85/5/10 PLA/$CaCO_3$/MSF, and 75/5/20 PLA/$CaCO_3$/MSF.

4.3 Thermogravimetric Analysis (TGA)

Figure 4.13 displays the TGA curves of neat PLA and 95/5 PLA/$CaCO_3$, thus indicating a significant improvement in the thermal stability of PLA upon the addition of 5wt% calcium carbonate. This enhancement can be attributed to the thermal stabilizing property of calcium carbonate, which absorbs and gradually releases heat, and thereby leading to a higher decomposition temperature.

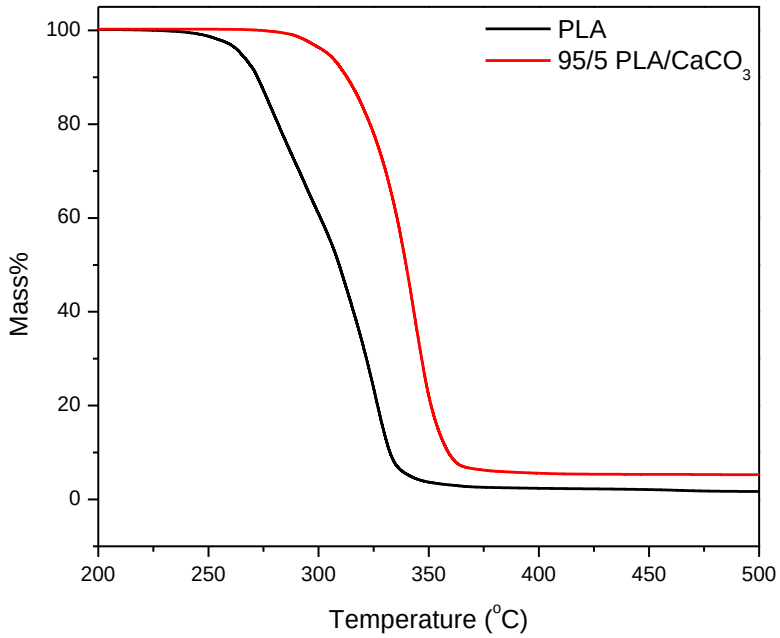

Figure 4.13 TGA graphs of neat PLA and 95/5 PLA/$CaCO_3$.

In a similar study, Elleithy *et al*. [22] investigated the thermal properties of HDPE/micro calcium carbonate composites and found an increase in $T_{50\%}$ with an increase in calcium carbonate content. The researchers attributed this effect to the high thermal resistance of micro calcium carbonate with an onset degradation temperature of 550°C, and its ability to minimize heat permeation into the HDPE matrix. Likewise, Liu *et al.* [23] examined the thermal stability of PVC/$CaCO_3$ composites, and reported that incorporating 40-nm $CaCO_3$ particles in concentrations over 2% improved the thermal stability of PVC. The addition of $CaCO_3$ nanoparticles increased both the onset temperature (T_{onset}), and maximum degradation temperature (T_{max}) of PVC with the effect becoming more pronounced as the concentration of nanoparticles increased. In the present study, the PLA/$CaCO_3$ composite exhibited TGA values at $T_{20\%}$ and $T_{80\%}$ of 322.61 ^{o}C, and 350.99 ^{o}C, respectively as shown in **Table 4.2**. These findings implies that a substantial enhancement of approximately 14% ($T_{20\%}$), and a notable 7.4% ($T_{80\%}$) increase when compared with neat PLA. **Figure 4.14** presents the TGA curves of neat PLA, 90/10 PLA/MSF, 85/15 PLA/MSF, and 80/20 MSF composites. Neat PLA, and its composites displayed a single step degradation. As depicted in **Figure 4.14** and **Table 4.2**, it is evident that all PLA composites containing maize stalk fiber exhibited enhanced thermal stability at $T_{20\%}$, in comparison to neat PLA. Notably, the composite with 90/10 PLA/MSF

demonstrated the highest thermal stability, thus reaching 301.73℃. Both PLA/MSF 85/15 and PLA/MSF 80/20 however showcased a low thermal degradation temperature at $T_{80\%}$ when contrasted with neat PLA. At lower fiber content, (i.e., 90/10 PLA/MSF), there were few fiber pullouts with most of the fiber interacting with fiber as a result enhancing the thermal stability of the composite. Nevertheless, at higher fiber content, there are more less interaction between the fiber and the PLA matrix; thus this poor interaction resulting in fiber acting as catalysts for the degradation of the polymer matrix at $T_{80\%}$. A study conducted by Bajpai *et al.* [24] analyzed the tribological behaviour of Nettle fibre, Grewia optiva, and sisal fibre reinforced PLA composites. Their TGA analysis revealed a reduction in the degradation temperature of PLA with the addition of natural fibers to the matrix. The authors attributed this difference in degradation temperature to various factors such as surface conditions, fiber nature, and poor interfacial bonding with PLA.

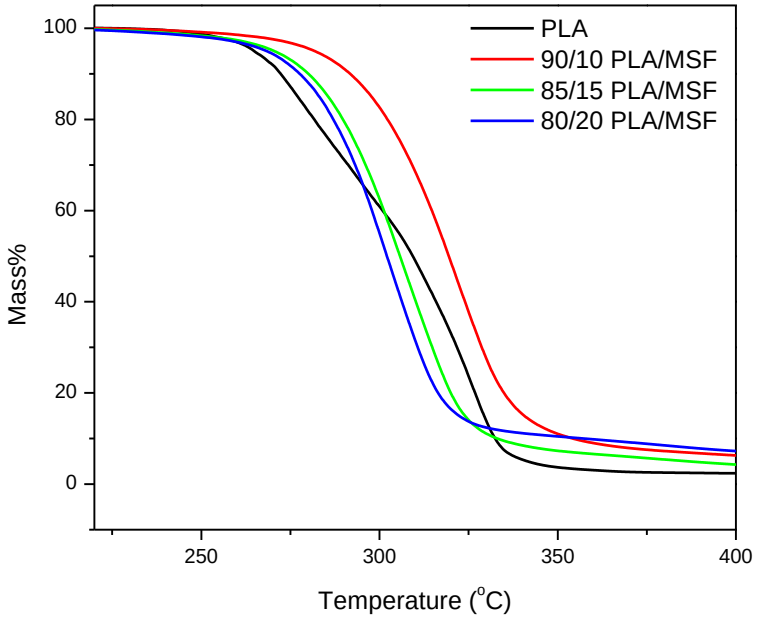

Figure 4.14 TGA graphs of neat PLA, 90/10 PLA/MSF, 85/15 PLA/MSF and 80/20 PLA/MSF.

Figure 4.15 depicts a comparison between the 95/5 PLA/$CaCO_3$ and 90/10 PLA/MSF composites. Both fillers at these contents had likely improved the thermal stability of the composites when compared to neat PLA. Calcium carbonate enhanced the thermal stability of the PLA matrix better when compared to the 90/10 PLA/MSF. As shown in section 4.2, the $CaCO_3$ can form a stable char residue, and such chars can trap volatile materials, and in the process, enhances the thermal stability of the composites.

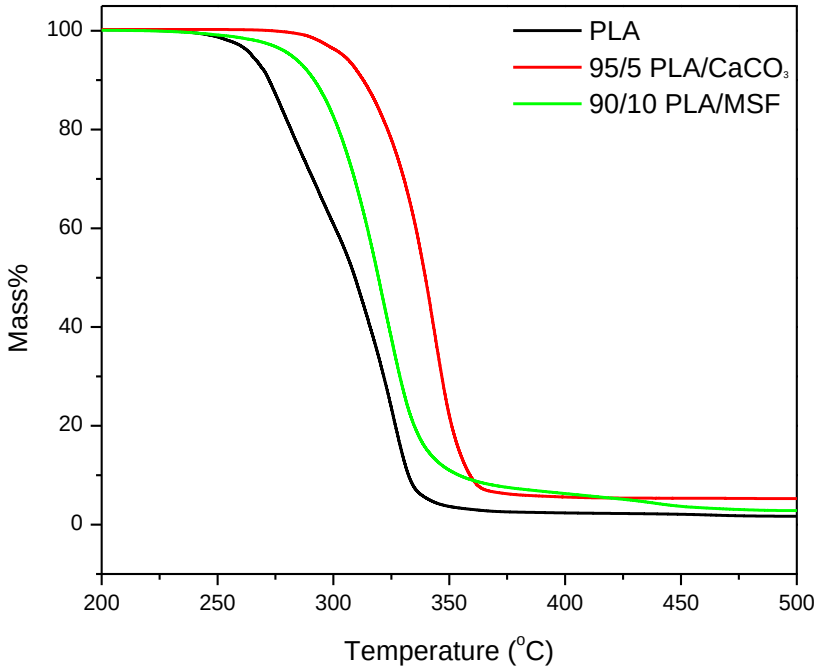

Figure 4.15 TGA graphs of neat PLA, 95/5 PLA/$CaCO_3$, and 90/10 PLA/MSF.

One can also realize that the presence of maize stalk had an impact on the thermal stability in the samples. Meanwhile, the incorporation of maize stalk at lower content somehow enhanced the thermal stability of the PLA matrix, but its presence showed lower thermal stability when in the PLA/$CaCO_3$ composites **(Figure 4.16)**. This indicates that the thermal stability of the 90/5/5 PLA/MSF/$CaCO_3$ is an intermediate thermal stability between the 95/5 PLA/$CaCO_3$ and PLA (**Table 4.2**).

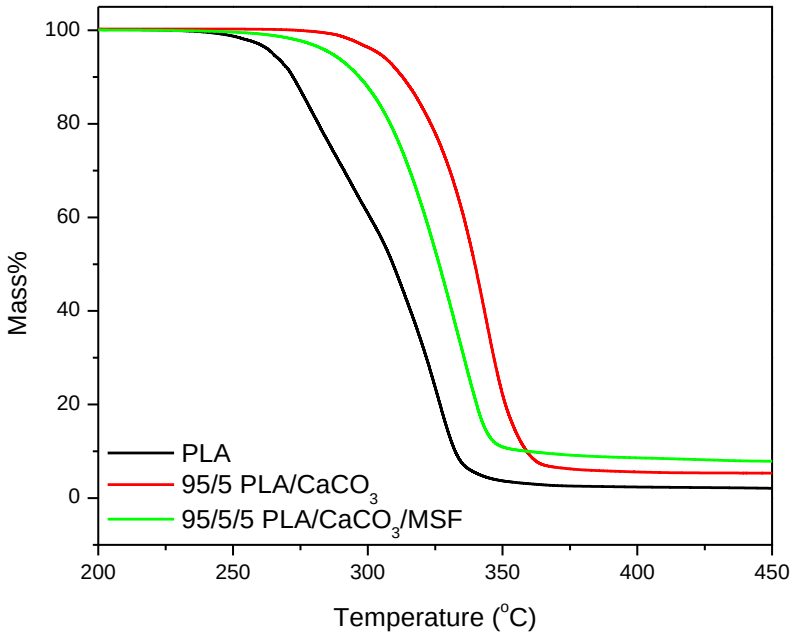

Figure 4.16 TGA graphs of neat PLA, 95/5 PLA/$CaCO_3$, and 90/5/5 PLA/MSF/$CaCO_3$.

Table 4.2 Summary of the TGA results for selective samples.

Samples	$T_{20\%}$	$T_{80\%}$
Neat PLA	280.54	326.73
95/5 PLA/$CaCO_3$	322.61	350.99
90/10 PLA/MSF	301.73	334.39
85/15 PLA/MSF	289.27	319.46
80/20 PLA/MSF	285.73	315.58
90/5/5 PLA/MSF/$CaCO_3$	308.07	340.14

$T_{20\%}$ and $T_{80\%}$ are the degradation temperatures at 20 and 80% mass loss, respectively.

The TGA curves of neat PLA, 95/5 PLA/$CaCO_3$, 90/5/5 PLA/$CaCO_3$/MSF, 85/5/10 PLA/$CaCO_3$/MSF, 80/5/15 PLA/$CaCO_3$/MSF, and 75/5/20 PLA/$CaCO_3$/MSF are displayed in **Figure 4.17**.

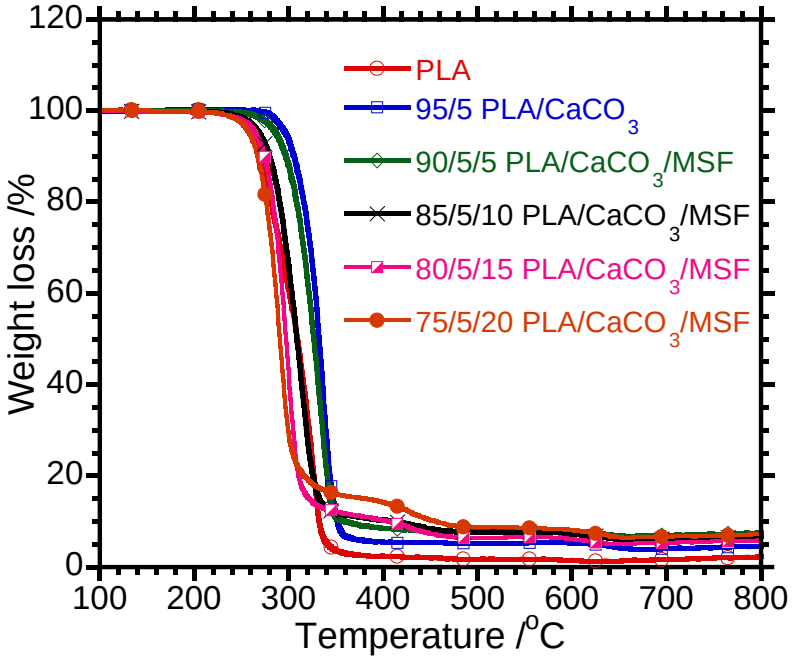

Figure 4.17 TGA graphs of neat PLA, 95/5 PLA/$CaCO_3$, 90/5/5 PLA/$CaCO_3$/MSF, 85/5/10 PLA/$CaCO_3$/MSF, 80/5/15 PLA/$CaCO_3$/MSF, and 75/5/20 PLA/$CaCO_3$/MSF.

According to **Figure 4.17**, the 95/5 PLA/$CaCO_3$ composites showed high thermal stability when compared to hybrid composites. It was found that the presence of MSF reduced the thermal stability of the PLA/$CaCO_3$, however the reduction was not below the thermal stability of the neat PLA. These results are different from the cone calorimeter, whereby the hybrid composites showed lower pHRR values when compared to pristine PLA, and PLA/$CaCO_3$. In **Figure 4.17**, the content of the calcium carbonate was kept constant at 5wt %, while varying the content of the fiber in the hybrid composites. According to **Figure 4.17,** and **Table 4.3**, an increase in fiber content decreased the thermal in the hybrid composites. For an example, $T_{10\%}$ and $T_{50\%}$ of the 90/5/5 PLA/$CaCO_3$/MSF recorded 296.7 and 326.98 °C, respectively when compared with the $T_{10\%}$ and $T_{50\%}$ of the 75/5/20 PLA/$CaCO_3$/MSF, which were revealed as 266.5 and 290.7°C. The above result suggests that there seems to be a better interaction between the fiber and the PLA matrix at lower content *viz* 5wt.%, with the interaction improving better in the presence of 5wt% of calcium carbonate. Also, a thermally stable calcium carbonate acts as a heat protective barrier, and such protective barriers ensures that it

takes longer for heat to reach the substrate, and a better interaction retards the degradation of PLA.

Table 4.3 Summary of the TGA results from all investigated samples.

Sample	**$T_{10\%}$ / °C**	**$T_{50\%}$ / °C**
PLA	272.2	309.4
95/5 PLA/$CaCO_3$	303.8	332.1
95/5 PLA/MSF	298.1	325.6
90/10 PLA/MSF	283.6	311.9
85/15 PLA/MSF	281.6	306.8
80/20 PLA/MSF	278.6	302.8
90/5/5 PLA/$CaCO_3$/MSF	296.7	326.98
85/5/10 PLA/$CaCO_3$/MSF	279.6	308.8
80/5/15 PLA/$CaCO_3$/MSF	274.5	296.7
75/5/20 PLA/$CaCO_3$/MSF	266.5	290.7
85/10/5 PLA/$CaCO_3$/MSF	293.1	321.9
80/10/10 PLA/$CaCO_3$/MSF	286.6	316.6
75/10/15 PLA/$CaCO_3$/MSF	272.1	297.7
70/10/20 PLA/$CaCO_3$/MSF	266.4	291.5

$T_{10\%}$ and $T_{50\%}$ are the degradation temperatures at 10 and 50% mass loss, respectively.

Figure 4.18 presents the thermal stability of the hybrid composites at 10wt% of calcium carbonate ($CaCO_3$). The thermal stability of the hybrid composites at 10wt% of calcium carbonate ($CaCO_3$) showed higher thermal stability for 5wt% when compared to 10, 15 and 20 wt% of the fiber. There were two reasons identified for such an observation. Firstly, there seems to be a better interaction between the fiber and the matrix at lower content of the fiber in the presence of calcium carbonate. A strong interaction between the components of the hybrid system inhibited the diffusion of the volatiles from the hybrid composites, and as a result, enhances thermal stability. Furthermore, low content of the fiber also contributed to an enhanced thermal stability when compared to higher content of the fiber. Based on **Table 4.3**, the 75/10/15 PLA/$CaCO_3$/MSF, and 70/10/20 PLA/$CaCO_3$/MSF showed lower thermal stability when compared to neat PLA. No obvious reason was established for such an

observation; however, one might suspect that this content of the $CaCO_3$ (viz 10wt%), and higher content of the fiber seemed to show trends of ineffectiveness. This behaviour was also observed for 75/5/20 PLA/$CaCO_3$/MSF hybrid, whereby a neat PLA showed higher thermal stability when compared with 75/5/20 PLA/$CaCO_3$/MSF hybrid. One can conclude that at higher content of the fiber, 20wt% calcium carbonate exhibited less impact in terms of improving thermal stability and flammability properties, however there was an improvement in flame resistance of such hybrid ratios**.**

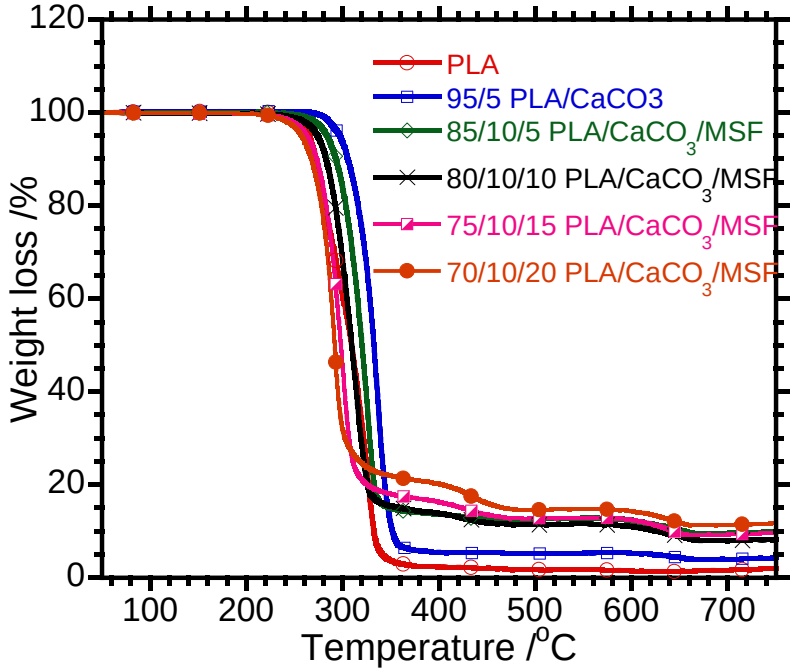

Figure 4.18 TGA graphs of neat PLA, 95/5 PLA/$CaCO_3$, 85/10/5 PLA/$CaCO_3$/MSF, 80/10/10 PLA/$CaCO_3$/MSF, 75/10/15 PLA/$CaCO_3$/MSF, and 70/10/20 PLA/$CaCO_3$/MSF.

4.4. Dynamic mechanical analysis (DMA) of the investigated samples

Figures 4.19 and **4.20** show the storage modulus and tan δ curves of neat PLA, 95/5 PLA/$CaCO_3$, 90/10 PLA/MSF, and 80/20 PLA/MSF composites. The storage modulus is usually associated with the viscoelastic rigidity of the material. The incorporation of the fiber at 20wt% of the fiber enhanced the storage modulus when compared with neat PLA, PLA/$CaCO_3$, and 90/10 PLA/MSF composites. There are various factors that affect the storage modulus of the polymer composites, and they include the nature of the filler(s), stiffness of the filler, interaction between the composite and crystallization of the composites and/or hybrid

composites. In this study, two factors were observed to have impact on the storage modulus of the systems (i.e., stiffness and the interaction between the calcium carbonate, fiber, and PLA matrix). An improvement in storage modulus was therefore attributed to the stiffness of the fiber (*viz* 20wt%) within the PLA matrix. This means that a stiff fiber has a tendency of immobilizing polymer chains, and as a result enhances the storage modulus of the polymer.

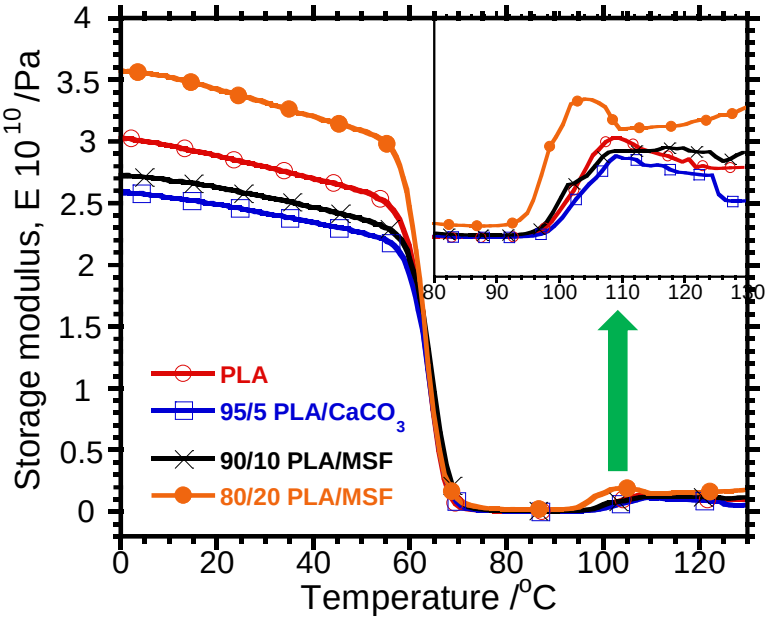

Figure 4.19 Storage modulus vs Temperature for neat PLA, 95/5 PLA/$CaCO_3$, 90/10 PLA/MSF, and 80/20 PLA/MSF composites.

Interestingly, the PLA/$CaCO_3$ had lower storage in comparison to PLA, 90/10 PLA/MSF, and 80/20 PLA/MSF composites. There is no clear explanation about the reduction in storage modulus of the PLA/$CaCO_3$ when compared with neat PLA. It should also be noted that the $CaCO_3$ improved the interaction between the fiber and PLA matrix, and its incorporation alone seems to impact the storage modulus of PLA matrix negatively. Gu *et al.* [25] investigated the dynamic mechanical analysis of PLA reinforced calcium carbonate composites. The results of the study showed that calcium carbonate content above 30% improved the storage moduli, loss moduli, and dynamic viscosities and calcium carbonate content below 20% seemed to reduce the mentioned properties. Notably, calcium carbonate generally has been reported to improve the stiffness of polymers. A study by Kemal *et al.* [26] investigated the toughening effect of nanoparticulate calcium carbonate on poly (vinyl chloride) composite. The results from the

study showed that an increase in calcium carbonate nanoparticles led to an increase in the composites stiffness, which then led to an increase in the storage modulus. **Figure 4.20** illustrates the tan δ vs temperature for neat PLA, 95/5 PLA/$CaCO_3$, 90/10 PLA/MSF, and 80/20 PLA/MSF composites.

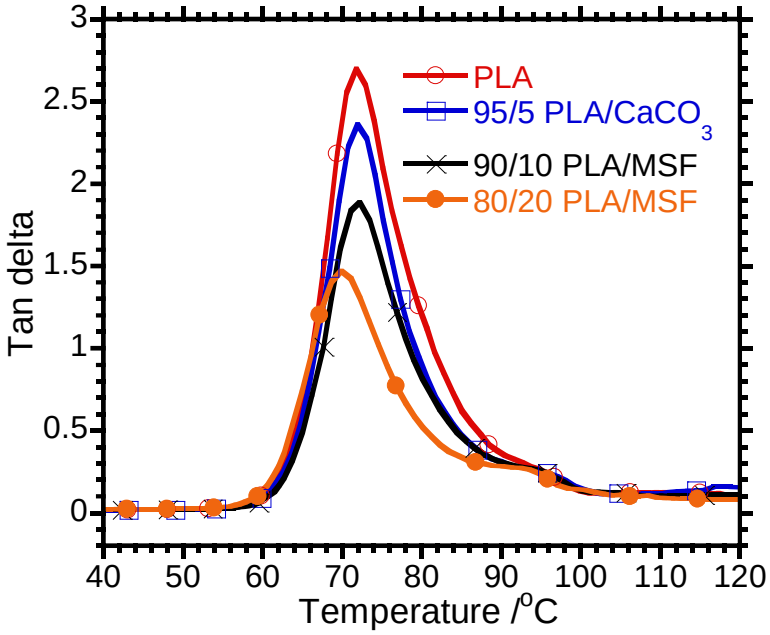

Figure 4.20 tan δ vs Temperature for neat PLA, 95/5 PLA/CaCO3, 90/10 PLA/MSF and 80/20 PLA/MSF composites.

According to **Figure 4.20**, there is a peak in the temperature range between 60 to 80 °C, which might be associated with the glass transition temperature of PLA. Additionally, there was no shifting in the glass transition temperature of PLA with the addition of fillers (*viz* $CaCO_3$ and MSF), and no obvious reason was found for such an observation. Moreover, the reduction in the tan δ peak intensity of PLA with the incorporation of fiber and calcium carbonate was identified. Two possible reasons are associated with such occurrence. Firstly, the incorporation of a stiff and rigid fiber material causes decrease in the tan δ peak; and secondly, the decrease may also be associated with reduction of PLA volume to dissipate vibration energy and fiber agglomerates at higher fiber content. The storage modulus, and tan δ as a function of temperature for PLA, PLA/$CaCO_3$, and PLA/$CaCO_3$/MSF composites are shown in **Figures 4.21** and **4.22**.

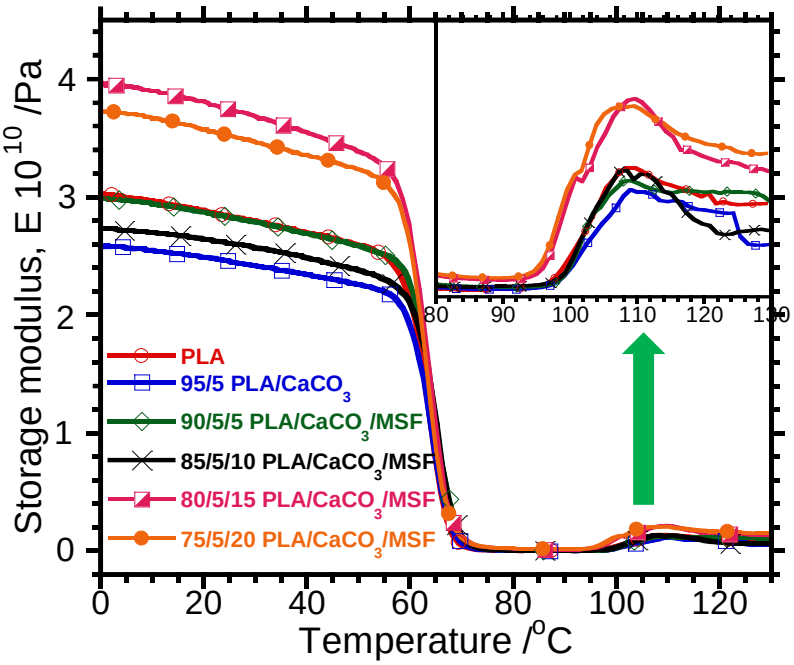

Figure 4.21 Storage modulus of: PLA, PLA/$CaCO_3$, and the natural fiber hybrid composites.

To further emphasize the impact of fiber stiffness at higher content, **Figure 4.21** shows higher storage modulus of the hybrid composites in the presence of 15 and 20wt% of the fiber. This is due to the ability of fibers in immobilizing the chains of the PLA matrix, and the process enhances the storage modulus. Similar observation was reported by Mofokeng *et al.* [27], whereby the presence of sisal fiber in the polypropylene (PP) restricted the segmental motion of the PP matrix due to a high stiffness of the fiber. As it was the case with the previous discussion, the incorporation of fillers into the PLA matrix reduced the tan δ peaks of the PLA matrix (Figure 4.22).

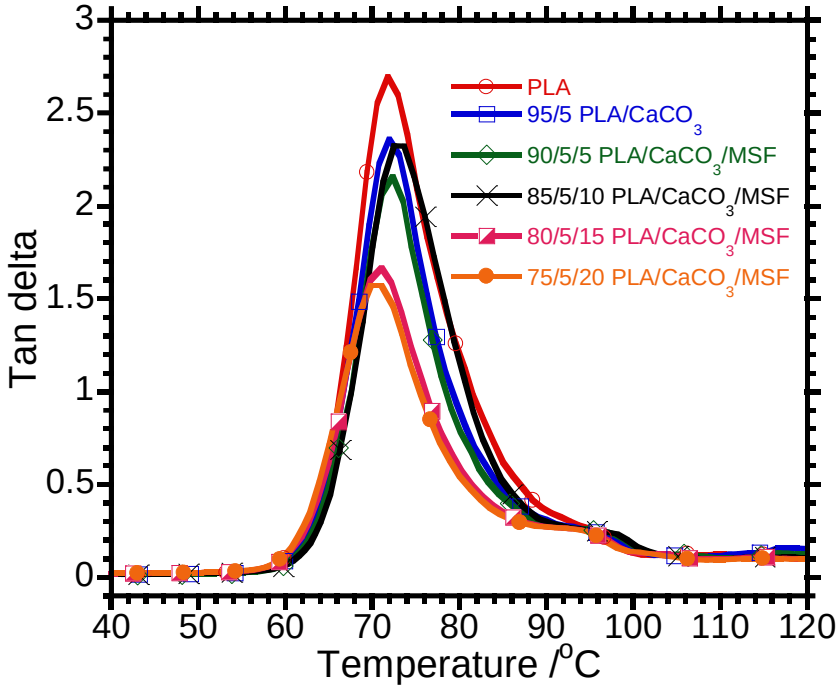

Figure 4.22 Tan delta curves of: PLA, PLA/$CaCO_3$, and the natural fiber hybrid composites.

Figures 4.23 and **4.24** depict the storage modulus and tan delta curves, with the emphasis on 10 wt.% of the calcium carbonate content. The content of calcium seems to have little effect in this case, as the storage modulus was found to increase with high fiber content (15 and 20wt%), as it was the case for 5wt% of calcium carbonate. Furthermore, the tan delta peak was still found to decrease with the addition of the filler(s). One can realize that the dominating factor in terms of enhancing the storage modulus is the stiffness of the fiber and to some extent the dispersion of the fibers within the PLA matrix, but this impact in dynamic mechanical properties of this systems is minimum compared to the stiffness of the rigidity of the fibers.

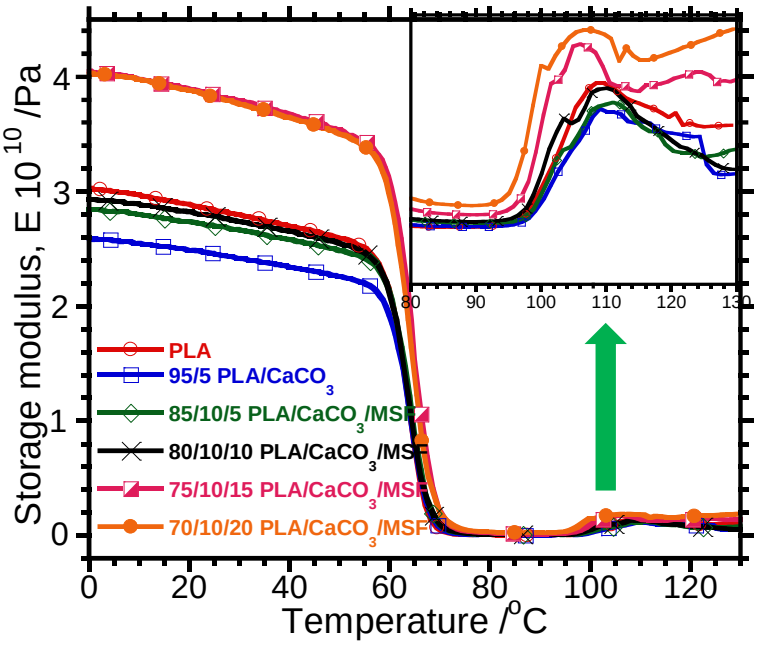

Figure 4.23 Storage modulus of: PLA and its natural fiber hybrid composites at 10wt% of calcium carbonate.

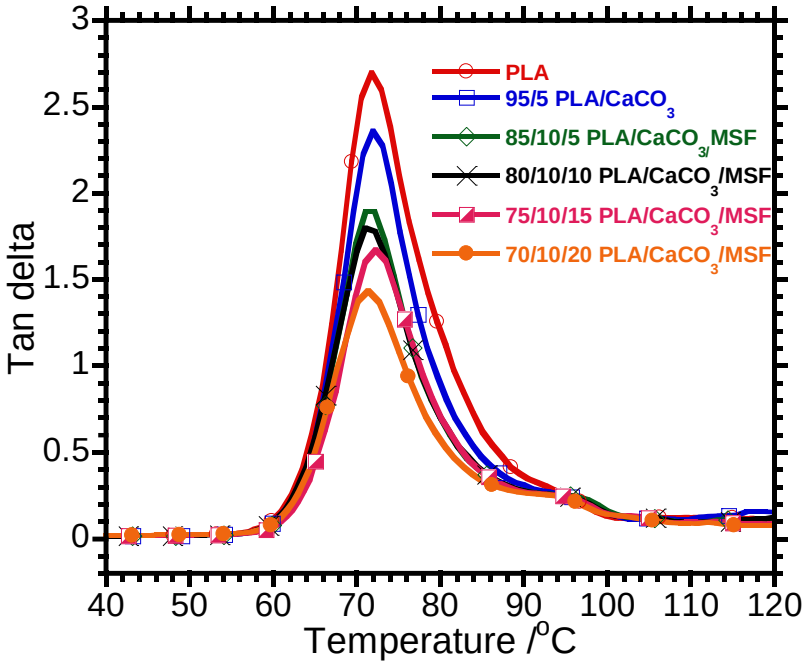

Figure 4.24 Tan delta peaks of: PLA, and its natural fiber hybrid composites at 10wt% of calcium carbonate ($CaCO_3$).

4.5 Rheology of all investigated samples

Rheology was performed to investigate the flow properties of the nanocomposites. The complex viscosity and loss modulus (G'') curves as functions of angular frequency for pristine PLA and binary composites are shown in **Figure 4.25**. The complex viscosity curves of pristine PLA and 95/5 PLA/$CaCO_3$ composite display a Newtonian behaviour for the tested angular frequencies. Incorporating 5wt% $CaCO_3$ to PLA slightly enhanced the complex viscosity and G''. The slight increase in the complex viscosity and G'' is attributed to the restriction of chain mobility induced by dispersion of $CaCO_3$ in PLA. The PLA/MSF composites with various MSF loadings display different viscoelastic behaviours. At low MSF loadings (5 and 10wt%), the complex viscosity and G'' were lower than those of pristine PLA at all tested frequencies. On the other hand, the complex viscosity and G'' were higher than those of pristine PLA at all tested frequencies for higher MSF loadings (15 and 20wt%).

The viscoelastic behaviours of polymer composites are influenced by several factors, namely the polymer matrix, specific polymer-filler interactions and filler network [28]. At lower MSF loadings (5 and 10wt%), the amounts of MSF are inadequate to form a percolation network. This results in the weakening of the molecular interactions between the PLA segments, hence a lower complex viscosity and G'' of 95/5 and 90/10 PLA/MSF than pristine PLA. In contrast, the complex viscosity and G'' of the 85/15 and 80/20 PLA/MSF composites are higher than those of neat PLA for lower frequencies. This suggests that a percolation threshold has been reached at 15 and 20wt% MSF loading, and that the MSF fillers form a network through MSF-MSF or MSF-PLA interactions, hence higher complex viscosity and G'' for 85/15, and 80/20 PLA/MSF composites, than for pristine PLA, and other composites. The complex viscosity and G'' curves for ternary composites at fixed $CaCO_3$ in **Figure A1** follow a trend similar to those in **Figure 4.25**.

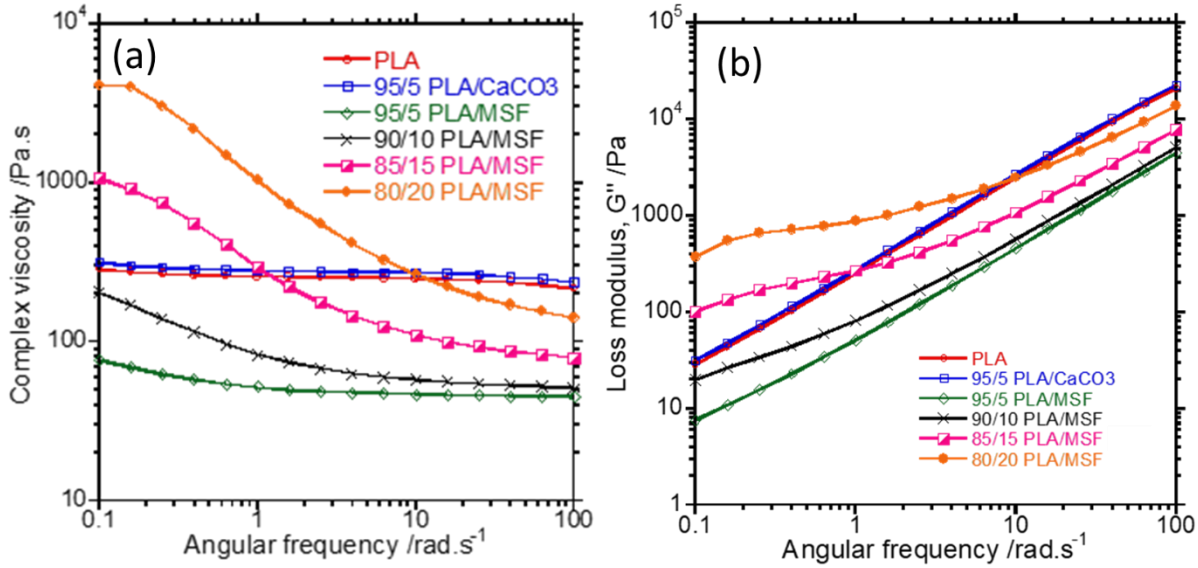

Figure 4.25 Reduced frequency dependence of (a) Complex viscosity, (b) loss moduli G″ of PLA, PLA/$CaCO_3$, and PLA/MSF composites.

4.6 References

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Chapter 5: Conclusions and future recommendations

The aim of the study was to investigate the effectiveness of maize stalk to be be utilized as a natural reinforcing filler in biopolymer matrix. In this study, the content of the fiber in the range of 0-20wt% was added into the PLA matrix and calcium carbonate ($CaCO_3$) was incorporated into the system to enhance the properties of the PLA/MSF composites. It can be concluded that the incorporation of MSF into the PLA matrix resulted in fiber pullouts and debonding, especially at higher fiber content *viz* 20wt%. Even though there was debonding of the fiber within PLA, the stiffness of the fibers improved the dynamic mechanical properties of the PLA matrix. Furthermore, there was an improvement in thermal stability of the composites. The presence of calcium carbonate (*viz* 5 and 10wt%) was found to reduce debonding of the fiber from the matrix, and it further enhanced its compatibility with the PLA matrix. Based on the above findings, one can conclude that calcium carbonate may be utilized as a compatibilizer in fiber reinforced biopolymer matrix. It was recognized that 5wt% of calcium carbonate performed better in terms of improving the adhesion between the fiber and PLA matrix when compared with 10wt% of the $CaCO_3$. Furthermore, the presence of calcium carbonate was found to improve the flame resistance properties of the PLA/fiber composite. Additionally, the dynamical mechanical analysis was found to be affected mostly by the stiffness of the fiber and probably the interaction between the fiber and the polymer. For example, the high fiber contents of 15wt% and 20wt% showed higher storage modulus in the presence of calcium carbonate, irrespective of the content of the calcium carbonate. In some cases, it was realized that the properties of the hybrid system were percentage dependent. The presence of fiber and calcium carbonate improved most of the PLA and PLA/fiber composites properties. This observation was associated with better wettability of the fiber in the presence of $CaCO_3$, and the stiffness of the fiber. It can be concluded that as much as both 5 and 10wt% of the fiber improved the properties of the hybrid composites, 5 wt% of $CaCO_3$ with lower fiber content seems to be dominant in improving majority of the properties. For future consideration, it is recommended to modify the fiber with alkali treatment and incorporate calcium carbonate into the hybrid system. The idea in this case means that the research will apply a synergistic effect of two modifiers to better improve the interfacial adhesion of the fiber and PLA , with the aim of improving the properties of the hybrid system for advanced applications. It would also be interesting to find the optimum ratio of the modifying material (i.e., $CaCO_3$: sodium hydroxide).

Appendix

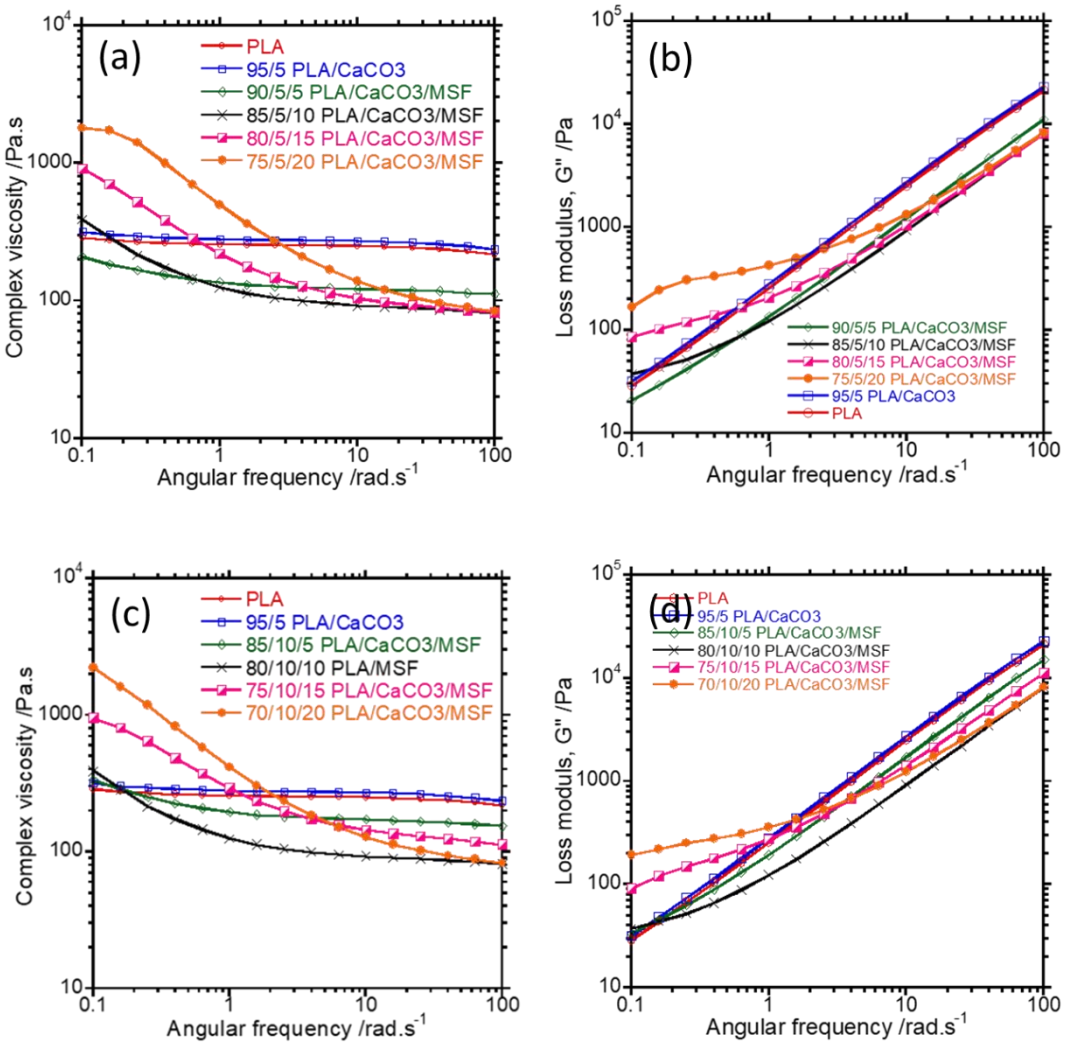

Figure A1. Reduced frequency dependence of (a,c) Complex viscosity, (b,d) loss moduli G″ of PLA, PLA/$CaCO_3$, PLA/MSF, and PLA/$CaCO_3$/MSF composites.