

POLY (LACTIC ACID)/GROUND TIRE RUBBER BLENDS: FLAME RETARDANCY AND WASTE MANAGEMENT

By

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A thesis submitted in fulfilment of the requirements for the degree

Master of Health Sciences:

Environmental Health

In the

Department of Life Sciences

Faculty of Health and Environmental Sciences

at the

Central University of Technology, Free State

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August 2024

DECLARATION

DECLARATION WITH REGARD TO INDEPENDENT WORK

I, Rethabile Bocibo, student number (#####), do hereby declare that this research report is my work. It is submitted for the master's degree in environmental health at the Central University of Technology, Free State. It has not been submitted before for any degree or examination at this or any other university.

AUGUST 2024

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DEDICATION

To God, the heavenly presence that has guided me persistently, providing unwavering strength and support throughout my entire research journey. Amidst challenges and hurdles, your calming influence has been my compass, leading me towards clarity and peace.

To my late great grandmother, Nkhokhoba, your radiant spirit lives on within me, an eternal echo of wisdom and resilience. With this thesis, I strive to continually earn your favour and honour your legacy, knowing you are watching over me.

And lastly, to myself, this thesis is a tribute to the strength I never knew existed within me. The sleepless nights, tireless research, and battles with self-doubt have revealed the depths of my capabilities.

ACKNOWLEDGEMENTS

- I extend my heartfelt gratitude to my supervisor Prof M.J. Mochane and co-supervisor Dr T.G. Mofokeng. Your guidance, knowledge and devotion contributed to this research study have been valuable. I am thankful for the knowledge and skills I have gained under your supervision; without you I wouldn't have been able to make it.
- To my beloved grandparents, Sarah Motaung, Maria and Meshack Nhlapo, I am very grateful for your continuous support and understanding during the whole period of my studies. Your endless prayers have kept me going strong throughout this journey.
- To my mother, Nokufa Bocibo, I am forever thankful for your constant support, sacrifices, and the unconditional love you continuously pour unto me. Your belief in me has been an on-going motivation. My only wish is to continuously make you proud, and I hope this only adds to that and more.
- To my father Godfrey Nhlapo, thank you for your support, love and the words of encouragement I have received to keep me strong and focused.
- To my dearest partner in crime, my steadfast companion, Lebohang Letsitsa, you have been my anchor during this strenuous journey. Those sleepless nights you've spent by my side to keep me company while I was doing research gave me strength and encouragement to continue.
- To my daughter Lesedi, thank you for your patience, compassion, and love throughout this journey. Your blissful presence and innocent laughter have reminded me of the significance of balance and the reason behind my accomplishments.
- To my aunts, Naledi Nhlapo, Gladys Matsi, Mapaseka Mthimkhulu and Dinono Nhlapo I am grateful for your support and words of wisdom. Your presence in my life has encouraged and inspired me to persevere and strive for excellence.
- To Dr T.C. Mokhena, thank you for your contribution in my research journey.
- A special thank you to the Faculty of Health and Environmental Sciences (Central University of Technology, Free State) for the opportunity to undertake my studies at the Department of Life Sciences.
- A special thank you to the National Research Funding and the Central University of Technology for funding me in my studies.
- Additionally, I would like to express appreciation to my family and friends for their well-thought words of encouragement and support through my studies.

ABSTRACT

In 2023, the global production of motor cars reached 94 million, which is 10% compared to the previous year, 2022. The management of waste generated by old car tires has been challenging throughout the world due to the chemical compositions and the vulcanization of tires. Unfortunately, this results in accumulation of waste car tires in landfills causing environmental harm. Nevertheless, there is one promising solution which can be applied to assist in minimizing the number of waste car tires, and it involves repurposing these tires to aid in improving properties of polymers. This approach paves the way to reduce the amount of waste tires disposed each year while improving the properties of polymers for diverse applications. This study investigates the effect of ground tire rubber (GTR) on the properties of poly (lactic acid) (PLA). However, both PLA and GTR are both extremely flammable; therefore, halloysite clay (HC) and zinc borate (ZB) at 3 wt% were added as flame retardants in pure PLA and PLA/GTR blend composites. Various techniques such as scanning electron microscopy (SEM), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), differential scanning calorimeter (DSC), cone calorimetry, rheology, tensile and impact testing were utilized to analyse the properties of the PLA, PLA/GTR, and PLA/GTR blend composites. The incorporation of GTR to neat PLA and PLA composites matrix seems to have affected most results acquired negatively. This is primarily due to the immiscibility of PLA/GTR blend. It also appears that GTR covers the nanoparticles within the PLA matrix hence hindering their effectiveness in enhancing properties of PLA. It was further observed that ZB interacted better with the PLA matrix when compared with HC. There was poor synergy between ZB and HC and this was shown in most of the results. The addition of GTR, HC and ZB seemed to have reduced the thermal stability of PLA, however the char residues of all investigative samples were greater than that of neat PLA. Cone calorimetry showed that the addition of HC to the PLA/GTR blend improved the flammability properties of the blend, with the GTR acting as a flame catalyst in majoring of the investigated samples. The addition of GTR to the PLA matrix seems to affect the mechanical properties adversely.

Keywords: blend composites, flame retardancy, ground tire rubber, polylactic acid, waste management

RESEARCH OUTPUTS

Published book chapter:

1. **Recent developments on the use of eco-friendlier phosphazenes as flame retardants for different polymeric materials**

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LIST OF SYMBOLS AND ABBREVIATIONS

ΔH_{cc}	Crystallization enthalpy
ΔH_m	Melting enthalpy
ΔH_m^{Norm}	Normalized enthalpy for melting
ABS	Acrylonitrile butadiene styrene
APP	Ammonium phosphate
C30B	Cloisite 30B clay
CO	Carbon monoxide
CO ₂	Carbon dioxide
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
DTG	Derivative thermogravimetric
E'	Storage modulus
E''	Loss modulus
EBS	N,N'-ethylenebis(stearamide)
EVA	Ethylene vinyl acetate
FR	Flame retardant
FTIR	Fourier transform infrared
Fe (OH) ₃	Iron chloride hexahydrate
GTR	Ground tire rubber
HC	Halloysite clay
HDPE	High-density polyethylene
H-FRs	Halogenated flame retardants
HNTs	Halloysite nanotubes
IFR	Intumescent flame retardant
LDPE	Low-density polyethylene
LNR	Liquid natural rubber
LOI	Limiting oxygen index
MPP	Melamine polyphosphate
OMMT	Organically modified montmorillonite
PBAT	Poly (butylene adipate-co-terephthalate)
PBS	Polybutylene succinate

PCL	Polycaprolactone
PDLA	Poly (D-lactic acid)
PDLLA	Poly (D,L-lactic acid)
PHA	Polyhydroxyalkanoates
pHRR	Peak heat release rate
PLA	Poly (lactic acid)
PLA-g-MAH	Maleic anhydride grafted
PLLA	Poly (L-lactic acid)
POP	Persistent organic pollutants
PP	Polypropylene
PVA	Poly (vinyl alcohol)
PVC	Poly (vinyl chloride)
PZM	Polyphosphazene
SEBS-g-MAH	Maleic anhydride grafted styrene-ethylene/butylene-styrene
SEA	Specific extinction area
SEM	Scanning electron microscopy
T _{10%}	Decomposition temperature at 10% mass loss
T _{50%}	Decomposition temperature at 50% mass loss
T _{cc}	Cold crystallization temperature
TEM	Transmission electron microscopy
T _g	Glass transition temperature
TGA	Thermogravimetric analysis
T _m	Melting temperature
TTI	Time to ignition
UL 94	Vertical burning test
wt%	Weight percentage
X _c	Degree of crystallinity
XRD	X-ray diffraction
ZB	Zinc borate
ZnO	Zinc oxide

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CHAPTER 1: Introduction

1.1. Background

Waste from car tires has been a global challenge to handle. The tire industry project for the World Business Council for Sustainable Development declares that 1 billion waste tires are produced yearly (Kościuszko *et al.*, 2022). Four billion of such tires are currently in stockpiles and landfills around the world. The Innovation for Sustainable Development Network estimates that 60 million waste tyres are on South African soil. These tires are highly resistant to photochemical decomposition, biodegradation, chemical reagents, and high temperatures due to their chemical compositions and cross-linked structures (Al-Malki *et al.*, 2013). Discarding of waste tires in landfills is one of the most harmful approaches, as it results in severe environmental problems and lacks potential development for the future (Fazli and Rodrigue, 2020).

Waste tires affect the environment negatively in many ways. They pose a fire threat when discarded in landfills. When they do catch fire, they release a black, dense smoke comprising toxic pollutants such as carbon monoxide (CO), carbon dioxide (CO₂) and sulphur dioxide (SO₂). The toxic gases cause air pollution and impair the visibility of fire fighters, which in turn result in failure to extinguish these fires (Ramarad *et al.*, 2015). In 2012, 1.3 million tires in a landfill at Iowa City in the United States of America caught fire. It took the fire fighters eight days to extinguish the fire successfully, due to thick smoke plume, which reduced their eyesight (Downard *et al.*, 2015). The burnt tires released 450 000 L of run-off pyrolytic oil. Studies show that these pyrolytic oils pollute the soil and can be carried by rainwater to nearby streams and rivers causing water pollution and affecting aquatic life (Machin, Pedroso and De Carvalho, 2017). At landfills, they become a breeding site for vectors, such as rats and mosquitoes, as well as dangerous animals (e.g. snakes). These put the health and safety of nearby communities at risk. In countries where malaria, dengue and yellow fever are prominent, these mosquitoes can transmit these viruses to nearby communities (Moasas *et al.*, 2022). Figure 1.1 illustrates an image of waste tires occupying a landfill site.

Developed countries such as Europe and China have restricted the discarding of waste tires at landfills due to the environmental concerns mentioned above. Several approaches have been investigated to reuse and recycle tire rubbers in several applications. For instance, research indicates that it is possible to generate biofuel through the combustion of discarded tires in

boilers and burners for energy recovery (Rowhani and Rainey, 2016). Studies show that tire pyrolysis can be used to produce products such as carbon black and in producing durable asphalt pavements (Alfayez, Suleiman and Nehdi, 2020). In 2012, the South African government permitted the recycling and economic development initiative of South Africa (REDISA) Integrated Industry Waste Tire Management Plan (IIWTMP)(Redisa, 2023). The plan initiated a distinctive strategy built around the concept of extended producer responsibility, meaning that both the domestic manufacturers and the manufacturers of tires that are imported would pay for the recycling of their own product.



Figure 1.1: Waste tires at a landfill site (Alfayez, Suleiman and Nehdi, 2020)

However, in the current study, poly(lactic acid) (PLA) is blended with ground tire rubber (GTR) as a strategy to help manage waste tires while improving the properties of PLA. PLA is a biodegradable plastic that is derived from renewable plant sources such as sugar and starch. It has been used in food packaging, biodegradable bags and bio-medicinal devices. It is estimated to replace petroleum-based polymers owing to its excellent mechanical attributes, ease of processing and semi-crystalline nature (Ye *et al.*, 2021; Lim, Auras and Rubino, 2008). Although biobased biodegradable polymers have higher production costs than traditional petrochemical plastics, they are eco-friendly and can degrade naturally in the environment. This reduces the number of plastic waste pollution at landfills and in the environment. These type of polymers are also less harmful to the environment, as they do not

release toxic chemicals when they decompose (Moshood, Nawanir and Mahmud, 2022). Polymer blends have been studied for more than 50 decades because of their theoretical and practical importance. A polymer blend is a material that is formed when two or more polymers are mixed together to create novel polymeric materials with different unique physical properties (Markovic and Visakh, 2017). Polymer blends are designed in a way that minimizes the weaknesses of the individual polymers while taking advantage of their strengths. Over the years, polymer blending has sparked a lot of interest from researchers as an easy and cost-effective way of creating versatile polymeric materials for commercial purposes.

Generally, there are two types of blends, namely miscible (homogenous) and immiscible (heterogenous) blends. Miscible blends contain polymers that mix well at molecular level and become evenly distributed, resulting in desired properties such as uniform morphology throughout. An example includes a blend of poly(vinyl chloride) (PVC) and butadiene/acrylonitrile, where the butadiene/acrylonitrile component serves as a permanent plasticizer for the PVC component in wire and cable insulation applications (Robeson, 1984). Immiscible blends consist of polymers that do not mix intimately at molecular level and tend to phase separately. An example is a blend of acrylonitrile butadiene styrene (ABS) and polysulfone in which desired properties increased toughness, heat, and distortion temperature (Robeson, 1984). The previously mentioned immiscible blend is used in food service trays, plumbing fixtures and other important industrial applications (Robeson, 1984). Blending rubber and polymers is an innovative way of developing new types of polymeric materials. It is another ideal solution of managing plastic and rubber waste discarded at landfills by recycling and reusing to create polymeric materials with advanced properties (Heller *et al.*, 2022). The particle size and distribution of GTR have a significant impact on producing a compound with suitable properties. Zhang *et al.* (2012) used a mechanical processing method called the solid-state mechanochemical milling using a pan-mill type equipment to prepare polypropylene (PP)/GTR blend to enhance the dispersion of GTR in PP matrix. The GTR particles were in the range of 40 to 500 μm and grinded into ultrafine particle size after 20 cycles of milling that evenly distributed in the polymer matrix. The results showed that the milled/treated GTR/PP blend had better mechanical properties than the untreated GTR/PP blend (Zhang *et al.*, 2012). Kościuszko *et al.* (2022) used injection moulding to prepare the PP/GTR blend. As displayed in Figure 1.2, the first stage was associated with grinding the 7 mm GTR particles into smaller size range of 100–600 μm using the original knife mill

method. The authors used modified and unmodified PP/GTR formulations comprised of 30 to 90 wt.% GTR. The addition of 1.5 wt% of 2,5-dimethyl-2,5-di-(tert-butylperoxy)-hexane modifier resulted in higher tensile strength, strain at break and impact strength due to adhesion between the components when compared to unmodified compositions. Moreover, the impact strength reduced when the GTR was incorporated at lower loadings (<50 wt%). However, samples with higher loadings of GTR (>50 wt%) did not break during impact tests. This was associated with the prevalence of the elastic phase within the material and an increase in the elongation at break. The study by Zhang *et al.* (2012), which used a pan mill, showed better dispersion of GTR in the PP matrix than that of Kościuszko *et al.* (2022), which used knife milling and injection moulding to prepare the PP/GTR blends.

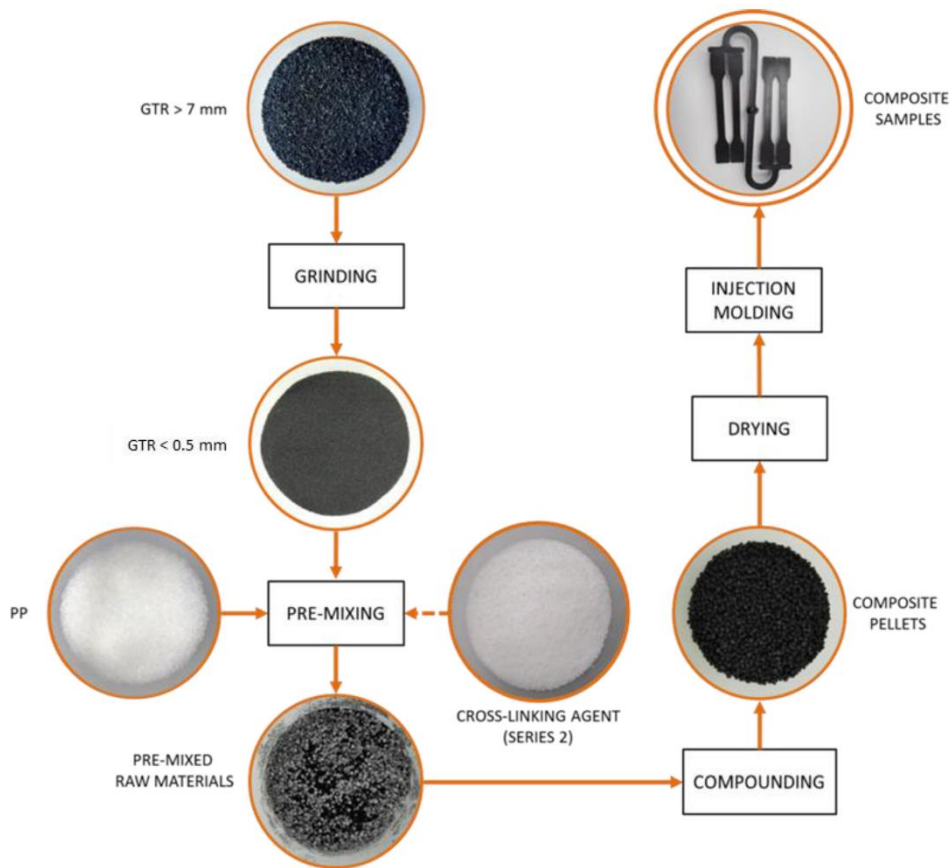


Figure 1.2: Preparation of PP/GTR blend (Kościuszko *et al.*, 2022)

Most polymeric materials are utilized across different industries and in day-to-day human life. However, most polymers are highly inflammable, which poses a risk to human health and property in case fire breakouts (Gao *et al.*, 2019). Flame retardants (FRs) have been applied to polymers to help reduce their level of flammability. These FRs can be divided into two, namely halogenated and non-halogenated FRs. Halogenated FRs were first used over the years due to their effectiveness and durability. However, the compounds released by them are

persistent organic pollutants (POP), meaning that they are able to stay in the environment for extended periods of time and accumulate in organisms. They are toxic to the environment and tend to release harmful gases, which are a threat to the environment and human health when exposed to fire (Mokhena *et al.*, 2022; Gao *et al.*, 2019). Non-halogenated or biobased FRs such as the zinc borate (ZB), and halloysite clay (HC) used in this study have gained more interest in research as a replacement for halogenated FRs due to their eco-friendlier features. These FRs work by releasing water to the surface of the polymer, forming a char layer and reducing the amount of smoke released (Mokhena *et al.*, 2022). Bao *et al.* (2023) developed a novel flame retardant consisting of halloysite nanotubes (HNT), polyphosphazene (PZM) and iron chloride hexahydrate ($\text{Fe}(\text{OH})_3$). The developed $\text{HNT@PZM@Fe}(\text{OH})_3$ flame retardant was added in the epoxy resin matrix to enhance its flame retardancy, as shown in Figure 1.3. The FR showed an improvement in the amount of char residue produced in the epoxy resin. It was deduced that the compact char structure significantly contributed to preventing further combustion of the epoxy resin and the emission of combustible gases.

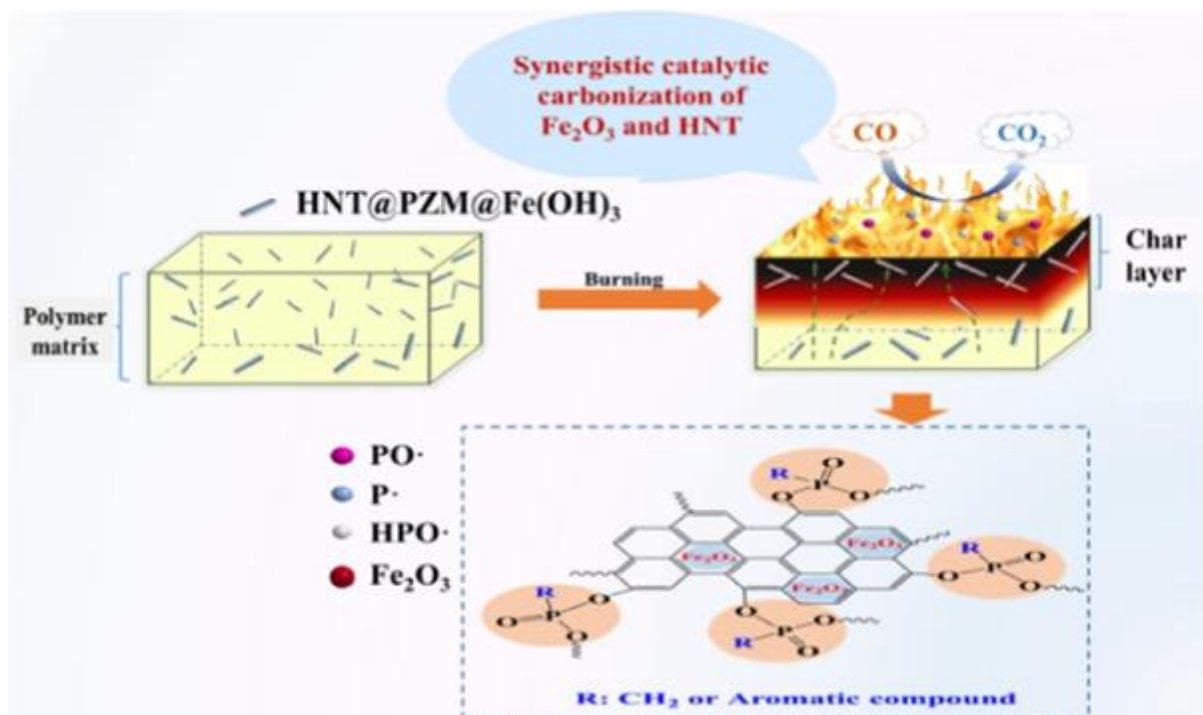


Figure 1.3: Flame retardancy mechanism of $\text{HNT@PZM@Fe}(\text{OH})_3$ on the epoxy resin matrix (Bao *et al.*, 2023)

1.2. Problem statement

Waste management of tires is a massive problem worldwide. At least two-thirds of the billions of used tires around the world each year end up dumped at legal or illegal waste sites. Excessive accumulation of waste tires in landfills causes soil pollution, water pollution and air pollution, which affect the environment, human and animal health negatively. It has been estimated that over 16 000 residential fires occurred in Cape Town between 2009 and 2016. Households have many items and appliances made of plastics that are highly flammable and which can easily catch fire and, once ignited, they can rapidly spread the fire, leading to serious hazards like loss of property, injury, or even death. Therefore, it is essential to develop effective strategies for converting rubber tire waste into valuable products that enhances the well-being of the environment and human life.

1.3. Aim

The aim of the research is to develop a PLA/GTR blend that is highly resistant to fire.

1.4. Objectives

- To develop a solution for managing waste tires in landfills
- To investigate the effect of GTR on the properties of PLA
- To investigate the effect of halloysite clay and zinc borate on the flammability properties of PLA/GTR blend
- To investigate the synergy of halloysite clay and zinc borate on the thermal stability of PLA and PLA/GTR blend

1.5. Thesis structure

This thesis consists of five chapters and an appendix. The chapter titles are listed below.

Chapter 1:	Introduction
Chapter 2:	Literature review
Chapter 3:	Materials and methods
Chapter 4:	Results and discussion
Chapter 5:	Conclusions and recommendations
Appendix	

1.6. References

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CHAPTER 2: Literature review

2.1. Overview on plastics

The demand for flame-retardant materials has risen significantly in recent years due to growing concerns about fire safety in various plastic industries. Petroleum plastics are derived from non-renewable resources and are characterized by their extended chains of molecules, which have found extensive use in numerous sectors due to their light weight, versatility and cost-effectiveness (Jiang *et al.*, 2018). The ease of processing and corrosion resistance properties of these plastics makes them attractive for both every-day and industrial use. One of their key attributes is their capacity to be moulded or shaped into various forms using processes such as injection moulding, extrusion, or blow moulding. Plastics can be categorised into commodity resins and specialty resins based on their properties, production volume, and specific applications. Commodity resins are produced in large quantities and are cost-effective for durable goods and commonly used disposable items. Alternatively, specialty resins are produced at low volume and higher cost. They are engineered to possess specific properties for specialized applications and have the ability to compete with die-cast metals in plumbing, hardware, automotive and agricultural applications (Atabek and Dogan, 2019). The examples and an overview of the commodity and specialty resins are provided in Table 2.1.

Table 2.1: Overview of the commodity and specialty resin's properties and applications

Properties	Uses	Examples
Commodity resins		
Good chemical resistance	Toys	Polypropylene
Corrosion resistance	Plastic bottles	Polyethylene
Ease of processing	Packaging	Polystyrene
Lightweight	Food packaging	Polystyrene
High production volume	Pipes	PVC
Specialty resins		
Heat resistance, light transmittance	Specialized applications such as Components for MRI scans	Polycarbonate

High performance	Automotive parts	Polyamide
Superior heat resistance	Plumbing components	Polyether ketone
Enhanced durability	Aerospace and defence	Polytetrafluoroethylene

However, the prolonged use of petroleum plastics has a negative impact on the environment, as they are difficult to degrade naturally. When dumped in landfills, petroleum plastics can stay in the environment for many years, thus contributing to land and water pollution. Moreover, the burning of petroleum plastics produces toxic fumes that cause air pollution. Over the years, a lot of research trends have focused on replacing petroleum plastics with environmentally friendly plastics. Biodegradable plastics are able to undergo decomposition in the environment by micro-organisms such as fungi and bacteria (Thakur *et al.*, 2018). Biodegradable polymers can be biobased or petroleum based. Biobased polymers are produced from natural renewable resources, such as starch, cellulose, or sugar. The examples include polyhydroxyalkanoates (PHA), poly(lactic acid) (PLA), polybutylene succinate (PBS), etc. Petroleum-based bioplastics are synthetic polymers that are produced from non-renewable resources. They are designed to break down through natural processes, and they contain hydrolysable functional groups such as esters, amides and urethanes (Olaiya *et al.*, 2019). Examples of petroleum-based bioplastics include polycaprolactone (PCL), poly(vinyl alcohol) (PVA), and poly(butylene adipate-co-terephthalate) (PBAT). Despite their existence in several variations, bioplastics have not yet fully replaced traditional petroleum plastics due to higher production costs. Amongst biodegradable polymers, PLA is one of the most promising biodegradable polymers due to its biocompatibility, mechanical strength and processability (Qi, Ren and Wang, 2017; Singhvi, Gokhale and Zinjarde, 2019). It is a biobased polymer derived from lactic acid (LA) that can be acquired using the fermentation of sugars derived from corn and sugarcane.

2.2. Properties of PLA

PLA is an aliphatic polyester with a constituent monomer, lactic acid ($\text{CH}_3\text{-CHOHCOOH}$). It has two types of stereoisomers, L- and D-lactic acid, due to an asymmetric carbon atom. These stereoisomers play a very vital role in the crystallization and mechanical properties of

PLA. There are three forms of PLA that can be produced, namely poly(L-lactide) (PLLA), poly(D-lactide) (PDLA), and poly(DL-lactide) (PDLLA)). PLLA and PDLA are semi-crystalline types of PLA with a glass transition temperature range from 55-60 °C and a high melting temperature of 180 °C. They have an estimated tensile modulus of 3 GPa, flexural modulus of 5 GPa, flexural strength of 100 MPa, tensile strength of 50-70 MPa and an elongation at break of about 4% (Farah, Anderson and Langer, 2016).

When compared to other aliphatic polyesters, PLA has exceptional properties, such as high mechanical strength, high modulus, bio-absorbability, transparency, energy savings and low toxicity. These properties make it suitable for various applications, such as biomedical devices, packaging, agricultural films, and automotive industries. The meso-lactide (PDLLA) is an amorphous type of PLA with low tensile strength, glass transition temperature of about 55 °C and no melting point (Vroman and Tighzert, 2009). Research studies have shown that semi-crystalline PLA is much more preferred than the amorphous PLA, especially when higher mechanical properties are desired. The lactide monomers are chiral and the mechanical properties of PLA can differ, depending on the ratio of L- and D-lactic acid.

PLA is industrially synthesized in two ways, namely direct condensation polymerization (polycondensation) of lactic acid (LA) and the ring-opening polymerization (ROP) of lactide. The direct condensation polymerization process is used to attain low molecular weight PLA and is regularly implemented in bulk by distilling off the condensation water. The process can be performed either with or without a catalyst in the presence of gradually increasing vacuum and temperature conditions (Mehta *et al.*, 2005). The production of low molecular weight is due to the equilibrium among the free acid, the oligomers, and the water produced during the reaction. The ring-opening polymerization is a vital method for obtaining a high-molecular weight of PLA. The key step in this procedure is the usage of high-purity lactide. This lactide is prepared via a decompression method, where water is removed from the system and then followed by the addition of catalysts in the reactor. After certain periods of hours, lactide is attained and undergoes its ring opening to polymerize into PLA (Cheng *et al.*, 2009). The degree of crystallinity of PLA will differ, depending on the molecular weight, the stereo chemical makeup of the backbone and the kind of functional groups that can be added to it. Displayed in Figure 2.1 is an example for the production of PLA. PLA is insoluble in water (hydrophobic) due to the presence of $-\text{CH}_3$ side groups. The produced PLA pellets have a clear transparent colour and can be processed

through injection moulding, blow moulding, film extrusion, thermoforming, fibre spinning, and film forming. The drawbacks of PLA, which limit its application in various industries are poor toughness, flammability and lower thermal stability. Therefore, there is a need for blending PLA with other polymers or the incorporation of different fillers to address its drawbacks. Fillers such as clay (Thanh *et al.*, 2023) and flame retardants (e.g. zinc borate) (Malucelli, 2022) are introduced into polymers to reduce their flammability.

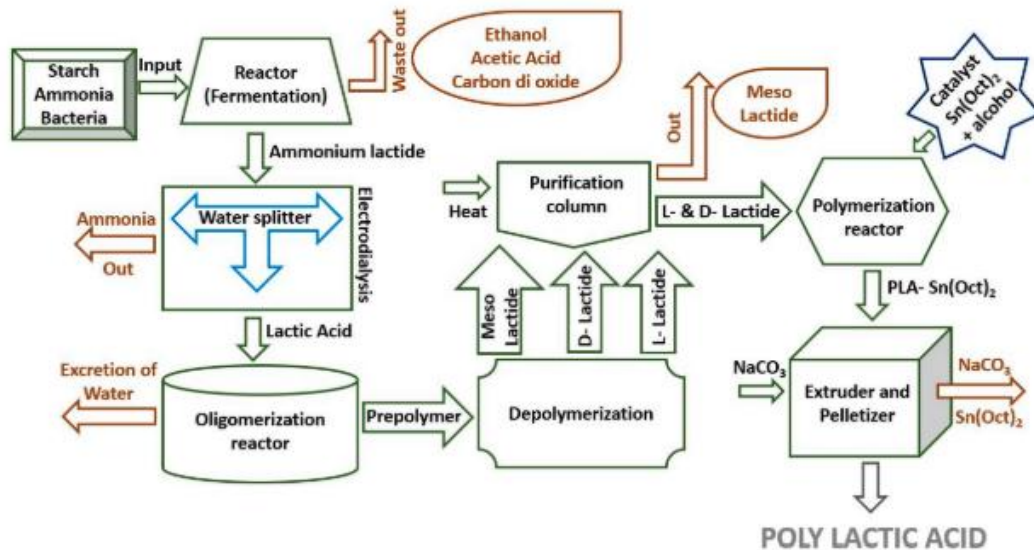


Figure 2.1: A step-by-step process for the production of PLA (Ranakoti et al., 2022)

2.3. Properties of halloysite clay

Halloysite clay, also called halloysite nanotubes (HNTs) is a 1:1 layer clay mineral of the kaolin group, where each layer is comprised of a tetrahedral (Si-O) and octahedral (Al-OH) sheet. The chemical composition ($\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5 \cdot n\text{H}_2\text{O}$) and structure of HNTs are similar to that of kaolinite, but halloysite has unit layers that are separated by the occurrence of the monolayer of water molecules (Abdullayev and Lvov, 2013; Yuan, Tan and Annabi-Bergaya, 2015). It exists in two forms, namely the hydrated form ($\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$) with an interlayer d_{001} spacing of 10 Å and the anhydrous ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) with a d_{001} spacing of 7 Å (Massaro, Noto and Riela, 2020; Capsoni *et al.*, 2022). HNTs can be found in soil, weathered or hydrothermally altered rocks and saprolites. It is found in various locations worldwide, especially in wet tropical and subtropical regions. There are more HNTs deposits in countries such as Brazil, United States of America, China, New Zealand and Turkey. When extracted from various sources pure halloysite appears to be a white colour, but the colour may vary from yellowish to brown in some deposits due to impurities

from Fe^{3+} , Cr^{3+} , or Ti^{4+} compounds and ions substituting for Al^{3+} or Si^{4+} (Abdullayev and Lvov, 2013). Halloysite comes in various morphologies such as platy, spheroidal, and tubular, depending on where it was found or mined and its crystallization. Despite various morphologies, the hollow tubular structure is the most common morphology of halloysite (see Figure 2.2) (Joussein *et al.*, 2005; Massaro *et al.*, 2020). The outer surface of halloysite is made up of siloxane (Si-O-Si) groups, which form the negatively charged outer surface. The hollow internal surface has gibbsite-like groupings of aluminol (Al-OH) groups, which form the positively charged inner one surface. The occurrence of reactive sites in the inner and outer surfaces of nanotubes is an excellent property of halloysite. This adds to its outstanding flame-retardant properties in polymers and makes it a good candidate for other applications such as controlled drug release, nanotemplating and adsorption (Capsoni *et al.*, 2022; Rawtani, Satish and Rao, 2023). The walls of HNTs comprises 10–15 bilayers, with an interlayer spacing of approximately 0.72 nm and a density of 2.53 g/cm³. When it comes to the size of HNTs, it is important to note that they will differ according to the geographical location of where they were sourced. Reported sizes on various studies include a length of 2–40 μm , an outer diameter of 10–50 nm, and an inner diameter of 5–20 nm. Goda *et al.* (2018) reported the HNTs length ranges from 0.2 to 2 μm , the inner diameter ranges from 10 to 40 nm, and the outer diameter of 40 to 70 nm. In another research study the tubes had a length in the range of 0.2–1.5 μm , the inner and outer diameters of the tubes were in the ranges of 10–30 nm and 40–70 nm, respectively (Massaro *et al.*, 2020).

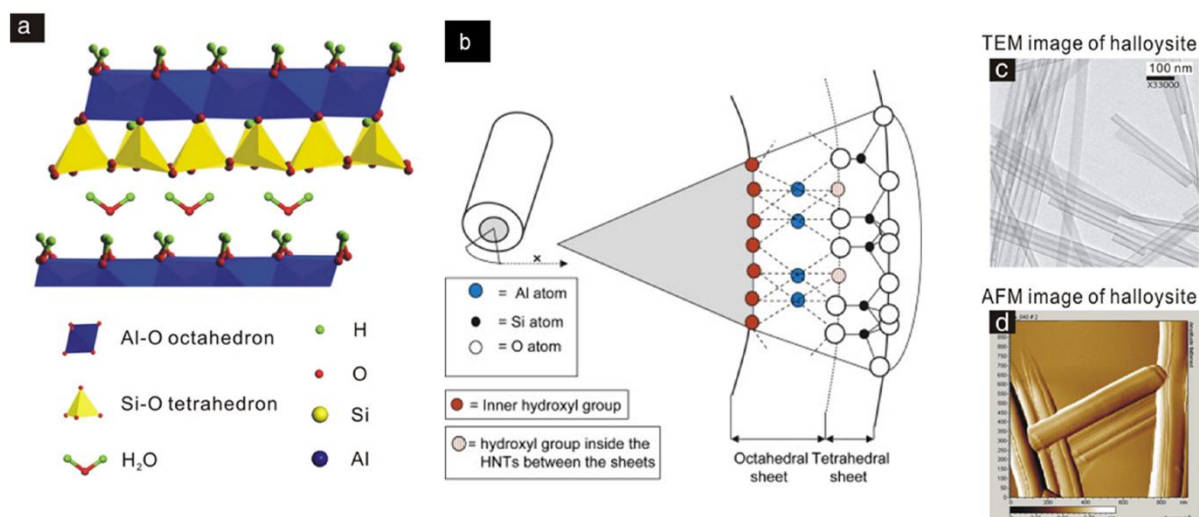
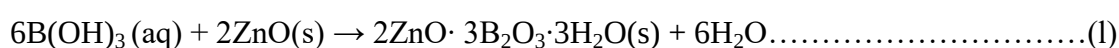


Figure 2.2: (a) displays the crystalline structure of HNTs, (b) tubular atomic configuration of HNTs, (c) Transmission electron micrograph of HNTs and (d) Atomic force micrograph of HNTs (Yuan *et al.*, 2015; Massaro *et al.*, 2020)

2.4. Properties of zinc borate

Zinc borate (ZB) is a white, odourless crystalline powder with a molecular weight of approximately 434.6 g/mol. Figure 2.3 shows the colour property of ZB (Fang *et al.*, 2013; Atabek and Dogan, 2019). ZB can be classified as either hydrous or anhydrous. Hydrous ZB contains water molecules that are chemically bound to the zinc and borate ions and are an essential part of the compound's structure. It is hygroscopic and absorbs moisture from its surroundings. Anhydrous ZB, on the other hand, does not contain water molecules, it is non-hygroscopic, and more stable in dry conditions (Gao and Zhang, 2015; Fatima *et al.*, 2018). Hydrated ZBs come in many variations, which differ in their zinc/boron ratios and water content, e.g. $4\text{ZnO} \cdot \text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$, $\text{ZnO} \cdot \text{B}_2\text{O}_3 \cdot 1.12\text{H}_2\text{O}$, $\text{ZnO} \cdot \text{B}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, $6\text{ZnO} \cdot 5\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$, $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, $3\text{ZnO} \cdot 5\text{B}_2\text{O}_3 \cdot 14\text{H}_2\text{O}$, and $\text{ZnO} \cdot 5\text{B}_2\text{O}_3 \cdot 4.5\text{H}_2\text{O}$. Hydrated ZB can be synthesized as either nanoparticles or micron-sized particles. The use of micron-sized particles affects both the flame-retardant properties and mechanical strength of polymer materials negatively, limiting the application of ZB inorganic powders (Savrik, Balkose and Ulku, 2011). This occurs because micron-sized particles disperse poorly on the polymer surface and tends to form more agglomerates, which adversely affect polymer properties. As a result, there is growing interest in nano-sized ZB due to its unique properties and ease of use.

ZB is synthesized by the reaction of zinc oxide and boric acid or borate salts or zinc salts and boric salts as seen below (Baltaci *et al.*, 2013):



The methods used for synthesizing ZB are precipitation in aqueous media, inverse micro-emulsion, ethanol supercritical fluid drying technique, homogeneous precipitation method, hydrothermal method, sonochemistry, and ultrasonication (Ipek, 2020). The factors that affect the formation of ZB include molar ratio, water volume, pH, sealing state, reaction time, and temperature (Baltaci *et al.*, 2013). Over the years, various methods have been developed for the synthesis of ZB. ZB has a wide range of applications, most notably its use as a flame retardant in polymer composites. Further research into the properties and potential uses of ZB will continue to expand its industrial applications and provide valuable insights into its potential benefits.

A study on the production of hydrated zinc borate ($2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$) through a single-step hydrothermal reaction between boric acid and zinc oxide in the presence of seed crystal was conducted (Yalçın *et al.*, 2021). The authors investigated the effects of reaction temperature (110 °C and 120 °C) and time while keeping other parameters constant. The scanning electron microscope (SEM) images showed that the morphology of ZB whiskers is noticeably influenced by the duration of the reaction, likely due to variations in the rates of crystallization and growth mechanisms. Overall, lower reaction times yielded agglomerated ZB, whereas longer reaction times yielded an almost homogenous mixture of ZB whiskers, with diameters and lengths of less than 1 µm and 1-10 µm, respectively. The developed ZB whisker structures have the potential for improving the mechanical properties of polymer composites. Zheng *et al.* (2009) synthesized ZB nano-whiskers at ambient conditions (70°C) with phosphate esters as a modifying agent. The resulting product manifested as a stable white powder. The X-ray diffraction (XRD) patterns of the synthesized samples exhibited a remarkable match with the characteristic peaks of the monoclinic crystal structure of $4\text{ZnO} \cdot \text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$, indicating a formation of a pure phase.

ZB effectively reduces flammability by releasing water vapour and forming a protective char layer during combustion, and it suppresses smoke generation during fire incidents. The morphology and particle size of zinc borate play an important role in its use as an additive for polymers. According to Yalçın and Gönen (2021), zinc borate whiskers, which resemble fibres with a high surface area due to their small dimensions, have been shown to enhance the mechanical properties and flame retardancy of polymers. It decomposes around 980 °C, indicating its high thermal stability. The boron trioxide (B_2O_3) moiety within zinc borate is capable of creating a glassy layer, which effectively blocks the oxygen in the air from entering the burning system, thus preventing further oxidation of the char. The study conducted by Ning and Guo (2000) shows that the incorporation of zinc borate in the polyvinyl chloride (PVC) matrix reduced the smoke density of PVC and promoted char formation during combustion. Zinc borate is known for its low toxicity and is not classified as hazardous. Moreover, zinc borate demonstrates anti-corrosion properties and offers protection against moisture and corrosive environments (Yalçın and Gönen, 2020). It is compatible with various materials, such as polymers, rubbers, textiles, coatings and wood, which enhance its applications in different industries (Zhang *et al.*, 2015; L. Wang *et al.*, 2021). Other than being a filler in polymer composites, it is also used in electrical cables,

building materials, automotive components, textiles, and coatings, and is commonly incorporated into materials during manufacturing.

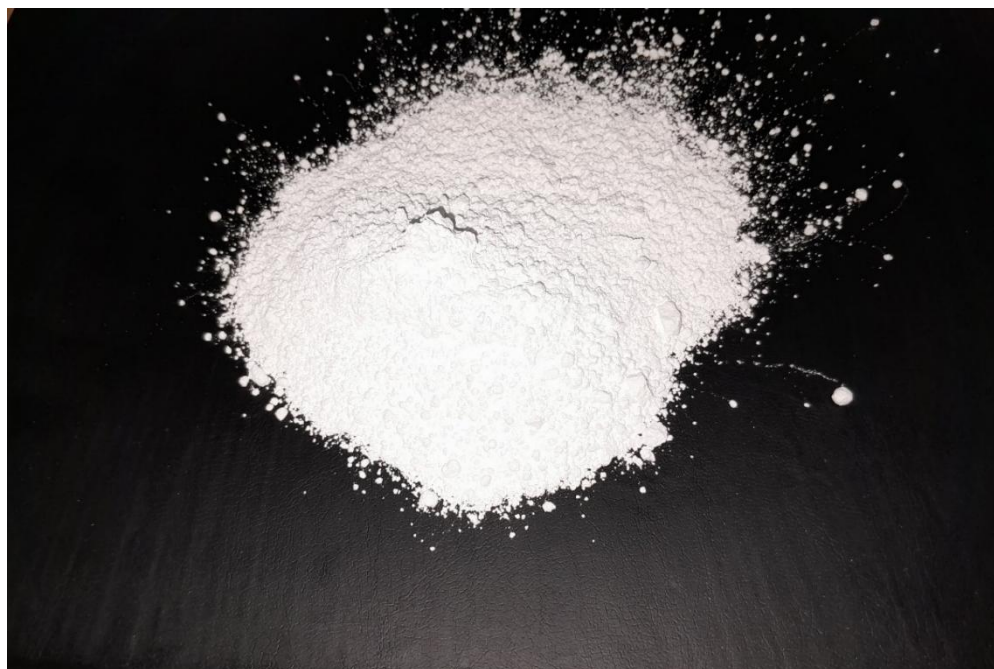


Figure 2.3: Zinc borate's colour property

2.5. Binary clay and zinc borate containing PLA nanocomposites

2.5.1 Morphological development of PLA/clay and PLA/zinc borate nanocomposites.

Understanding of the morphological features is important in the polymer nanocomposite world, because the overall performance is dictated by nanostructures and morphology. The morphology of filled PLA composites is often analysed using scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR) and x-ray diffraction (XRD). XRD and FTIR have been utilized proficiently to determine the crystalline structure and functional groups of polymeric materials, respectively. Over the years, the morphological features of PLA/HNT composites have been reported by many authors. Chen *et al.* (2017) prepared PLA and rod-like HNTs using melt extrusion. The SEM micrographs showed good dispersion and few aggregates of HNTs within the PLA matrix. In addition, there were voids in the matrix, indicating a probability that adhesion between PLA and HNT did not always occur. In another study, PLA/HNTs were prepared by conventional extrusion compounding followed by injection moulding (Montava-Jorda *et al.*, 2019). The field emission scanning electron microscopy (FESEM) images showed fine

particle dispersion of HNTs embedded in PLA. However, increased loadings of HNTs resulted in the formation of aggregates. Risyon *et al.* (2016) used solution casting to prepare PLA/HNT films. The authors used FTIR to show that there is a likelihood of interaction between PLA and HNTs *via* hydrogen bonding in PLA/HNT films, resulting in interfacial adhesion. Therefore, it can be deduced that the preparation method of PLA/HNT composites plays a role of influencing interfacial adhesion between the constituents. Research has also shown that interfacial adhesion between HNTs and PLA is not perfect due to a low concentration of hydroxyl groups on the exterior surface of unmodified HNTs. Guo, Qiao and Zhang (2016) treated HNTs with sodium hydroxide (NaOH) to increase a number of hydroxyl groups on the external surface of HNTs, a feature that would promote better dispersion of HNTs on the PLA matrix. Although the authors used melt mixing to prepare the PLA/HNT composites, their SEM images showed that the increased loading of unmodified HNTs resulted in the formation aggregates within the PLA matrix with evidence of microvoids suggesting debonding between the constituents of the composites. However, the modified HNTs showed a relatively better dispersion and adhesion in the PLA matrix due to better hydrogen bonding between the modified HNTs and PLA (Montava-Jorda *et al.*, 2019). Similar findings were reported in a study where HNTs were modified with quaternary ammonium salt (Prashantha *et al.*, 2013). Murariu *et al.* (2012) pre-treated HNTs with a silanization reaction of 3-(Trimethoxysilyl) propyl methacrylate and melt blended it with the polyester matrix (HNT (QM)) and then later incorporated in PLA. The TEM micrographs showed well dispersed individualized HNTs in PLA. This was associated with the presence of the organomodifier (HNT (QM)) on the HNTs surface, reducing the surface-free energy and nanotube/nanotube interactions, inhibiting the formation of aggregates during melt mixing. Based on these studies, it seems that modifying HNTs results in better dispersion and distribution of HNTs with fewer aggregates, which in turn could result in enhanced mechanical properties of PLA. In addition to modification of HNTs, solution mixing can also improve dispersion further.

According to my literature search, until recently, there have been no studies that report the morphology of PLA/ZB composites. Zhan *et al.* (2014) and Long *et al.* (2019) only incorporated ZB into PLA in the presence of other fillers to form hybrid PLA/ZB/filler composites without producing a PLA/ZB composite sample. Therefore, there is a need to investigate the effect of ZB on the properties of PLA in binary PLA/ZB composites. However, for the purpose of this review chapter, zinc oxide (ZnO) has been used as a

substitute to survey its effects on the properties of PLA. PLA/ZnO composites have been prepared by solution casting method, melt compounding, flat die extrusion and the volatilizing method (Benali *et al.*, 2015; Murariu *et al.*, 2015; Nasab, Tabari and Azizi, 2018; Shankar, Wang and Rhim, 2018; Shojaeiarani *et al.*, 2019; Tang *et al.*, 2020; Da Cruz Faria *et al.*, 2021). In most studies of PLA/ZnO composites, there seems to be a homogenous dispersion of ZnO nanoparticles on the PLA matrix. However, there was a formation of larger aggregates within the PLA matrix at higher ZnO loadings (Shojaeiarani *et al.*, 2019; Tang *et al.*, 2020). Doumbia *et al.* (2015) prepared PLA/ZnO composites using a melt spinning process. The ZnO nanoparticles were treated with triethoxy-caprylsilane (ZnO_T), while others were left untreated (ZnO_{NT}). TEM images showed the poor dispersion of ZnO_{NT} and the formation of aggregates, whereas ZnO_T resulted in the finest dispersion within the PLA matrix. Murariu *et al.* (2015) incorporated epoxy-functional styrene-acrylic oligomers in the PLA/ZnO composites to evaluate their chain extension capabilities. These chain extenders are often utilized in a single processing step to greatly improve the molecular weight, the mechanical and rheological properties without requiring complete drying. The TEM images show that even though that the chain extender increased the viscosity of PLA in molten state, the ZnO nanoparticles were well dispersed on the PLA matrix. The study by Da Cruz Faria *et al.* (2021) investigated the crystallization behaviour of PLA/ZnO nanocomposites. They prepared the PLA/ZnO by flat die extrusion and analysed the morphology by use of XRD. The XRD curves of neat PLA and PLA/ZnO displayed amorphous halos, signifying low degree of crystallinity in these films. In the investigation of FTIR spectra of a study conducted by Nasab *et al.* (2018), the percentage of bonds between ZnO and PLA increased by enhancing the zinc oxide percentages. Avci *et al.* (2024) investigated the impact of various boron compounds as fillers on PLA. The study examined ulexite, ZB, and a combination of boric acid and borax. The composites were mixed by a twin-screw co-rotating extruder and injection moulded into various test specimens. All three boron compounds dispersed well within the PLA matrix.

2.5.2 Thermal properties of PLA/clay and PLA/zinc borate nanocomposites

Thermal stability refers to the capability of a material to sustain desirable mechanical properties, such as strength, toughness, or elasticity at a given temperature (Kholodovych and Welsh, 2007). The main source of thermal stability in polymers is the bond energy between atoms within the polymer chain. The strength of the chemical bond executes an upper limit

on the vibrational energy a molecule may have without bond breakage (Rezakazemi, Sadrzadeh and Matsuura, 2018). Generally, polymers can behave either as thermoplastics or thermosets when subjected to heat. Thermoplastics melt and become mouldable when exposed to heat, and then solidify upon cooling. However, the chemical nature of polymers remains unaltered during the melting or solidification process. Thermosets undergo irreversible changes when heated due, to their crosslinked networks (Beyler and Hirschler, 2002). In order to measure the thermal stability and thermal transitions of polymeric materials, most researchers use thermogravimetric analyser (TGA) and differential scanning calorimetry (DSC), respectively. TGA is a technique used to study the changes in mass of a sample as a function of temperature or time under controlled heating conditions (Rezakazemi, Sadrzadeh and Matsuura, 2018; Zainal *et al.*, 2021). This method yields valuable insights into the thermal stability, decomposition behaviour, moisture content, and other pertinent properties of the sample. DSC is amongst the best extensively used techniques for determining thermal characteristics and phase transition of polymers as a function of temperature and time. It involves simultaneous heating of a sample and a reference material. This method provides significant information about the melting temperature (T_m), crystallization temperature (T_c), cold crystallization temperature (T_{cc}), glass transitions (T_g), and other thermal events (Avci *et al.*, 2024).

Most researchers have shown that the incorporation of zinc oxide within the PLA matrix reduces the thermal stability of PLA (Ghozali *et al.*, 2018; Shankar *et al.*, 2018; Shojaeiarani *et al.*, 2019; Bajwa *et al.*, 2021; Da Cruz Faria *et al.*, 2021). Da Cruz Faria *et al.* (2021) attribute the decrease in thermal stability of PLA/ZnO composites to the catalytic effect of ZnO nanoparticles, which promotes earlier degradation of PLA. Generally, it is known that fillers such as nanoclay (Najafi, Heuzey and Carreau, 2013) and graphene (Chieng *et al.*, 2014) improve the thermal stability of PLA. Therefore, the lower thermal stability of PLA/ZnO nanocomposites can be overcome by forming hybrid systems such as PLA/ZnO/nanoclay and PLA/ZnO/graphene nanocomposites. Chu *et al.* (2017) investigated ZnO in synergy with silver nitrate ($AgNO_3$) on the antimicrobial characteristics of PLA. Their DSC results show that the T_g , T_m and T_c of PLA/ZnO, PLA/ $AgNO_3$ and PLA/ZnO/ $AgNO_3$ decrease when compared to neat PLA. They associated the decrease in T_c of PLA/ZnO with the fact that the ZnO nanoparticles within the PLA might have acted as the heterogeneous nucleus and progressed the cold crystallization of PLA chains at lower temperatures. There were double melting peaks, and this was explained as the result of

annealing that occurs during the taking of DSC scans. This means that crystals had time to recrystallize a few degrees beyond the melting point and then remelted. In another study (Shojaeiarani *et al.*, 2019), the decrease in T_g was associated with the fact that the addition of ZnO interrupted the intermolecular attraction of PLA chains, which in turn promoted enhanced chain mobility. In a study conducted by Zhou *et al.* in 2014, ZnO was coated with kenaf and then covered with flame-retardant resorcinol di(phenyl phosphate) (RDP) and blended with PLA. The addition of ZnO-coated kenaf and RDP increased the thermal properties of pure PLA under nitrogen and the air atmosphere. The degradation temperatures values at 10% ($T_{10\%}$) of neat PLA and PLA-2 (85 wt% PLA, 1.2 wt% kenaf, 0.3 wt% ZnO and 13.5 wt% RDP) were 354.03 °C and 363.48 °C, respectively. The RDP that covered the ZnO coated with kenaf hindered the catalysing effect of ZnO that usually promotes a decrease in the thermal stability of polymers, hence an improvement in the thermal stability of PLA. Another study reports on the effects of green synthesized fillers such as zinc-modified melamine phytate (MPAZn) on the thermal stability and the flame retardancy of PLA (Wang *et al.*, 2021). Their results show reduced thermal stability of PLA in PLA/MPAZn composites and the presence of MPAZn resulted in increased char formations. Shankar *et al.* (2018) show that the T_g , T_m and T_c of neat PLA and PLA/ZnO composites remain unchanged while the degree of crystallinity (X_c) improves. The authors suggest that the ZnO nanoparticles are compatible with the PLA matrix to form well-miscible composite films. On the study examining the effects of different boron compounds (ulexite, zinc borate, borax and boric acid) on PLA matrix (Avci *et al.*, 2024), the DSC results indicated that all the boron compounds slightly decreased the T_g and increased the T_m and degree of crystallinity. The increase in the degree of crystallinity was associated with the boron compound's surface shape and roughness. The T_c was reduced for all samples, meaning that boron compounds caused PLA to crystallize at lower temperatures. It can be deduced that the boron compounds have an anti-nucleating effect on PLA.

Russo *et al.* (2014) investigated the effect of HNTs and sepiolite clay (SEP) on the PLA matrix. The samples were nonannealed and annealed at 80 °C overnight. Annealing is a heat treatment process that causes an increase in mechanical properties such as modulus and tensile strength. It can also be used to reduce gas permeability. There were no significant changes in the T_m and T_g when either HNT or SEP was introduced to PLA at 0.1-5 wt% loading. The T_{cc} of PLA in annealed PLA/HNT remained the same at 0.1 wt% HNTs loadings, but then disappeared for the higher loadings due to the formation of agglomerates.

Despite the formation of residual char due to the catalytic effect, the addition of HNTs reduced the thermal stability of PLA. Nevertheless, annealing PLA in the presence of low loadings of SEP introduced polymorphism. Beltrán, De la Orden and Martínez Urreaga (2018) investigated how the addition of modified HNTs could enhance properties of recycled PLA. The HNTs were modified with aminosilane and then added to the recycled PLA. The addition of raw HNTs to recycled PLA showed an increase in enthalpies of crystallization ΔH_{cc} and fusion ΔH_m , which was attributed to the nucleating effect of HNTs. The addition of modified HNTs to the recycled PLA increased the T_{cc} and reduced the ΔH_{cc} and ΔH_m . These results were attributed to the ability of modified HNTs to develop stronger interactions with PLA. This feature resulted in the reduction of mobility of PLA chains and their capability to rearrange into crystalline structures. In a study conducted by Murariu *et al.* (2012), the HNTs were added to the polyester matrix (HNT (QM)), then HNT (QM) was added to PLA matrix. TGA results showed that the addition of 12% HNT (QM) to PLA enhanced the thermal stability of PLA and increased the formation of char residues. PLA showed double melting enthalpies, which were attributed to the slow rates of PLA crystallization and recrystallization. In another study, glycerol was added to the PLA/HNT blend. The DSC results compared PLA/HNT with and without glycerol. DSC showed that PLA/HNT with and without glycerol decreased T_g , T_c and the T_m of PLA (Othman *et al.*, 2016). Liu, Zhang and Zhou (2013) report that the addition HNTs on the PLA matrix did not influence the T_g and T_m ; however, the degree of crystallinity increased with the addition of HNTs. TGA also showed that the addition of HNTs increased the thermal stability of PLA, and this was attributed to uniformly dispersed HNTs within the PLA matrix. Based on the above summarised studies, it can be deduced that there is no direct relationship between the amount of residual char and thermal stability in PLA/HNT composites.

2.5.3 Flammability properties of PLA/clay and PLA/zinc borate composites

Flame retardants (FRs) are chemicals or substances that are applied to materials to increase their resistance to ignition and slow the growth of fire or flames. They work by forming a protective layer on the surface of the material, which helps to inhibit the material from catching fire. The essential advantage of flame retardants is reducing flammability of polymeric materials, which in turn enhances fire safety. The factors that affect the system's success of a FR on thermoplastics are dependent on the type of FR used, size, shape, loading percentage, dispersion rate and its thermal stability (Vahabi and Kandola, 2019). Fire hazards

encompass a range of factors that contribute to the potential danger of a fire. These factors include the material's ability to ignite, how easily it can be extinguished, the flammability of the volatile substances produced during combustion, the amount of heat released during burning, the rate at which heat is released, the spread of flames, the level of smoke generated, the reduction in visibility caused by smoke during a fire, and the toxicity of the smoke (Levchik, 2007). Most polymers are highly flammable and release toxic gases and smoke to the environment during combustion, which in turn results in their limited application for other industries (Chen *et al.*, 2009; Yang *et al.*, 2013; Yan, Xu and Wang, 2019). Excessive carbon monoxide concentrations released during real fires could result in loss of consciousness in four minutes. South African statistics show that fires reported from 2002 to 2009 decreased from 47 699 to 40 481 (Fire Protection services of South African, 2011). Fires in the United States of America decreased from 6 000 in 1977 to about 3 500 in 1993. This decrease can be due to a variety of factors that have improved over time, including advancements in the design of appliances, electronic equipment, cars, heating systems, houses, and other relevant products; most importantly, the application of FR polymeric materials. These FR-polymeric materials have proven to be highly valuable in enhancing fire safety and reducing the risk of casualties. In 1988, the National Bureau of Standards conducted tests involving room combustion (Enright and Fleischmann, 1995). These tests compared the performance of FR plastics with non-FR plastics commonly used in various applications such as printed wiring boards, television set, cables, and upholstered furniture. The results indicated that FR materials allowed for an escape time that was more than 15 times longer compared to non-FR materials. Furthermore, FR materials exhibited a 75% reduction in heat release, produced significantly less smoke, and resulted in a lower concentration of toxic gases. The presence of FRs in materials contributed to a decrease in overall toxicity during fires. This proves that flame retardants can help to minimize the extent of property loss, give people sufficient time to escape in case of fire breakouts and provide valuable time for fire-fighters to respond effectively. The most widely used laboratory tests to assess the fire behaviour and flammability of material include the cone calorimeter test (CCT), vertical flame test (UL 94), oxygen index and limiting oxygen index (LOI). The main characteristics evaluated with CCT includes the peak of Heat Release Rate (pHRR), Total Heat Release (THR), and Time-To-Ignition (TTI). When analysing CCT, it is very crucial that the pHRR values are reduced for fire safety. The pHRR indicates a moment during combustion when heat is the most likely to spread further or ignite close objects (Liu *et al.*, 2015). UL 94 determines the flammability characteristics of polymeric materials by observing their behaviour when exposed to a small

flame source (Patel, Hull and Moffatt, 2012). The UL 94 rates the flames in the following order:

- V-0: The highest classification showing excellent flame resistance. The material should self-extinguish within 10 seconds and not produce any dripping flames.
- V-1: The material self-extinguishes within 30 seconds and does not produce dripping flames.
- V-2: The material self-extinguishes within 30 seconds but can produce dripping flames.
- HB: This classification indicates a lower level of flame resistance. The material is not required to self-extinguish and may continue to burn.

The oxygen index test determines the minimum concentration of oxygen necessary to sustain the burning of a material, providing an indication of its flammability in the process. The LOI test, like the oxygen index test, is employed to determine the minimum oxygen concentration needed to sustain combustion. However, it is specifically applied to evaluate the flammability of materials that are known for their enhanced flame resistance. In this test a vertical strip of a polymer composite is ignited at its top using a Bunsen burner or a pilot candle-like diffusion flame (Suzanne, Delichatsios and Zhang, 2014). The LOI value needs to increase to achieve the improvement of flame retardancy on a polymer.

The mechanism of halloysite clays as FRs involves the formation of a char layer on the polymer matrix (see Figure 2.4). Stoclet *et al.* (2014) investigated the effect of HNTs on PLA by using water-assisted extrusion. The peak heat release rate (pHRR) of pure PLA was 419 kW/m², while that of PLA/HNTs was 346 kW/m². This reduction was attributed to the sample preparation method, where the presence of water aided in the dispersion of HNTs during extrusion. In another study (Jin *et al.*, 2020), the incorporation of HNTs into a bamboo fibre/PLA (BPC) blend resulted in reduced total smoke production (TSP), THR and pHRR. The LOI value of the BPC slightly changed from 19.1% to 21.3% with the addition of HNTs. The results show that HNT indeed improved the flame retardancy of bamboo/PLA composites. The research conducted on the flame retardancy of HNTs on PLA is limited in the literature. The effects of HNTs and other clays on the flame-retardant properties of other biopolymers and PLA, respectively, have been investigated. Wang *et al.* (2019) investigated the effect of HNTs on the flame-retardant properties of intumescent flame retardant (IFR)/poly (butylene succinate) (PBS) composites. The addition of HNTs to the binary

PBS/IFR composite enhanced LOI and the maximum value was obtained at 1.5 wt.% HNTs loading. Moreover, the UL-94 rating of the composites was assigned to V-0. The authors associated the improvement of flame retardancy to the good synergistic effect between HNTs and IFR. Hasan *et al.* (2022) investigated the effect of different HNTs loadings on the flammability of jute fibre/poly(3-hydroxy-butyrate-co-3-valerate) (PHBV) composites. The residual mass formation increased with the increasing content of HNTs, and this contributed to the enhancement of flame retardancy. The authors associated their results with the ability of HNTs to create a barrier effect which restricts the transfer of heat produced during the combustion of a polymeric material. In another study of PBS/HNTs composites, the addition of HNTs reduced the pHRR value of neat PBS from 809 to 630 kW/m², whereas residual char increased in the process. The improvement in flame retardancy was because of good dispersion of HNTs in the PBS matrix (Dumazert *et al.*, 2018). González *et al.* (2012) studied the effect of sepiolite and organically modified montmorillonite (OMMT) on the PLA matrix. The addition of both clays did not change the LOI values of PLA. The pHRR value of neat PLA remained at 332 kW/m² in the presence of sepiolite. However, the presence of OMMT clay and its combination with sepiolite on PLA increased the pHRR values to 371 and 345 kW/m², respectively. The inadequate fire performance of sepiolite was associated with its inter-channel networks. These networks can hold accumulated heat and utilize it as a heat source in combination with external heat flow to quicken the decomposition process of PLA. Various studies have shown that the pHRR values of PLA reduce when OMMT is used in synergy with IFRs, thus not improving the flame retardancy of PLA (Fontaine, Gallos and Bourbigot, 2014; Liu *et al.*, 2015; Ye *et al.*, 2016). In another study (Li *et al.*, 2009), the influences of incorporating IFR and OMMT on the flame retardancy and melt stability of PLA were investigated. The addition of OMMT to PLA slightly increased the LOI value to 21.8 %, but the PLA/OMMT composite dripped, indicating OMMT is ineffective for making the composite self-extinguishable, despite its known ability of enhancing the thermal stability of PLA. However, the UL-94 results revealed a V-2 and V-0 rating for the PLA/IFR and PLA/IFR/OMMT composite, respectively. Moreover, OMMT showed non-dripping behaviour when used in combination with IFR. This behaviour was attributed to the ability of OMMT to reduce the heat release of the composite and increase thermal stabilization.

Zinc-based FRs work by forming a protective char layer on the surface of the polymer, which prevents the breakdown of the polymer from flames, as illustrated in Figure 2.4 (Avci *et al.*, 2024). They can be used solely or in synergy with other FRs for improvement of flame-

retardant properties of PLA (Dogan *et al.*, 2021). Various studies in Table 2.2 have shown an improvement in the flame retardancy of PLA through different analysis, namely UL-94 test rating of V-0, reduced pHRR and increasing LOI values. The reported results depended on the amount of zinc-based flame retardant used in synergy with other FRs. A summary of studies where zinc-based FRs were used to enhance the flammability is shown in Table 2.2.

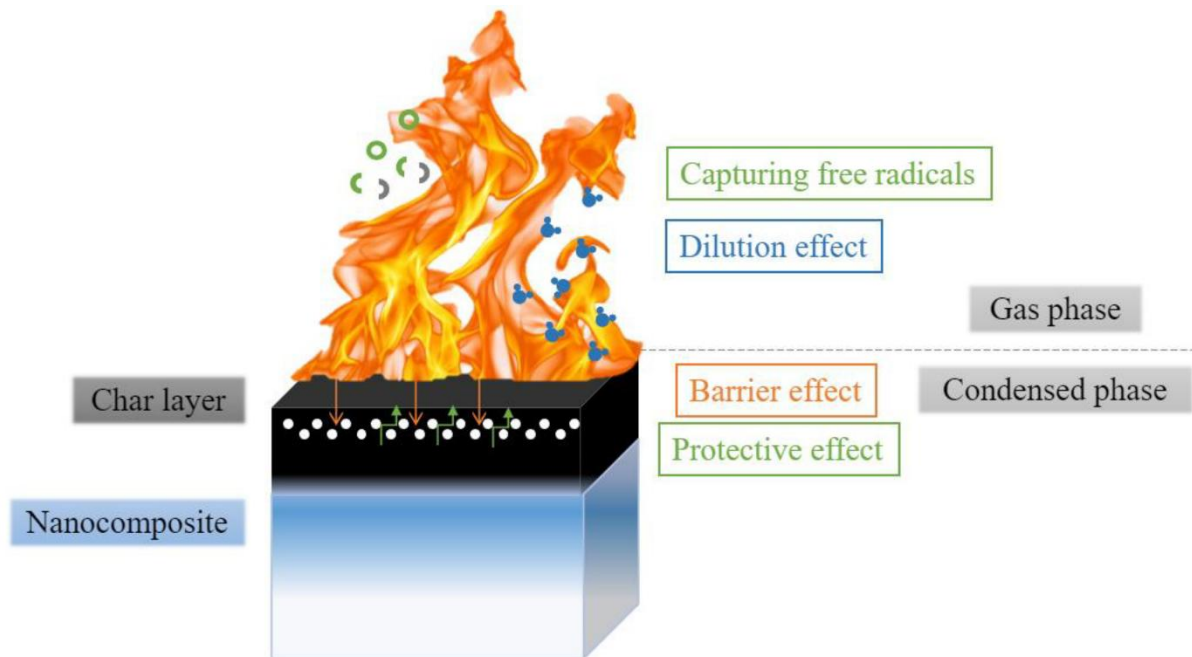


Figure 2.4: Mechanisms of flame retardancy of nanoparticles on polymers (Dowbysz *et al.*, 2024)

Table 2.2: Selective studies on zinc FRs in synergy with oth

PLA/Zinc FRs	Summary of results	References
ZnO+Chain extender were added to intumescent flame retardant (IFR) PLA.	The LOI values obtained for neat PLA, IFR/PLA and IFR/PLA/ZnO are 20.2, 36.8, and 37%, respectively. It was only when ZnO was added to IFR/PLA that the sample got V-0 rating. CCT showed a reduction in pHRR and increased char residues.	(Chen <i>et al.</i> , 2021)
ZB/PLA/IFR	The addition of 3 wt.% ZB to the PLA/IFR slightly enhanced the LOI rating and a V-0 UL-94 rating was achieved.	(Zhan <i>et al.</i> , 2014)
LDPE+PLA/ZB	The addition of ZB alone to LDPE/PLA did not change the LOI value of LDPE. However, incorporation of ZB in synergy with other flame retardants increased the LOI of LDPE/PLA blend from 20 to 40%.	(Arslan and Dilsiz, 2020)
PLA/FR (composites containing a phenethyl-bridged 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide derivative (DiDOPO) /ZB	When compared to PLA/FR composite, the addition of 1 wt.% ZB did not change the LOI value as they are both at 27,1%. Both samples obtained a V-0 UL-94	(Long <i>et al.</i> , 2019)



	rating. The	
	PLA/FR decreased the pHRR value from 488 to 475 kW/m ² . The PLA/FR/ZB composite had more char residues than neat PLA and PLA/FR composite.	
PLA/resorcinol di(phenyl phosphate) (RDP) with ZnO-coated kenaf	The addition of ZnO/RDP increased the LOI value of neat PLA from 20 to 30% with V-0 rating being achieved.	(Zhou <i>et al.</i> , 2014)
FRPLA/organomodified zinc aluminum layered double hydroxide (Zn-Al-LDH)	The addition of Zn-Al-LDH to FR/PLA decreased the total heat release and the highest amount of char residue was obtained.	(Wang <i>et al.</i> , 2010)
PLA/IFR/Nano ZnO	The addition of nanoZnO to the PLA/IFR composite slightly enhanced the LOI value and V-0 rating was achieved. Moreover, the pHRR of the PLA/IFR composite decreased from 331 to 196 kW/m ² . The THR reduced and increased char residues.	(Chen <i>et al.</i> , 2019)

2.5.4 Mechanical properties of PLA/clay and PLA/zinc borate nanocomposites

The tensile and impact tests are often used to assess the mechanical properties of polymer composites. The thermomechanical properties of polymer composites are determined through dynamic mechanical analysis (DMA). The tensile test measures the maximum stress that a polymer can withstand being stretched before cracking (Othman *et al.*, 2016). It is used to assess tensile strength, Young's modulus, and elongation at break. Impact test is used to measure the ability of the material to absorb energy and resist fracture under sudden, impact loads or shocks (Savadori, 1985). PLA has excellent mechanical properties. However, its brittleness, poor impact strength and low heat resistance might limit its applications in various industries that require very durable bioplastics (Seki *et al.*, 2023). Therefore, to overcome these drawbacks of PLA, research studies have shown that PLA can be blended with other polymers or fillers to enhance its mechanical properties.

The DMA results in a study by Prashantha *et al.* (2013) showed that the addition of HNTs in the PLA matrix increased the storage modulus. It was also observed that the tan delta peaks shifted to higher temperatures with the addition of HNTs. This was attributed to a decrease in the segmental movements in the PLA matrix. Chow, Tham and Seow (2013) investigated the effect of maleic anhydride grafted poly(lactic acid) (PLA-g-MAH) on the properties of the polylactide/halloysite clay (PLA/HNC) composites. The introduction of HNC and a combination of PLA-g-MAH and HNC to PLA increased the flexural strength of PLA, and this was associated with the reinforcing effect and the rigidity of HNT. The improvements were also associated with the ability of PLA-g-MAH to enhance the interfacial interaction between PLA and HNC. A similar study that involves incorporating PLA-g-MAH into natural-fibre-reinforced PLA/HNT composites was conducted (Ertas *et al.*, 2019). Their results showed that the presence of PLA-g-MAH improved the flexural strength of natural fibre-filled PLA/HNT composites. The authors attributed the improvements to the ability of PLA-g-MAH to form a bridge between the fillers (HNT and natural fibre), thus enhancing adhesion between the constituents of the polymer composites. However, the impact strength of PLA remained the same in the presence of HNT and due to agglomerates, which created stress concentration points promoting failure. The study of Ling and Teik (2014) evaluated the combined effects of 2 wt.% HNTs and *N,N*-ethylenebis (stearamide) (EBS) on PLA. EBS was added in the composites to improve the dispersion of HNTs and toughening of the

PLA/HNT nanocomposites. The impact strength values of the PLA/HNT composite improved in the presence of EBS and the largest improvement was attained with the 93/2/5 PLA/HNT/EBS formulation. This improvement was associated with the dispersion of EBS in the composites, which acted as a core for crack enhancing the spread of many fine cracks from under the applied impact load. This occurrence of these cracks (known as crazing) creates a stress-whitening phenomenon, which in turn creates numerous shear zones at the fracture surface, increasing the energy absorption during deformation. In another study (Othman *et al.*, 2016), the addition of 1-3 wt.% of HNTs increased the toughness of PLA due to the uniform dispersion of HNTs in the PLA matrix. This in turn resulted in an increased surface attraction between the HNTs and the PLA matrix. Chen *et al.* (2017) reported an increase in stiffness, tensile strength, and young's modulus in PLA/HNT composites at lower loadings of HNT. In another study (Eperk, Ozkoc and Yilmazer1, 2015), the reduced tensile strength in PLA/HNT blend was associated with the absence of intercalated structures and agglomeration of HNTs within the PLA matrix (Eperk, Ozkoc and Yilmazer1, 2015). It is deduced that the ability of HNT to reinforce the PLA matrix is influenced effectively by its dispersion.

Sun *et al.* (2018) investigated the effect of zinc bisdiethylphosphinate (ZnPi) and melamine polyphosphate (MPP) on the properties of PLA. The tensile and impact test results showed an increase in the elongation at break and impact strength of the PLA/ZnPi system, respectively. However, the tensile strength and Young's modulus were decreased. Jandíková *et al.* (2018) also reported similar results in terms of the Young's modulus, tensile strength, and elongation at break in their study of the effects of stearate silver coated ZnO (ZnSt-Ag) on PLA. They associated the reduction in the earlier mentioned properties to the dispersion of ZnSt-Ag within the PLA matrix which disrupted the homogeneity of PLA matrix and in turn affected the mechanical properties of the composites. A decrease in molecular weight could have also affected tensile strength. Lower molecular weight is associated with lower entanglement which yields lower mechanical properties. Other studies have reported a decrease in elongation at break when ZnO was added to the PLA matrix (Luzi *et al.*, 2017; Marra *et al.*, 2017; Heydari-Majd *et al.*, 2022). The decrease in elongation at break was ascribed mainly to the weak adhesion amid the phases, rather than agglomeration of ZnO nanoparticles phenomena. The weak interfacial bonding allowed fractures to propagate through the voids (Marra *et al.*, 2017). Seki *et al.* (2023) investigated the effect of zinc borate, ammonium phosphate and triphenyl phosphate on the PLA/polycarbonate (PC) binary blend. The

addition of ZB for synergy in PLA/PC/FR system increased the tensile modulus and flexural strength and modulus. In a study by Ding, Rui and Li in 2013, ZnO was modified with titanium ester (NDZ-201) and silane coupling agent (KH550) then added to PLA. The addition of untreated ZnO nanoparticles enhanced tensile strength, impact strength and elongation at break. Treated ZnO further increased the mechanical properties of PLA. Geng *et al.* (2019) also report an increase in tensile strength, elongation at break, and impact strength. Rodríguez-Tobías *et al.* (2014) associated the increase in tensile strength and Young's modulus with the agglomeration of ZnO that eventually acted as failure points in their study. Most authors reported that the addition of higher contents of ZnO products resulted in a decrease in mechanical properties (Ding *et al.*, 2013; Rodríguez-Tobías *et al.*, 2014; Geng *et al.*, 2019). In summary, it can be deduced from the above studies that improvements in the mechanical properties of filled polymer composites can be attained either by pre-treatment of the filler or pre-treatment of the polymer.

2.6 Overview of polymer blends

Polymer blends represent a category of materials in which at least two polymers or copolymers are mixed. Polymer blending is beneficial from the economic view. In comparison to polymerization of new polymers using expensive monomers, polymer blending is cost effective for the development of polymeric materials with enhanced properties using existing polymers. It is also essential for converting recycling industrial waste and/or municipal plastic waste into usable materials (Utracki, 1982). The mixing of polymers is a thermodynamic issue that can be represented by the Gibbs free energy equation of mixing:

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (2.1)$$

where ΔG_m , ΔH_m , and ΔS_m are the Gibb's free energy, enthalpy, and entropy of mixing at temperature (T), respectively. Polymer blends are generally categorized into three classes, namely miscible, partially miscible and immiscible blends. Miscible polymer blends are homogenous or single phase and made of polymers with similar chemical structures. In addition, $\Delta G_m < 0$ and a single glass transition temperature lying between that of the virgin constituent polymers is observed in the case of binary miscible blends. The blends of polylactide (PLA) with polyacrylics such as polymethyl methacrylate (PMMA) were found to be miscible in all investigated compositions (Charasseangpaisarn *et al.*, 2023). Partially

miscible polymer blends are those with the glass transition temperatures of the virgin constituent polymers shifting towards one another. Immiscible polymer blends are those with heterogenous phases and multiple glass transition temperatures related the constituent polymers. Immiscibility of polymer blends is characterized by $\Delta G_m > 0$ and the absence of interactions between the blended polymers. Immiscible blends have multiple glass transition temperatures associated with the blend polymers. PLA is a biobased, and biodegradable polyester that has been researched for its use in numerous applications such as food packaging, biodegradable bags, and biomedical devices. The drawback of PLA is its rigidity, low-impact resilience, elongation, and flammability which limit its applications. PLA can be blended with polycaprolactone (PCL) to enhance its impact resilience and elongation (Urquijo, Guerrica-Echevarría and Eguiazábal, 2015). Natural rubber (NR) in dynamically vulcanized PLA/NR has been reported to enhance the impact resilience of PLA (Chen, Yuan and Xu, 2014).

In the current study, PLA was blended with waste-ground tire rubber (GTR) to develop a model system of the 80/20 PLA/GTR blend and filled PLA/GTR composites. The choice for the beneficiation of waste GTR materials for the development of PLA/GTR blend and filled composites is motivated by participation in circular economy, which requires minimization and elimination of waste materials. Generally, the PLA/GTR blends are immiscible due to poor interfacial interactions between the blended components resulting in a decline of the properties. Therefore, the current study is devoted to tailoring the morphology by incorporating fillers such as clay and zinc borate (ZnBrO_3) to maximise the use of PLA/GTR blends.

The information on distribution and localization of nanofillers in immiscible blends is essential for understanding their role in compatibilizing immiscible blends. The distribution and localization of nanofillers in immiscible blends are controlled either by thermodynamic or kinetic factors, or the combination of both factors (Mofokeng *et al.*, 2018). In the earlier stages of mixing, the localization of nanofillers in immiscible blends is more likely to be dominated by the kinetic factors. The nanofiller particles are more likely to favour localization in a lower melting and lesser viscous polymeric phase during the earlier stages of melt mixing. The nanofillers would likely remain confined in a lower melting and lesser viscous polymeric phase if there is better enthalpic interaction between the filler and the lower melting polymeric phase. However, both the thermodynamic and kinetic factors play a role on the localization of nanofillers in the presence of favourable enthalpic interactions

between the filler and the high melting polymer. Nanofillers will favour localization in the polymer phase that melts earlier, followed by migration to the high melting phase due to favourable enthalpic interactions between the filler and the high melting polymer. The resulting different nano/microstructures of the filled immiscible blend ternary composites influence the properties differently. Hence, the next section will describe the characteristics of the filled PLA/elastomer composites.

2.7 PLA/elastomer/clay and zinc borate containing PLA/elastomer/ ZnBrO_3 nanocomposites

2.7.1 Morphological development of PLA/elastomer/clay and zinc borate containing PLA/elastomer/ ZnBrO_3 nanocomposites

Blending PLA with flexible polymers such as elastomers is an effective way of improving its flexibility and impact resilience. However, the improvements may come at the expense of stiffness and tensile strength. The stiffness and tensile strength can be improved by introducing fillers such as nanoclay. The properties of PLA/elastomer/clay composites are dependent on their morphology. Numerous studies have reported on the effects of nanoclay on the morphologies of PLA/elastomer blends, wherein the elastomer is the dispersed minor phase (Harinatharavimal Balakrishnan Iman Masoumi and Wahit, 2012; Wang *et al.*, 2016; Chen *et al.*, 2017). Wang *et al.* (2016) used OMMT to investigate its compatibilization of the PLA/ethylene-propylene-diene rubber (EPDM) blends. The SEM results showed that the PP/EPDM blends were incompatible due to the hydrophilic and hydrophobic natures of PLA and EPDM, respectively. The TEM results showed that most OMMT layers favoured localization at the interface between PLA and EPDM, while some dispersed within the minor EPDM, thus enhancing compatibility. The authors attributed their results to high affinity between OMMT and EPDM. Chow and Lok (2009) examined the effects of OMMT and maleic anhydride-grafted-ethylene propylene rubber (EPMgMA) on the morphological properties of PLA. The XRD results showed intercalation in the PLA/OMMT composite, which enhanced further for PLA/OMMT/EPMgMA composite. Intercalation occurs when the polymer chains penetrate the interlayer regions of clay. However, the authors did not report on the localization and spatial distribution of OMMT in different phases of the PLA/EPMgMA blend. Harinatharavimal Balakrishnan Iman Masoumi and Wahit (2012) report that intercalation of PLA chains in the clay galleries occurs in the PLA/ethylene-co-

polymer (Biostrong)/OMMT composites. The authors attributed their results to hydrogen bonding interactions between ammonium groups in the surfactant of OMMT with the carbonyl groups of PLA. It is essential to note that better intercalation was achieved at the highest OMMT loading (4 phr) despite its tendency to form agglomerates. Nevertheless, the above studies show that OMMT can tailor the morphology of the immiscible blend.

In a study by Chen, Shahdan and Ahmad (2017), PLA, liquid natural rubber (LNR) and nickel zinc (NiZn) ferrite were prepared by melt blending. The SEM images of neat PLA/LNR blend displayed a one-phase surface morphology with visible holes. The holes represent localization of rubber particles which were removed during fracturing, thus confirming poor interfacial adhesion between PLA and LNR. The addition of NiZn decreased the number of holes as it homogenously dispersed on the PLA matrix filling up the holes. However, at higher loading of NiZn, there was formation of nanoparticles agglomerates. In a similar study (Tarawneh, Shahdan and Ahmad, 2013), the good dispersion of NiZn ferrite in PLA/LNR blend was associated with good interfacial interactions, which enhanced interparticle bonding, reducing agglomerations. Shahroodi, Moshkriz and Momeni (2023) investigated the effect of chloroprene rubber on the PLA matrix in the presence of treated ZnO. The SEM images indicated a droplet morphology of chloroprene rubber dispersed in the PLA matrix for lower rubber loading (<40 wt.%), which changed to co-continuous at 40 wt.% chloroprene rubber loading. The authors attributed the change in morphology to the affinity of chloroprene rubber drops to coalesce, and the inadequate PLA phase present to transfer the force and break the coalescing chloroprene rubber drops. The surface-treated ZnO particles showed a tendency for agglomerating when incorporated into the blend. Maroufkhani *et al.* (2021) reported on the super tough dynamically vulcanized blends (DV) of polylactide (PLA) and acrylonitrile butadiene rubber (NBR). The rubbery phase was vulcanized with ZnO and stearic acid as activators, while dibenzothiazole disulfide (MBTS) and tetramethyl thiuram disulfide (TMTD) were utilised as accelerators. The FTIR results showed carbonyl absorption peaks PLA within the dynamic vulcanized samples, proving that NBR reacted with PLA during rheomixing. Furthermore, the carbonyl peaks moved to higher wavenumbers suggesting enhanced interfacial interactions between the two phases.

2.7.2 Thermal properties of PLA/Elastomer/clay composites

Numerous authors have reported on the T_{cc} of PLA/elastomer/clay composites using DSC (Tham, Mohd Ishak and Chow, 2014; Talbamrung *et al.*, 2016). Different types of clays and

melt mixing method were used for preparing the composites. Generally, the authors observed a reduction in the T_{cc} of PLA with incorporation of clay, and this was associated with the nucleating effect of the clays. However, the addition of maleic anhydride-grafted styrene-ethylene/butylene-styrene (SEBS-g-MAH) to PLA/HNC composites seemed to increase the T_{cc} . The authors suggested that the inclusion of SEBS-g-MAH slowly prevented the formation of large crystallites within the PLA matrix. One question that can be asked is “In PLA/SEBS-g-MAH/HC composites, which constituent play a dominant role on the T_{cc} of PLA?” It is important to mention that Tham *et al.* (2014) did not report on PLA/ SEBS-g-MAH blends. It is probable that there are two opposing effects on the T_{cc} of PLA for the PLA/SEBS-g-MAH/HC composites. To be specific, HC reduces T_{cc} due to its nucleating effect, whereas SEBS-g-MAH counters by increasing the T_{cc} . The net effect is higher than that of neat PLA. It can be deduced that the effect of SEBS-g-MAH on the T_{cc} of PLA/SEBS-g-MAH/HC composites is more superior than that of HC. The TGA results showed that the addition of SEBS-g-MAH improved the thermal stability of PLA/HNC composite, and this was attributed to the presence of highly thermally stable phenyl groups in SEBS-g-MAH. In another study, Bijarimi, Ahmad and Rasid (2013) investigated the thermal properties of PLA in Cloisite (C30B)-filled PLA/liquid natural rubber (LNR) blends. The addition of LNR and C30B seemed to reduce the T_g of neat PLA. This was attributed to increased free volume of polymer chains within in the composites, arising due to molecular weight loss during processing. Introduction of increasing amounts of C30B clay to the PLA/LNR blend reduced the T_c and this was associated with the ability of clay particles to act as an effective nucleation sites of PLA crystallization. Hoidy, Al-Mulla and Essa (2019) added dioctadecyl dimethylammonium bromide (DODAB) modified MMT clay to PLA/NR (natural rubber) blend to investigate its effectiveness on thermal properties. Their TGA results showed that initial degradation temperatures for neat PLA, PLA/NR, PLA/NR/DODAB MMT were 268.0, 290.1 and 299.5 °C, respectively. The improvement of the thermal stability with addition of the modified clay can be associated the good dispersion of the clay and improved interfacial adhesion between NR and the PLA matrix. It is known in polymer/clay composites that clay in its well-dispersed state creates a physical barrier that retards degradation of polymer matrix and diffusion of volatiles. The study of Li and Turng (2006) show that the addition of core-shell rubber and modified MMT to PLA have no significant effect on the thermal stability of PLA. The authors suggest that rubber and clay contents are relatively low in the composite to effect changes on the thermal stability. Chow, Leu and Ishak (2014) investigated the effect of ethylene propylene rubber grafted with maleic anhydride (EPR-g-

MAH) on PLA/OMMT nanocomposites. Their TGA results showed that the addition of OMMT to the PLA matrix decreased the thermal stability of PLA. This effect may be due to the decomposition of the organic modifier of the OMMT and subsequent catalytic effect on the decomposition of PLA. However, the PLA/EPR-g-MAH/OMMT had higher thermal stability and this was attributed to the addition of 20 wt.% EPR-g-MAH to PLA/OMMT, which improved the thermal stability of PLA.

2.7.3 Flammability properties of PLA/elastomer composites

Given the limited research on the flammability of PLA/elastomer/clay nanocomposites, the author supplemented this review chapter with papers related to other toughening polymers such as low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP) and ethylene vinyl acetate (EVA) for PLA. Flammability properties were investigated using alternative halogen-free flame retardants. Arslan and Dilsiz (2020) investigated the effect of metal hydroxides, melamine (MLM), boron compounds, ammonium phosphate (APP) and pentaerythritol (PER) on the flammability of the LDPE/PLA blend. LOI was used to analyse the flammability of the polymer composite. The LDPE/PLA blend had an LOI value of ~21%, and the addition of ZB in the polymer blend did not greatly affect the LOI, as it was just 21.3%. However, the highest LOI of 40% was attained when a mixture of ZB, APP, PER and MLM was incorporated into the LDPE/PLA blend, indicating good synergy between the FRs. In another study, PP and PLA were melt blended together with styrene-ethylene-butylene-styrene-g-maleic anhydride (SEBS-g-MAH) in the presence of intumescent flame retardant (IFR) (Lin *et al.*, 2012). The IFR was made up of phosphorus and nitrogen compounds to aid in enhancing the flame retardancy of PP/PLA/SEBS-g-MAH. The results indicated that the LOI of the PP/PLA/SEBS-g-MAH blend was 18% and the blend obtained a non-rating (NR) on the UL-94 test. However, the incorporation of the IFR to the blend greatly increased the LOI value to 34%, achieving a V-0 rating on the UL-94 test, reduced the pHHR and increased the char residues. Chaiwutthinan *et al.* (2019) investigated the effect of wood flour (WF) and wollastonite (WT) on the FR properties of the PLA/EVA blend. The results indicate that the LOI value for PLA/EVA is higher when compared to the blend composite samples containing WF and WT. The authors attribute the lower LOI values of the filled PLA/EVA composites to the low LOI of WF, aggregation of the filler in the blend, and interstices at the matrix–particle interface. A V-2 for PLA/EVA and V-1 rating

was attained for the PLA/EVA blend and (WF and WT) containing composites, respectively. In addition, the WF and WT containing blend composites had anti-dripping capability. Based on the results of Chaiwutthinan *et al.* (2019), it can be deduced that WF and WT are not effective for reducing the flammability of PLA/EVA matrix because a V-0 rating was not achieved. A solution would be to incorporate either WF or WT in combination with ZB and clay to the PLA/EVA blend. Other researchers (Yang *et al.*, 2019) utilised oxidized wood flour as a charring agent, ammonium polyphosphate (APP) to enhance flame retardancy, and polyethylene glycol (PEG) as a toughening agent for PLA. Their results showed that neat PLA had a LOI value and UL-94 rating of 20.4% and V-2, respectively. The addition of both oxidised wood flour and APP to PLA increased the LOI value to 30.6% attaining a V-0 rating. Their CCT results showed that the addition of both oxidised wood flour and APP significantly reduced the pHRR and THR of neat PLA. This suggested good synergy between oxidised wood flour and APP in improving the flame retardancy of the polymer matrix. In an almost similar study but without the wood flour, the addition of APP to PLA/ polyethylene glycol enhanced the flame retardancy of the polymer matrix (Sun *et al.*, 2017).

2.7.4 Mechanical and thermomechanical properties of PLA/Elastomer/clay

In a study conducted by Baouz *et al.* (2015), the PLA/OMMT composite was toughened by ethylene-methyl acrylate-glycidyl methacrylate (E-MA-GMA) rubber. The addition of OMMT alone increased the tensile modulus of neat PLA from 2046.7 to 2373.4 MPa. This increase was associated with PLA molecules being replaced by OMMT with high intrinsic stiffness and high-aspect ratio. The addition of the E-MA-GMA rubber to PLA/OMMT reduced the tensile modulus and tensile strength due to the soft nature of rubber. The elongation at break increased with the increasing rubber content in the PLA/OMMT blend composite. Another study by Chow *et al.* (2014) shows that the incorporation of maleic anhydride-grafted-ethylene-propylene rubber (EPR-g-MAH) on the PLA/OMMT composite also reduces the tensile strength and tensile modulus due to low modulus of the rubber. The authors also report that the elongation at break and impact strength (notched and un-notched) significantly increases with increasing rubber content in the PLA/OMMT. This was associated with the ability of the rubber to act as an efficient stress concentrator, triggering the micro-deformation mechanisms which in turn enhanced the ductility of the PLA nanocomposites. Leu, Ishak and Chow (2012) report similar results with the addition of malleated styrene-ethylene/butylene-styrene (SEBS-g-MAH) rubber to a PLA/OMMT. The

DMA results in a study by Bijarimi *et al.* (2013) show that the addition of liquid natural rubber (LNR) to PLA decrease the storage modulus of PLA. However, the addition of Cloisite clay (C30B) to the PLA/LNR blend increases the storage modulus of the PLA nanocomposite, showing that the clay has a reinforcing effect on the elastic properties of the PLA/LNR blend. The tan delta curves of the PLA/LNR blend and PLA/LNR/C30B composite show two T_g peaks, one associated with rubber and the other for PLA. This suggests that PLA and LNR in the PLA/LNR blend and PLA/LNR/C30B composite are immiscible. Tham *et al.* (2016) investigated the effects of the two types of impact modifiers (SEBS-g-MA and N,N'-ethylenebis (stearamide) (EBS) on the mechanical properties of the PLA/HNT composites. The impact strength of PLA nanocomposites was measured prior to and post water exposure. Prior to water absorption, the impact strength of PLA/HNT composite increased with introduction of impact modifiers. However, the impact strength of PLA/HNT composite decreased with introduction of impact modifiers post water absorption. This reduction was associated with the weakened interfacial adhesion induced by diffusion of water molecules within the PLA matrix. The above studies show that the elastic behaviour of elastomers prioritizes reducing the brittleness of PLA over increasing ultimate strength. However, the incorporation of nanoparticles such as clay to PLA/rubber blends has the potential for maintaining the ultimate strength of PLA.

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CHAPTER 3: Materials and methodology

3.1 Materials.

3.1.1 Polylactic acid

Polylactic acid (PLA) pellets were supplied by 2M Biotech, India. It appears as a transparent resin shown in Figure 3.1. It has a melting temperature, density and melt flow index of 155 °C, 1.24 g/cm³ and 6g/10 min, respectively.



Figure 3.1: Neat PLA

3.1.2 Ground tire rubber

An old car tire was supplied by Dunlop tyres South Africa. The car tire was initially shredded into pieces ranging from 5 to 15 cm using a BS 400 dual shaft shredder. In the secondary stage, a granulator further reduced the pieces to smaller fragments, approximately 9 mm in size. During this stage, metals and textiles were also removed from the tire material. The 9 mm pieces were further subjected to ambient grinding, where they were ground into finer particles or powder at room temperature. The ground tire rubber with an average particle size of 0.4 mm is displayed in Figure 3.2.



Figure 3.2: The ground tire rubber that was utilized in samples

3.1.3 Zinc borate

Zinc borate (ZB) was supplied by Sigma-Aldrich, South Africa. It is a white powder that contains $\geq 45\%$ ZnO basis and $\geq 36\%$ B₂O₃ basis. It has a molecular weight of 127.21 g/mol.

3.1.4 Halloysite clay

The Halloysite nanoclay powder (HC) was supplied by Sigma-Aldrich, South Africa. It appears beige in colour. It has a formula weight of 294.19 g/mol and a pore size of 1.26-1.34 ml/mol. Its particles have a diameter of 30-70 nm and a length of 1-3 microns.

3.2 Preparation of the PLA/GTR/flame retardant blend nanocomposites.

Prior to compounding, PLA, GTR, ZB and HC were dried at 60 °C in a vacuum oven for over 12 hours. The sample designations and compositions are listed in Table 3.1. Neat PLA, PLA/GTR blend, and PLA blend composites were melt processed in a TE-30 Co-rotating twin-screw extruder (Nanjing Only extrusion Machinery Co., Ltd) shown in Figure 3.3(a). The temperatures of the heating zones near the hopper to the die ranged from 120 °C to 180 °C. The extrusion speed and feed rate were set at 178.8 rpm and 4.4 kg/hr, respectively. The extrudates were quenched in water, pelletized, and dried in an oven at 60 °C for 24 hours.

The dried pellets were injection moulded to form various test specimens using an injection moulding machine (ENGEL e-mac50) shown in Figure 3.3(b). The heating zones of the injection moulder were set at 36, 160, 170, 180, and 190 °C. The clamping force, metering, specific back pressure, injection pressure, and injection speed were set at 500 kN, 29 mm, 100 bars, 550 bars, and 100 m/s, respectively. The test specimens were cooled to 22 °C and stored in a zip-lock bag.



Figure 3.3: Machines used for (a) compounding and (b) moulding test specimens

Table 3.1: Percentage compositions of investigative samples

Samples	Percentages %
PLA	100
PLA/GTR	80/20
PLA/HC	97/3
PLA/ZB	97/3
PLA/ ZB/HC	97/3
PLA/GTR/HC	77.6/19.4/3
PLA/GTR/ ZB	77.6/19.4/3
PLA/GTR/ ZB/HC	77.6/19.4/3

3.3 Characterization and sample analysis

3.3.1 Scanning electron microscopy (SEM)

SEM microscopy is used for imaging the surface of materials at a very high resolution or magnification, which can reach 300 000x and even 1 000 000x. This technique has been used worldwide in many applications to determine the surface morphology and composition of organic and inorganic materials on a nanometre to micrometre scale. In SEM the electron beam is focused down to a specific point and is moved or scanned in sequence across the

specimen. As the beam interacts with the specimen at each specific location or point, it releases signals that are collected by the detectors. The detector signals are used to adjust the intensity of the corresponding image pixel and they are then used to create detailed images of the surface of the samples (Inkson, 2016). The morphology of the samples was determined using a Shimadzu ZU SSX 550 Superscan scanning electron microscopy as displayed in Figure 3.4. The analysis was done at room temperature and the samples were fractured by freezing them in liquid nitrogen. The samples were broken into appropriate sizes to fit the specimen chamber. The fractured samples were gold coated by sputtering to produce conductive coatings onto the samples.

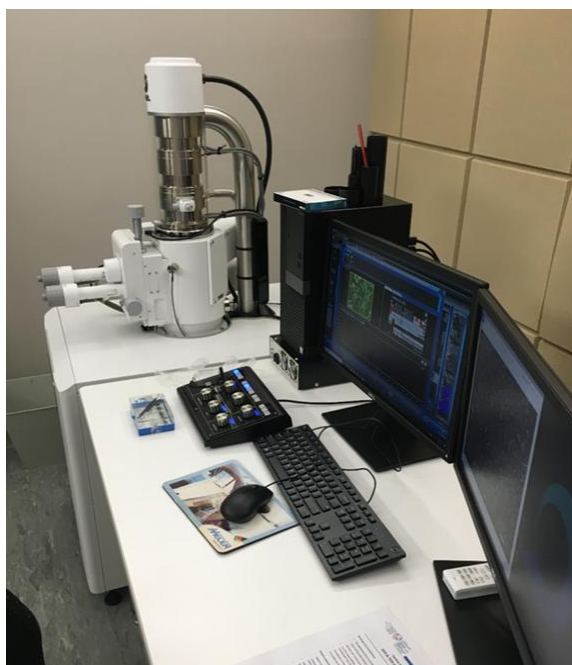


Figure 3.4: Scanning electron microscopy used to examine the surface morphology of samples

3.3.2 Thermogravimetric analysis (TGA)

TGA is a technique used for measuring thermal stability of materials as they undergo temperature changes. During the analysis, the technique works by examining and recording down the variations in weight of a sample as it undergoes the process of being heated or cooled in a controlled atmosphere (Price, Hourston and Dumont, 2000; Loganathan *et al.*, 2017) Thermal stability of samples was determined using a TG analyser (model Q500, TA Instruments) shown in Figure 3.5. Samples weighing between 8 and 10 mg were heated at a heating rate of $10\text{ }^{\circ}\text{C.min}^{-1}$ from 25 to $800\text{ }^{\circ}\text{C}$ under nitrogen. Three independent runs were conducted per sample.



Figure 3.5: Thermogravimetric analyser used to analyse thermal stability

3.3.3 Cone calorimeter

Cone calorimeter as demonstrated in Figure 3.6 is one of the flammability tests that can be compared to real-life fires (Goff, 1993). It measures quantities such as heat-release rate (HRR), time to ignition (tig), total heat release (THR) and mass-loss rate (MLR). It can also quantify the smoke output as well as carbon monoxide and carbon dioxide yields (Koo *et al.*, 2000). It will be performed on a Dual Cone calorimeter using a cone-shaped heater at an incident heat flux of 35 kWm^{-2} . The specimens, with dimensions of 6 mm x 100 mm will be prepared by injection moulding.



Figure 3.6: Cone calorimeter used for the analysis of the flammability of samples

3.3.4 Rheology

Rheometers are often utilized to study flow and deformation of a polymeric material under the effect of stress, which aids in optimizing manufacturing processes, thereby saving costs. The flow properties were determined using a Modular compact rheometer (Anton Paar) shown in Figure 3.7. The 25 mm-diameter parallel-plates configuration was used. The tests were carried out at 180 °C under atmospheric conditions. Preliminary experiments were performed to determine the linear viscoelastic region of the samples, and the strain amplitude was fixed at 1.00%. The zero-gap was set at 1.1 mm for all tests. Experiments were performed in replicates to confirm reproducibility.



Figure 3.7: Equipment that was used to determine the dynamic rheological measurements

3.3.5 Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis is used to study the viscoelastic behaviour of polymeric materials with respect to time and temperature, under conditions of low applied mechanical force (Akay, 1993). This analysis uses a system of clamps for mechanical testing of solid polymeric materials, so a polymer sample that is to be tested needs to be trimmed, cut or moulded into a shape that will match the clamp that is to be used (Debra Dunson, 2017; Bashir, 2021). DMA tests were performed on the samples in the temperature range of –30 °C to 130 °C in the dual-cantilever bending mode using a PerkinElmer DMA 8000 analyser shown in Figure 3.8. The heating rate, frequency, and strain amplitude were set as 2

$^{\circ}\text{C}.\text{min}^{-1}$, 10 Hz, and 0.02%, respectively. Three trials were conducted for each DMA test to confirm the reproducibility.



Figure 3.8: Perkin-Elmer DMA used to determine mechanical properties

3.3.6 Tensile testing

A tensile tester is a machine used for measuring the force needed to break a sample and the level at which a sample stretches before it breaks. It determines tensile properties such as energy to break, tensile strength, tensile modulus and % elongation at break (Gilmer and Williams, 1996). A tensile test was performed on injection-moulded, dog-bone-shaped specimens using an Instron 5966 tester (Instron Engineering Corporation) shown in Figure 3.9. The instrument has a load cell of 10 kN. The test was carried at a single strain rate of $50 \text{ mm}.\text{min}^{-1}$ and at a temperature of 25°C . The obtained results are an average of at least six tests per sample.

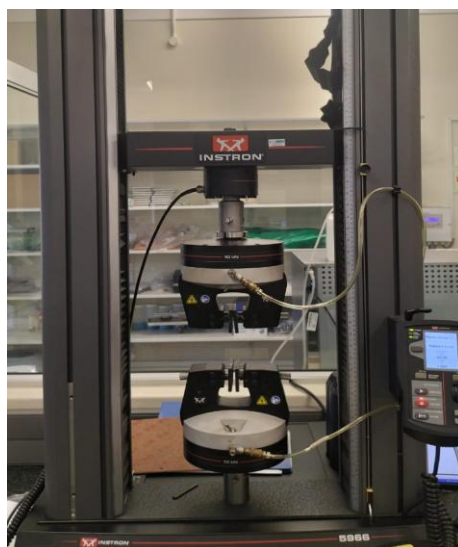


Figure 3.9: Equipment that was utilized to determine tensile properties of sample

3.3.7 Charpy impact test

The Charpy impact test is a traditional and standardized high-strain technique that evaluates the energy that a specimen absorbs either notched or unnotched during fracture induced by an impact load at high strain rates (Krausz *et al.*, 2021). During the test, the polymeric material shaped like a small rectangle is placed in the equipment that holds it firmly. Then a pendulum of a known mass is swung from a certain height to strike the polymeric material at a known force (Hufenbach *et al.*, 2008). A Charpy impact test was conducted on injection-moulded specimens with dimensions of approximately 80 mm × 10 mm × 4 mm (L×W×B) by adhering to the ISO179 standard. The specimens were notched on one side with a notch root radius of 0.25 mm at a 2 mm depth using a CEASt Automatic Notchvis Plus shown in Figure 3.10(a). The notched Charpy impact strength (ISO179) was measured at 25 °C using a fully automated CEASt Pendulum Resil Impactor II shown in Figure 3.9(b). The drop velocity was 3.7 m.s⁻¹ for a hammer energy of 14 J. The obtained results are an average of at least six tests per sample.

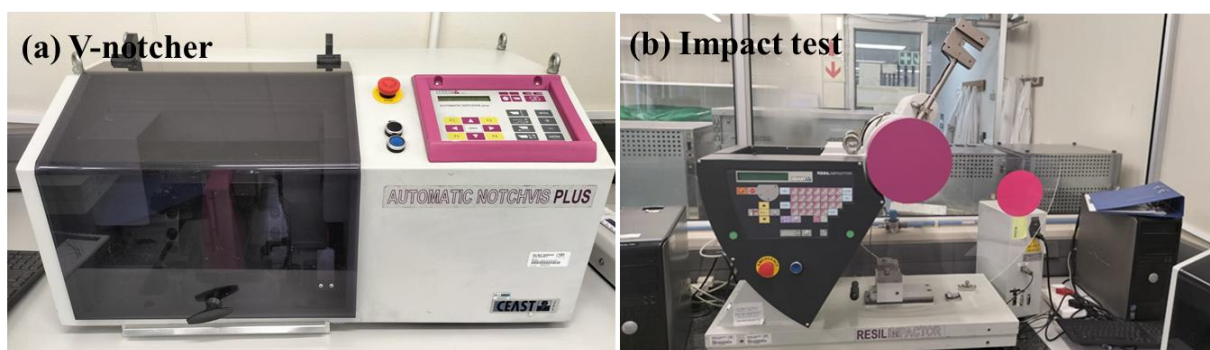


Figure 3.10: Machines used for (a) notching and (b) determining the impact strength of samples

3.3.8. Differential scanning calorimetry (DSC)

DSC is a thermal analysis technique that scans and measures the difference between the heat flow or capacity of a sample and a reference pan as they are subjected to the same temperatures and atmospheric pressure throughout the experiment (Demetzos, 2008). DSC analysis was performed using a DSC-2500 from TA Instruments shown in Figure 3.11. The samples weighing 6 mg were heated from $-60\text{ }^{\circ}\text{C}$ to $200\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C}.\text{min}^{-1}$, cooled to $-60\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C}.\text{min}^{-1}$, and reheated to $200\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C}.\text{min}^{-1}$ in a nitrogen atmosphere with a nitrogen flow rate of $50\text{ mL}.\text{min}^{-1}$. Three independent runs were conducted per sample.



Figure 3.11: DSC machine used to measure the heat transfer of samples

3.9 References

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CHAPTER 4: Results and discussion

4.1 Morphology of the investigated samples (SEM)

Figure 4.1 depicts SEM images of 80:20 PLA/GTR blend. According to Figure 4.1(a) (symbol A), the GTR agglomerates have fairly dispersed and formed an immiscible blend within the PLA matrix. An immiscible blend (sometimes called heterogeneous) refers to a mixture of two or more polymers that do not mix well at molecular level (Sarathchandran, 2020). It was observed that GTR particles do not melt during mixing; hence the GTR and PLA separate into two different regions, with each material maintaining its unique properties. This resulted in a phase separation where GTR formed dispersed droplets within the PLA matrix, which further led to poor mechanical properties of the PLA/GTR blend (later discussed in this document). Furthermore, the immiscibility of the two components also indicated agglomerates of the GTR component (see symbol B in Figure 4.1(b)). Zhang *et al.* (2012) investigated the effect of mechanochemical milling of PP/GTR blend. The results indicated that the PP/GTR blend that did not undergo milling showed a poor dispersion of GTR in the PP matrix due to the formation agglomerates. Marín-Genescà *et al.* (2020) observed the same trend in their study, as the dispersed GTR particles could be clearly seen in the LLDPE matrix and this lead to poor interfacial adhesions between the two components. Lu *et al.* (2017) also reported a two-phase structure in PP/GTR blend, which is attributed to thermodynamic incompatibility of the hard (PP) and soft (GTR) phase. In a study by Luo and Isayev (1998), different mixing methods were investigated on PP, ground rubber tire (GRT), and ultrasonically devulcanized GRT. The SEM results indicated that the twin-screw extruder rubber particles appeared smaller and more uniform than those mixed in the internal mixer. The SEM micrographs also indicated a two-phase morphology. This two-phase morphology trend was also observed for different polymers such as recycled polyethylene, LDPE and HDPE (Tian *et al.*, 2013; Sulcis *et al.*, 2014; Wang, Chen and Rodrigue, 2018). When GTR particles are dispersed in a manner like small voids, they act as stress concentrators in the PLA matrix. This is due to the differences in stiffness between the GTR particles and the PLA matrix. In a study conducted by Datta and Marcin (2015), the recycled polyethylene, ground tyre rubber, and thermoplastic poly(ester-urethane) were blended together. It was found that when GTR was added at higher concentrations within the polymer matrix, it resulted in the formation of agglomerates. Similarly, Heller *et al.* (2022) reported that the

addition of 20% GTR to the w-HPDE/ABS disrupted the continuity and uniformity of the structure, as demonstrated by the formation of voids around GTR particles.

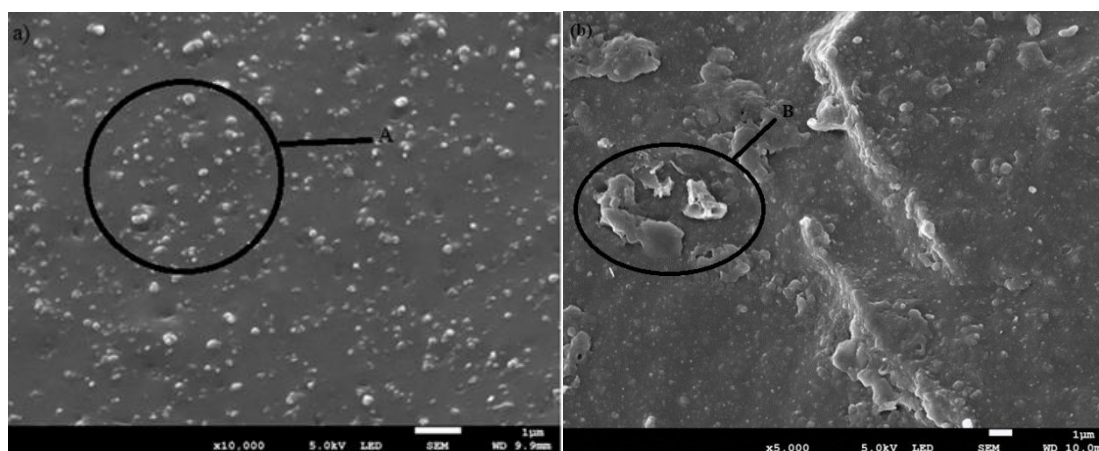


Figure 4.1: SEM images for 80:20 PLA/GTR blend

Figures 4.2(a) and (b) show that the halloysite clay had a fairly good dispersion within the PLA matrix. Symbol A depicts a typical tubular structure of halloysite clay. However, some HC particles are embedded within the matrix while others are debonding and pulling out of the PLA matrix (as can be seen by micro-voids or holes formed in symbol B and C), and this can be associated with the fact that HC in this study was not functionalized. It could also be related to poor interaction between HC and PLA because of different chemical structures. Wu *et al.* (2013) observed that HC formed fewer agglomerates and that most of the HC dispersed uniformly in the PLA matrix. Furthermore, the SEM pictures showed that some of the HC was visible, and a significant number of cavities were observed on the PLA matrix. This was associated with a poor interaction between HC and the PLA matrix. Othman *et al.* (2016) conducted a study on the mechanical and thermal properties of PLA/halloysite bio-nanocomposite. In this study HC was modified with glycerol and a uniform dispersion of the clay was reported within the PLA matrix. Silva *et al.* (2014) conducted a study where PLA/natural halloysite nanotubes (HNTs) films were prepared by solution-casting method to examine their properties for packaging applications. The SEM micrographs showed that there was a fairly uniform dispersion of HNTs in the PLA matrix at 5 w/w%. They also observed that HNTs formed agglomerations and that there was a presence of micro-voids, which resulted from the pulled-out HNTs during tensile testing. Generally, it was the case in the current study; the trend of a uniform dispersion of HC within the polymer matrix is accompanied by agglomerates.

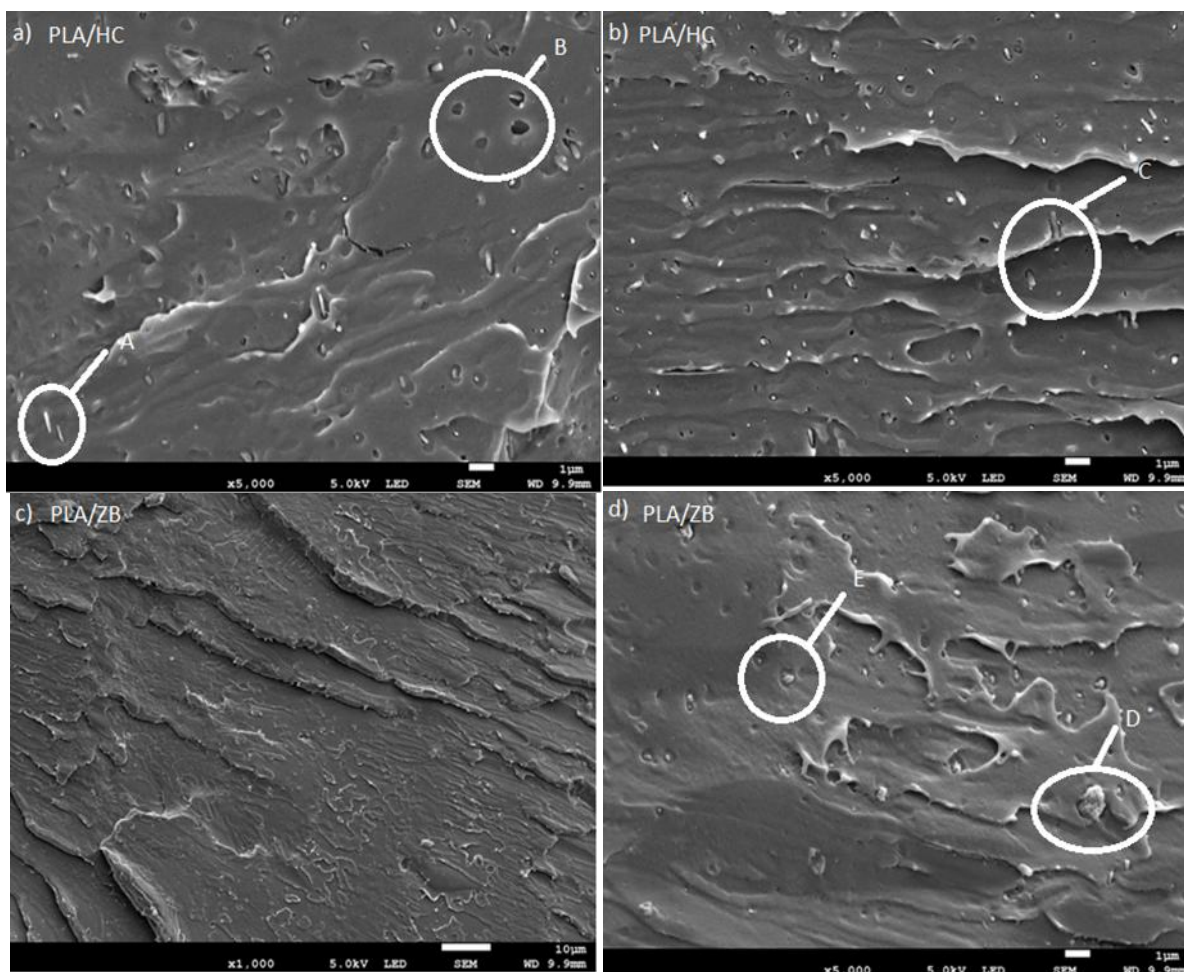


Figure 4.2: SEM images for 97:3 PLA/HC (a and b) and 97:3 PLA/ZB (c and d)

Figure 4.2(c) illustrates the effective dispersion of zinc borate within the PLA matrix. On the other hand, Figure 4.2(d) indicates a reduced number of zinc borate agglomerates (symbols D and E) which resulted in higher tensile modulus, which will be discussed later in this document. Symbol E provides a view of the ZB structure embedded within the PLA matrix. In a study conducted by Baltaci *et al.* (2013), the presence of cumene-terminated poly(styrene-co-maleic anhydride) (PSMA) in ZB resulted in a homogeneously dispersed ZB particles in poly(ethylene terephthalate) (PET). Pi, Guo and Ning (2002) studied the mechanochemical improvement of flame retardancy of poly(vinyl chloride) (PVC) by infusion of zinc borate and zinc borate/aluminium trihydrate (ATH). The SEM micrographs showed that the addition of untreated zinc borate (ZB) to the PVC matrix resulted in a significant number of aggregates of ZB particles. However, the treated ZB displayed a homogeneous dispersion of ZB in the PVC matrix. Elsewhere, Köytepe, Vural and Seçkin (2009) reported on a well-dispersed ZB in the polyimide matrix, with little agglomerates. When comparing the two nanoparticles in the current study, it seems like ZB is better dispersed in the PLA polymer matrix than HC. This can be attributed to the fact that ZB used

in this study had a lower molecular mass than HC (refer to Chapter 3), which could have allowed it to flow easily during mixing and interact better within the PLA matrix.

Figures 4.3(a) and (b) depict a SEM micrograph of PLA/HC/ZB. Symbol A shows HC tubular structure within the matrix, and symbol B shows aggregation of ZB particles within the PLA matrix. There seems to be no interaction between ZB and HC, which might indicate an anti-synergy on the two nanoparticles. This resulted in the decrease of tensile modulus and a reduced thermal stability of the PLA matrix, as discussed elsewhere in this document. It was observed that HC and ZB undergo phase separation and work well separately. In Figure 4.3(b), symbol C shows micro-voids where HC has debonded from the PLA matrix.

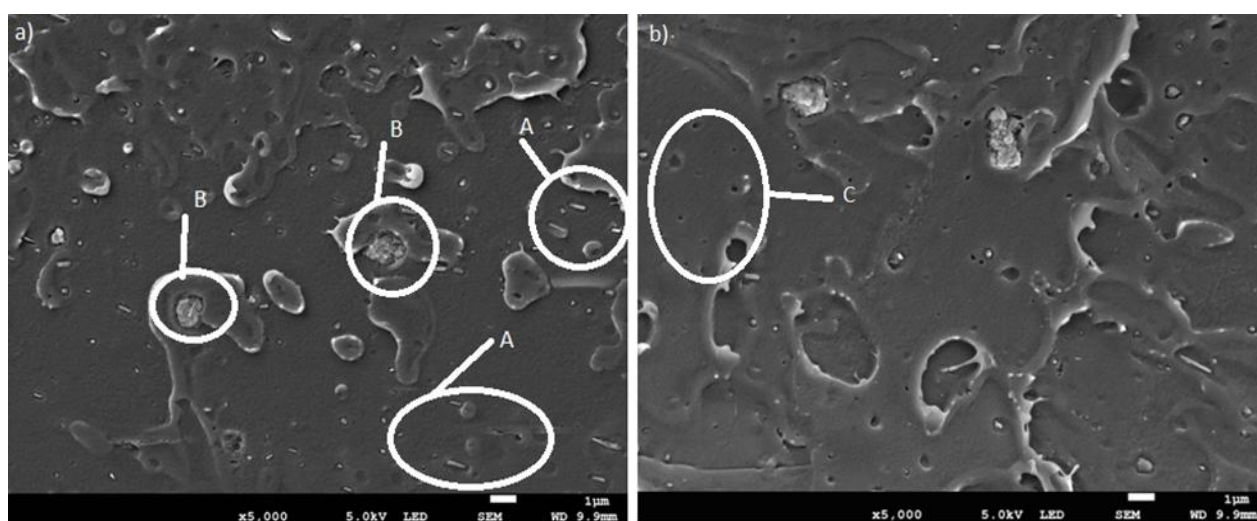


Figure 4.3: SEM micrographs for 97:3 PLA/HC/ZB

Figures 4.4(a) and (b) depict PLA/GTR/HC blend composite, with symbol A displaying the GTR within the PLA matrix. The HC seems to have dispersed fairly on the PLA matrix; however micro-voids are visible on the surface of the PLA matrix. Furthermore, the GTR seems to encapsulate the HC nanoparticles, which has a negative impact on the properties of PLA. Due to this encapsulation, the GTR and HC both separate from PLA matrix, resulting in lower tensile strength, impact strength and a reduced thermal stability, which will be discussed later in this document. Figures 4.4(c) and (d) show the micrographs for PLA/GTR/ZB, with symbol C displaying the GTR structure. Symbol D shows the agglomeration of ZB within the blend. The ZB agglomerates have dispersed well in the blend; however ZB and GTR underwent phase separation. This resulted in reduced mechanical properties as well as thermal stability.

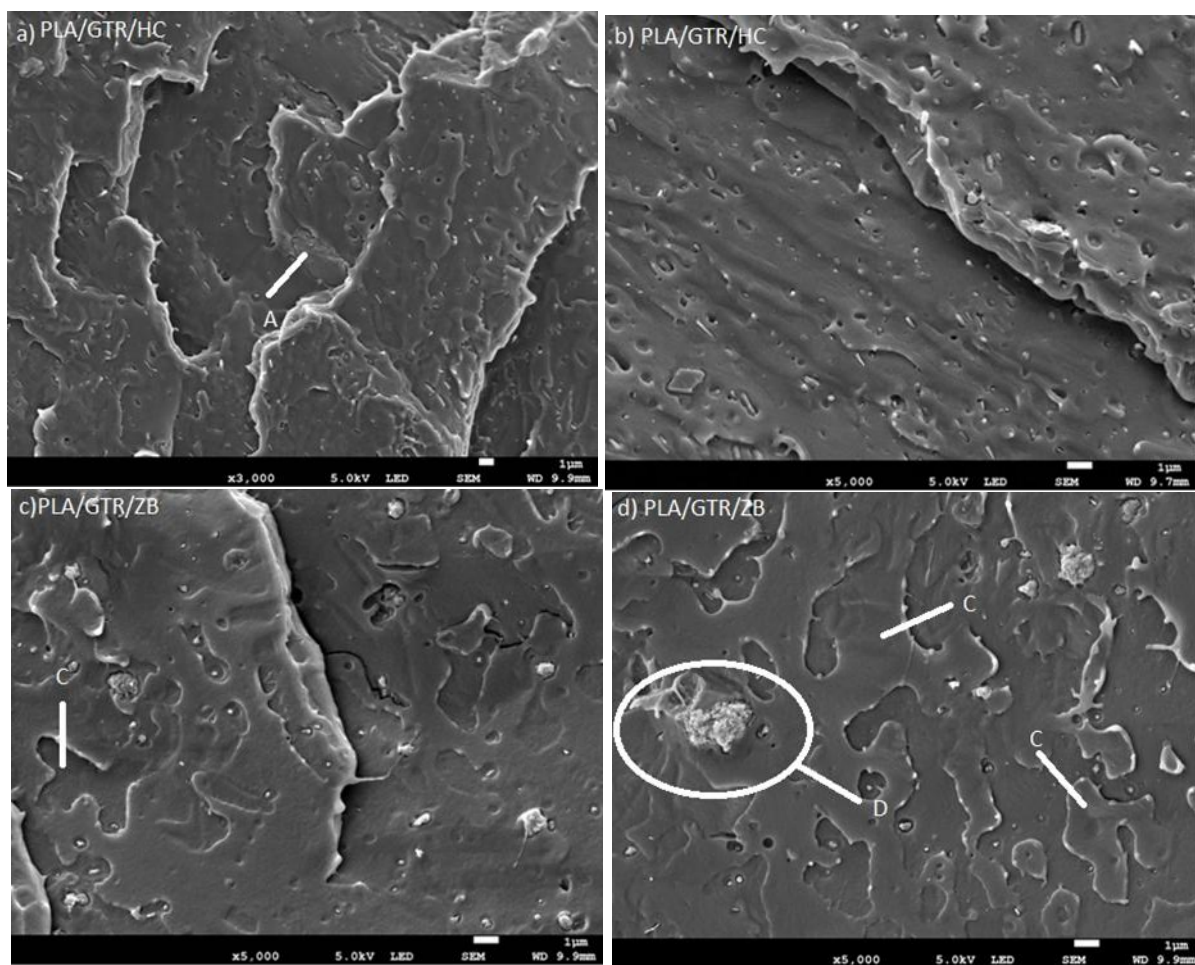


Figure 4.4: SEM micrographs for 77.6:19.4:3 PLA/GTR/HC (a and b) and 77.6:19.4:3 PLA/GTR/ZB (c and d)

In Figure 4.5(a), symbol C represents the presence of GTR. Symbol B illustrates the debonding of HC from the matrix, while symbol A indicates the agglomeration of ZB. Symbol E reveals the existence of numerous micro voids, and symbol D depicts large agglomerates of ZB. Each of these fillers operate independently within the PLA matrix, which unfortunately results in a negative impact on both the mechanical and thermal properties of PLA. ZB and HC were unable to interact with GTR, which in turn made the GTR to start working as a catalyst, affecting flammability properties of the blend. There is anti-synergy between HC, ZB and GTR within the polymer matrix. Furthermore, there is a possibility that the nanoparticles are only localized in the PLA phase and the interphase between PLA and GTR, but not in the GTR phase. This behaviour can be attributed to the fact that GTR does not melt during mixing, which prevents it from attracting the nanoparticles into its phase.

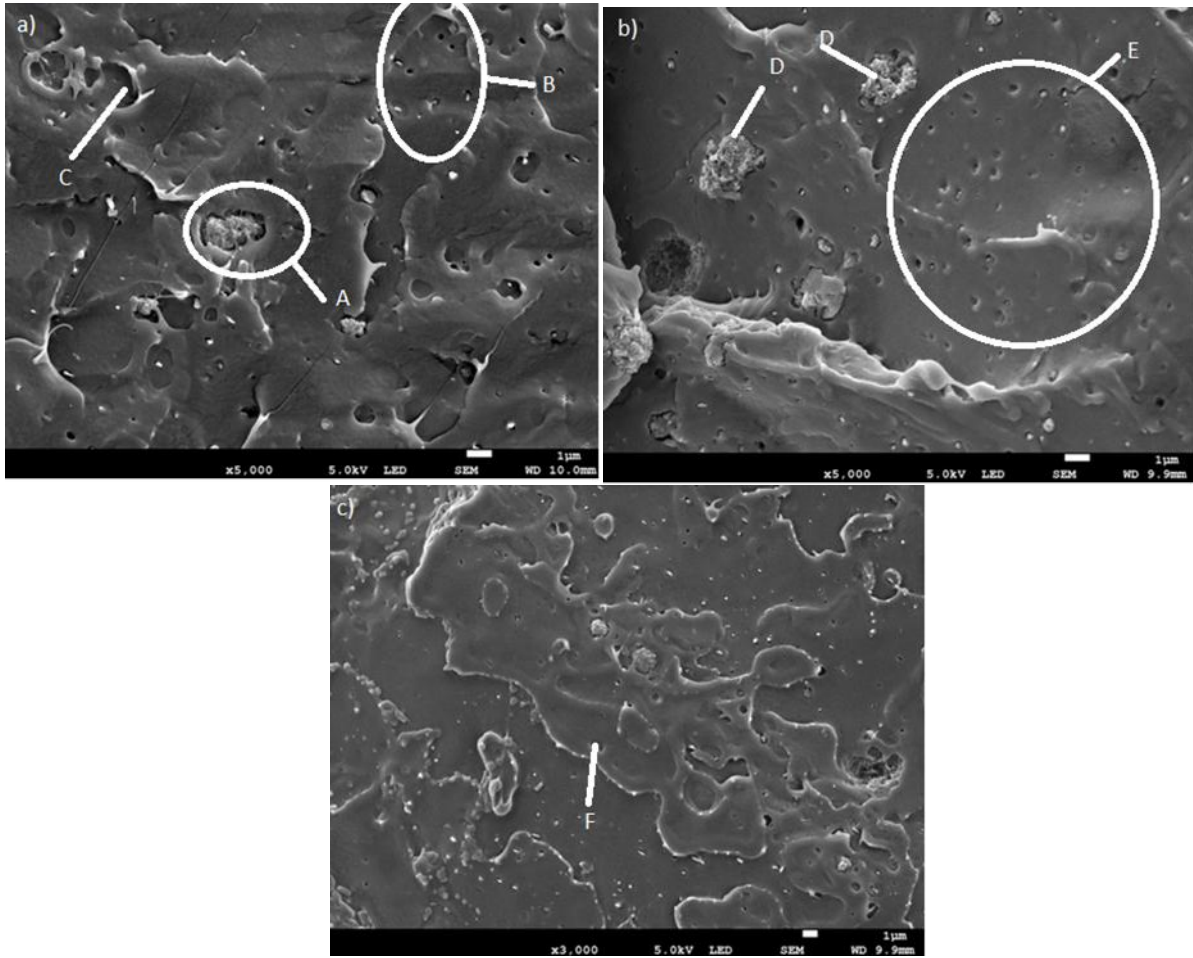


Figure 4.5: SEM micrographs for 77.6: 19.4: 3PLA/GTR/HC/ZB

4.2 Differential scanning calorimetry (DSC)

The second heating DSC thermograms of PLA nanocomposites and PLA/GTR hybrid composites are shown in Figures 4.6(a), and (b), respectively. Thermal properties such as the glass transition temperature (T_g), melting temperature (T_m), cold crystallization temperature (T_{cc}), change in melting enthalpy (ΔH_m) and the degree of crystallinity (X_c) are summarised in Table 4.1. The data in Table 4.1 are an average of two tests (with standard deviations). The normalized enthalpies of melting in Table 4.1 was determined using the following equation (1),

$$\Delta H_m^{Norm} = \frac{\Delta H_{m,PLA}}{W_{PLA}} \quad (4.1)$$

whereby, $\Delta H_{m,PLA}$ is the experimentally observed melting enthalpy for neat PLA, and ΔH_m^{Norm} is the calculated normalized enthalpy of melting for PLA weight fraction (w_{PLA}) in

the composite. The following equation (2) was used to calculate the degree of crystallinity (X_c):

$$X_c (\%) = \frac{\Delta H_m^{Norm}}{\Delta H_m^0} \times 100 \quad (4.2)$$

whereby, ΔH_m^0 is the melting enthalpy of a 100% crystalline PLA, with a value of 93 J/g (Solariski, Ferreira and Devaux, 2005; Yang *et al.*, 2010; Mngomezulu, Luyt and John, 2019). Figure 4.6(a) illustrates three distinct peaks for neat PLA. The first peak, denoted by symbol ‘A’, represents the glass transition temperature at 57.4 °C. The second peak, symbolized by ‘B’, corresponds to the cold crystallization temperature at 111.0 °C. Finally, the double melting peaks are observed (symbolized by ‘C’), with the initial peak at 147.8 °C and the following one at 151.9 °C. Chapple, Anandjiwala and Ray (2013) observed the same double melting peaks when they investigated the mechanical, thermal, and fire properties of polylactide/starch blend/clay composites. The authors associated the double peaks with the melting of crystallites that vary in size and/or the degree of their structural perfection. Wu *et al.* (2013) associated these peaks with the formation of different crystal structures when reporting on the polylactide/halloysite nanotubes composites. This occurrence has been extensively reported in the literature; these structures are divided into two forms (Mngomezulu *et al.*, 2019; Lendvai *et al.*, 2021). Firstly, the α -form is characterized by a pseudo-orthorhombic structure, which melts at higher temperatures. The second one is associated with the β -form, which exhibits an orthorhombic structure and melts at lower temperatures, making the α -form much more stable than the β -form (Pongtanayut, Thongpin and Santawitee, 2013; Russo *et al.*, 2014). The addition of GTR and HC into the PLA matrix did not have a significant effect on the glass transition temperature, with minimum change observed. The addition of GTR displayed a slight reduction in T_g temperature when compared to neat PLA. The presence of HC and ZB showed a slight or minimum improvement in the T_g of the PLA. Neat PLA recorded a T_g value of 57.4 °C, while the two composites, i.e. PLA/ZB and PLA/HC, recorded T_g values of 57.9 °C and 57.7 °C, respectively. Wu *et al.* (2013) reported a slight improvement in the T_g when 7 wt% of halloysite clay was incorporated in the PLA matrix. This was ascribed to the ability of halloysite clay in delaying the migration and diffusion of PLA molecular chains. The addition of GTR into the PLA matrix increased the cold crystallization temperature of neat PLA, and this can be associated with the stiffness of the crosslinked GTR. The blend composites (PLA/GTR/HC, PLA/GTR/ZB and PLA/GTR/HC/ZB) show the same increase in T_{cc} , due to

the presence of GTR, together with the stiffness of the fillers. There is a reduction in the degree of crystallinity with the addition of GTR, ZB and HC. A careful inspection of Table 4.1 shows that the PLA/GTR recorded the lowest degree of crystallinity value. This may be due to the presence of GTR in the inter- and intra-spherulitic regions of the crystalline component of the PLA. As a result, the rubber particles in the blend hinder the formation of crystallites and reduces the crystallinity. One can realize that the blend composites consisting of GTR (PLA/GTR/ZB and PLA/GTR/HC/ZB) show the lower degree of crystallinity values when compared to the PLA/HC, PLA/ZB and PLA/HC/ZB. The low degree of crystallization in the presence of GTR may be ascribed to the encapsulation of the ZB and HC, which hinders the crystallization of the PLA matrix.

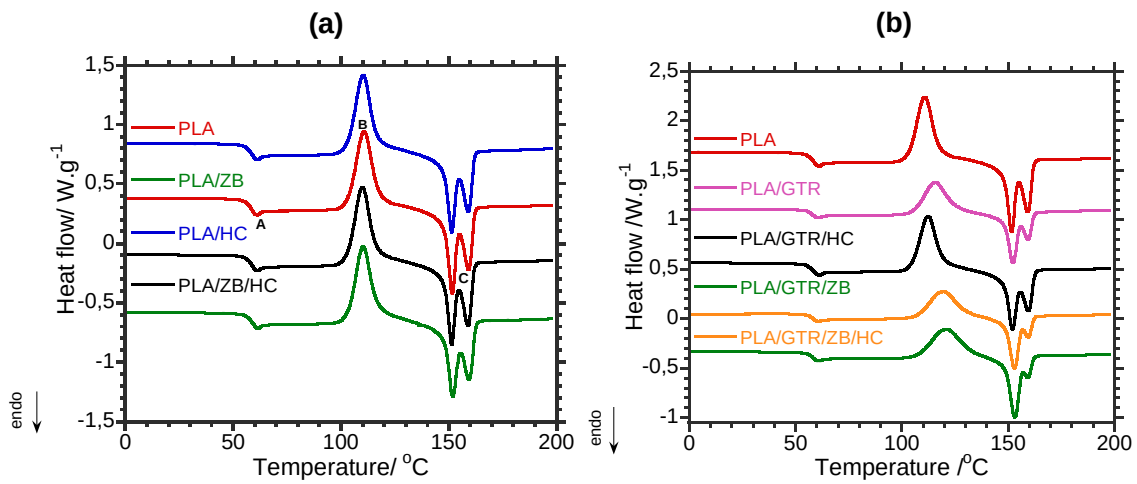


Figure 4.6: DSC thermograms for PLA and PLA composites

Table 4.1: The crystallization and melting temperatures of PLA and PLA composites

Sample ID	T _g °C	T _{cc} °C	T _m °C	ΔH _m ^{norm}	ΔH _m (J/g)	X _c (%)
PLA	57.4 ± 0.4	111.0 ± 0.21	^a 147.8 ± 0.1 ^b 151.9 ± 0.3	45.5	45.5 ± 2.3	48.9
PLA/GTR	56.0 ± 0.2	116.6 ± 1.2	^a 148.1 ± 0.3 ^b 152.3 ± 0.3	28.5	22.8 ± 5.1	30.6
PLA/GTR/HC	57.4 ± 0	113.0 ± 0.8	^a 148.0 ± 0.2 ^b 152.2 ± 0.2	42.6	33.1 ± 7.6	45.8
PLA/GTR/ZB	57.1 ± 0	121.5 ± 0.4	^a 148.5 ± 0.02 ^b 153.3 ± 0.1	34.4	26.7 ± 2.9	36.9
PLA/GTR/HC/ZB	57.2 ± 0.1	119.6 ± 0.1	^a 148.5 ± 0.1 ^b 153.0 ± 0.2	34.1	26.5 ± 2.6	36.6
PLA/HC	57.7 ± 0.2	110.5 ± 0.2	^a 147.5 ± 0.04 ^b 151.6 ± 0.3	40.7	39.5 ± 1.5	43.7
PLA/ZB	57.9 ± 0.1	110.6 ± 0.3	^a 147.9 ± 0.2 ^b 151.9 ± 0.2	41.2	40.0 ± 1.2	44.3
PLA/HC/ZB	57.8 ± 0.3	110.2 ± 0.3	^a 147.7 ± 0.1 ^b 151.5 ± 0.2	40.5	39.3 ± 2.3	43.5

a) Represents the melting peak temperatures

b) Represents the peak shoulder temperatures

4.3 Thermal stability of investigative samples (TGA)

Figures 4.7(a) and (b) display the TGA and derivative thermogravimetric (DTG) curves of neat PLA and PLA/GTR blend. The addition of GTR seems to decrease the thermal stability of PLA, and this can be associated with the fact that the rubber consists of volatile organic compounds (VOCs) that easily act as a catalysts in enhancing the degradation of PLA. Detected VOCs in various studies include cyclic hydrocarbons, benzene, styrene, toluene, 4-vinylcyclohexene, and limonene (Formela, 2022; Wiśniewska *et al.*, 2022). Gisbert *et al.* (2007) conducted a study on thermal degradation kinetics of GTR and the results showed that GTR consists of 7.0 ± 0.2 of volatile compounds, 56.3 ± 2.1 of rubbers (natural rubber and synthetic rubber) and 36.7 ± 2.2 of carbon black ash. The present volatile products evaporated at lower temperatures, thus reducing the thermal stability of PLA matrix. The degradation of the PLA/GTR blend initially started at about $288.8\text{ }^{\circ}\text{C}$ and this can be supported by the DTG curve. Table 4.2 shows that the degradation temperature for neat PLA at $T_{10\%}$ and $T_{50\%}$ is at $335.4\text{ }^{\circ}\text{C}$ and $358.7\text{ }^{\circ}\text{C}$, respectively, while the PLA/GTR blend recorded the $T_{10\%}$ and $T_{50\%}$ values of $321.5\text{ }^{\circ}\text{C}$ and $347.9\text{ }^{\circ}\text{C}$ respectively, clearly indicating that PLA has higher thermal stability than the PLA/GTR blend. However, it can also be observed that the incorporation of the GTR results in a higher weight percentage (wt%) char residue at $500\text{ }^{\circ}\text{C}$, whereas PLA degrades completely. This can be associated with the fact that GTR contains carbon black. It is well known that carbon black is utilized to strengthen the physical properties of rubber and enhances vulcanization. Piszczyk and Hejna (2015) observed a similar trend when they conducted a study between GTR and polyurethane foams. It was reported that the blend of GTR/polyurethane foam had a huge impact on the wt% char residue at $510\text{ }^{\circ}\text{C}$ when compared to neat polyurethane foam. This was associated with the presence of carbon black in the GTR.

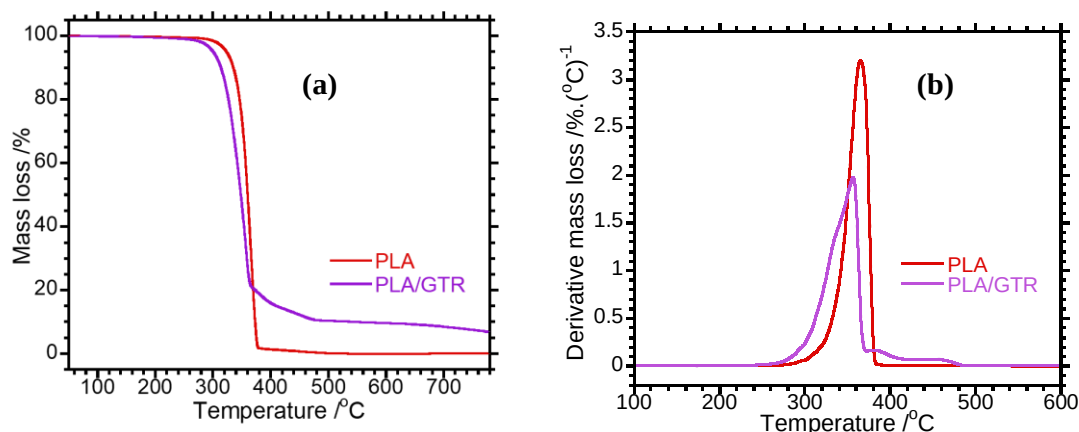


Figure 4.7: TGA and DTG curves of PLA and the PLA/GTR blend

Figure 4.8 illustrates the TGA and DTG curves of neat PLA and PLA composites. PLA has higher thermal stability than all the other investigative samples. For example, according to Table 4.2 at $T_{50\%}$, there is an 11% reduction of thermal stability when ZB is added to the PLA matrix; however there is an increase in the percentage char residue. This can be associated with the release of water, boric acid and boron oxide from ZB at higher temperatures. Song *et al.* (2019) reported similar findings with silicone rubber composites and hydrated ZB blends. ZB accelerated the thermal decomposition of the silicone rubber blends thereby reducing thermal stability due to the release of water molecules. According to Table 4.2, the addition of HC to the PLA matrix shows a slight reduction of 0.5 % in thermal stability when compared to neat PLA. This may be associated with the catalytic behaviour of clays that may be linked to the decomposition of alkylammonium cations modifiers. These modifiers can catalyse the polymer matrix. The process involves replacing the ammonium linkage on the clay structure with a hydrogen proton due to β -carbon fracture. This fracture acts as a Brønsted acidic site, seemingly accelerating PLA degradation. The reduction can also be associated with the release of water found within the tubular structure of HC at elevated temperatures and the decomposition of the hydroxyl groups. Ling and Teik (2014) reported that at $T_{5\%}$ the neat PLA had a temperature value of 334.8 °C, which is higher than that of PLA/halloysite nanotubes (HNT), which is 329.1 °C. This observation was attributed to the presence of a free hydroxyl group on the surface of halloysite clay and the moisture that is situated inside their tubular structure acting as catalysts to degrade PLA. Murariu *et al.* (2012) reported the same results from their study and associated this behaviour with degradation of ammonium organo-modifiers normally found in clays. When comparing 97/3 PLA/HC and 97/3 PLA/ZB, the PLA/HC composite at $T_{10\%}$ and $T_{50\%}$ revealed higher thermal

stability. There is no clear explanation for such an observation. There is an 8.9% reduction of thermal stability when ZB and HC are combined together in the PLA matrix, and this can be related to the anti-synergy between the two nanoparticles.

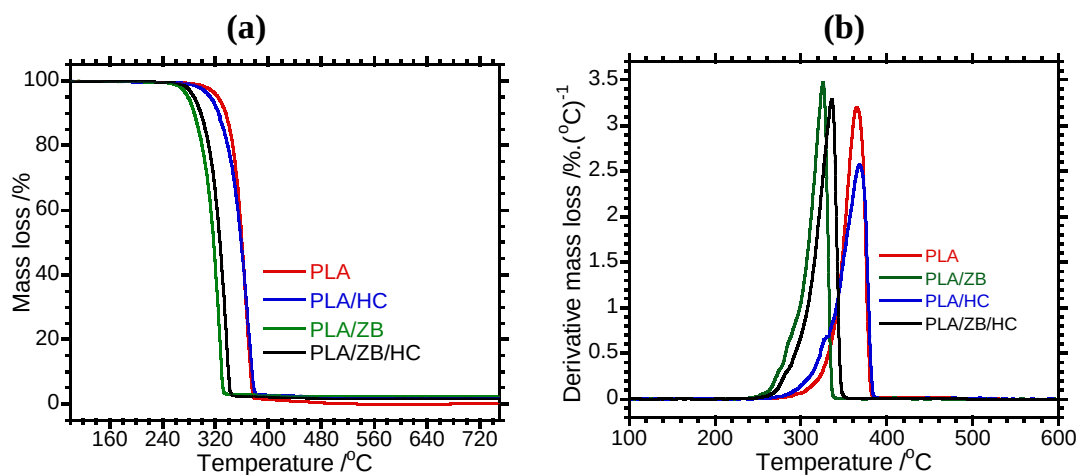


Figure 4.8: TGA and DTG curves of PLA and PLA composites

Table 4.2: Degradation temperature at 10 and 50% mass for all the investigative samples

Sample ID	T _{10%}	T _{50%}	% Char
PLA	335.4	358.7	0.01
97/3 PLA/ZB	289.2	318.5	2.22
97/3 PLA/HC	326.7	356.8	1.97
97/3 PLA/HC/ZB	298.2	326.7	1.72
80/20 PLA/GTR	321.5	347.9	10.33
77.6/19.4/3 PLA/GTR/ZB	289.4	319.5	19.31
77.6/19.4/3 PLA/GTR/HC	316.0	355.2	14.05
77.6/19.4/3 PLA/GTR/HC/ZB	287.5	317.8	9.42

Figure 4.9 and Table 4.2 show that the addition of GTR to the PLA composites resulted in low thermal stability of PLA, which is to be associated with the presence and release of volatile gases in the GTR. The blend composite of PLA/GTR/ZB has a higher char residue at 500 °C than neat PLA and all the other investigative samples. It is well known that ZB degrades at approximately 300 °C, which results in the release of boric acid, which in turn accelerates the formation of a glassy char layer. All the investigated samples have lower thermal stability than neat PLA, and for PLA/GTR/HC this can be induced by the presence of

alkylammonium cation in halloysite clay, as the temperatures rises from 180 °C. The kinetic energy of these cations increases, which causes the cations to break free from the clay structure and release gases such as ammonia. The blend composites have a two-step degradation phase that represents the decomposition of different organic materials. The first step is associated with the decomposition of volatile compounds, followed by the second decomposition phase, which is a combination of GTR and PLA. The low thermal stability of PLA with the addition of GTR, ZB and HC can be a limitation in various applications that require high thermal stability.

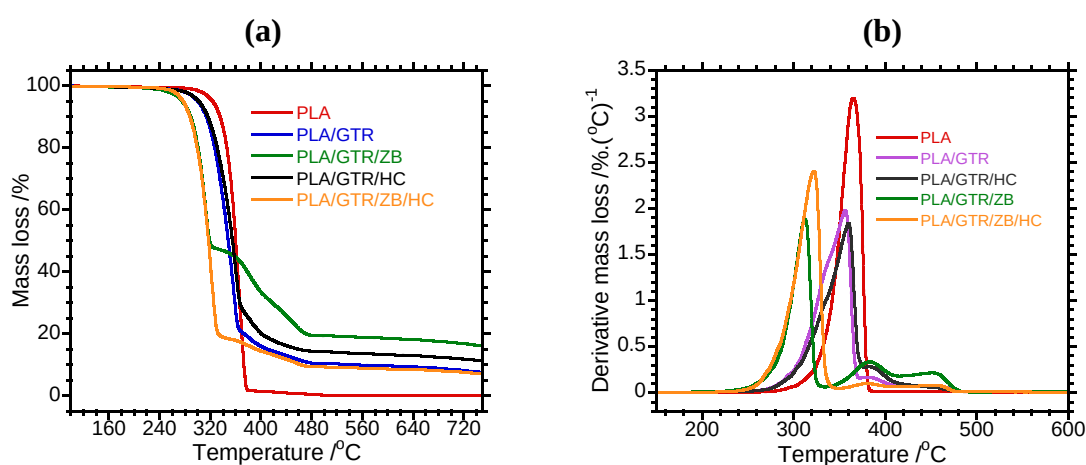


Figure 4.9: TGA and DTG curves of PLA, PLA/GTR blend and blend composites

4.4 Tensile and Impact tests of the investigated samples

The mechanical properties of all the studied samples are shown in Figure 4.10 and summarized in Table 4.3. All the stress-strain curves are shown in the Appendix. The incorporation of the ZB into the PLA slightly increased the tensile modulus when compared to the neat PLA, PLA/HC and PLA/ZB/HC composites (Figure 4.10(a) and Table 4.3). An improvement in the presence of ZB might be associated with better interaction between the filler and PLA matrix. A study conducted by Chellamuthu and Vasanthanathan (2023) shows that the addition of 5 and 10 wt% ZB in epoxy resin/glass fibre blend increased the tensile modulus of the polymer blend. This was attributed to the fact that ZB improved the bonding between the glass fibre and the epoxy resin matrix. However, the presence of the halloysite clay (HC) showed a slight decrease in the tensile modulus in comparison to neat PLA (Table 4.3 and Figure 4.10(a)). This might be due to poor interaction between the HC and PLA, with the clay nanoparticles somehow acting as defect points, which resulted in stress cracking.

Contrary to the current results, numerous researchers found an increase in tensile modulus with the addition of HC to polymers due to the dispersion of HC and the its level of stiffness (Heddicke-Höchstötter, Lim and Altstädt, 2009; Carli, Crespo and Mauler, 2011; Silva *et al.*, 2014; Ertas, Altuntas and Donmez Cavdar, 2019). The composites (PLA/ZB, PLA/HC and PLA/ZB /HC) showed higher tensile strain than neat PLA. In the presence of ZB, the tensile strain increases due to the ability of the ZB acting as a stress concentrator in the process absorbing a high amount of energy during the deformation. However, there is no clear explanation for an increase in tensile strain in the presence of HC. Ludwiczak, Frąckowiak and Leluk (2021) studied the effect of MMT clay as an additive in a PLA/polybutylene adipate-co-terephthalate (PBAT) blend. The addition of 5 wt% MMT in PLA/PBAT blend increased the elongation at break of the blend composite from 3.1 ± 0.3 to $42.9 \pm 3.0\%$. To further explain the increase in elongation at break, it was suggested that a polymer went through a forced deformation, whereby holes developed at MMT and PLA interface, reducing the sharpness of any formulated cracks and preventing further expansion of the cracks.

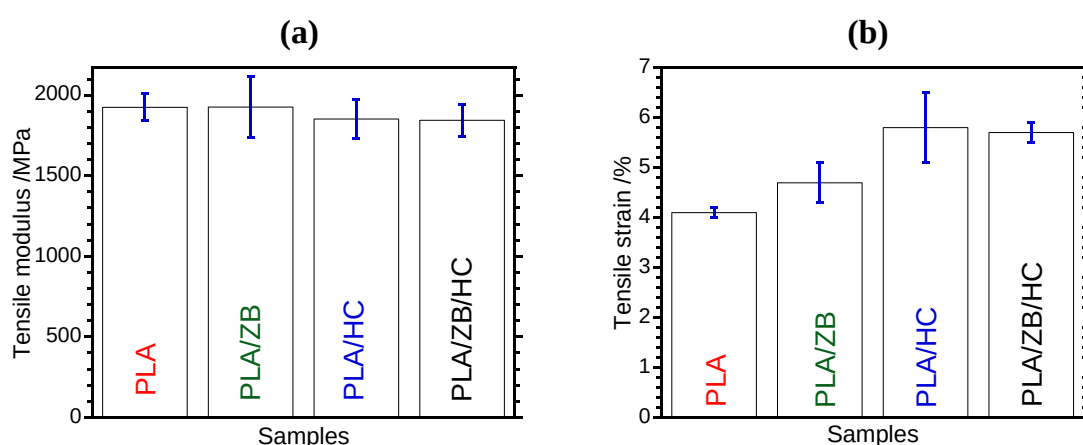


Figure 4.10: (a) Tensile strength and (b) tensile strain of PLA. PLA/ZB, PLA/HC and PLA/ZB/HC

Table 4.3 and Figure 4.11 show that the addition of the GTR in the PLA reduced the tensile modulus of PLA from 1926 ± 83 MPa to 1207 ± 39 MPa. Poor interaction between the GTR and PLA resulted in a reduction in tensile strength. One might argue that GTR acted as stress concentration sites and enhanced the material failure during stress-strain analysis and reduced the tensile modulus. Furthermore, it is apparent that the incorporation of GTR in the composites reduced the tensile modulus and tensile strain. As stated above, because of poor interactions between the GTR and PLA, the GTR acted as high stress concentrations, which resulted in low tensile modulus and tensile strain. It seems as if the presence of GTR in ZB-based composites counteracted the positive impact of ZB in terms of mechanical properties.

One can realize that the GTR encapsulated the ZB, with the GTR acting as the defects side for the initiation and propagation of stress cracking, which in turn reduced the mechanical properties of the ZB based systems. Fazli and Rodrigue (2021) studied the effect of GTR particle size on the properties of recycled HDPE. The addition of the GTR to the recycled HDPE resulted in a decrease in tensile modulus and elongation at break. This was attributed to the poor interfacial interaction between the GTR and recycled HPDE and the limited stress transfer between the phases. It was also associated with the fact that the recycled rubber and plastic get exposed to oxygen/ozone, grinding, processing and also thermal and mechanical stresses during their service life, which result in their degradation. In another study conducted by Prat and Rahhali (2012), the addition of GTR to PP, despite different particle sizes, reduced the tensile modulus and elongation at break of the PP matrix. This was due to the poor particle interface attachment, which led to cracks and fractures in the polymer matrix.

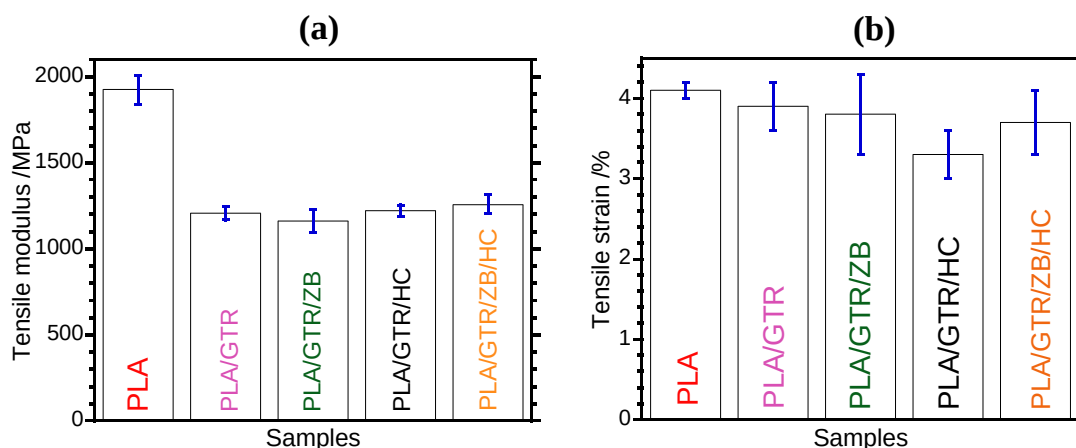


Figure 4.11: (a) Tensile strength and (b) tensile strain of the PLA, PLA/GTR blend, PLA/GTR/ZB, PLA/GTR/HC, and PLA/GTR/ZB/HC blend composite

Figure 4.12 illustrates the impact resilience of all the investigated samples. The incorporation of the ZB slightly enhanced the impact strength of the PLA, i.e. PLA recorded an impact strength of 5.75 ± 0.31 , while the PLA/ZB recorded a value of 5.77 ± 0.57 (Table 4.3 and Figure 4.12(a)). Better interfacial interaction between the PLA and ZB enhanced the stress-transfer between the PLA matrix and filler. Better interaction between the two components enhanced the resistance of the composite and provided better propagation of the energy. However, the PLA/HC composite showed a lower impact strength when compared to neat PLA. Because of poor interaction between the clay and PLA, there was an acceleration in relation to the crack propagation between the PLA/HC interface, which caused a debonding and reduced the impact strength. Contrary to these results, the addition of modified and

unmodified HC added to the PP matrix increased the impact strength of PP (Prashantha, Lacrampe and Krawczak, 2011). For the modified samples this was due to the better dispersion of HC, whereas for the unmodified this increase was associated with the intrinsic toughening properties of HC. The presence of the GTR in the blend composites reduced the impact strength of the blend composites. The interaction between GTR and PLA was poor, and as a result it seems as if the GTR covered the HC and ZB, which reduced the impact strength of the blend composites. The GTR acted as stress concentrators, initiating propagation and reducing the impact strength.

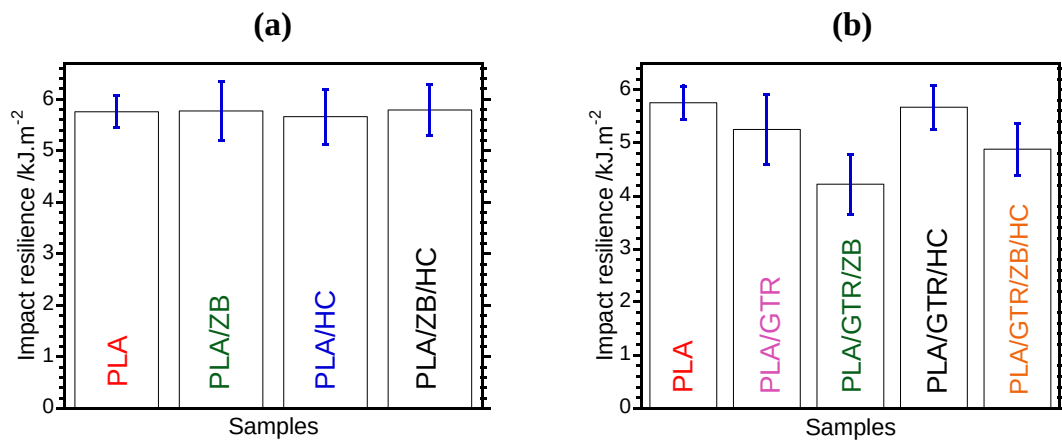


Figure 4.12: Impact strength of all the investigated samples

Table 4.3: Summary of the mechanical properties of all the investigated samples

Sample	Tensile modulus /MPa	Tensile strain /%	Impact resilience /kJ.m ⁻²
PLA	1925.5 ± 83.1	4.1 ± 0.1	5.75 ± 0.31
PLA/ZB	1926.8 ± 189.1	4.7 ± 0.4	5.77 ± 0.57
PLA/HC	1852.3 ± 119.1	5.8 ± 0.7	5.66 ± 0.53
PLA/ZB/HC	1843.9 ± 101.4	5.7 ± 0.2	5.79 ± 0.50
PLA/GTR	1207.2 ± 38.6	3.9 ± 0.3	5.25 ± 0.65
PLA/GTR/ZB	1161.3 ± 65.9	3.8 ± 0.5	4.22 ± 0.57
PLA/GTR/HC	1220.9 ± 33.5	3.3 ± 0.3	5.67 ± 0.41
PLA/GTR/ZB/HC	1257.5 ± 54.8	3.7 ± 0.4	4.88 ± 0.49

4.5 Dynamic Mechanical Analysis (DMA)

Figure 4.13 depicts the E' and $\tan \delta$ curves of the investigative samples. All the loss modulus curves will be shown in the Appendix. Various factors are known to affect the storage modulus of the polymeric materials. Stiffness, dispersion and the preparation method of polymer composites are found to be those factors affecting the storage modulus. The addition of ZB and HC improved the storage modulus of PLA (can be seen in Figure 4.13(a)). The improvement might be associated with two factors, i.e. stiffness of the fillers and their interaction with PLA. Firstly, better interaction between the PLA and ZB enhanced the rigidity of the polymer chains, leading to higher storage modulus. Furthermore, a high aspect ratio of clay nanoparticles reduced the chain mobility of the polymer chains, which enhanced the storage modulus. Murariu *et al.* (2012) associated the increase in storage modulus of PLA/HNT primarily to the contribution of the mechanical loss produced at the interface regions between halloysite nanotubes and PLA matrix. Shojaeiarani *et al.* (2019) reported an increase in storage modulus when zinc oxide (ZnO) was added to the PLA matrix and attributed it to the uniform dispersion of ZnO to the PLA matrix, which led to strong interfacial interaction between the two components, resulting in a stiffer PLA/ZnO blend. The addition of the combination of ZB and HC further increased the storage modulus of the PLA matrix. This can be attributed to the high aspect ratio of HC and the better interaction of ZB with the PLA matrix. The 97/3 PLA/ZB and 97/3 PLA/HC seem to have performed equally in increasing the storage modulus. There is little or no shifting of the $\tan \delta$ peaks of all the investigative samples when compared to neat PLA. According to the $\tan \delta$ peaks, the glass transition temperature (T_g) of PLA is 70 °C.

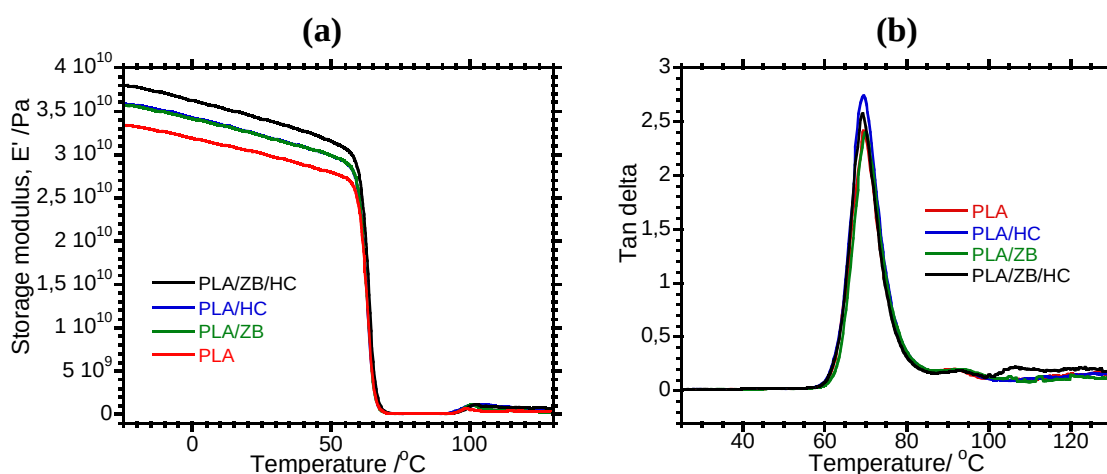


Figure 4.13: (a) storage modulus and (b) $\tan \delta$ peaks of the PLA based composites

Figure 4.14 displays the DMA results of PLA/GTR blend composites. The addition of GTR in the PLA matrix decreases the storage modulus of PLA (as can be seen in Figure 4.14(a)). This can be attributed to the immiscibility of the PLA/GTR blend shown in SEM images. Neat PLA has the highest storage modulus when compared to PLA/GTR, PLA/GTR/HC, PLA/GTR/ZB and PLA/GTR/ZB/HC. This is a very interesting observation, since ZB, HC and GTR have a higher stiffness than neat PLA. However, stiffness is not the only factor that affects the DMA results; dispersion and interfacial interaction also play a role. The reduction can also be attributed to poor interaction of the fillers within the PLA matrix, for example SEM images showed that HC mostly debonded from the PLA matrix forming voids. It can also be deduced that the addition of the GTR in the PLA matrix resulted in phase separation, which is known to decrease the properties of polymers. The PLA/GTR/HC and PLA/GTR/ZB/HC blend composites have a higher storage modulus than that of PLA/GTR/ZB blend composite. This can be attributed to higher stiffness of the components and the better interaction of ZB in the PLA matrix. All the storage modulus graphs showed that at a glassy state (T_g) the storage modulus seems to be higher for all components, but as temperature increases the storage modulus drops due to polymer chain mobility in the system. Tan delta shows that the peak of neat PLA decreases with the addition of all components. This can be associated with poor interaction of the components in the polymer matrix, and the reduced mobility of segments within polymer chain, which led to decreased energy that was absorbed. Lendvai (2021) studied the effect of natural rubber (NR) on toughening PP. This study reported that the addition of NR to PP decreased the storage modulus, and this was attributed to the fact that the existence rubber domains resulted in softening effect of PP. The tan delta peaks also reduced with the addition of NR to the PP matrix due to poor interaction between the two components.

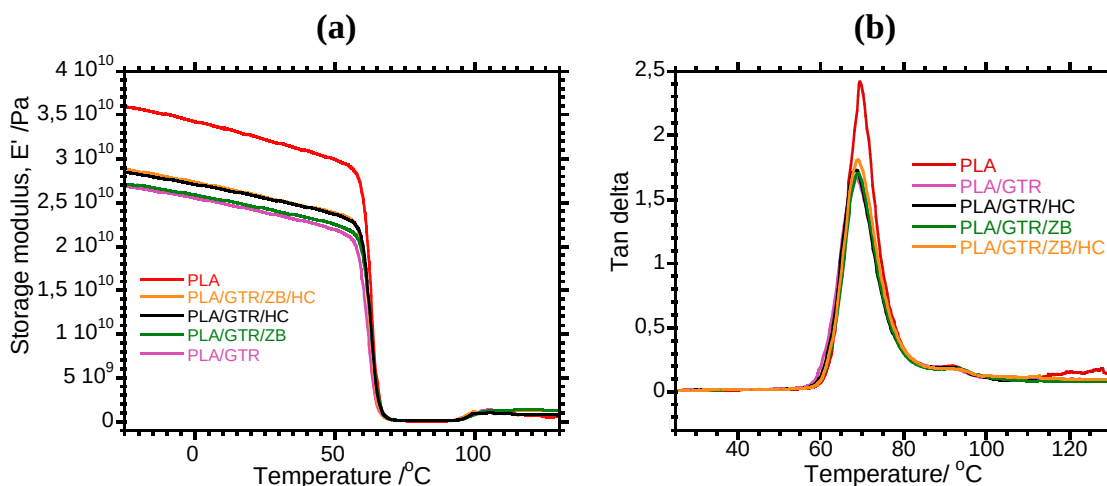


Figure 4.14: DMA results for PLA/GTR blend and blend composites (a) Storage modulus, and (b) Tan delta

4.6 Rheology

Figures 4.15(a) displays the rheological behaviour of neat PLA and PLA composites, while Figure 4.15 (b) depicts the rheological behaviour of the PLA/GTR blend. Various factors affect the complex viscosity of polymers and these include the dispersion of fillers in the polymer matrix, level of stiffness, aspect ratio and interaction of the fillers with the polymer matrix (Kalyon and Aktaş, 2014; Rueda *et al.*, 2017). In Figures 4.15(a) and (b), the complex viscosity curves of the tested samples display a non-Newtonian behaviour for the tested frequencies. In Figure 4.15(a), neat PLA has the lowest complex viscosity, but incorporation of ZB to PLA raises the viscosity. A higher complex viscosity for the PLA/ZB than the neat PLA is attributed to the dispersed ZB filler particles, which restrict the mobility of PLA chains, leading to the enhancement of elasticity. The PLA/HC composite has higher viscosity than the PLA/ZB composite, despite the equal amount of fillers (3 wt.%) in the two composites. Generally, HC is known for its tubular structure, large aspect ratio and high surface area. The tubular structure of HC allows confinement of more PLA chains, leading to a relatively better restriction in the mobility of the PLA chains than in the case of using ZB. The PLA/ZB/HC composite has the highest complex viscosity than both the PLA/ZB and PLA/HC composite. The total amount of filler in the PLA/ZB/HC composite is 3 wt.%. This shows that the presence of both 1.5 wt.% HC and 1.5 wt.% ZB in the PLA/ZB/HC composite enhanced the viscosity of PLA due to enhanced restriction in the mobility of the PLA chains because of the stiffness of the nanoparticles. In Figure 4.15(b), the complex viscosity of PLA/GTR blend is relatively higher than that of neat PLA. This is attributed to the higher

viscosity of GTR than PLA due to its crosslinked structure, leading to a higher viscosity of PLA/GTR blend. The PLA/GTR/filler blend composites could not be run on the rheometer due to the instrument limitations, such as a higher normal force exceeding the instrument specification. Nevertheless, it is expected that the filled PLA/GTR blend composites would display higher viscosity than the neat PLA/GTR blend.

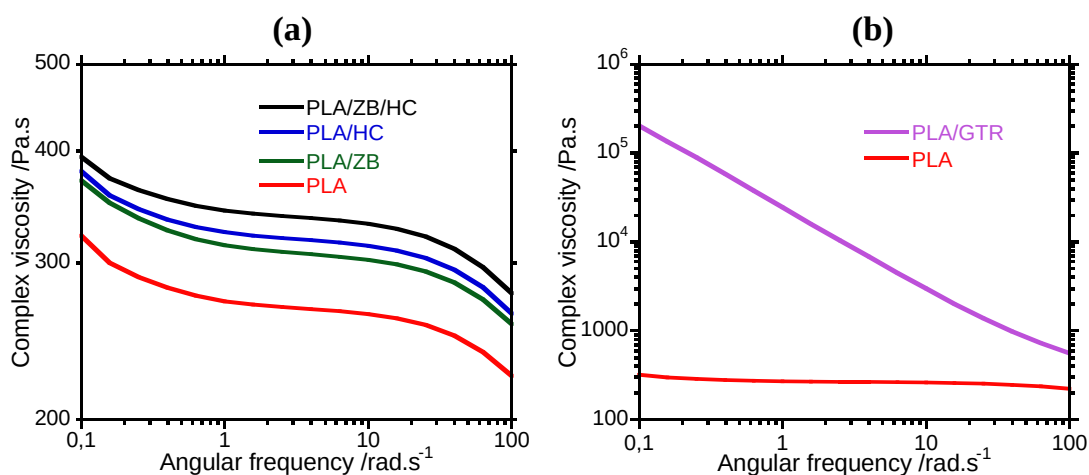


Figure 4.15: The plot of complex viscosity for neat PLA, PLA composites (a), neat PLA and PLA/GTR blend (b) as a function of angular frequency

4.7 Flammability properties of selective composites

The cone calorimetry technique is utilized to measure fire-associated properties of materials. The cone calorimetry collects data such as the heat release rate (HRR), time to ignition (TTI), carbon monoxide production (COP), carbon monoxide production (CO₂P), and mass loss rate (MLR). A low HRR peak value symbolizes a highly flame-resistant material and/or system. The incorporation of the clay slightly reduced the HRR peak value of the PLA/GTR from 461.72 kW/m² to 420.36 kW/m² (Figure 4.16(a) and Table 4.4). The flame-retardant property of the PLA/GTR/HC when compared to the PLA/GTR is associated to the formation of the char layer, which forms on the outer surface of the blend composite during combustion. It is well-known that the inorganic nanoparticles, such as halloysite can convert into a ceramic char layer, which can enhance the oxidation resistance. The formation of the char layer acts as an excellent heat insulator, slowing down the oxygen supply into the system and in the process trapping down the volatile products from leaving the system. The PLA/HC composite showed the lowest HHR peak value when compared to the GTR containing samples. In the absence of GTR, it seems as if the halloysite clay is more effective in trapping the volatiles from the system and blocking heat from entering the system. The reason for a difference in

HRR values between the PLA/HC and PLAGTR/HC blend is due to the encapsulation of the clay nanoparticles by the ground tire rubber (GTR), which hinders the clay nanoparticles to be an effective flame-retardant filler. Sun *et al.* (2018) studied the effect of kaolinite and halloysite clay on the IFR polypropylene. The addition of both clays reduced the pHRR value of 75:25 PP/IFR from 438 ± 20 to 263 ± 14 kW/m² (75PP/23.5IFR/1.5 (9Kaol:1HNT)). This reduction was associated with the barrier effect both clays have on the PP/IFR matrix, which plays a role in inhibiting the emission of flammable gases.

Another parameter of importance in cone calorimetry is the total heat release (THR). The total heat release (THR) of the GTR samples showed higher THR values when compared to the PLA/HC composite (Figure 4.16(b)). This can be associated with the presence of carbon black in GTR acting as a catalyst and the GTR releasing volatile organic compounds during combustion. The ZB-based composites showed the highest PHRR values when compared to other investigated samples. This is evidence of a poor flammability resistance in the presence of GTR and ZB. This might be due to the encapsulation of the ZB by a flammable GTR, resulting in the formation of an inhomogeneous char layer. This kind of chars allow the evaporation of volatile materials out of the system and ease of entrance of the heat into the system. To verify the flame retardancy of the PLA/HC composite, the flame performance index (FPI) was calculated (Table 4.4). A higher FPI value means that there is a better flame-retardant performance of the polymeric material (Wang *et al.*, 2019). PLA/HC composite showed the highest FPI value of 0.23, with the ZB and GTR-based composites showing the lowest FPI values. The higher FPI value of the PLA/HC composite is due to the formation of an effective char layer, which can prevent the heat transfer between the burning material and flame zone, further protecting the underlying material from burning and hindering the pyrolysis of the polymers.

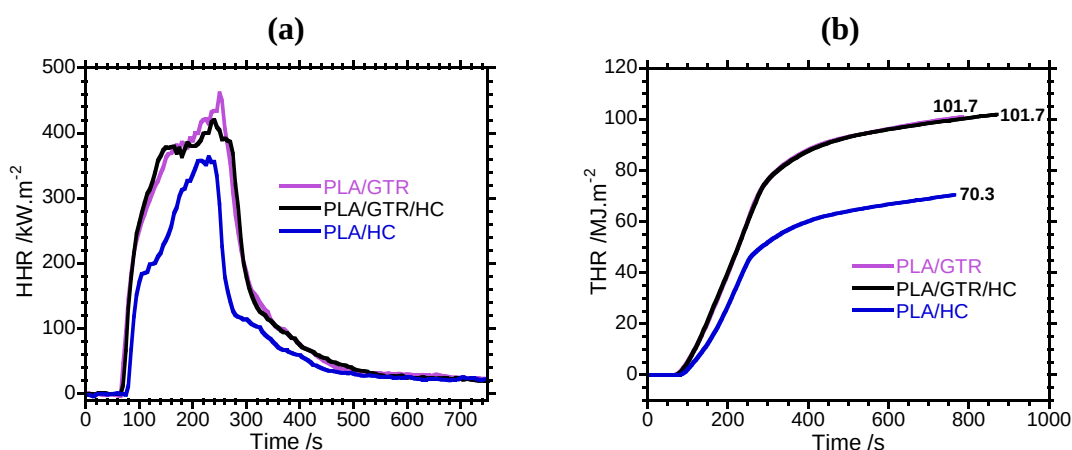


Figure 4.16: Heat release rate (HRR) and total heat release (THR) of the PLA/GTR, PLA/GTR/HC blend composite and PLA/HC composite

The smoke generation (SEA) of the PLA/GTR, PLA/GTR/HC and PLA/GTR/ZB was found to be higher than the PLA/HC as well as PLA/ZB. The GTR-based composites showed higher SEA values because GTR converts easier into smoke when it burns.

Table 4.4: Parameters from the cone calorimeter analysis of the investigated samples

Sample ID	HRR Peak (kW/m ²)	THR (MJ/m ²)	TTI (s)	FPI	SEA(m ² /kg)	Time to pHRR (s)	FIGRA
PLA/GTR	461.72	101.1	69	0.15	472.82	250	1.85
PLA/GTR/HC	420.36	101.9	72	0.17	576.92	240	1.75
PLA/HC	363	70.3	85	0.23	43.67	230	1.58
PLA/GTR/ZB	486.5	100.3	59	0.12	681.50	230	2.12

The toxicity of the gases involved in the combustion of the polymer blends and blend composites was also reported by cone calorimetry. There was a reduction in the carbon dioxide production with the addition of the halloysite into the PLA matrix (Figure 4.17(a)). This is due to the formation of an effective compact structure that hinders the toxic gases from escaping the system. Carbon monoxide is a very dangerous gas and when inhaled it has the potential to carry oxygen to the body tissues. A small content of carbon monoxide may reduce the haemoglobin ability to supply oxygen. There was a reduction in carbon monoxide production with the addition of the halloysite. This may be ascribed to the ability of halloysite in trapping the carbon monoxide from escaping the system. However, the GTR-based composites showed higher carbon monoxide production due to the formation of poor char layer. The GTR covers the HC nanoparticles in such a way that there is no effective formation of the char layer, which allows the escape of the carbon monoxide production. In a study conducted by Attia *et al.* (2014), the addition of halloysite clay to acrylonitrile butadiene styrene (ABS) reduced the emission of CO and the CO₂ concentrations, and this was attributed to the formation of a barrier on the surface of ABS–HNT nanocomposites, which delayed the thermal degradation of ABS. As a result, combustion remains incomplete, leading to reduced CO₂ emissions

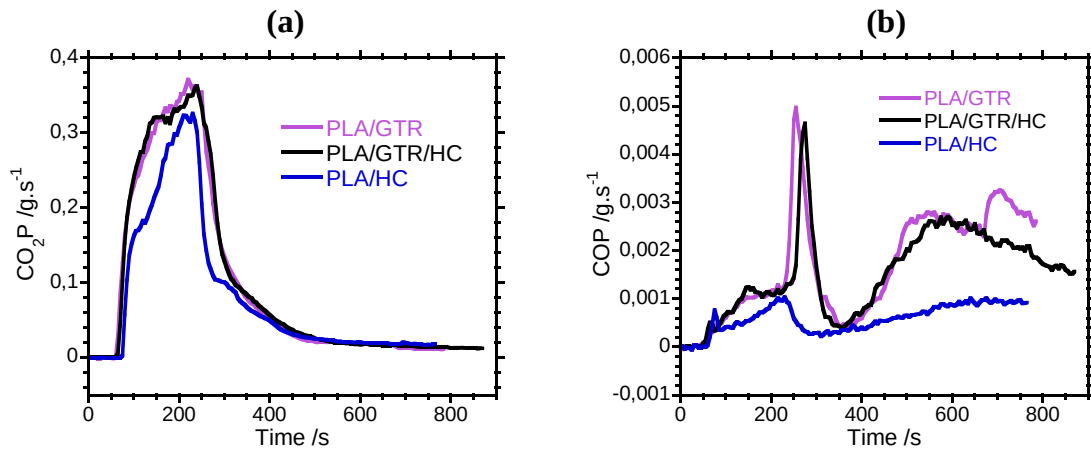


Figure 4.17: Carbon dioxide and carbon monoxide production of the investigated samples

Another parameter of importance in flammability properties is the mass loss rate (MLR). Figure 4.18 illustrates the MLR vs time for the PLA/GTR, PLA/GTR/HC and PLA/HC.

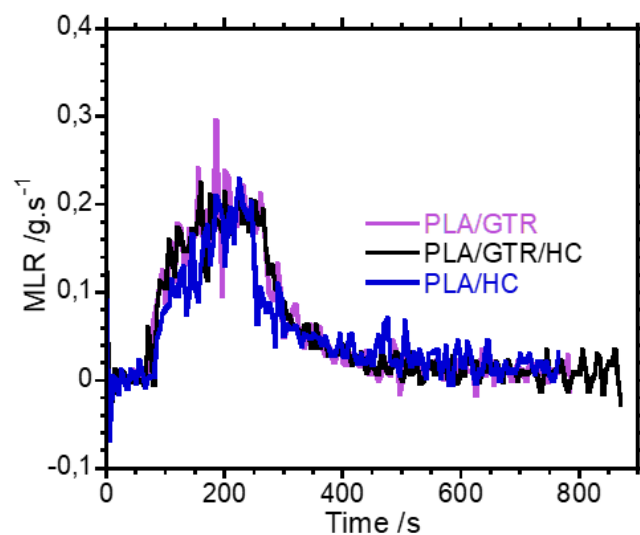


Figure 4.18: Mass loss rate (MLR) of the PLA/GTR, PLA/HC and PLA/GTR/HC

The MLR value of the PLA/HC seems to be lower than the PLA/GTR and PLA/GTR/HC blend composites. The MLR data indicate that the presence of GTR decreases the flame retardancy of the samples, whereas HC enhances it.

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CHAPTER 5: Conclusion and recommendations

The purpose of this work was to investigate the effect of GTR, HC and ZB on the morphology, flammability, thermal stability, rheological, mechanical and thermomechanical properties of PLA. SEM showed that the 80/20 PLA/GTR blend resulted in immiscibility and poor interfacial interaction between GTR and PLA. HC dispersed fairly; however, it seemed to have debonded from the PLA matrix, forming voids which adversely affected the properties of PLA. ZB interacted better with the PLA matrix, as it was dispersed fairly good with little aggregation. The release of volatile compounds from GTR resulted in lower thermal stability of PLA. Although all fillers resulted in the reduction of the thermal stability of PLA, the 97/3 PLA/ZB had higher thermal stability when compared to all the investigative samples. The incorporation of GTR in PLA led to an increase in complex viscosity of PLA because of the crosslinked structures of GTR, which resulted in a rubber that is highly stiff. This was also observed for the addition of HC and ZB to PLA, as they increased the complex viscosity of PLA. DMA results showed that the addition of nanoparticles enhanced the storage modulus of PLA. Interestingly so, the stiffness of GTR did not aid in enhancing the storage modulus of PLA or PLA blend composites. This was due to the poor interfacial interaction of GTR within the PLA matrix. Some mechanical properties were improved while others were reduced. For example, the addition of the nanoparticles to PLA increased the tensile strain of PLA. However, the addition of GTR to PLA blend composites decreased the tensile strain and tensile modulus. PLA/ZB and PLA/ZB/HC were able to increase the impact strength of PLA. However, PLA/HC reduced the impact strength due to poor interfacial interaction between the HC and PLA. The incorporation of HC in the PLA/GTR blend enhanced the flame retardancy of the blend. However, the addition of ZB did not improve the flame retardancy of the PLA/GTR blend; in fact, it acted as catalysts to increase the propagation of flames on the PLA/GTR blend matrix. Although GTR had an adverse impact on most results in this study, the use of it in polymers to reduce waste management of old car tyres can still be achieved. For future purposes the reduction of GTR particle sizes and the addition of certain compatibilizers can be used to enhance the interfacial interaction of GTR and the PLA matrix. To improve flame retardancy, ZB and HC can be functionalized or used in synergy with strong halogen-free FRs, such as ammonium polyphosphate (APP) and

magnesium hydroxide ($\text{Mg}(\text{OH})_2$) at higher wt%. Because of the poor interaction of HC in this study, in future, HC can be modified or surface treated to enhance the interaction and dispersion of it to the PLA matrix.

Appendix

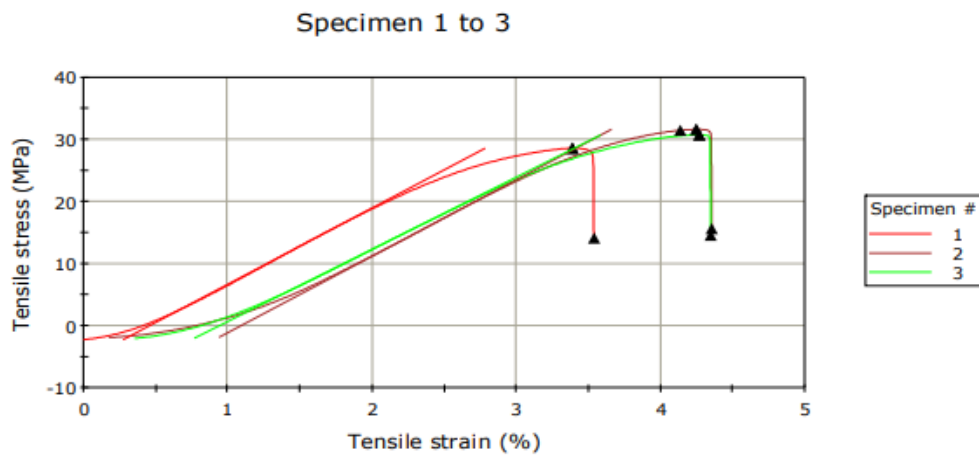


Figure A1: Tensile stress vs tensile strain of 80/20 PLA/GTR

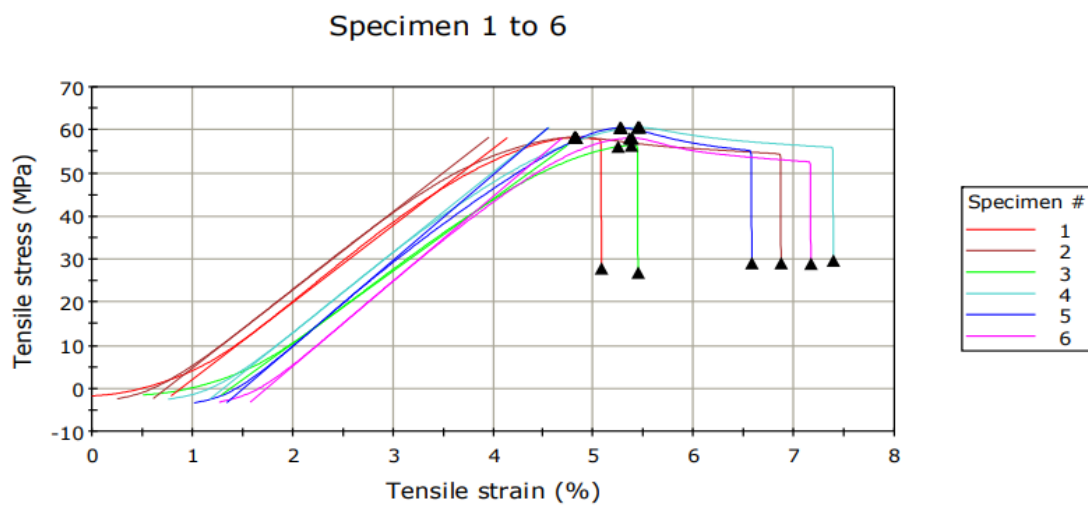


Figure A2: Tensile stress vs tensile strain of 97/3 PLA/HC

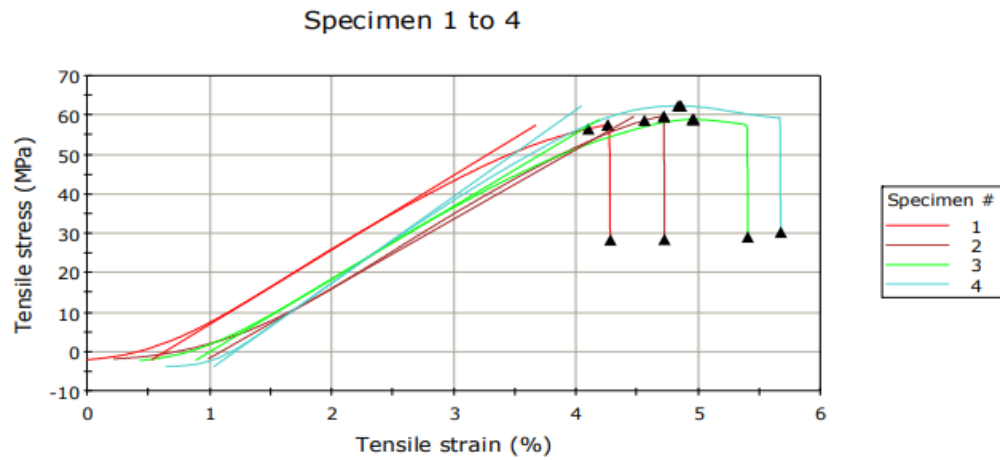


Figure A3: Tensile stress vs tensile strain of 97/3 PLA/ZB

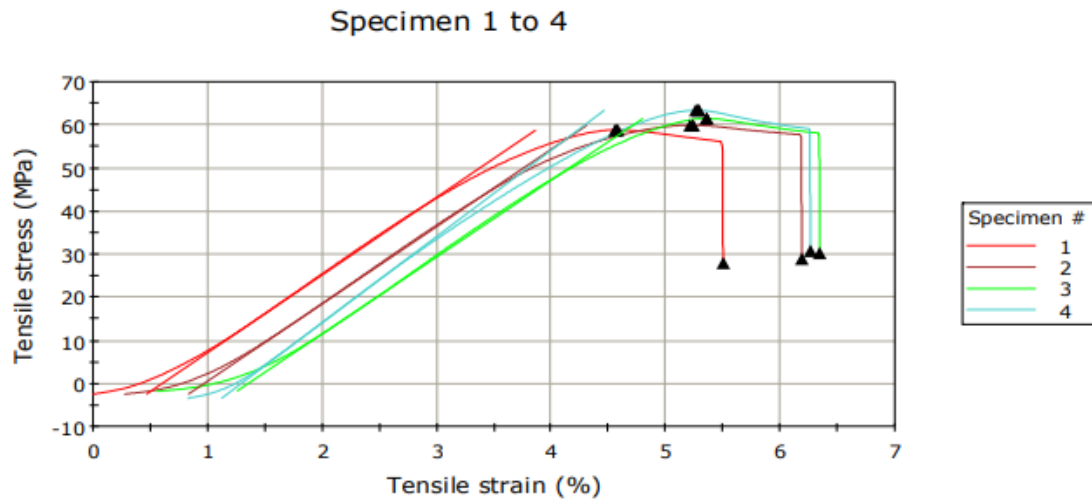


Figure A4: Tensile stress vs tensile strain 97/3 PLA/ZB/HC

Specimen 1 to 5

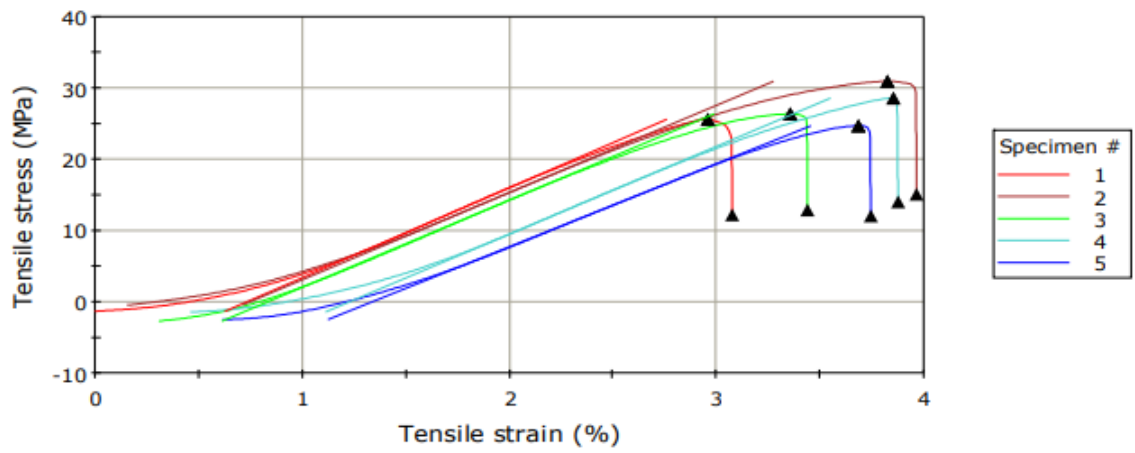


Figure A5: Tensile stress vs tensile strain of 77.6/19.4/3 PLA/GTR/HC

Specimen 1 to 4

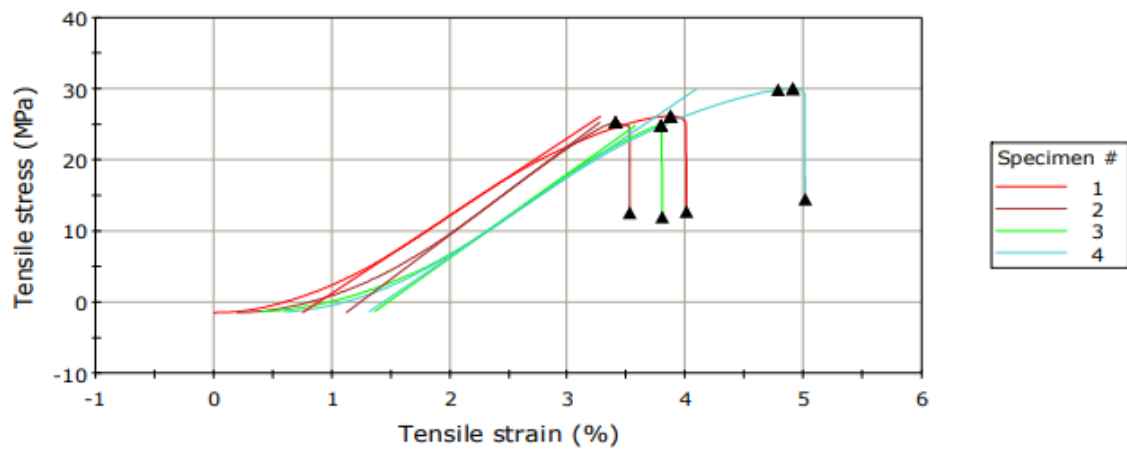


Figure A6: Tensile stress vs tensile strain of 77.6/19.4/3 PLA/GTR/ZB

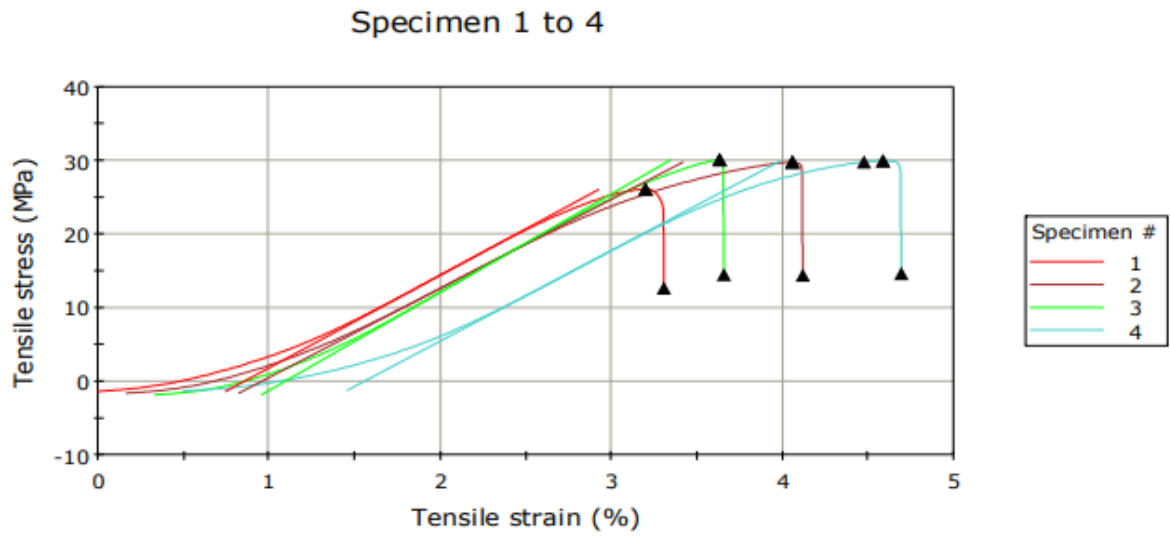


Figure A7: Tensile stress vs tensile strain of 77.6/19.4/3 PLA/GTR/ZB/HC

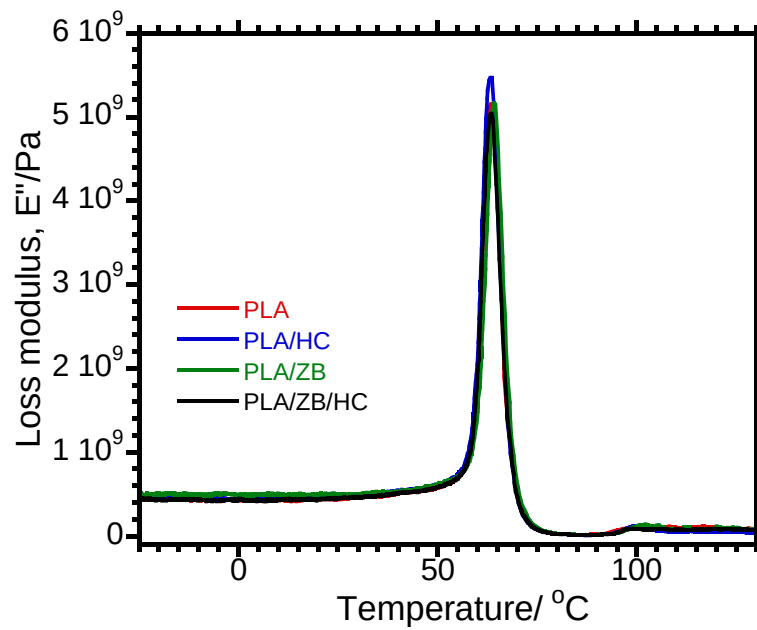


Figure A8: Loss modulus of neat PLA and PLA composites

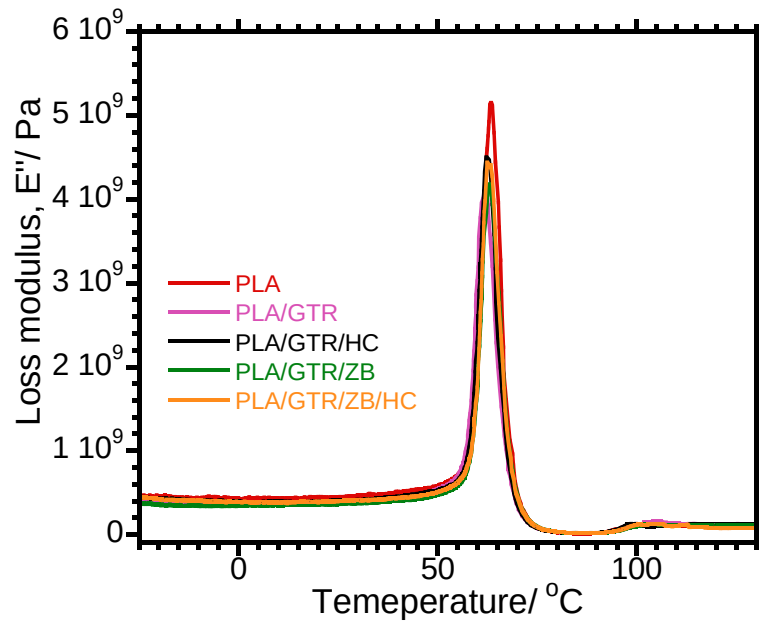


Figure A9: Loss modulus for neat PLA and PLA/GTR blend composites