STUDIES ON FLAX/POLYPROPYLENE-REINFORCED COMPOSITES FOR AUTOMOTIVE APPLICATIONS

by

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Declaration

I, Nobuhle Yvonne Biyana, student number 2013507439, hereby declare that this thesis for the Master's degree is my own work and that it has not previously been submitted for assessment of any postgraduate qualification to another University or for another qualification.

Nobuhle Biyana

Dedication

This work is dedicated to the entire Biyana family for their love and support. To (Mom & my late Father), siblings, my nephews and my nieces, special thanks to everyone that contributed towards this work in order to be successful more especially CSIR friends. I would also like to show appreciation to the love of my life, Mr Sithembele Ndum-ndum and to my beautiful angels, Olothando and Lundanele, your love kept me going.

"Psalm 91"

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Abstract

The use of natural fibers as reinforcement in thermoplastics presents an interesting alternative for the production of low cost and ecologically friendly composites. One of the advantages of using natural fibres is their low specific weight, resulting in higher specific strength and stiffness when compared to glass reinforced composites. Natural fibres also present safer handling and working conditions. They are non-abrasive to mixing and can contribute to significant cost reduction.

This work is divided into two phases: Phase 1 deals with developing nonwoven mats composites from flax/polypropylene (PP) and evaluating their properties. Flax/polypropylene fibres (at different weight ratios) were processed by needle-punching technique in order to form nonwoven mats. The mats were compression-molded at a temperature of 180°C to form composite materials. The mechanical, thermal and viscoelastic properties of the composites were analyzed. Composites (untreated and silane-treated) were also subjected to varying conditions of temperature and humidity and the tensile properties of the conditioned and unconditioned composites were investigated.

The mechanical properties (tensile, flexural and impact) of flax/PP composites were found to increase and reach maximum values at 30% fibre loading and then decrease at higher fibre content. Thermal studies revealed that the composites were stable up to 320°C and samples containing 40% flax fibres were found to exhibit greater thermal stability than neat PP. The dynamic mechanical analyses of the composites showed that the incorporation of flax in the composites resulted in an increase of the storage modulus with a maximum value exhibited by composite containing 40% fibre loading. Composites containing chemically modified fibres exhibited low tensile modulus after conditioning.

Phase 2 is based on the investigation of the effect of nano-calcium carbonate (CaCO₃) on the properties of two types of polymer matrices: recycled PP and virgin PP. In this case, composites were prepared by melt-mixing and injection molding. The mechanical and thermal properties of the composites were characterized. The tensile modulus of the nano-

 $CaCO_3$ filled PP (virgin and recycled) composites were found to increase and reach maximum at 30% nano-CaCO₃ loading, while the tensile strength decreased with increasing filler content. Thermal studies showed that the nano-CaCO₃ filled PP samples exhibited a one-step degradation pattern and are thermally stable up to 450°C. The thermal stability of the samples was found to decrease following the addition of nano-CaCO₃. SEM micrographs of the tensile fractured surfaces of composites of the nano-CaCO₃ filled virgin and recycled PP revealed the presence of nano-CaCO₃ agglomeration.

List of Abbreviations and Symbols

GFRP	Glass Fibre Reinforced Plastics
CO_2	Carbon Dioxide
PP	Polypropylene
CaCO ₃	Calcium Carbonate
(rPP)	Recycled Polypropylene
(vPP)	Virgin Polypropylene
TS	Tensile Strength
FRP	Fibre Reinforced Polymer
(PEI)	Poly (Ether Imide)
(PPS)	Poly (Phenylene Sulphone)
(PES)	Poly (Ether Sulphone)
(PEEK)	Poly (Ether Ether Ketone)
(PA-6,6)	Polyamide-6,6
(PET)	Poly (Ethylene Terephthalate)
(PBT)	Poly (Butylene Terephthalate)
MAH-gPP	Maleic Anhydride Grafted Polypropylene
TiO ₂	Titanium Oxide
PNCs	Polymer Nanocomposites
(PCC)	Precipitated Calcium Carbonate
NaOH	Sodium Hydroxide
°C	Degree Celsius
DMA	Dynamic Mechanical Analysis
TGA	Thermogravimetric Analysis
ESEM	Environmental Scanning Electron Microscopy
wt %	Weight Percent

(T _g)	Glass Transition Temperature
(PF)	Phenol-Formaldehyde
Tan (δ)	Tan Delta
T _{max}	Maximum Temperature

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CHAPTER 1

Overview

1.1 Introduction

The depletion of petroleum resources and the emerging environmental legislations have spurred the research community to search for environmentally-friendly and biodegradable materials that will substitute the use of traditional non-biodegradable composites^{1,2}. Over the last decade, research has been conducted increasingly on renewable materials from sustainable resources for a variety of applications. This has been influenced by the ever increasing demand for newer, stronger, recyclable, fire repellent, less expensive and lighter weight materials in the aerospace, automotive, construction and packaging industries. Factors, such as: increased environmental and health concerns, a need for waste management solutions particularly landfills, more sustainable methods of manufacturing and reduced energy consumption, are reasons for the need to replace conventional composites (glass, carbon and synthetic fibres). Therefore, natural fibres and biodegradable polymers can be considered as viable alternatives for the development of new biodegradable composites or biocomposites³⁻⁷.

This growing interest in natural fibre materials is brought by the biodegradability and decomposability at the end of their life time cycle that helps in creating a positive environmental impact. In addition, as these fibres are usually extracted from plants and/or plant waste, they are inexpensive. They are also non-abrasive to mixing and present safer handling conditions when compared to synthetic fibres. The continuous use of petroleum based plastics will create more environmental problems, such as increasing number of landfills for disposal purposes, depletion of petroleum reserves and increasing amount of CO_2 emitted into the atmosphere resulting in global warming^{8,9}. Natural fibres result in composites with lower specific weight (in comparison to glass-filled counterparts) and possess favourable properties such as improved thermal and acoustic insulation characteristics^{1,10-13}.

The automotive industry is constantly looking for products that are lighter, more eco-friendly and are suitable for mass production at low cost. Therefore, the use of low weight, inexpensive and more sustainable materials in automotive is more favourable, due to environmental concerns and cost efficiency. Studies indicate^{14,15} that shifting to green materials is not only an initiative towards sustainability, but also a demand of current environmental regulations. European car manufacturers have shown a lot interest in the use of natural fibre-reinforced thermoplastic composites for interior applications, such as: door panels, seat backs, headliners, package trays and dash boards. Automakers also estimate that cars made of composites could be between 50–67% lighter than similarly sized steel autobody as compared to with a 40-55% mass reduction for aluminium auto-body and a 25-30% mass reduction for an optimized steel auto-body^{4,14,15}. Hence, substituting glass fibres with natural fibres in automotive composite parts, would reduce the material weight by \approx 30% and their cost by 20% ^{16,17}.

Nano filler based polymer composites represent an interesting class of materials containing dispersed nano-sized filler materials (nanoparticles, Nano clays, nanotubes and nanofibers) within the polymer matrices. Owing to their nanoscale size features and very high surface-to-volume ratios, they possess unique combination of multifunctional properties. Nanocomposites are an emerging class of polymeric materials exhibiting excellent mechanical properties, enhanced modulus and dimensional stability, flame retardancy, superior thermal and processing properties and enhanced impact resistance therefore, making them suitable to replace metals in automotive and other applications. The key drivers for the use of Nano filler systems in the automotive industry are reduction in vehicle's weight, improved engine efficiency (fuel saving), reduction in carbon dioxide (CO_2) emissions and superior performance (greater safety, increased comfort and better driveability)¹³⁻¹⁹.

This work is divided into two phases: the first phase of the work is aimed at developing flax/polypropylene (PP) composite materials from nonwovens by compression molding and the evaluation of their mechanical, thermal, viscoelastic and aging properties. The second phase investigates the effect of nano-CaCO₃ on properties of two types of polymer matrices: recycled PP and virgin PP. In this phase, composites were prepared by melt-mixing and injection molding. The mechanical and thermal properties of the nano filler based composites were characterized.

The advantage of using polypropylene as the matrix in the composite material is due to their relatively low processing temperature which is essential because of low thermal stability of

natural fibres, as well as their good properties and low cost. Nonwovens are one of the products popularly used as reinforcements in composites production for many applications (especially automotive) since they possess a good combination of strength, lightweight and flexibility when compared to conventional materials. The use of recycled polymers is also on the increase as it contributes to energy savings and re-use of materials²⁰⁻³³.

1.2 Problem statement

The mass production of glass fibre and other synthetic fibre reinforced petroleum based plastics has been causing many environmental problems. These problems include: increasing pollution caused by the use of plastics and emissions during incineration and depleting petroleum resources. Glass fibre-reinforced plastics have several disadvantages such as: high fibre density, difficulty to machine and poor recycling properties and the attendant potential health hazards, posed by glass fibre particulates. It is, therefore, crucial to examine alternative sources that are environmentally-friendly and sustainable.

This study focuses on the use of composites prepared from flax fibres and polypropylene for automotive applications. The study will also investigate the effect of nano-CaCO₃ inclusion on the properties of two types of polymer matrices: recycled PP and virgin PP^{34-37} .

1.3 Objectives

The objective of the study is to examine the effect of flax fibres and nano-fillers on the properties of polypropylene composites. The tasks of the study are as follows:

- 1. Preparation of non-woven substrates from flax fibres and high strength polypropylene fibres
- 2. Processing of flax/polypropylene composites by compression moulding
- 3. Characterization (mechanical, thermal, viscoelastic and aging) of flax/polypropylene composites
- Preparation of nano-filler/PP composites from nano-CaCO₃ and PP (recycled and virgin PP) by injection moulding
- 5. Evaluation of nano filler influence on PP properties
- 6. Mechanical and thermal characterisations of the injection moulded composites.

The outline of the thesis is as follows: Chapter 1: Overview Chapter 2: Literature review Chapter 3: Experimental Chapter 4: Results and Discussion Chapter 5: Conclusion

CHAPTER 2

LITERATURE REVIEW

2.1 Background

There is a growing urgency to develop new bio-based and innovative products from sustainable and renewable resources. Research in the field of bio-composites development, using materials obtained from renewable resources as reinforcements and matrices have been on the increase. A detailed review on bio-fibres, biodegradable polymers and biocomposites highlighting the advantages of bio-based materials have been documented by Mohanty et al¹². Natural fibres have now become an attractive reinforcement in composites due to its favourable properties of high strength, low cost and weight as well as their biodegradable nature²⁰⁻²¹.

Natural fibres can be sourced from plants, animals and minerals. Hence, these fibres are in abundance around the world. The major chemical components of plant fibres are cellulose, lignin, hemicellulose and pectin. The industry at large is looking for green materials to use in its products, both for reducing the pollution and to shift towards a growing environmentally conscious market³⁴. The automotive industry in particular is constantly looking for products that are lighter, eco-friendly and are still sufficient for mass production at low cost. Natural fibres, such as: hemp, flax and wood are already in use in the automotive industry to reduce weight and create a positive environmental impact ^{38,39}.

2.2 Classification of natural fibres:

2.2.1 Animal fibres

Animal fibres generally contain proteins; e.g. mohair, wool, silk, alpaca and angora. Animal fibres are the fibres taken from animals or hairy mammals. Silk fibres are collected from secretions of the silkworm. Avian fibres are the fibres collected from bird feathers.

2.2.2 Mineral fibres

Mineral fibres are the naturally occurring fibres or slightly modified fibres procured from minerals. Examples include: asbestos fibres, ceramic fibres and metal fibres.

2.2.3 Plant fibres

Plant fibres are classified into the following categories:

- Fruit fibre: These are extracted from the fruits of the plant. Examples include coir, oil palm.
- Bast fibre: These are found in the stems of the plant providing the plant its strength. Usually, they run across the entire length of the stem and are therefore very long. Examples include: jute, flax, kenaf, hemp and ramie
- Leaf fibre: These are the fibres extracted from the leaves. Examples include sisal, henequen and pineapple

2.3 Flax fibres

Flax plant (*LinumUsitatissimum*) a member of the family Linaceae, has been used since olden times as the fibre for fabric. The plant grows in moderate temperature and moist climates, and it is cultivated in Belgium, the Netherlands, France, Ireland and Italy. The flax fibre in the stem of the plant forms about 25% by weight, although the amount of fibre recovered after isolation is a lot smaller than this 25%. In all native cellulose (elementary) fibres, the cell-wall consists of long thin threads termed as microfibrils (**Figure 2.1**). Natural fibres can be considered as composites containing varying volume fractions of cellulosic microfibres embedded in a matrix of hemicellulose and lignin⁴⁰.



Figure 2.1: Schematic view of the cross-section of the stem of flax plant (a), and the cross-sectional view of the flax stem (b).

2.3.1 Flax fibre processing

As mentioned earlier, the properties of natural fibres vary according to crop variety and weather conditions during growth and harvesting. The processing of bast fibres comprises of the following steps:

a) Harvesting and Pre-treatment: Plants are harvested at optimum maturity by pulling or mowing (either manually or mechanically). Thereafter, they are spread out in the field to dry. The retting processes elaborated below are the most prominent in use today.

b) **Retting:** The removal of the bast fibres from bark and woody stem parts is promoted by a biological process called retting which is an enzymatic or bacterial action on the pectinous matter of the stem. Appropriate retting is of great importance; under-retting would mean that the required fibre bundles are not easily separated from the wood and excess retting results in a weakened fibre. Several methods are used for the retting process.

Dew retting involves the action of dew, sun, and fungi on the plants, resulting in the dissolution of the cellular tissue and the larger part of the gummy substances. It requires between 4-6 weeks and the action is not uniform. In *water retting* (also called pool and tank retting), bundles of plants are immersed in stagnant pools, rivers, or ditches and the biological

effect is achieved through bacterial action. The retting time is usually between 2-4 weeks. Water retting gives a uniform product. In stream retting the plants are immersed in slow moving streams for a longer time and the quality of the product can be high. In chemical retting, the dried plants are placed in a tank and treated with chemicals, such as sodium hydroxide, carbonate or sulphuric acid^{22,40}.

2.4 Properties of natural fibres

Table.2.1:

The interest in natural fibre-reinforced polymer composite materials is rapidly growing in terms of their industrial applications and fundamental research. Plants, such as: flax, cotton, hemp, jute, sisal, kenaf, pineapple, ramie, bamboo, banana and wood have been used as reinforcement in composites. Their availability, renewability, low density and price as well as satisfactory mechanical properties make them an attractive ecological alternative to glass, carbon and man-made fibres used in the manufacturing of composites. Natural fibrecontaining composites are more environmentally-friendly and are used in transportation (automobiles, railway coaches, aerospace), construction industries and for packaging etc^{39,40}.

Fibres	Density	Tensile strength	Young's Modulus
	[g/m ³]	[MPa]	[GPa]
Hemp	1.4	514	24.8
Jute	1.3-1.45	393-773	13-26.5
Flax	1.50	345-1100	27.6
Sisal	1.45	468-640	9.4-22
Coir	1.15	131-175	4-6
Cotton	1.51	400	12

Table 2.1 Represents a summary of the common properties of natural fibres

Common properties of Natural Fibres

Natural fibres, such as hemp, flax and wood are already used as composite reinforcements particularly in the automotive industries. Table 2.2 presents the use of natural fibres in the automotive sector⁴¹⁻⁴⁶

Manufacturer Model	Application (dependent on model)			
Audi A3, A4 ,A6, A8,	Seat back, side and back door panel, boot lining, hat rack, spare tire			
Coupe	lining			
Avant, Roadster,				
BMW 3, 5 and 7 Series	Door panels, headliner panel, boot lining, seat back			
Daimler/Chrysler	Door panels, windshields/dashboard, business table, pillar cover			
A-Series, C-Series, E-	panel			
Series, S-Series				
Fiat Punto, Brava,	Door panels, B-pillar, boot liner			
Marea, Alfa Romeo				
146, 156				
Ford Mondeo CD 162,				
Focus				
Opel Astra, Vectra,	Headliner panel, door panels, pillar cover panel, instrument panel			
Zafira				
Peugeot New model	Insulation, rear storage shelf/panel			
406,	Saab Door panels			
Renault Clio	SEAT Door panels, seat back			
Rover 2000 and others				
Volkswagen Golf A4,	Door panel, seat back, boot lid finish panel, boot liner			
Passat Variant, Bora				

Table 2.2:Use of natural fibres in the automotive sector

2.4.1 Advantages of natural fibres

The main advantages of natural fibres are:

- Low specific weight, resulting in a higher specific strength and stiffness than glass fibres
- It is a renewable source, the production of natural fibres requires little energy, and CO₂ is used while oxygen is given back to the environment.

- Producible with low investment at low cost, which makes the material an interesting product for developing countries
- Reduced wear of tooling, healthier working conditions and no skin irritation.
- Thermal recycling is possible while glass fibres causes problem in combustion furnaces.
- Good thermal and acoustic insulating properties.

2.4.2 Disadvantages of natural fibres

One of the major issues of natural fibres is that their properties are basically dependent on where they are grown (locality), what part of the plant they are harvested from (leaf seed or stem), the maturity of the plant (age) and how the fibres are harvested and pre-conditioned in the form of mats or chopped fibres. These factors result in a significant variation in properties when compared to their synthetic fibre counterparts (glass, aramid and carbon)^{47,48}. Other disadvantages associated with natural fibres are:

- Variations in fibre quality and uniformity
- Moisture sensitivity of natural fibres during processing and application.
- Limited heat resistance
- Limited fire resistance

2.5 Thermoplastic Matrix Based Composites

Fibre reinforced polymer (FRP) composites have found applications in the aerospace, automotive and construction industries. The lightweight aspect has been the key motivating force behind the use of fibre reinforced composite materials as replacements for metal materials. Composite materials comprising of a polymer matrix with fibre reinforcements have given a completely new dimension to the use of plastics in automobiles. When compared to their metal counter parts, plastic composites are easier and economical to process, lighter in weight and have comparable impact resistance, thus giving a better stiffness to weight ratio than metals. Since these composites are composed of fibre and

polymer matrix, they can be individually formulated to meet the needs of the specific application. Another advantage with composites is that, it is also possible to reinforce the weak areas of the structure by considering uni-directional reinforcements ^{47,49-53}. These different materials work together to give the overall composite material enhanced properties that are better than those of the separate constituents.

The introduction of thermoplastic resins as matrices for continuous-fibre-reinforced composites has attracted considerable attention since the mid-80s. As matrix materials for composites, thermoplastics offer a wide range of advantages over thermosets. These include: high toughness, increased moisture resistance, rapid processing, unlimited shelf-life and better recyclability. Hence, research activities have been focused on various types of hightemperature polymers, such as: poly (ether imide) (PEI), poly (phenylenesulphone) (PPS), poly (ether sulphone) (PES) and poly (ether ether ketone) (PEEK). The processing of these high-performance materials generally requires high temperatures and pressures and due to their high price, applications are limited to niche markets, such as aerospace. Therefore, current research activities have shifted towards the development of 'cost-performance', rather than 'high-performance' thermoplastic composites. Since cost-effectiveness depends on raw material cost, most composite systems that are considered as an attractive candidate for this 'cost-performance' market are based on resins such as: polypropylene (PP), polyamide-6,6 (PA-6,6), poly(ethylene terephthalate) (PET) and poly(butylene terephthalate (PBT). PP offers a number of favourable characteristics as matrix material for high volume applications of composite materials. It exhibits many beneficial properties, such as: low price, high toughness, low density, relatively high thermal stability, good di-electrical properties and chemical resistance. Moreover, PP can easily be processed and recycled and it is available in a large number of grades ^{54,55}. Recent researches focusing on improving stiffness, strength and thermal stability, have been very successful in closing the gap between the commodity PP and the engineering thermoplastics. Polypropylene is used in automotive components, plastic parts, food packaging, textiles and reusable containers ⁵⁶⁻⁶⁹.

2.6 Natural Fibre Reinforced Polymer Composites

The mechanical properties of natural fibre-reinforced composites depend on many parameters, such as fibre strength, modulus, fibre length, fibre orientation and fibre-matrix interfacial bond strength. A strong fibre-matrix interfacial bond is critical for high mechanical properties of composites. A good interfacial bond is required for effective stress transfer from the matrix to the fibre, whereby maximum utilization of the fibre strength in the composite will be achieved ⁷⁰. Modification to the fibre also improves resistance to moisture-induced degradation of the interface and the composite properties. In addition, factors such as: processing conditions and techniques have significant influence on the mechanical properties of fibre reinforced composites. The specific properties (specific strength and modulus) of natural fibres, e.g flax, coir, hemp, jute and sisal is comparable with that of glass fibre. A number of investigations have been conducted on several types of natural fibres, such as: kenaf, hemp, sisal, flax, bamboo and jute in order to study the effect of these fibres on the mechanical properties of composite materials ⁵⁸.

Mansur and Aziz ⁷¹ studied bamboo-mesh reinforced cement composites and found that the reinforcing materials could enhance the strength and toughness of the cement matrix, and significantly increase its tensile, flexural and impact strengths. On the other hand, jute fabric-reinforced polyester composites were tested for the evaluation of their mechanical properties and compared with wood composites. It was found that the jute fibre composites have better strength than wood composites.

In a fibre reinforced polymer, the fibres serve as reinforcement and therefore have to exhibit high tensile strength and stiffness, whereas the task of the matrix is to hold the fibres together, conduct the shear forces and to work as a coating. Natural fibres offer a competitive advantage over synthetic fibres with a possibility of replacing them for various industrial applications. Increasing environmental concerns over widespread pollution by non-degradable materials, particularly long lasting plastics promoted a growing tendency towards the substitution of synthetic fibre composites. Several reviews and research articles have been dedicated to natural fibres as replacement to synthetic fibres in composites. Natural fibre reinforced plastics have found application in many sectors and these include: aerospace, automotive and construction industries³⁹⁻⁴³.

It is a generally accepted factor that the strength of a fibre-reinforced polymer matrix composite is dependent on the strength of fibres. Amongst all natural fibres, flax has the highest tensile strength. The tensile strength of flax fibres is found to be in the region of 1500 MPa and flax fibres have been successfully used to reinforce PP matrix in a number of studies ⁵⁸.

Moreau et al⁷² successfully developed nonwovens that contained a high percentage of kenaf fibres. This resulted in the increased utilization of kenaf fibre, thereby enhancing markets for the U.S. kenaf farmers. Nonwoven techniques aim to produce mats or fabrics more economically than the traditional means of weaving and knitting. Recently, de Guzman et al¹⁰¹ investigated new materials for novel textile products from abaca, kenaf, flax and pineapple fibres using nonwoven techniques of needle-punching and adhesive-bonding processes. The advantage of nonwoven mats is that they can be tailored by blending with another fibre in order to achieve the desired mat properties.

Tao et al⁷³ prepared nonwoven mats containing 100% kenaf and kenaf/cotton blends. They showed that adding cotton fibres into kenaf mat increases the mat strength and oil retention capacity and that the blended mats have potential to be used for prevention of soil erosion, weed control and clean-up of waste. Magurno⁴⁰ has given a detailed account of properties of compression molded composites from kenaf and jute fibres for automotive interior components.

2.7 Natural Fibre Modification

A lot of work has been done by many researchers on fibre treatment in order to improve the mechanical properties of natural fibre/PP composites. Researchers⁵⁸ have reported that pretreatment can be used for cleaning and modification of the fibres in order to prevent moisture absorption process in natural fibres. The use of silane and peroxide treatments on natural fibres has achieved various levels of success in improving fibre-matrix adhesion⁵⁸. Coupling agents usually improve the degree of crosslinking at the interface region and offer improved bonding between fibre and matrix. Among the various coupling agents, silane coupling agents were found to be effective in modifying the natural fibre-matrix interface. Appropriate treatment of fibres with silane can increase the interfacial adhesion to the target polymer matrices and improve the mechanical performances of the resulting fibre/polymer composites. Silane coupling agents undergo hydrolysis forming reactive silanols and it is then adsorbed and condensed on the fibre surface (sol-gel process)^{74,75}.

John and Anandjiwala⁷⁶ investigated the chemical modification of flax reinforced polypropylene composites by using bio-based coupling agent. Zein (protein from corn) was used as coating on natural fibres and they investigated the influence of zein on the interfacial bonding between fibre and matrix. Zein modification was reported to be successful in enhancing the mechanical properties of composites due to the better interfacial bonding between PP and nonwovens.

In another study, Nurdina et al⁴⁹ reported that silanes, with different functional groups, have been successfully applied for the treatment of fillers in thermoplastic resin matrices. The addition of silane and titanate coupling agents improves the interaction between fillers and polypropylene, leading to high and effective transfer of stress from polypropylene to the fillers, thus increasing the tensile strength of polypropylene composites ^{77,78}.

Researchers have reported studies on the effect of adding maleic anhydride grafted PP (MAH-g-PP) on the microstructure and mechanical properties of abaca reinforced polypropylene composites. It was observed that the mechanical properties were maximum at 40 weight% fibre loading and the adhesion between abaca fibre and PP had significantly improved, due to the addition of the compatabiliser which improved the mechanical properties ⁷⁵⁻⁷⁶.

Arbelaiz et al⁵⁰ investigated the effect of flax fibre surface modification using maleic anhydride, maleic anhydride grafted polypropylene, vinyl-trimethoxysilane and alkalization on the properties of flax fibres. They reported that the hydrophilic nature of treated fibres decreased and the treated fibres showed higher modulus values when compared to the untreated fibres.

Devi et al⁵⁸ investigated the tensile, flexural, and impact behaviour of pineapple leaf fibre (PALF) reinforced polyester composites, as a function of fibre loading, fibre length, and fibre surface modification. A comparison of the effect of two silane coupling agents on the mechanical properties was carried out. A 40% increase in the tensile strength was observed

when the fibres were treated with silane A172 [vinyl tri (2-ethoxymethoxy) silane]. The flexural strength of these composites also increased by about 7%.

Pickering et al²³ investigated the effect of silane coupling agents on pine fibre reinforced polyethylene composites. Improved tensile strength was observed for treated composites when compared to the untreated fibre-reinforced composites and this was attributed to the improved compatibility of fibre surface with polyethylene.

Mansur et al⁷¹ studies were based on impact, mechanical and morphological properties of flax/PLA nonwoven composites. It is reported that flax content is the most significant factor in influencing the physical and mechanical properties of the biocomposites, and it was found that increasing the flax fibre content in the bio-composites, increases the mechanical properties and the impact strength increases with increasing flax fibre content and decreases with increasing moulding temperature and time. 60% flax content was the optimum recommended as it produced the highest tensile strength and flexural properties.

Joseph et al⁷⁹ studied the effect of different environmental conditions on banana-fibre reinforced phenol-formaldehyde (PF) composites by subjecting them to water aging, thermal aging, soil burial and outdoor weathering. The degradation level was measured as changes in weight and tensile properties after aging. Weight on water aged composites was found to increase due to absorbed water while chemical treatment and hybridization decreased the water absorption capacity of the composites. The highest weight loss was obtained for the soil buried untreated fibre/PF composites.

Devi et al⁷⁸ studied the ageing of pineapple leaf fibre reinforced polyester composites. Ageing studies showed a decrease in tensile strength of about 6%, for samples subjected to thermal ageing, whereas composite specimens subjected to water ageing showed considerable loss in tensile strength, of about 34%. The water uptake of the composites was found to increase with fibre loading and levelled-off at longer times.

2.8 Nano filler based polymer composites

As the use of composites increases, there is a need to produce novel composite materials that can stand the test of demanding applications while being lightweight and durable, as illustrated in **Figure 2.2**. With recent advances in polymer composites, various new materials have been identified which have potential as fillers in producing advanced composite materials with polymers as the matrix material. The most promising among them are nano-fillers, such as: calcium carbonate (CaCO₃), titanium oxide (TiO₂) and carbon nano-tubes. A considerable amount of research is currently going on in this field in order to exploit their properties for producing superior composites, as nano-filler based composites could greatly outweigh traditional composites in terms of physical properties and performance in various environments⁵⁹⁻⁶¹.



Figure 2.2: Illustration of the usage of nanocomposites in automotive sector

The new polymer nano-composites are made-up generally, of three categories of reinforcing materials, such as: particles (e.g., silica, metal and other organic and inorganic substances),

layered materials (e.g., graphite, layered silicate) and fibrous materials (e.g., nanofibres and nanotubes). When compared to their conventional counterparts, these nanocomposites have been found to possess promising mechanical properties, such as: hardness, tensile modulus, strength and toughness at both low and high temperatures. In addition, the composites are found to have significantly improved barrier properties, thermal stability and flame retardant characteristics with the advantage of being light-weight as well. Thus, these are used as excellent materials for food packaging, membranes, adhesives, automotive parts and textiles^{67,80}.

Calcium carbonate (CaCO₃) is by far the most widely used filler material, particularly as filler in paper and plastics. Traditionally, CaCO₃ is mined from natural resources (limestone) and processed by milling techniques. Its synthetic counterpart is called precipitated CaCO₃ (PCC) which exhibits finer particle sizes and smaller particle size distribution. It is available in fine and ultra-fine grades whereby the latter is sometimes referred to as nano-precipitated CaCO₃. Particle sizes range from between 60 nm and 150 nm. It is used as filler in adhesives and sealants in order to adjust the rheological properties and also in plastics in order to improve the mechanical strength and durability ⁶⁷⁻⁷². The world market for precipitated CaCO₃ was 13 million tonnes in the mid-2000, mostly due to the paper industry. The share of nanoscale precipitated CaCO₃ is significantly smaller; one of the world's biggest producers is the Chinese based Shengda Tech with a current production capacity of approximately 250,000 tonnes. According to literature reports⁶⁷, major producers of nano-CaCO₃ are German based Evonik and Wacker together with US-based Cabot and Japanese Tokuyama.

2.9 Calcium carbonate (CaCO₃) – PP composites

Nanocomposites have attracted attention in recent years because of improved mechanical, thermal and fire retardant properties when compared to the pure or conventional composite materials. The introduction of nano sized fillers or reinforcements into PP, often modifies the crystalline structure and morphology of PP and consequently results in property changes, such as: high impact strength and toughness⁵⁹. Hence nano filler-PP systems are used for automotive components, home appliances and other industrial applications.

Among the promising nano-fillers that have generated a lot of interest among researchers, are organo-clay, nano-silica, carbon nanotubes and nano-calcium carbonate. Studies have shown

that the large surface area possessed by these nano-fillers promotes better interfacial interactions with the polymer matrix when compared to the conventional micrometer sized particles, leading to better property enhancement. There are a number of inorganic mineral fillers used in polypropylene. The most common of these fillers are talc, calcium carbonate and barium sulphate. It is reported in the literature that the use of CaCO₃ in PP, typically runs from 10 to 50%, although concentration as high as 80% has been reported. CaCO₃ is usually selected as filler when a moderate increase in stiffness is desired. The main secondary additive employed in CaCO₃ is a stearate. Stearic acid acts as a processing aid, helping to disperse the CaCO₃ particles. It also helps to prevent the absorption of stabilizers into the filler. Finally, as an added benefit, it acts to cushion the system, resulting in improved impact. The dispersion qualities of CaCO₃ particles play a crucial role in its toughening efficiency^{60-65,73}.

Zuiderduin et al^{81} studied the toughening of PP with calcium carbonate particles and it is reported that these particles resulted in composites with higher stiffness and higher impact resistance. However, particle distribution was found to be critical at higher filler loading due to aggregation of nano fillers in the system. Buasri et al^{75} studied the effect of modified nano-CaCO₃ particles on the thermal properties of polypropylene and it was found that the presence of CaCO₃ significantly affected the mechanical and crystallisation characteristics of the composites. Impact strength was found to have improved by 65% and hardness by 5%. The modification of CaCO₃ with sodium stearate resulted in improved dispersion of the nano fillers within the system⁸²⁻⁸⁵.

Leong et al⁶¹ studied the effect of filler treatment on the mechanical, flow, thermal and morphological properties of talc and CaCO₃-filled PP hybrid composites and it was reported that for both silane and titanate treated hybrid and single filler composites, there was a dramatic increase in the elongation-at-break values, whereas treatment with stearic acid improved the dispersion of filler in the composites. Nezhad-Shelesh et al⁷⁴ investigated the influence of nano-CaCO₃ on the production consistency, shrinkage and melt flow rates and the mechanical properties of nano-CaCO₃/PP nanocomposites. The compatibiliser (MAH-g-PP) with maleic anhydride content of 0.05 wt% was used to improve the interfacial adhesion between nano-CaCO₃ and PP and the dispersion of the nanoparticles in polymer matrix. The modulus and impact strength of the composites also registered increase^{80,86-90}.

CHAPTER 3

EXPERIMENTAL

3.1 Materials

3.1.1 Polypropylene (PP)

High strength polypropylene fibres with dTex 7.0 and staple of 60 mm were sourced from Asota GmbH, Austria. Recycled polypropylene (rPP) pellets were obtained from Tufflex Plastic Products, South Africa. Virgin polypropylene (vPP) pellets was obtained from Sasol, South Africa. It has the following properties: melting point range 130 - 165 °C, flash point > 350 °C, auto-ignition temperature > 390 °C and density 0.88 - 0.92 g/cm³.

3.1.2 Flax Fibres

Flax (*Linum usitatissimum*) fibres were supplied from a farm in Graff-Reinet near Port Elizabeth, South Africa. It has a diameter range of 40-600 μ m, average tensile strength of 345–1500 MPa, average modulus of 27.6–80 GPa and elongation-at-break of 1.2–3.2 %. The chemical composition of flax fibres comprises of: 71 % cellulose, 18.6–20.6 % hemicellulose, 23 % pectin and 2.2 % lignin^{91,92}.

These fibres were initially cottonised using Temafa cottonising machine and they were processed via a single pass lomy and a single pass cottoniser.

3.1.3 Chemicals

Sodium hydroxide (NaOH) pellets of 98 % purity was obtained from Minema Chemicals, South Africa.

The silane coupling agent (3-aminopropyl tri-ethoxysilane) (A1100) was supplied by Sigma Aldrich (density 0.946 g/mL and a boiling point of 217°C).

Calcium carbonate (CaCO₃) SOCAL 312- ultrafine surface treated precipitated calcium carbonate with mean particle diameter of between 0.05-0.03 μ m was obtained from Solvay Chemicals International, France.

3.2 Manufacturing Techniques

3.2.1 Needle-punching technique for preparation of nonwovens

Various ratios of flax and polypropylene fibres were prepared accordingly, using an electronic scale. Dilo needle punching machine was used for the preparation of nonwoven mats from cottonised flax fibres and polypropylene fibres. The processing parameters set for needle punching machine for the processing of blended fibres of flax/PP into nonwovens are tabulated in **Table 3.1**.

Parameter	Setting			
	20/80	30/70	40/60	100%PP
Feeding speed (m/min)	0.74	0.75	0.75	0.75
Output from vertical lap (m/min)	0.75	0.8	0.9	0.65
Incline conveyer (m/min)	0.75	0.8	0.9	0.65
In-feed apron (m/min)	0.75	0.85	0.95	0.65
In feed rolls m/min	0.8	0.85	0.95	0.7
Needle depth (mm)	7	7	7	7
Stroke (min ⁻¹)	232	250	280	280
Dilo output (m/min)	1.05	1.10	1.25	1.00

 Table 3.1:
 Processing parameters used for preparation of flax/PP nonwovens

3.2.2 Compression moulding technique

Composites were prepared from nonwovens at varying fibre weight loadings. The flax/PP nonwovens were cut into small uniform squares (30 cm x 30 cm) and wrapped in Teflon sheets and placed between the platens of the compression moulding press, compressed at a pressure of 6 bars and temperature of 180°C for 10 minutes, followed by cooling under pressure for approximately 3 minutes. Nonwoven mats were chemically modified with silane coupling agent.

3.2.3 Injection moulding technique

Injection-moulded samples were prepared by mixing virgin polypropylene (vPP)/nano-CaCO₃ and recycled PP (rPP)/CaCO₃ in a Brabender Plastograph. They were processed at a temperature of 180 °C, and at a speed of 60 rpm for 13 minutes. The mixing time was divided in the following manner: the first 1 minute 30 seconds was for melting the polymer matrix (vPP and rPP), the next 1 min. 30 sec. was for the addition of filler, and then the last 10 minutes were allocated for thorough mixing of the two components. The samples were then cut into small pieces with a pair of scissors and then allowed to cool to room temperature. Samples were prepared at varying filler weight loadings of CaCO₃ namely; 10, 20 and 30 %. The melt mixed samples were injection moulded in order to obtain specimens for mechanical and thermal testing

3.3 Methods

3.3.1 Fibre preparation

Flax and polypropylene (PP) fibres were mixed accordingly, at three formulations, namely: flax/PP (0/100, 20/80, 30/70 and 40/60). Fibres were processed by opening and feeding them into a silo chute machine. They were then opened and channelled into the carding machine for cleaning and were further orientated to form a loose web. The fibres were then passed through a cross lapper for web laying and needle-punched to form the nonwoven fabric.

3.3.2 Chemical treatment of nonwovens

Nonwovens were soaked in 2 % (by weight) solution of NaOH for the duration of 2 hours for alkalization process. The alkalized fibres were repeatedly washed with distilled water, followed by neutralisation with few drops of acetic acid in order to maintain the pH of 5. Fibres were then washed with distilled water, followed by silane treatment ⁷⁶.

Silane used was 3-aminopropyl tri-ethoxy and 0.4% (by weight) of the silane was prepared by mixing with an ethanol/water mixture, in the ratio 6/4 and was allowed to stand for 1 hour. The pH of the solution was maintained at 4 with the dropwise addition of acetic acid. The alkalized treated nonwovens were soaked in this solution and were allowed to stand for 1.5 hours. The fibres were then washed with distilled water and dried in an oven at 70°C, until they were completely dry (took approximately two days)^{49,79}.

3.4 Characterisations

3.4.1 Mechanical testing

Tensile test is a fundamental mechanical test where a specimen is prepared and loaded in a controlled manner, while measuring the applied load and the elongation of the specimen over a distance of 60mm. It is a measure of the stress that a material can withstand while being stretched or pulled apart before breaking. Tensile modulus (also known as Young's modulus) is a measure of the stiffness of an elastic material and it is a quantity widely used to characterise the tensile properties of materials. Tensile tests are used to determine the modulus of elasticity, elongation and tensile strength of materials.

Tensile tests were performed using an Instron model 3369, in accordance with ASTM D638 standards. The specimens were tested at a speed of 50 mm per minute and a gauge length of 60 mm. Flexural tests were performed on the same machine using the 3-point bending method as per ASTM D790 standard ⁵⁰⁻⁵¹. The specimens were tested at a speed of 5mm/min and span length of 60mm. A total of 5 samples for each material were tested and the average data were reported ^{93,94}.

Impact strength experiment is performed in order to check the capability of a specimen's resistance to break under applied stress. Impact toughness of a material is a very important factor that determine the brittleness of the material. Impact tests were performed on an Instron Dynatup 9250 HV. The test method adopted was consistent with ASTM D256. Notched specimens [(2 mm V notch (45° C)] were tested, at a span length of 80 mm and drop weight of 6.39 kg (**Figure 3.1**). A total of five samples were tested and the mean value of the absorbed energy obtained was calculated²³.



Figure 3.1: A typical example of notched impact specimen (D-breadth and w-width, and L-length)

3.4.2 Dynamic mechanical analysis (DMA)

DMA is a very useful technique for investigating the dynamic mechanical behaviour of a material, based on its viscoelasticity. It measures the stiffness and the damping factor and these are reported as modulus and tan delta. A dynamic mechanical test measures the response of a material as it is deformed by a sinusoidal or other periodic stress⁸⁰.

Dynamic mechanical analyses were performed⁵⁷ on PerkinElmer DMA 8000 and samples of dimensions 50 mm x 10 mm were used for testing, in a temperature range of between -20° C to 160°C. The samples were tested under a dual cantilever mode, at a strain amplitude of 0.05 mm.

3.4.3 Environmental aging

Environmental ageing allows for a laboratory simulation of the effects of temperature and humidity on samples for the purpose of predicting long-term durability of materials exposed to out-door environment. Composite samples of dimensions 150 mm x 10 mm were conditioned in an environmental chamber at (a) 55° C and 90 % RH for 48 hours and (b) 90° C for 16 hours. Weights of samples were taken before and after conditioning. The mechanical properties of samples after conditioning were compared to the unconditioned samples⁷⁶.

3.4.4 Thermogravimetric analysis (TGA)

Thermogravimetric analysis is a method of thermal analysis, in which changes in physical and chemical properties of materials are measured as functions of increasing temperature (at a constant heating rate), or as functions of time (at a constant temperature and/or constant mass loss). TGA can be used to evaluate the thermal stability of a material. In a desired temperature range, if a material is thermally stable, no mass change will be observed. Small mass loss corresponds to little or no slope in the TGA thermograms. TGA also gives the upper use temperature of a material. Beyond this temperature the material will begin to degrade.

TGA analyses were performed on a PerkinElmer Pyris-1 TGA, in a flowing nitrogen atmosphere (20 ml /min). Samples with masses of between 6–7 mg each, were heated from 30 to 700 $^{\circ}$ C at a rate of 10 $^{\circ}$ C per min^{23,51}.

3.4.5 Scanning electron microscopy (SEM)

SEM is a commonly used technique to analyze the surface morphology of fibres, crack initiation and failure process in composites. SEM studies were conducted using ESEM Quanta 200 fitted with EDAX genesis XTE475 to study the fracture behavior in conditioned and unconditioned samples. The fracture ends of tensile specimens were mounted on aluminium stubs and gold-coated in order to avoid electrical charging during examination.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Flax Fibre-PP Composite

4.1.1 Mechanical properties

Generally, the mechanical properties of different polymeric materials are enhanced by the incorporation of various fillers. Tensile testing is frequently used to evaluate the strength of the material. **Figure 4.1** shows the tensile strength and tensile modulus of flax/PP reinforced composites. It can be clearly seen that as the loading of fibres increases from 10 to 30%, tensile modulus of the composites increases, to a maximum of 30% fibre loading and then declines thereafter. A similar trend was observed where a maximum of 30% fibre loading was obtained whereas there was a decrease at 40% fibre loading. The decrease at 40% fibre loading is attributed to agglomeration of fibres, causing inefficient stress transfer within the composite⁷⁶.



Figure 4.1: Effect of fibre loading on the tensile strength and modulus of flax/PP composites



Figure 4.2: Effect of fibre loading on the flexural strength and modulus of flax/PP composites

When fibre reinforced composite is subjected to load, the fibres act as the carrier of load and stress is transferred from matrix along the fibres, leading to effective and uniform stress distribution and results in composite with good mechanical properties. Uniform distribution of stress is dependent on two factors: i) population of fibres, ii) dispersion of fibres. At low levels of fibre loading, the dispersion of fibres is poor and fibres cannot participate effectively in stress transfer. At high levels of fibre loading, it is usually seen that increased population of fibre leads to agglomeration and stress transfer gets blocked.

The variation of flexural strength and modulus with fibre loading is presented in **Figure 4.2**. Flexural strength is a combination of the tensile and compressive strengths, which directly varies with the interlaminar shear strength. It was observed that flexural strength and flexural modulus are directly proportional to the fibre loading as they increase with an increase of the fibres in composite materials. When the fibre loading increases from 10% to 30%, the flexural modulus increases from 1059 MPa to 1763 MPa and to a maximum of 2172 MPa of treated composites, respectively. The flexural modulus also is resembling a similar pattern when compared to flexural strength in that as the fibre loading increases, the flexural modulus increases^{80,76,95}.



Figure 4.3: Effect of fibre loading on impact strength of flax/PP composites

In general, impact test gives information about the toughness of a material. The variation of impact strength with fibre loading is shown in **Figure 4.3**. It can be seen that the impact strength increases from 10 kJ/m² and reaches a maximum at 46 kJ/m² (30% weight fraction of fibres) and then decreases to 11 kJ/m² that corresponds with the 40% fibre loaded composites. This may be the results of the energy dissipating mechanisms operating during impact fracture, namely matrix and fibre fracture, fibre-matrix debonding and fibre pull-out. At higher fibre content, the friction between the fibres can also contribute to the fracture process, resulting in lower energy dissipation and hence impact strength decreases.^{880,82,84}

4.1.2 Thermogravimetric analysis (TGA)

Usually, thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) curves are used to determine the weight loss and to identify the degradation profiles of the material and thereby gives the thermal behaviour of composites. **Figures 4.4** show the thermograms depicting the weight percent loss as function of temperature curve for all representative samples under nitrogen atmosphere⁹⁶. In the literature, it is stated that degradation of natural

fibres involves two main steps, the first peak around 300°C is associated with the thermal depolymerisation of the hemicellulose and the cleavage of glycosidic linkages of cellulose, and the second peak at around 360°C is attributed to the decomposition of α -cellulose. Previous research indicates that, Lignin decomposes ⁹⁷⁻¹⁰² at a broad range of temperature between 200°C and 500°C.



Figure 4.4 TG curves of flax/PP reinforced composites

Thermal properties of natural fibre reinforced PP composites show two degradation peaks, a minor peak at 348°C which is also associated to the depolymerisation of hemicellulose and glycosidic linkages of cellulose and a major peak at 533°C. PP exhibits one-step degradation profile with T _{max} at around 480°C (**Table 4.1**). The samples are found to be thermally stable up to 320°C and composites containing 40% fibres exhibit greater thermal stability than neat PP. This can be attributed to the fact that at high fibre content, there is higher consolidation effects within the composite structure ¹⁰³⁻¹⁰⁵.

Weight of flax fibres in	T _{onset} [°C]	Maximum degradation temperature [T _{max}] [°C]		
sample		Peak I	Peak II	
[%]				
0	380	-	480	
20	342 - 390	417	471	
30	342 - 431	433	480	
40	342- 410	452	533	

 Table 4.1:
 Thermal properties of flax/PP composites

4.1.3 Dynamic mechanical analysis

Storage modulus provides input into the stiffness of the samples. It is most useful for studying the viscoelastic behaviour of polymers. The most common application of natural fibre reinforced composites is in the automotive sector, where components are exposed to varying temperatures. DMA is very useful in establishing a wide range of temperature and load dependent material data. In **Figure 4.5**, it can be seen that the storage modulus decreases with increasing temperature for the neat PP and the various composites with different fibre loadings. This is because as the temperature increases, the molecules move from the frozen state (below 0°C) to rubbery state at around 4°C resulting in low stiffness. The incorporation of flax fibres in the composites has resulted in an increase of the storage modulus and maximum value is exhibited by composite containing 40% fibre loading. This is attributed to the incorporation of stiff flax fibre, thus increasing the stiffness of the samples^{76,106}.



Figure 4.5: Variation of storage modulus with temperature at different fibre loading

The ratio between the loss modulus and storage modulus is referred to as mechanical loss factor or tan δ . The damping properties are influenced by the type of fibres, fibre dispersion, fibre-matrix interaction and void content. The position and height of the tan delta peak are indicative of the structure and properties of the material under test. The tan δ curves show a peak at around 4°C for all samples investigated (**Figure 4.6**). This peak is related to the glass transition (T_g) or β -relaxation of the PP amorphous domains. There is no significant change on the glass transition temperature with the incorporation of nonwovens; however, there is a slight decrease in the intensity of the β -relaxation. This is probably due to the presence of flax fibres which inhibited the mobility of the polymer chains, hence suppressing the damping peak (at ~4°C). Similar results were observed by John et al⁷⁹ in the case of flax fibre reinforced polypropylene composites¹⁰⁷.



Figure 4.6: Variation of tan δ with temperature at different fibre loading

4.1.4 Environmental conditioning of composites

Environmental aging behaviour of flax/PP reinforced composites was assessed by subjecting tensile specimens to high humidity and temperature in an environmental chamber. In the literature, Joseph et al⁷⁹ studied the environmental aging behaviour of banana fibre reinforced phenol-formaldehyde (PF) composites by subjecting it to water aging, thermal aging, soil burial and outdoor weathering. The tensile strength and modulus of the banana/PF composites were found to have decreased due to water aging and when compared to glass fibre loading, in water intake increased. However, water absorption was found to decrease by chemical treatment and hybridization.

Cantero et al⁸⁵ reported on the effects of treatment on the wettability and mechanical behaviour of flax/PP composites. It was observed that wettability of fibres improved by the

action of maleic anhydride and vinyl trimethoxysilane. In another study, George et al.⁸⁶ reported that as the fibre content increases, water uptake increases and that there was reduction of water uptake in chemically modified composites for low density polyethylene composites reinforced with pineapple leaf fibre. In a number of studies^{92,93} silane coupling agent treatment was also found to be effective in modifying the natural fibre-matrix interface.

One of the drawbacks of natural fibre composites is that it absorbs moisture which affects the mechanical properties of the composites. Hence, it is crucial to investigate the effect of high temperature and humidity on the mechanical properties of composites. In this particular study, composites containing silane treated fibres were also aged and compared to untreated samples. Silane coupling agent acts as bridges between fibres and matrix, resulting in better bonding and stronger interface in the composites. When natural fibres are exposed to very high humid conditions (~90 % RH), they absorb moisture due to its hydrophilic character. Moisture absorption in polymer composites is governed by three mechanisms: the first involves the diffusion of water molecules inside the micro-gaps between polymer chains. The second mechanism involves capillary transport of water into the gaps and flaws at the interfaces between fibre and matrix while the third relates to transport of water through micro-cracks in the matrix arising from the swelling of fibres (particularly in natural fibre composites). Among the three mechanisms, diffusion is considered to be the major mechanism of moisture absorption.

In the case of flax-PP composites, moisture uptake is entirely dependent on the fibres, since PP is hydrophobic. In the present study, samples were aged at two conditions: (a) 55° C and 90% RH for 48 hours and (b) 90°C for 16 hours. These conditions are similar to the testing parameters used in the automotive sector for non-load bearing components.

Figures 4.7 and **4.8** present the tensile properties of untreated and treated composites before and after conditioning at 55°C and 90% RH for 48 hrs. The results in **Figure 4.7** show that the tensile strength of flax/PP (30/70) composites was not influenced by the conditioning of the composites at 55°C and 90% RH for 48 hrs. On the other hand, the tensile modulus of the composites decreased by 35% after conditioning. **Figure 4.8** shows that the silane-treated flax/PP (30/70) composites were also conditioned at similar parameters as untreated samples. The tensile strength of the silane-treated composites shows no difference when compared to the samples after conditioning at 55°C and 90% RH for 48 hrs. Nevertheless, the tensile modulus of the silane-treated composite registered a decrease of only 7% after conditioning. This behaviour of the tensile properties in both scenarios, before and after conditioning are attributed to the silane treatment, carried out on the fibres which improved the interaction between the fibres and polymer matrix⁸⁷⁻⁸⁹. Generally when samples are exposed to high temperatures and humidity, swelling of composites is observed, leading to poor tensile properties. In the case of silane treated composites, there were better bonding and adhesion which resulted in a tight compact structure that makes penetration of water difficult and hence a relatively small decrease in tensile properties is observed.



Figure 4.7: Effect of conditioning on the mechanical properties of untreated flax flax/PP (30/70) composites at (55°C and 90% RH for 48 hrs)



Figure 4.8: Effect of conditioning on the mechanical properties of silane treated flax flax/PP (30/70) composites at (55°C and 90% RH for 48 hrs)

Figures 4.9 and **Figure 4.10** show the tensile properties of untreated and treated composites, before and after conditioning at 90°C for 16 hours. It can be observed that after conditioning, the tensile strength reduced by 6.8% for untreated composites, whereas for treated composites, the tensile strength reduced by 6.1%. In this case, as samples were exposed to very high temperatures for a long period, it is possible that the silane coupling agents might have disassociated and proved inefficient in increasing the bonding between the fibre and matrix. However, the results from both figures indicate that the silane treatment had no influence on the tensile strength of composites in both cases, before and after conditioning.



Figure 4.9: Effect of conditioning at (90°C for 16 hrs) on the mechanical properties of untreated flax flax/PP (30/70) composites.



Figure 4.10: Effect of conditioning at (90°C for 16 hrs) on the mechanical properties of silane treated flax/PP (30/70) composites

4.1.5 Morphological studies

SEM is one of the useful techniques to analyze the surface morphology and diameters of fibres, degraded areas, crack initiation and failure process in composites. Kamath et al¹⁰⁸ studied the bonding between cotton fibres and binder polymers, such as polyolefins and polylactic acid (PLA). They reported better bonding between natural fibres and thermoplastic binder polymers.

Figure 4.11 (a) and **(b)** represents the SEM micrographs of untreated surfaces of tensile fractured specimens after conditioning at 55°C and 90% RH for 48 hrs. Natural fibres are hydrophilic in nature and are prone to water sorption. When composites are exposed to conditions of high humidity, the fibres absorb water, resulting in swollen fibres. In Figure 4.11 (a), SEM images of solid and strongly bonded fibres are observed, while fibrillated ends in **Figure 4.11(b)** indicate poor bonding between fibre and the matrix. When natural fibre polymer composites are exposed to moisture, water penetrates and confers onto hydrophilic groups of fibres establishing intermolecular hydrogen bonding with fibres, while reducing interfacial adhesion between fibre and matrix.



Figure 4.11: SEM micrographs of tensile fractured surfaces and untreated composites after conditioning at 55°C and 90% RH for 48 hrs

SEM micrographs of silane treated composites that were conditioned at 55°C and 90% RH for 48 hours. Although **Figure 4.12(a)** shows some few fibrillated ends, the fibres appears to have smoother surfaces when compared to the untreated composites that were subjected to the similar conditions. **Figure 4.12 (b)** indicates SEM image of silane-treated fibres in composites that were also prepared under the same conditions as untreated samples. However, the treated composites showed solid and continuous fibres that are stuck together. This is due to the fact that when natural fibres are subjected to the treatment with silane coupling agent, there exists improved interaction between fibres and matrix. This resulted in a good fibre-matrix adhesion and thus the fibres were well embedded in the matrix.



Figure 4.12: SEM micrographs of surfaces tensile fractured chemically treated composites after conditioning at 55°C and 90% RH for 48 hrs

4.2 Nanofiller – PP composites

4.2.1 Mechanical Properties

The use of fillers in the fabrication of polypropylene and other thermoplastic composites is on the rise as they find applications in many areas, such as automotive and construction. The use of fillers can improve properties such as: shrinkage, stiffness and flammability and can also be cost effective. Recently, the introduction of nano-sized fillers (CaCO₃, silica) in composites has resulted in a new area of research. The advantages of using nanofillers, when compared to their micro-sized counterparts, is that high level of reinforcements can be obtained at low fibre loadings leading to stronger and lighter structures. However, this is attributed to the large surface area that contribute to effective interaction.

This section deals with the mechanical and thermal studies of nanofiller reinforced PP composites. The effects of nano-CaCO₃ on the mechanical properties of recycled and virgin PP composites have been investigated and the results are presented in **Table 4.2**. The mechanical properties of virgin PP and recycled PP composites, loaded with different nano-CaCO₃ contents show that the tensile strength decreases, while the tensile modulus increases with an increasing nanofiller loading. In virgin PP composites, as the nanofiller content increased from 0 to 30%, the tensile strength decreased from 30.2 MPa to 25.2 MPa, whereas the tensile modulus increased from 777 to 1059 MPa.

Nano-CaCO ₃ (%)	Virgin PP		Recycled PP	
	Tensile	Tensile	Tensile	Tensile
	strength	modulus [MPa]	strength [MPa]	modulus [MPa]
	[MPa]			
0	30.2 ± 0.2	777 ± 2	22.9 ±0.3	609±28
10	28.4 ± 0.1	908 ± 19	20.8 ± 0.1	701 ± 14
20	26.2 ± 0.2	936 ± 28	20.1 ± 0.2	775 ±13
30	25.2 ± 0.2	1059 ± 15	19.3 ± 0.3	861±21

 Table 4.2:
 Mechanical properties of nano-CaCO₃/PP composites

The results in **Table 2** indicate that in recycled PP composites, the tensile strength decreased from 22.9 MPa to 19.3 MPa as the nano-CaCO₃ content increased, the tensile strength is usually dependent on the adhesion and stress transfer between filler and matrix, while modulus is dependent on filler loading and generally increases with filler content. The decrease of tensile strength may be attributed to the poor interaction between non-polar PP

and polar nano-CaCO₃ resulting in poor dispersion of the filler. This resulted in poor stress transfer leading to lower tensile strength. Similar results were reported by Nezhad et al^{74} where tensile tests showed that the inclusion of nano-CaCO₃ slightly increased the modulus and decreased tensile strength of the PP composites.

Figure 4.13 shows the impact test results for virgin PP, as the nano-CaCO₃ content increased from 0 to 30%. The impact strength exhibits a maximum of 78 kJ/m² at 20% nanofiller loadings and thereafter, the trend becomes unstable. On the other hand, for the recycled PP, the impact strength increases from 58 kJ/m² to a maximum of 83 kJ/m² as the nano-CaCO₃ increases from 0 to 20%, respectively. At 30% nanofiller loading, the virgin and recycled PP showed a decline in impact strength when compared to their maximum impact strength. On contrary, Fuad et al¹⁰⁹ reported that the addition of precipitated calcium carbonate increased the impact strength of neat PP, reaching a maximum (impact strength) at 5% filler loading.



Figure 4.13: Effect of nano-calcium carbonate on impact strength of recycled and virgin polypropylene composites

4.2.2 Thermal analysis

Thermal analyses of nano-CaCO₃ incorporated in virgin and recycled PP were determined. **Figures 4.14** and **15** represent the thermograms of nano-CaCO₃ incorporated virgin polypropylene composites. It can be seen that all the samples exhibits a one-step degradation pattern. The thermal stability was found to decrease upon the inclusion of nano-CaCO₃. This may be attributed to the poor bonding between nanoCaCO₃ and polypropylene, resulting in a weak consolidated structure. Another observation is that char residue of composites increased with increasing loading and this is attributed to high thermal stability of CaCO₃. In addition, it has been observed that the composite samples are thermally stable up to 450° C.



Figure 4.14 TGA curves of nanoCaCO₃/virgin PP composites



Figure 4.15 DTG curves of nanoCaCO₃/virgin PP composites

Figure 4.16 represents the thermograms of nano-CaCO₃ incorporated recycled polypropylene composites. It can be seen that thermal stability increases with increasing filler content. In the literature, Buasriet al⁷⁵ studied the thermal and mechanical properties of modified CaCO₃/PP nano composites and indicated that the addition of fillers enhanced the thermal stability of the composites. They also observed that the presence of CaCO₃ significantly affected the crystallization behaviour of PP, and concluded that the presence of nanosized CaCO₃ in the matrix decreased the size of crystalline domains. In the present study, composites were found to be thermally stable up to around 430°C, whereas for the recycled PP, degradation started at around 300°C. A one-step degradation is observed for all samples and the T_{max} for composites manifested at approximately around 550°C while that of recycled PP is around 430°C.



Figure 4.16 TGA curves of recycled nanoCaCO₃/PP composites

4.2.3 Scanning electron microscopy

SEM micrographs surfaces of tensile fractured surface of composites of nano-CaCO₃ filled virgin and recycled PP are shown in **Figures 4.17** and **Figure 4.18**, respectively. **Figure 4.17(a)** shows SEM images of virgin PP with porous and non-uniform structure. **Figure 4.17(b)** reveals the morpholgy of virgin PP loaded with 10% nano-CaCO₃ content. The SEM micrographs indicate a distorted surface morphology due to nano-CaCO₃ agglomeration. This indicates that the dispersion of nano-CaCO₃ is not uniform due to the poor bonding between PP and nano CaCO₃. This was also reflected in the low tensile strength values of the composites. Similar results were observed by Fuad et al¹⁰⁹, who reported that at low levels of nano-CaCO₃ content in PP composites, agglomeration was more prominent in extruded composites than in melt mixed composites^{87-90,74}.



Figure 4.17: SEM micrographs surfaces of tensile fractured specimens of nano-CaCO₃ /virgin PP (a) 0/100 (b) 10/90 (c) 20/80 and (d) 30/70

Figure 4.17 (c) shows the SEM image of virgin PP with 20% nano-CaCO₃ loading. The micrograph clearly indicates the surface with uniform patterned morphology resembling some parallel grooves in the composite material. On the other hand, **Figure 4.17** (d) shows a scaly but rather connected and non-porous structure. Therefore, the surface morphology of nano-CaCO₃ loaded virgin PP shows improved surfaces when compared to virgin PP, which is due to a good dispersion of nano-CaCO₃ filler.

This indicates the fact that surface treatment of nano-fillers is required in order to obtain good dispersion within the matrix.



Figure 4.18: SEM micrographs surfaces of tensile fractured specimens of nano-CaCO₃/recycled PP (a) 0/100 (b) 10/90 (c) 20/80 and (d) 30/70

Different surface morphologies were obtained for SEM micrographs in Figure 4.18 (a), (b), (c) and (d), with respect to nano-CaCO₃ loadings on recycled PP. Figures 4.18 (a) and (b) shows structures with fibrillated edges while Figure 4.18 (c) indicate agglomeration surface due to 10 % nano-CaCO₃ filler. The morphology in Figure 4.18 (d) demonstrates a highly agglomeration surface that indicate a good dispersion on the nano filler.

The results above clearly indicate that as the nano-CaCO₃ loading increases, the extent of agglomeration increases.

CHAPTER 5

5.1 Conclusions

The aims of this project was to develop flax/polypropylene (PP) composite materials and to evaluate their properties for automotive applications. The study also investigated the effect of nano-CaCO₃ on the properties of two types of polymer matrices: recycled PP and virgin PP.

The mechanical properties (tensile, flexural and impact) of flax/PP composites were found to increase and reached a maximum at 30% fibre loading and then decreased at higher fibre content. This was attributed to the agglomeration of fibres, causing inefficient stress transfer within the composite. Thermal studies revealed that the composites were stable up to 320 °C and samples containing 40% flax fibres were found to exhibit greater thermal stability than PP. The dynamic mechanical analyses of the composites showed that the incorporation of flax in the composites resulted in an increase of the storage modulus and maximum was exhibited by composite containing 40% fibre loading. This was attributed to the fact that the presence of flax fibres increased the stiffness of the samples. Glass transition temperature (T_g) was observed at 1.2 °C for PP; in the case of the composites, T_g was not significantly altered but there was a slight decrease in intensity of the relaxation region. This was attributed to the fact that the presence of flax fibres acted as barriers to the mobility of polymer chains, leading to lower degrees of molecular motion and resulted in lower tan δ values.

A major issue restricting the use of natural fibres composites in industrial applications is that natural fibres are hydrophilic and hence absorb moisture. This leads to the deterioration of mechanical properties in composites and hence chemical modifications are usually employed in order to inhibit water absorption in composites. In the automotive/aerospace sector, components are often subjected to variable conditions of temperature and relative humidity during the service life; this affects the long term strength and durability of the composites. With a view to investigate the use of flax/PP composites for automotive applications, aging studies were performed for untreated and silane treated composites at two conditions: (a) 55°C and 90 % RH for 48 hours and (b) 90°C for 16 hours. These conditions are similar to the testing parameters used by the automotive sector for non-load bearing components. It was

found that after conditioning samples at 55 °C and 90% RH for 48 hrs, the tensile modulus of composites decreased by 35% but composites containing chemically modified composites registered a decrease of only 7%. This was attributed to the fact that in silane treated composites, the better bonding and adhesion resulted in a solid compact structure which made penetration of water difficult and hence decrease in tensile properties is observed. However, for composites conditioned at 90 °C for 16 hours, it was observed that the tensile strength before and after conditioning did not alter significantly.

SEM studies of tensile fractured surfaces specimens of untreated composites after conditioning revealed fibrillated fibre ends and swollen fibres, while for the silane-treated composites, embedding of fibres in the matrix and smoother fibre surfaces were noticed. This indicates improved interactions between fibres and matrix.

The tensile modulus of nano-CaCO₃ filled PP (virgin and recycled) composites were found to increase and reached maximum at 30% nano-CaCO₃ loading, while the tensile strength decreased with increasing filler content. The decrease of tensile strength was attributed to the poor interaction between the non-polar PP and the polar nano-CaCO₃, resulting in poor dispersion of the filler. Modulus is dependent on filler loading and thus increased with filler content.

Thermal studies showed that nano-CaCO₃ filled PP samples exhibited a one-step degradation pattern and are thermally stable up to 450° C. The thermal stability was found to decrease following the incorporation of nano-CaCO₃. This was attributed to the lack of bonding between nano-CaCO₃ and polypropylene, resulting in a weak consolidated structure. Another observation is that char residue of composites increased with increasing CaCO₃ loading and this is attributed to high thermal stability of CaCO₃. Nano-CaCO₃ filled recycled PP samples also exhibited similar results, but were found to be thermally stable up to around 430 °C

SEM micrographs of tensile fracture surface of composites of nano-CaCO₃ filled virgin and recycled PP revealed the presence of nano-CaCO₃ agglomeration. This indicates that the dispersion of nano-CaCO₃ was not uniform due to lack of bonding between PP and nano CaCO₃. This was also reflected in the low tensile strength values of the composites. This indicates that surface treatment of nano-CaCO₃ is an important requisite in obtaining good dispersion and properties in composites.

6.1 References

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