

**PHYSICAL, MECHANICAL AND DURABILITY PROPERTIES OF
SUGARCANE ASH ENHANCED COMPRESSED EARTH BLOCKS
STABILIZED WITH FLY ASH AND LIME POWDER**

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2019

UNIVERSITY OF ZULULAND



**Physical, Mechanical and Durability Properties of Sugarcane Ash Enhanced
Compressed Earth Blocks Stabilized with Fly Ash and Lime Powder**

Cellulose chemistry and applications

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M.Sc. Polymer Chemistry (University of Free State)

THESIS

Submitted in Fulfillment of the Requirements for the Degree

DOCTOR OF PHILOSOPHY IN CHEMISTRY

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DECLARATION

I hereby declare that the work described in this thesis entitled “Physical, mechanical and durability properties of sugarcane ash enhanced compressed earth blocks stabilized with fly ash and lime powder” is my own work and has not been submitted in any form for another degree or qualification of the University of Zululand or any other University or Institution of tertiary education. Information derived from the published or unpublished work of others has been acknowledged in the text and a list of references is given.

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DEDICATION

This work is dedicated to everyone who believes in my potential, my family, and my late grand-father, Tatolo Molebatsi. May his soul rest in peace.

AKNOWLEDGEMENTS

I would like to express my sincere gratitude and indebtedness to my supervisors, Prof. T.E. Motaung, Dr. L.Z. Liganiso and Prof. S.P. Songca for their guidance and support during my studies.

I would also like to express my gratitude to staff of Nelson Mandela University, in the department of chemistry for helping me in preparing and characterizing my samples.

I am also thankful to the staff of University of Johannesburg, department of civil engineering for their input and conducting the compressive testing of the bricks in their laboratory.

Many thanks to chemistry staff and Organic Research Group of the University of Zululand for their input in this work.

Lastly, I would like to thank my family for their continuous support throughout this wonderful journey.

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ABSTRACT

The construction sector is one of the principal component of anthropogenic activities and a major contributor of greenhouse gases (GHGs) emissions. Large quantities of solid wastes are being produced every year by industrial and agricultural industries which lead to environmental and health concerns such as flooding, air pollution and other public health scarce. These wastes have potential pozzolanic reactivity and may be used to develop cementitious materials that are sustainable, while maintaining requirements as affirmed in various standards. The sector is also an important economic sector that has a large environmental impact in terms of large quantities of construction and demolition wastes (C&DW) which are generated. These is mainly due to severe shortage of natural aggregates (NA) for the production of new concrete materials, and a boom in construction activities currently taking place worldwide. The utilization of recycled masonry and concrete (RCA) from C&DW will conserve the natural resources and reduce the environment impact of concrete manufacturing. Sugarcane bagasse ash (SCBA) is an industrial waste material obtained from sugar milling industry that can be used as pozzolanic material for the development of greenbricks. In this research, the application of various waste materials and the effects of fly ash and lime on the mechanical and durability properties of compressed earth bricks (CEBs) are investigated. Secondly, the applications of fly ash, recycled cement and masonry as industrial waste materials in construction industry are reviewed. Lastly, The SCBA greenbricks were developed using lime as a chemical stabilizer and tested for physical, mechanical and durability properties.

In addition, several agricultural by-product such as sugar cane bagasse (SCB) and soft wood (SW) were treated as wastes until recent times when researchers considered incorporating them in polymeric matrices to mainly avoid environmental pollution and cost of a new synthesis. The properties of untreated sugarcane bagasse (SCB) and soft wood (SW), their respective celluloses, and corresponding composites and blends with thermoplastics (polypropylene and polyethylene) were analysed by DMA, SEM, XRD, FTIR, DSC and TGA. Three degradation models, Kissinger-Akahira-Sunose (KAS), Flynn-Wall-Ozawa (OFW), and Kissinger (KGR) methods were employed to determine apparent activation energy values of untreated SCB and SW, and their respective celluloses. The apparent activation energy values obtained from OFW and KAS models vary with the degree of conversion, and showed similar

trends. The activation energies TGA analysis shows that the untreated SCB and SW degrade earlier than their respective celluloses and the prolonged treatment affects the onset of main degradation. PP/SCB were least thermally stable compared to PP/SW composites. The addition of extracted cellulose decreased the thermal stability of PP/SCB composites at higher filler content due to poor interfacial bonding as compared to PP/SW composites. Likewise, the cellulose containing blend composites were thermally stable compared to untreated fibre, and are less stable compared to neat PP/PE blend. DMA of both PP/SCB and PP/SW composites indicated improvement in the storage modulus compared with neat PP. Similar results were obtained for all blend composites, with the cellulose containing blend composites displaying higher values than untreated fibre. SEM results confirmed a rough morphology and the presence of many voids resulting from fibre pull-out in composites, especially for the ones with higher fibre content. However, a stronger interaction between PP/PE/SW as compared to PP/PE/SCB took place in the blend composites. DSC analysis reveals that the introduction of SCB or SW did not significantly change the melting and crystallization behaviour of both the PE and PP.

LIST OF ABBREVIATIONS

Acrylic acid	AA
American Society for Testing and Materials	ASTM
Billet scale	BS
Brick powder	BP
Calcium aluminate hydrates	C-A-H
Calcium aluminate silicate hydrates	C-A-S-H
Calcium silicate hydrates	C-S-H
Cement stabilized masonry block	CSMB
Compressed earth blocks	CEBs
Construction and demolition wastes	C&DW
Corn fiber	CF
Crystalline size	CS
Crystallinity index	CI
Degree of polymerization	DP
Digital scanning calorimetry	DSC
Differential thermogravimetry	DTG
Dynamic mechanical analyser	DMA
Empty fruit bunch fibre	EFBF
Fine recycled concrete aggregate	FRCA
Fourier transform infrared spectroscopy	FTIR
Full width at half maximum	FWHM

Fly ash	FA
Flynn Wall Ozawa	FWO
High density polyethylene	HDPE
Greenhouse gases	GHGs
glycidyl methacrylate	GMA
International Standards	IS
Kissinger Akahira Sunose	KAS
Kissinger	KGR
Lime powder	LP
low-density polyethylene (LDPE)	LDPE
Maleic anhydride	MAH
Maleic anhydride polyethylene	MAPE
Maleic anhydride polypropylene	MAPP
Microcrystalline cellulose	MCC
Million tonnes	Mt
Municipal solid waste	MSW
Natural aggregates	NA
Ordinary Portland cement	OPC
Oil palm shell	OPS
Poly(butylene succinate)	PBS
Polycaprolactone	PCL
Polyhydroxyalkanoates	PHA

poly(3-hydroxybutyrate-co-3-hydroxyvalerate)	PHB
Polyethylene	PE
Polylactic acid	PLA
Polypropylene	PP
Polyvinylchloride	PVC
Quarry dust	QD
Recycled aggregate	RA
Recycled brick masonry aggregate	RBMA
Recycled concrete aggregate	RCA
Recycle high density polyethylene	R-HDPE
Recycled-low density polyethylene	R-LDPE
Rice husk ash	RHA
Rice husk	RH
Rice husk-polystyrene	RH-PS
Scanning electron microscopy	SEM
Self-compacting concrete	SCC
Silica fume	SF
Soft wood	SW
South African National Standards	SANS
Stockpiled circulating fluidized bed combustion ash	SCFBCA
Sugarcane bagasse	SCB
Sugarcane bagasse ash	SCBA

Thermogravimetric analysis	TGA
Waste tire rubber	WTR
Wood fibre	WF
Wood powder	WP
X-ray diffraction	XRD

LIST OF SYMBOLS

kg	kilogram
kW/h	kilowatt per hour
%	percentage
μm	micro meter
MPa	mega Pascal
g/cm ³	grams per cubic centimetre
Mt	million tons
mm	millimeter
°C	degree celsius

CHAPTER ONE:

GENERAL INTRODUCTION

1.1 Introduction

An increasing interest in ecological issues has pressured various industries, including the construction industry to develop products and materials that are environmentally friendly. This interest is mainly driven by current global environmental concerns for sustainable development, impoverishment of natural resources and emission of greenhouse gases (GHGs) within the sector [1-3]. The manufacturing process of conventional construction materials such as cement and bricks is energy intensive and generates large amounts of GHGs emissions. For example, the production of 1 kg of ordinary Portland cement (OPC) consumes approximately 1.5 kWh of energy and releases about 1 kg of CO₂ to the atmosphere. In addition, quarrying operations for producing the aggregates are energy intensive, adversely affect the landscape, and release large quantities of waste materials [4, 5]. These environmental concerns have generated an interest to develop alternative building materials that are sustainable while maintaining the material requirements affirmed in the standards [6, 7].

Large quantities of unmanaged solid wastes are generated every year by industrial and agricultural production that lead to environmental and health concerns such as flooding, air pollution and other public health scarce [8-10]. The construction industry which is a major sector when it comes to environmental control, remain a viable option for waste disposal due to its high volume consumption of waste materials [11, 12]. The application of waste to develop construction materials offers an attractive alternative to their disposal, and number of advantages including low cost, abundant raw material availability and lower degree of industrialization. These wastes are potential source of materials with pozzolanic reactivity and could reduce the emission of CO₂ and minimize the volume of waste in landfill [13, 14].

Sugarcane bagasse ash (SCBA) is an agricultural by-product of sugarcane bagasse combustion in the sugarcane and alcohol industries. It is generally disposed of in landfills creating environmental problems. It is classified as a pozzolanic material which poses economic potential to be used in cementitious materials [15, 16]. It has gained acceptability in the construction industry with much emphasis on its performance as a supplementary material due to its positive effect on the strength and durability of concrete [17]. SCBA has silica in high content and also contains aluminium, iron, alkalis and alkaline earth oxides in smaller amounts. The pozzolanic activity and the composition of SCBA depends on factors such as

temperature of combustion, surrounding environment, nature of soil, and ash fineness amongst others [18-20].

Conventional bricks are produced from clay with high temperature kiln firing or OPC. However, these conventional methods of brick manufacturing have not yet been changed or converted to more sustainable ones [21-23]. These methods are energy intensive, adversely affect the landscape, and releases substantial quantity of greenhouse gases. [24, 25]. Hence, researchers are developing alternative construction bricks by utilizing waste materials not only to reduce the environmental challenges but also to meet economical and sustainable solution. Various studies have been directed towards partial or total substitution of OPC by pozzolanic binders such as lime, fly ash (FA) and SCBA as raw materials in the development of compressed or stabilized bricks. The advantages of this brick is that there is no need for high curing temperatures and the release of CO₂ into the atmosphere is 80% less than production of cement bricks. The degree of compaction can be achieved with hydraulic equipment or hand levers. In addition, the bricks have comparable performance in terms of appearance, durability and structural properties such as water absorption and compressive strength [26, 27].

There is also a growing interest of utilizing agricultural waste products as reinforcing fillers in the development of polymer composites due to the demand for green materials, depletion of renewable resources and increasing awareness of environmental safety [28]. Accumulation of this waste in large quantities results not only in environmental and health challenges, but also represents an economic difficulties for companies. Agricultural wastes are normally incinerated or dumped in landfill causing environmental problems such as air pollution and soil erosion [29-31]. Amongst these wastes, agricultural fibers such as sugarcane bagasse (SCB) and soft wood (SW) are increasingly used as an alternative to conventional and inorganic fillers such as carbon fiber, glass fiber and silica [30, 31]. Sugarcane is one of the most abundant biomass in the tropical countries such as Brazil and India, creating about 54 million dry tons of residue bagasse per year. About 50.3% of this production is used to manufacture ethanol (22.9 billion liters), 47.3% to make sugar (36.9 million tons) and 2.4% used to produce alcoholic beverages/candies [34]. Several processes and products have been reported that utilize bagasse as a raw material for industrial applications. These include electricity generation, pulp and paper production, amongst others [35, 36].

The utilization of SCB for processing of composites and blends materials has attracted growing interest because of their ecological and renewable characteristics. This is mainly due to their low densities, low cost, non-abrasiveness, high filling levels, recyclability, higher solvent compatibility, higher thermal resistance, low toxicity and renewable nature compared to composites reinforced by inorganic materials [37, 38]. Apart from their abundance and renewability, the utilization of agricultural residues is advantageous to the economy, environment, and technology due to their low manufacturing energy demand, low CO₂ emission, and high level of biodegradability, when compared to thermoplastic polymer composites reinforced by inorganic fillers [39]. The convenience of these composites lies in the fact that the ingredients are obtained from natural wastes and hence the composites can be made relatively easily [40]. Additionally, composites derived from natural organic materials have high specific strength and modulus compared to composites reinforced by inorganic materials [41]. However, the poor compatibility between hydrophilic fibers and hydrophobic polymers often leads to a weak interface, resulting in poor mechanical properties and high moisture sensitivity. There are nevertheless many chemical and physical surface treatments that have been applied in the literature to achieve high performance composites [42–44]. These treatments influence the fibers structures such that moisture absorption tendency by the fiber is reduced by facilitating better bonding with the matrix materials. In addition, the suitable fiber content and processing parameters must be carefully examined in order to achieve optimum property of composite. The final properties of composite materials depend further on the incorporated fiber properties (morphology, surface chemistry, chemical composition and crystalline contents), as well as matrix properties (nature and functionality) [45–47].

1.2 Statement of the research problem

OPC remains the primary and attractive material of choice in construction due to its performance, durability, and availability of raw precursors. However, the production of OPC consumes large amount of raw materials and releases quantifiable amounts of CO₂ to the atmosphere. There are also large quantities of solid wastes generated by industrial and agricultural activities which causes both environmental and health challenges. In addition, the conventional construction bricks are produced from clay with high temperature kiln firing or OPC concrete. These methods consume large quantities of raw materials and releases large amounts of greenhouse gases. Hence, researches are using waste materials such as SCBA, FA and lime as partial or total substitution of OPC in the development of cementitious products.

These waste materials are rich in silica concentration and possess little or no cementitious activity, unless they are chemically activated. They have recently gained acceptability in the construction industry as supplementary materials in OPC due to their positive effect on the strength and durability of OPC.

1.3 Scope of work

The main aim of this study is to find alternative ways of replacing cement by other lower carbon materials with cementitious properties in order to reduce emission of GHGs. The work further intends to address the challenges experienced by the agricultural and industrial sectors in terms of minimizing unmanaged waste and landfill scarcity in production and development of polymer composites and greenbricks. Industrial and agricultural waste such as sugarcane bagasse, sugarcane bagasse ash and lime are amongst some of the waste materials used. The research intends to use sugarcane bagasse ash in combination with lime as chemical stabilizer in production of green bricks. This work is thus aimed at contributing towards the existing knowledge of manufacture of compressed earth bricks using cementitious waste materials.

1.4 Objectives

There are two main focus of this work.

- *Development of green bricks using sugarcane bagasse ash, stabilized with industrial waste products such as lime and fly ash (Chapter 2-7). The objectives include:*
 1. To investigate the balance of ingredients and the optimization of compressed green brick production.
 2. To review the mechanical and durability properties of compressed bricks using agricultural waste stabilized with fly ash and lime.
 3. To review the application of fly ash, recycled cement and masonry as industrial waste in the construction industry.
 4. To investigate factors that can mitigate GHGs reduction in the construction industry and application of SCB waste in development of green bricks.
 5. To investigate physical, mechanical and durability properties of compressed green bricks using sugarcane bagasse stabilized with lime.

- *Application of agricultural waste (sugarcane bagasse and soft wood) in the development of polypropylene composites (Chapter 8-13). The objectives are as follows:*
 1. To investigate thermal degradation kinetics of sugarcane bagasse cellulose and soft wood cellulose.
 2. To investigate the effect of extraction period on properties of sugarcane bagasse and softwood chips celluloses.
 3. Comparison of alkali treated sugarcane bagasse and softwood cellulose/polypropylene composites.
 4. To investigate the effect of bagasse and soft-wood on mechanical and thermal properties of polypropylene (PP)/polyethylene (PE) blend composites.
 5. To investigate influence of extraction methods on the properties of PP/SCB cellulose composites.

1.5 Thesis layout

This thesis is composed of fifteen chapters:

- Chapter 1: General introduction
- Chapter 2: An overview on the mechanical and durability properties of compressed earth blocks (CEBS) stabilized with fly ash and lime
- Chapter 3: Transforming construction and demolition wastes into aggregates in concrete materials
- Chapter 4: The application of fly ash as industrial waste material in building construction industries
- Chapter 5: Recycled cement and masonry
- Chapter 6: Sustainable green brick using sugarcane bagasse ash waste
- Chapter 7: Mechanical and durability strength of green brick developed using sugarcane bagasse ash waste
- Chapter 8: Thermal degradation kinetics of sugarcane bagasse cellulose and soft wood cellulose

- Chapter 9: The effect of extraction period on properties of sugarcane bagasse and softwood chips celluloses
- Chapter 10: Comparison of alkali treated sugarcane bagasse and softwood cellulose/polypropylene composites.
- Chapter 11: The effect of bagasse and soft-wood on mechanical and thermal properties of PP/PE blend composites
- Chapter 12: Influence of extraction methods on the properties of polypropylene sugarcane bagasse cellulose composites
- Chapter 13: Conclusion and recommendations

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CHAPTER TWO:

OVERVIEW ON THE MECHANICAL AND DURABILITY PROPERTIES OF COMPRESSED EARTH BLOCKS (CEBS) STABILIZED WITH FLY ASH AND LIME

(Article submitted on Asian Journal of Civil Engineering)

AN OVERVIEW ON THE MECHANICAL AND DURABILITY PROPERTIES OF BRICKS STABILIZED WITH FLY ASH AND LIME

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Abstract

Large amounts of solid wastes are being generated every year by industrial and agricultural industries, which leads to environmental and health related concerns. These waste materials are a source of pozzolan materials that can be used in the construction sector to develop cementitious materials that are environmentally friendly and sustainable. This article reviews the mechanical and durability properties of compressed earth bricks (CEBs) manufactured with fly ash and lime as cementitious binders. The CEBs do not need high curing temperature in their production and the release of greenhouse gases is less compared to conventional bricks. The bricks reviewed are not compromising on structural strength and durability properties with regard to their compressive strength, water absorption and densities and can be adopted within the construction sector. The application of various waste materials and the effects of fly ash and lime on the mechanical and durability properties of bricks are reviewed and recommendations are suggested.

Keywords: Compressed Earth bricks, Waste Materials, Fly Ash, Lime, Construction materials

2.1 Introduction

Recently, there is an increasing interest within the construction sector to develop and manufacture materials that are environmentally sustainable. This is due to current global environmental concerns for sustainable development, scarcity of natural resources and emission of GHGs within the sector. In addition, the construction sector consumes high energy input and generates large quantities of waste materials [1-3]. Moreover, the cost of conventional building materials keeps increasing because of high energy needed for production and transportation. These ecological and economic concerns have generated interest in construction techniques that are sustainable while maintaining the material requirements affirmed in the standards [4-6].

Cement and bricks are major materials that are mostly used within the construction and building sector, and will probably remain so in the near future. The current worldwide production of construction bricks is about 1.391 trillion units per year, and the demand is constantly rising [7-9]. The modern methods of brick production are divided into i) conventional firing [10-12], cementing [13-15] and iii) alternative geopolymerization [16-18] categories. The conventional methods are energy intensive, adversely affect the landscape, and generate large quantity of greenhouse gases [8, 19]. Geopolymerization method relies on the chemical reaction of silica and alumina with alkaline solution to form aluminosilicate inorganic bonds. However, the high cost of alkaline solution makes this method uneconomical, unless the construction is located near an alkali reserve [20, 21]. Other alternative types of bricks are made from industrial or agricultural waste materials stabilized with cement or lime and then forming the bricks by compaction [7, 22]. These alternative type referred as compressed earth bricks (CEBs) have gained popularity due to the sector's willingness to adopt and promote sustainable construction materials [3, 23].

The brick industry is one of the most designated sector to absorb solid waste. This is due to the large amount of raw material used and large volume of final products generated in the sector. There are many studies available in the literature that incorporated various waste materials in the production of bricks; for instance, the use of industrial waste such as silica fume [3], sludge [20], granite fines [24], billet scale [25], waste paper mill [26], polystyrene fabric [27], cigarette butts [28], waste marble powder [29], crumbed rubber [30], briquette ash [31], and ceramic waste [32] to develop environment friendly building materials. Agricultural

materials such as flax [1], cotton [26], oil palm [33], rice husk [34], barley straw [35], wheat straw [36], hemp [37], date palm [38], sunflower seed [39], cassava peels [40], coconut fiber [41], sugarcane baggase [42] and banana leaves [43] have also been used (see Table 2.1). The pozzolan and cementitious materials such as fly ash [44] and lime [45] also find extensive application in the manufacturing of bricks [46, 47].

CEBs have over the years showed potential to absorb large quantities of solid waste generated by both industrial and agricultural activities. These bricks are generally manufactured by mixing the earth with chemical stabilizers such as cement, lime and fly ash, and following the existing brick manufacturing practices and standards [48-56]. When a brick is compacted it loses about 30% of its volume due to the mechanical compression of the press driving out air pockets, improving both the compressive strength and water resistance. CEBs are typically produced by a simple manual press or motorized or hydraulic machines (see Figure 2.1) for small and commercial production, respectively [57, 58]. There is a lack of specialized labour in manufacturing process, low usage of energy and abundant availability of raw materials if waste materials are incooperated. The advantages of these bricks is that there is no need for high curing temperatures as it is required for clay, and the release of CO₂ is less compared to fired bricks and cement bricks [59-62]. Despite the promising characteristics of CEBs, the final properties of these bricks are dependent on the raw materials utilised and manufacturing process executed to achieve acceptable compressive strength and water resistance in comparison to mainstream materials like concrete masonry units and fired bricks [63-65].

2.2 Industrial and agricultural waste

The large volume of solid wastes generated by industrial and agricultural sectors has created an interest to incooperate these wastes in developing construction brick materials. The interest is also due to shortage of landfill space, increase volume of unmanaged waste and awareness to protect the environment [66-68]. The use of industrial and agricultural waste as brick materials provide solution to solid waste management and generation of alternative raw materials. The waste materials are otherwise land filled and thus, add to ever escalating cost of disposal [47, 69, 70]. Both industrial and agricultural wastes present advantages from an economic and ecological point of view i.e., the reduction of costs related to use of alternative

raw materials; the reduction in consumption of virgin raw materials; reduction on transport and production energy costs [71-73].

Table 2.1. Agricultural and industrial waste used in the manufacture of bricks

Waste material	Type of brick	Reference
Flax	Compressed earth brick	[1]
Silica fume	Compressed earth brick	[3]
Sludge	Geopolymer	[20]
Granite fines	Cementing	[24]
Billet scale	Compressed	[25]
Waste paper mill	Cementing	[26]
Cotton	Cementing	[26]
Polystyrene fabric	Compressed earth brick	[27]
Cigarette butts	Fired clay	[28]
Waste marble powder	Fired clay	[29]
Crumbed rubber	Cementing	[30]
Briquette ash	Cementing	[31]
Ceramic waste	Fired	[32]
Oil palm	Cementing	[33]
Rice husk	Fired	[34]
Barley straw	Compressed earth brick	[35]
Wheat straw	Fired	[36]
Hemp	Compressed earth brick	[37]
Date palm	Compressed earth brick	[38]

Sunflower seed	Fired	[39]
Cassava peels	Compressed earth brick	[40]
Coconut fiber	Cementing	[41]
Sugarcane baggase	Compressed earth brick	[42]
Banana leaves	Cementing	[43]

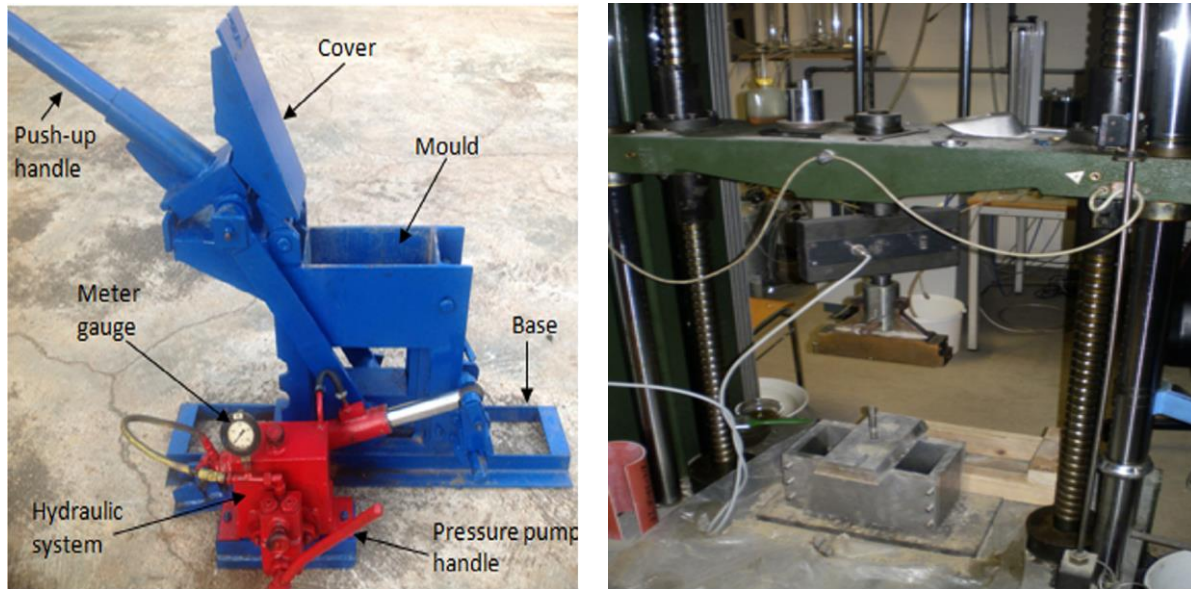


Figure 2.1. (from left to right) Simple manual press and a motorized hydraulic machine (adapted from [71] and [4])

Large volumes of unmanaged solid wastes are generated every year by industrial and agricultural production that leads to environmental and health concerns such as flooding, air pollution and other public health scarce. According to the World Bank statistics on solid waste management, the world cities are currently generating about 1.3 billion tons of solid waste per year and this volume is expected to increase to 2.2 billion tons by the year 2025 [74-76]. In addition, the increase of population and urbanization are also contributing to an increase in the amount of wastes produced. The building construction industry continue to be a viable option for waste disposal and land filling due to its high volume consumption [6, 26, 74). The application of wastes as raw materials offers an attractive alternative to their disposal, and has a number of advantages including low cost, low density, and lower degree of industrialization. The inclusion of wastes in construction materials will reduce the emission of carbon dioxide

and minimize the volume of waste in landfill [77, 78]. Hence, researchers are developing environment friendly, low-cost and lightweight construction materials obtained from these wastes as a response to environmental awareness [79, 80, 81].

2.3 Stabilization

Stabilization is an important step in the manufacture of CEBs in order to achieve desirable mechanical and physical properties such as compressive strength, water resistance, and durability. The three basic methods of stabilization are mechanical, physical and chemical. Mechanical stabilization typically means compaction of the material to change the density and mechanical strength, and decrease its permeability and porosity. Physical stabilization includes texture change and involve heat and electrical treatment. Typical method of chemical stabilization involves the application of cement, lime, fly ash and other hydraulic binders used in the construction industry [82-84]. Cement is the most popular stabilizer due to higher and faster strength gain, durability, availability and ability to obtain acceptable properties with low percentage. These binders typically improve the mechanical strength, erosion resistance and dimensional stability of CEBs [85, 86]. The choice of the stabilizer to be employed is dependent on the type of soil to be stabilized, the purpose for which the stabilized layer will be used, the type of soil quality improvement desired, the required strength and durability of the stabilized layer and cost and environmental conditions [87, 88].

2.3.1 Lime

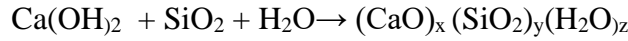
Lime is a by-product of stone crushing operations in limestone quarries and normally presents a serious problem in terms of disposal, pollution, and health hazards because of its fine powder. This white alkaline material consists of calcium oxide, which is obtained by heating limestone, and used in the production of hydrated lime. It performs better with very fine particles such as clay to form a stable pozzolanic material [89-92]. Adding lime to clay soil in the presence of water, several chemical reactions occur, namely, cation-exchange, flocculation and agglomeration, carbonation, and pozzolanic reactions that are similar to the mechanisms of cement. Then, lime causes the pH level to rise which causes the silica and alumina sheets of the clay minerals to partially dissolve and react with calcium to form calcium silicate hydrates (C-S-H) and calcium aluminate hydrates (C-A-H) bonds [82, 85, 93]. The

cementitious products formed in lime reactions are similar to those formed during hydration of OPC. However, in the case of cement, the reactions are mainly hydraulic, while with lime they are pozzolanic. This means that cement needs only water to react and improve in strength; while lime needs water and the addition of a secondary stabiliser or pozzolan, i.e. fly ash. The reaction of lime with water mainly depend on the specific surface and is typically based on calcium and siliceous compounds [94, 95].

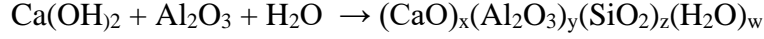
2.3.2 Fly ash

FA is a by-product of the combustion of pulverized coal in thermal power plants and is gathered by electrostatic precipitators from the combustion gases before they are discharged into the atmosphere [96, 97]. FA is generally grey in colour, abrasive, mostly alkaline, and pozzolanic in nature [98-100]. FA pozzolanic activity is attributed to the presence of silica (60–65%), alumina (25–30%), and magnetite, Fe_2O_3 (6–15%), which are similar to the chemical composition of clay [99-101]. The pozzolanic properties of FA makes it useful for the manufacture of cement, building materials concrete, road construction materials and solid bricks [102-104]. FA stabilized bricks typically exhibit excellent physiochemical and mechanical properties including low density, negligible shrinkage, thermal stability, fire and chemical resistance than conventional clay bricks [105, 106].

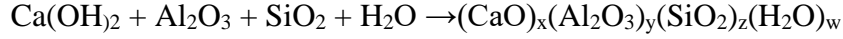
Depending upon the source of the coal being burned, the components of FA vary considerably. In general, the components of FA typically include SiO_2 , Al_2O_3 , CaO and Fe_2O_3 , which exists in the form of amorphous and crystalline oxides or various minerals. FA also contains many other trace metal elements, such as Ti, V, Cr, Mn, Co, As, Sr, Mo, Pb and Hg, and can be classified as Class C and Class F types based on their calcium oxide contents. Class C fly ash has high calcium content, and is mainly generated from the burning of lignite coal sources. Class C FA has a total SiO_2 , Al_2O_3 and Fe_2O_3 content between 50 wt.% and 70 wt.% and CaO content more than 20 wt.%. Class F FA has low calcium content, and is generated from burning anthracite or bituminous coal. Class F FA has a total SiO_2 , Al_2O_3 and Fe_2O_3 content over 70 wt.% and CaO content less than 10% [107, 108]. The major reactions and products of FA during hydration with calcium hydroxide to form C-S-H and C-A-H which are effective in forming dense, durable and resistant cementitious products are as follows:



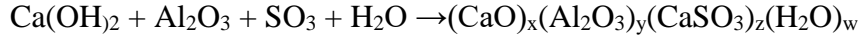
(calcium silicate hydrates [C-S-H])



(calcium aluminate hydrates [C-A-H])



(calcium aluminate silicate hydrates [C-A-S-H])



(calcium aluminate calcium sulfate hydrates)

The amount of water available for the reaction must also be taken into consideration as it is an important factor affecting the type of hydrate products for both C-S-H and C-AS-H systems. The coefficients x , y , z and w can vary over a range of values and depend on the chemical composition of FA [109-111].

2.4 Mechanical and durability properties of CEBs

CEBs are becoming one of the most popular materials for building construction due to their excellent properties such as durability, fire resistance, and weathering resistance and are expected to have a wider usage as masonry of choice in future. Therefore, there is also a necessity of ensuring adequate performance in CEBs with respect to mechanical and physical properties i.e. compressive strength, flexural strength, water absorption and density parameters.

2.4.1 Compressive strength

Compressive strength test is the most common test conducted for quality control, because most of the desirable characteristic properties of blocks are quantitatively related to it. It can be defined as, “the capacity of structure or a material to withstand axial pushing forces which are compressive in nature and also the maximum stress that a material can sustain under crushing load” [7, 24]. The compressive strength in general depends on soil composition, type and amount of stabilizer, method and duration of curing, block density and the compaction pressure used in compressing the brick [12, 53].

The literature cites a few applications of FA-lime compositions used to manufacture masonry blocks (see Table 2.2). Turgut [111] and Chindaprasirt and Pimraksa [109] produced masonry blocks by using lime powder (LP) waste and FA materials compressed under high pressure. Both studies showed that the compressive and flexural strengths of the brick samples increased with an increase in FA content and curing. Chindaprasirt and Pimraksa [109] reported that the application of fine FA results in better compressive strengths as compared to the coarse ash. Da Rocha et al. [69] related an increase in strength with an increase in the amount of amorphous material available, which enhances cementitious reactions in the presence of hydrated lime and water. In another study of FA-lime masonry composites, Cicek et al. [98] and [104] produced light-weight building bricks cured under high pressure steam using a pilot scale autoclave. The results showed that the compressive strength of the bricks increased with an increase in lime content (optimum of 12%) and curing. However, the introduction of sand in the mixture reduced the optimum FA content from 88% to 68% and increased the compressive strength of the specimen. The improved strength by addition of quartz sand was explained by the increased amount of free SiO_2 which is more readily reactive with LP than FA. Patowary et al. [60] also reported that the usage of lime at constant proportion of sand, clay and FA increased the compressive strength of materials.

Several additives such as silica fume (SF) [3], phosphogypsum [80] and stockpiled circulating fluidized bed combustion ash (SCFBCA) [62] were also introduced in the mixture of FA–lime used to make masonry blocks. Turgut [3] observed an increase of compressive and flexural strengths with an increase of SF content (optimum 20%) and curing. The addition of SF increased the amount of C-S-H gel and pozzolanic reactions, resulting in a denser structure. Moreover, visible hairline cracks did not develop in the samples containing SF, unlike in the samples without SF. Kumar [80] also reported an increase in compressive strength with an increase in phosphogypsum content and curing. The author related to the fact that FA acts as a source of reactive silica and alumina to give calcium sulphoaluminate and silicate hydrate, which are responsible for the development of strength. Shen et al. [68] explained that the inclusion of phosphogypsum in the mixture was responsible for high early strength, and increases the pozzolanic reaction between the lime and FA. In another study, Shon et al. [62] evaluated the potential usage of SCFBCA combined with lime and FA to develop CEBs. The results showed that SCFBCA addition reduces the compressive strength, and replacement of SCFBCA by clay increasing the compressive strength of bricks.

Some studies looked at the replacement of lime with additives like waste tyre rubber [79], cement [112], and bagasse ash [58] in FA mixture. Yilmaz and Degirmenci [79] evaluated the possibility of using waste tire rubber (WTR) and FA with OPC as construction materials. The study findings showed that compressive strength decreased by increasing the rubber content while increased by increasing the FA content for all curing periods. The reduction in compressive strength was attributed to the physical properties of the rubber particles and the poor bond between the cement paste and the rubber particles. Kumutha et al. [112] studied the feasibility of using laterite soil to produce stabilized earth blocks with cement and FA. Laterite is highly weathered soil which contains large proportions of iron and aluminium oxides, as well as quartz and other minerals. The results showed that compressive strength increased with an increase in the percentage of laterite with the optimum achieved at 40%. The blocks made with 100% cement were found to have highest strength compared with the blocks made with 70% cement and 30% FA. Furthermore, Prasanth et al. [58] investigated the impact on soil sieves on the compression strength of CEBs produced by different types of soil mixed with lime, FA and bagasse ash. The maximum compression strength was found when cement was used, as compared to lime and FA. The study found that the compression strength of bricks depends on the grain size, with the maximum value noted to the soil that passes through 600 μ sieve, as compared to 1.18mm and 300 μ sieves. Lokeshwari and Jagadish [24], and Rahman et al. [33] attributed the higher compressive strength of blocks with finer particles with high surface area which increases the pozzolanic activity. Likewise, the increase in the percentage of the sandy soil in building material reduces the compressive strength of the brick due to larger particles that led to more voids and higher porosity.

Attempts have also been made to independently utilize lime and cement in the absence of FA in preparation of CEBs. However, utilization of lime compared to cement as a stabilizer in the preparation of CEBs has not found popularity. Nagarag et al. [48] compared the influence of lime and cement in long-term strength of compressed stabilized blocks. The results showed that the compressive strength of cement stabilized brick was higher than lime stabilized compacts, and both increased with additive increase and curing. There was initial high compressive strength in cement prepared blocks as compared to lime due to quick hydration of cement, which helps in formation of cementitious compounds. Similar results were also reported by Reddy and Latha [92] examining the role of clay minerals in the cement and lime stabilised brick. When cement and lime are used as stabilizers, special attention should be paid to the water content in the mixture. High water contents may lead to more porous structure

resulting in low compressive strength. Cement stabilized bricks need curing time of at least three weeks, while lime requires a minimum of four weeks to attain a maximum strength [1, 53].

LP has also been used to produce masonry blocks with different kinds of waste materials, including rice husk ash (RHA) [54], ground granulated blast furnace slag [113], and date palm fibers [85]. Muntohar [54] studied the utilization of sand, lime and RHA in production of CEBs. The compressive and flexural strength of brick were increased by addition of lime and RHA. Moreover, the compressive strength of the dry specimens was also higher than the compressive strength of the wet specimens. Similar behavior of wet and dry compressive strengths was also reported by El-Mahllawy and Kandeel [93] investigating the engineering and mineralogical characteristics of stabilized bricks treated by different curing methods. In other studies, Yu et al. [22], and Oti et al. [113] reported that the compressive strength of stabilized bricks generally increases with curing age, lime and cement content increase. However, when the additive content reached higher volume especially higher than 60%, the block strength typically decreases [83]. Taallah and Guettala [85] reported a decrease of the compressive strengths with an increase in date palm fibers content, in blocks stabilized with lime and filled with untreated and alkali-treated date palm fibers. The decrease in compressive strength was explained by the low fiber/matrix adhesion due to the manufacturing process, specifically the decompression of the block after discharge during its manufacturing process. However, the strengths values of alkali treated fibers were slightly greater than that of CEB filled with untreated fibers. Alkali treatment increases surface roughness resulting in better mechanical bonding and increases the number of possible reaction sites and allows better fiber wetting [56]. Pimraksa and Chindaprasirt [110], and Torkaman et al. [13] also reported a decrease in compressive strength by addition of gypsum, and wood fiber waste respectively. The mixtures with gypsum result in reduction of the compressive strength due to several factors, such as the high water content and high binding speed of gypsum. A high water–gypsum ratio leads to low strength and to low interconnection between the gypsum crystals. Furthermore, if gypsum solidifies fast during the mixing process, the formed gypsum crystals could be interrupted in their connections or they could be destroyed, reducing the strength [1].

Several studies compared the physical and mechanical properties of bricks developed by quarry dust (QD) and clay bricks stabilized with lime and/or FA. Sivagnanaprakash et al. [105] conducted a comparative study of conventional clay brick and QD/FA brick mixed with

cement. The results showed that compressive and flexural strength of QD/FA brick were 15% higher and almost twice than that of clay bricks respectively. Madurwar et al. [76] compared the physico-mechanical properties of commercially burnt clay and FA brick developed by QD, LP and sugarcane baggase ash (SBA–QD–LP) brick. The compressive strength of SBA–QD–L brick was equal to the compressive strength of FA brick and doubles the compressive strength of burnt clay bricks. The superior results of compressive strength than that of conventional clay bricks were also reported by Shakir et al. [25] and Vijayabharathi et al. [103]. Both studies showed that the compressive strength of the quarry developed bricks increased with an increase in curing and additive content. The inclusion of quarry dust in the brick reduces the cost of concrete, save large quantity of natural sand, and reduced the pollution created due to the disposal of the quarry dust on valuable fertile land.

2.4.2 Water absorption

Water absorption is the principle factor that affects the durability of bricks, and provides information about open porosity. It can be defined as “the action of surface tension on capillaries that allows the transport of liquid in porous solids” [7, 22]. Low values of water absorption (below 18%) imply good resistance to the natural environment and acceptable permeability of bricks. However, high values of water absorption (above 18%) can lead to volume changes that result in cracking of the bricks and structural damage in building [7, 28]. Water absorption should also not be more than 17% for bricks developed for areas with severe weathering resistance and 22% for moderate weathering resistance [12]. Water absorption typically increases with the amount of incorporated matter added, depend on the nature of the additive, the particle size and the porosity generated and level off at higher additive content [4, 26].

There is a handful of publication on the literature that investigated water absorption of FA-lime specimens. The water absorption results obtained by Turgut [111] for FA-LP bricks increased with an increase of FA content. The corresponding values obtained were 13.74%, 17.29% and 19.35% for 10%, 20% and 30% FA content respectively. The values obtained were within the allowable range for water absorption of masonry bricks. Chindaprasirt and Pimraksa [109] reported that the use of coarse graded FA provides slightly less connected voids in comparison to those using finer FA, therefore resulting in slightly less water absorption. The results of the water absorption tests bricks in a study by Cicek and Tanrverdi [104] were ranging

from 33% to 40% depending on the sand particle size. The specimens with quartz sand gave higher water absorption values than the specimens with river sand. These water absorption values of the specimens are quite high and general not preferred in construction bricks. The water absorption of FA-Lime-Gypsum (FaL-G) hollow blocks in the investigation by Kumar [80] was obtained between 19.2% and 37.2%. Clearly, the water absorption of the FaL-G hollow blocks is more compared to that of the traditional hollow clay bricks and gypsum seem to have influenced the rate of absorption of the specimen.

The literature showed that other added additives used in FA-lime mixtures have an influence on the water absorption of the resulting specimens. The water absorption of the bricks decreased with an increase of SF in a study by Turgut [3]. The water absorption values were varying between 17.32% and 16.52% g/cm³, and within a range of acceptable values for solid masonry bricks. The water absorption of FA-Lime bricks produced by Shon et al. [62] ranged from 23.2% to 43.5% incorporating SCFBCA. The results showed that water absorption increased with SCFBCA increase, and decrease with a higher amount of sand. The study clearly showed that there was an adverse effect caused by SCFBCA on the mixture of FA-lime. In a study Yilmaz and Degirmenci [79], water absorption decreased with the increase in the size of the rubber particles and increased with the increase in the WTR content. The incorporation of rubber particles in cementitious matrix tends to restrict the water absorption of the composite since the rubber particles do not absorb water. Similar water absorption reductions were also reported Torkaman et al. [13] incorporating RHA and wood fiber particles to the mixture. Kumutha et al. [112] results showed that water absorption increased with an increase in the percentage of laterite with the optimum achieved at 40%. But beyond 40%, the durability properties of the blocks start decreasing.

The blocks produced by Nagarag et al. [48] displayed a continuous reduction in the water absorption with an increase in lime content. The reduction was attributed to the micro-level changes taking place due to the interactions of admixtures with the soil and water to form cementitious products. The values of the water absorption for all the series were around 7–8%. Muntohar [54] observed that the amount of the absorbed water decreases as the lime and RHA ratio increases. The block mixed with clay-sand showed lesser water absorption than the stabilized block with lime and RHA. This phenomenon explained that the stabilized clay-sand mix is more impermeable than the stabilized clay specimens. The water absorption investigated by El-Mahllawy and Kandeel [93] decreased with curing time, and increased with OPC and

lime content addition. Moreover, the specimens cured by moisture method achieved better water absorption values compared to those treated by spray method. Similar results were also reported by Oti et al. [113] who also found that water absorption rate decreased with increasing curing and OPC content. The values of water absorption were between 17-22% for all specimens investigated. Fopposi et al. [45] and Alam et al. [50] explained that lime bricks are less durable and showed lesser greater resistance to rain caused by weathering compared to cement. The more the binders (cement and lime) are added as stabilizers, the low is the absorption of water.

Table 2.2. Studies on production of bricks from waste materials through addition of lime and FA

Waste material	Fillers	Cementing material	Brick size	Curing conditions	Pressure	Reference
SF and FA	n/a	LP	105 × 75 × 225 mm ³	Cured in water at room temperature for 7, 28 and 90 days.	20 MPa	[3]
SCFBCA and FA	Sand and clay	LP and OPC	90 × 65 × 90 mm ³	Cured in air, at room temperature.	55.2 Mpa	[63]
FA	n/a	LP	105 × 150 × 225 mm ³	Cured in air at room temperature for 24hrs. Afterwards the samples were cured in water at 22°C for 7, 28 and 90 days.	20 Mpa	[78]
FA	n/a	LP	200× 200 × 110 mm ³	6 hrs of curing in autoclave at 12 bars of steam temperature.	12 bar	[98]
FA	Sand	LP	45 × 45 × 45 mm ³	6 hrs of curing at room temperature in autoclave at 4Mpa.	20 Mpa	[104]
FA	n/a	OPC and LP	1.5 × 6.5 × 1.0 cm ³	Autoclaved at 130±5 °C and 0.14 MPa for 4hrs.	26 MPa	[109]
FA and Gypsum	n/a	LP	150 ×150 × 150 mm ³	Water curing at room temperature.	n/a	[80]

LP	Soil and sand	OPC		30.5×14.5×10.0 cm ³	Moist curing in shade for 28 days.	n/a	[48]
LP	Soil	OPC		190 × 100 × 20 mm ³	Cured in open air 25±2°C at for 28 days.	n/a	[45]
RH	Sand and soil	LP		230 × 110 × 55 mm ³	Moist cured for 28 days at the room temperature of ±30 °C.	15 MPa	[54]
WFH and RH	Sand	OPC and LP		150 × 150 × 150 mm ³	Cured in open air 25±1°C and 65±5°C for 28 days	n/a	[13]
SCBA	Quarry dust	LP		230 × 110 × 80 mm ³	7 days continuous wet curing and 7 days sun-drying.	20 Mpa	[76]
LP	Soil	OPC		260 × 125 × 80 mm ³	Cured in open air 20±3°C at room temperature for 3 days.	8 Mpa	[22]
Gypsum	Soil	LP		3.5 × 7.5 × 15 cm ³	Autoclaved at 0.14 MPa and 130 °C in a saturated steam environment for 4hrs.	3.5 Mpa	[110]
Oyster shells and FA	n/a	OPC and lime		240 × 115 × 53 mm ³	Cured at 80 ± 2 °C and 95 ± 2% relative humidity for 7 days and then in air at room temperature (24 ± 5 °C) to different testing ages of 14, 28 and 108 days.	5 kN/s	[73]
FA	Soil Aggregates	OPC		19 × 9 × 19 cm ³	Water curing in open air.	n/a	[112]
FA	Quarry dust	OPC		320 × 80 × 150 mm ³	Cured in open air for 28 days.	n/a	[105]
FA and	Quarry dust	OPC		200×90×60 mm ³	Curing at 22 °C at 95% humid	n/a	[25]

2.4.3 The bulk density

The bulk density value is the key indicator used to classify solid bricks and correlates inversely with water absorption capacity [7]. The most common result obtained by the scientific community in this field is a decrease in bulk density with an increase in the additive content [36, 42, 55]. The results showed that adding agricultural wastes into the building structure leads to a decrease of the bulk density and of lightening of the material [39]. Lower density bricks can be advantageous in construction as they reduce the structural dead load, are easier to handle, and can be transported at lower costs. It is acceptable to substitute bricks with a lightweight alternative in most applications, except when a higher strength brick is needed or when a particular look is required for architectural purposes [28, 33].

The effect of lime and FA content on the bricks was investigated by Turgut [111], Chindaprasirt and Pimraksa [109] and El-Mahllawy and Kandeel [93]. The density of FA-lime samples in a study by Turgut [111] increased with an increase in lime content, and decrease with the percentage of FA replacement. The values obtained were lower than the 2.200 kg/m^3 and greater than the 1.500 kg/m^3 , which are in the range of masonry bricks. The increase in the FA/LP ratio also yielded a decrease in the density of the samples because the density of FA is less than that of LP. Similar behavior was reported by Chindaprasirt and Pimraksa [109] who obtained the bulk density in the range of $1.60\text{--}1.66 \text{ kg/m}^3$, the normal range of unfired FA–lime brick bulk density. Furthermore, the bulk density of the unfired stabilized clay specimens prepared by El-Mahllawy and Kandeel [93] increased with lime and cement content increase.

The density of bricks incooperated with SCFBCA ranged between 2.5 g/cm^3 and 2.1 g/cm^3 in a study by Shon et al. [62]. The density of the brick decreased with an increase in SCFBCA content. The results further showed that the replacement of SCFBCA by clay increased the density of bricks. The average density of WTR bricks were in the range of 1000 and 1200 kg/m^3 in a study by Yilmaz and Degirmenci [79]. The density of the mixtures decreased with the increase in the percentage of rubber content. This was related to low specific gravity of rubber compared to the FA it replaces. The density of the bricks obtained by Turgut [3] decreased with an increase with SF, with density values varying between 1.78 and 1.79 g/cm^3 .

In a study by Taallah and Guettala [85], the bulk density of the CEB was reduced with the addition of untreated and alkali treated fibers. The values of bulk density ranged between 1892 kg/m³ and 1910 kg/m³. These values of bulk density were found to be in the interval of CEB values, which are commonly ranging between 1700 kg/m³ and 2200 kg/m³. The density of the block was observed to decrease with wood fiber and LP loadings in a study by Torkaman et al. [13]. The brick produced was about 30% lighter than the conventional concrete block at an optimum of 25 wt% wood fiber and 25 wt% LP. SBA–QD–LP bricks manufactured by Madurwar et al. [76] were having lower density compared to conventional burnt clay and FA bricks. Furthermore, the results by Kumutha et al. [112] showed that density increased with an increase in the percentage of laterite with the optimum achieved at 40%. The average values were in the range shown 1978 kg/m³ to 2261 kg/m³.

2.5 Summary

In this study, the mechanical and durability properties of bricks manufactured by utilizing different wastes, lime and FA were reviewed (see Table 2.2). Utilization of wastes in manufacturing of CEBs was due to an interest in construction industry to develop products and materials that are environment friendly. The main advantage of introducing FA and lime is that they do not require additional processing like aggregates and clay which need extensive crushing, due to their fine form. The bricks reviewed in this study do not need high curing temperatures in their production and emission of greenhouse gases and consumption of energy is less compared to conventional bricks. The materials reviewed in this study are typically stabilized with cement, lime and/or FA to achieve acceptable masonry properties such as compressive strength, water absorption, permeability and prolong durability.

Table 2.3. Comparison of FA/Lime bricks produced by various researchers in this study

Properties	[111]	[62]	[3]	[104]	[109]	[103]
Composition	FA, LP, SF.	FA, LP, SCFBCA , C.	FA, LP	FA, LP, Sand.	FA, LP, OPC.	FA, LP Gypsum.

Compressive strength (MPa)	26.5	34.6	14.7	10.25	62.5	44
Flexural strength (MPa)	4.1	n/a	1.07	n/a	n/a	10.5
Water absorption (%)	16.5	31.3	19.35	40.5	18.5	9
Density (g/cm ³)	1.78	2.44	1.79	1.14	1.66	1.45
Compaction (MPa)	20	55.2	20	20	26	n/a

Note: FA= Fly ash; LP= Lime powder; SF= Silica fume; C= Clay; S= Sand; QD=quarry dust.

The reviewed studies indicate that compressive strength of CEBs depends on type and amount of stabilizer, and block density used in compressing the brick. In addition to this, strength and durability of CEBs depend ash fineness and method used for curing. The compressive and flexural strength values of the samples generally increase with additive content increase and curing. The compressive strength of lime stabilized can be increased by replacement with cement and increasing curing. However, the high water content and poor bond between the FA-lime cement paste and additives may result in reduction in compressive strength. Water absorption is affected by the amount and type of incorporated matter, curing duration and method and the particle size. The review showed that increasing the additive content, compaction pressure and curing, decreased the density of the composites, resulting in lightweight materials. The mixtures using combined FA and lime as a binder were showing the best performance in the compressive strength, density and water absorption tests and can be used to manufacture CEBs (see Table 2.3). It can be observed that the mechanical properties were highly influenced by the addition of different additives.

2.6 Conclusion

The review is very crucial and useful for various stakeholders researching the utilization of industrial and agricultural waste materials to develop sustainable construction material. The CEBs manufacturing process is environment friendly, emits less greenhouse gases and can be produced without firing or with replacement of cement with pozzolan materials. The CEBs properties like compressive strength, density, and water absorption are influenced by the addition of FA, LP and waste materials. In addition, application of waste in CEBs manufacturing contribute to the conservation of raw materials, environmental and health awareness and landfilling challenges. Significant research work exists on masonry blocks incorporating different types of waste material. However, commercial production and application is slow due public misconception and lack of standard guidelines related to waste incooperation. Further research and studies on sustainable development related to waste application are required for commercial application of these bricks.

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CHAPTER THREE:

TRANSFORMING CONSTRUCTION AND DEMOLITION WASTES INTO AGGREGATES IN CONCRETE MATERIALS

(Book Chapter in “Waste-to-Profit” (W-T-P), *Value added products to generate wealth for a sustainable economy Volume 1*, edited by Linda Zikhona Liganiso (**2018**) Chapter 2, 147-160; New York, Nova Science Publishers).

TRANSFORMING CONSTRUCTION AND DEMOLITION WASTES INTO AGGREGATES IN CONCRETE MATERIALS

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Abstract

The construction industry is an important economic sector that has a large environmental impact in terms of large quantities of construction and demolition wastes (C&DW) which are generated. The impact is also due to higher proportion of mineral resources excavated from nature and substantial amount of greenhouse gases generated causing severe ecological challenges. There is also a severe shortage of natural aggregates (NA) for the production of new concrete materials, due to a boom in construction activities that are currently taking place worldwide. Recently, significant efforts have been made to the management of C&DW due to their negative impact on environment, economy and society. Recycling and reuse of C&DW is one such attempt which is done by reintroducing them as recycled aggregates (RA) in new concrete materials. Application of recycled aggregates constitutes a significant step towards a sustainable green construction and creates a new market opportunity to be exploited.

Keywords: Construction and Demolition Wastes; Waste Management; Recycled Aggregates

3.1 Introduction

The construction industry is one of the largest sectors of economy and major solid waste generator around the world associated with large environmental impact, energy consumption and greenhouse gases emissions. A great number of construction, renovation and demolition activities result in huge volumes of construction and demolition wastes (C&DW) that have to be disposed in landfills and managed of, with serious financial and environmental implications [1-4]. Significant efforts have been made to the management of C&DW, due to their weighty impact on environment, economy and society. One way to manage the volume of C&DW is to recycle and reuse C&DW as aggregates for the production of new concrete materials, because of a shortage of good quality natural aggregates (NA) mainly due to a boom in construction activities. Recycled aggregate (RA) offers both a solution to waste disposal problems, enables preservation of NA and creates a new market opportunity to be exploited, and one which is favourable to the environment [5-8].

The growth in the amount of solid waste generated has caused environmental and ecological concerns worldwide due to rapid urbanization, industrial growth, construction booms, and unsustainable consumption patterns. Globally, it is estimated that approximately 10-30% of waste disposed of in landfills originates from construction and demolition activities. However, the amounts differ considerably between countries from Japan (16%), Germany (19%), USA (29%), China (30-40%), Hong Kong (38%), Australia (42%), the UK (50%), and Spain (70%). The C&DW generation statistics are generally not tracked in many countries, and thus, the corresponding predictions seem to vary dramatically [8-10].

Effective C&DW management is considered to be essential for achieving the vision of landfill space conservation, environmental impact awareness, job opportunity creation, and to develop sustainable integrated management programs [11]. Waste reduction to landfill continues to be a challenge despite the adoption of several waste management strategies and legislation. Most legislation outlines the obligations of all the stakeholders involved in construction to implement all necessary measures to generate less C&DW and efficiently manage such wastes in many countries and regions such as the EU countries, the US and Hong Kong [12-13]. In addition, evidence shows that despite increasing waste management research and policies, proportion of construction waste landfilled increases. For instance, proportion of C&DW in UK landfill sites increased from 33% in 2010 to 44% in 2013. This increasing

proportion of C&DW is not necessarily because of increasing construction activities, and suggests that existing strategies for managing construction waste remain largely ineffective and poorly conceptualised [14].

3.2 C&DW generation

C&DW is generated whenever a building, road, bridge, industrial structure or a manufacturing facility is constructed, renovated or demolished. C&DW is typically composed of bricks, wood, plaster, concrete, cement, roofing materials, glass, plastics, metals, insulating materials, carpeting, and other similar materials depending on its origin. However, the lack of knowledge on the composition and other characteristics generally results in the landfilling of vast quantities of these materials without any previous treatment. This happens despite widely available and environmentally effective alternative methods of waste management, such as reuse and recycling [15-17]. The construction industry consumes nearly 40% of raw materials and generates about 35% of waste to landfill across the globe every year. Moreover, construction, demolition and renovation activities generate remarkable levels of solid waste and greenhouse gases that put an overwhelming force on waste management solutions. In Europe, the US and Japan, an estimated 900 million tons (Mt) of C&DW are produced annually. In China, more than 200 Mt of wastes are currently produced due to rapid urbanization and industrialization [18-20].

C&DW also amounts to about 110 Mt in the UK, which is over 60% of national waste generated. Construction related waste is up to 40% in Brazil, 27% in Canada, 44% in Australia, and 25% in Hong Kong. There is an administrative rule which specifies that C&DW containing more than 20% inert material by volume (or 30% by weight) cannot be disposed of at landfills in Hong Kong. This is because C&DW consumes a huge space, produce harmful chemicals such as organic waste materials, and other contaminants, all of which contribute to acidification and toxic impact on the ground and surface water and soil by putrefaction [21-23].

Table 3.1. C&DW proportion in the total amount of waste generated in EU-27 [2, 24, 25]

Country	Total quantity of waste (Mt)	C&DW amount (Mt)	C&DW proportion (%)	C&DW reuse (%)
Austria	56.3	31.4	55.8	n.a
Belgium	48.6	15.4	31.7	n.a
Bulgaria	286.1	1.8	0.6	n.a
Cyprus	1.8	0.4	22.2	n.a
Czech Republic	25.4	10.7	42.1	n.a
Denmark	15.2	5.7	37.5	94.9
Estonia	19.6	1.51	5.6	91.9
Germany	372.2	197.2	53.0	86.3
Greece	68.6	6.8	9.9	5
Finland	81.8	24.5	30.0	26
France	345.0	253.0	73.3	45
Hungary	20.1	5.2	25.9	16
Ireland	23.6	n.a.	n.a.	80
Italy	179.0	69.7	38.9	9
Latvia	1.5	0.0	0.8	46
Lithuania	6.8	0.4	5.9	60
Luxembourg	9.6	8.3	86.5	46
Malta	1.5	1.1	73.3	0
Netherlands	99.6	59.5	59.7	98.1
Poland	140.3	6.9	4.9	28
Portugal	36.5	8.1	22.2	5
Romania	189.3	0.3	0.2	0
Slovenia	5.0	1.4	28.0	53
Slovakia	11.5	1.3	11.3	0
Spain	149.3	44.9	30.1	14
Sweden	86.2	3.3	3.8	0
United Kingdom	334.1	101.0	30.2	75.1

3.3 C&DW utilisation

The most common practice for utilisation of C&DW includes substitution of virgin aggregates in construction of roads, parking areas, pavements, and embankments, thereby contributing to potential savings of natural resources and landfill capacity [18]. Utilization of C&DW is a well-established end-of-life strategy in many European countries (see Table 3.1); utilisation rates over 80% are reached in the Netherlands (98.1%), Denmark (94.9%), Germany (86.3%), Estonia (91.9%), and United Kingdom have rates upward of 75%. In many other countries around the world, including Greece, Hungary and Spain, Hong Kong, Brazil, and Turkey, the rates are under 16% due to lack of recycling plants. In Portugal, the low recycling rates are mainly due to the abundance of natural aggregates of very good quality and the lack of technical regulations for the use of recycled aggregates. When looking at the situation in USA, 73.5% of the C&DW is recovered with a 35% recycling rate for the mixed C&DW, 85% for the bulk aggregate, and over 99% for the reclaimed asphalt pavement [10, 13, 26, 27]. In China, less than 10% of C&DW is recycled while the majority of waste is disposed via landfilling or directly sent to dumping sites without any environmental protection measures. Waste dumping sites included gravel pits, farmland, abandoned residential land, borrow pits, river side, and low lying areas. In fact, there is no national or local regulation to guide the disposal of C&DW via landfilling. To make things worse, there are no specific regulations on sorting and safe treatment measures for non-inert or hazardous C&DW debris, such as the asbestos, brominated flame retardant thermal insulation material, and lead paint debris used in old buildings [6, 28].

3.4 C&DW structure

C&DW consists mostly of diverse non-hazardous, uncontaminated materials that may contain residual hazardous materials which need to be separated and processed or disposed of, as enforced by national regulations [2]. In general, C&DW can be divided into two categories i.e., inert materials and non-inert materials. The inert materials (e.g., concrete, bricks and sand) are the components that hardly participate in chemical reactions under common circumstances, and believed to have little damage to the environment. The non-inert materials are readily involved in chemical reactions, such as asbestos, plastics, glass, wood, and particulate matter. Theoretically, C&DW have high potentials of recycling and high economic value, 80% of

which could be reused. However, massive C&DW is disposed via simple landfilling or dumping, which would become a potential risk that threatens ecological security and sustainable development [11, 29, 30].

3.5 Waste management of C&DW

Governments worldwide are becoming increasingly informed about environmental issues caused by construction activities and drafting policies accordingly. Waste reduction, reuse and recycling are the most effective elements in waste management resulting in natural resources conservation, landfill space reduction, raw materials reduction, air and water pollution control and potential job creation. There are however, some constraints on reusing and recycling waste materials; the materials must fulfil some engineering requirements in terms of physical and compositional properties and they should not contain excessive amounts of harmful components which might cause environmental and ecological concerns [24, 31-33].

The recycling of C&DW has the following advantages: i) minimization of the resource consumption, which is causing serious environmental problems in many parts of the world; ii) it minimizes energy consumption and CO₂ emissions generated from crushing quarry rocks for aggregates production, mitigating the global warming iii) it prevents illegal deposits and landfilling of the fine fraction of C&DW and iv) utilization of waste which would otherwise be lost to landfill sites, and job creation. However, the main barriers for recycling C&DW are: lack of information related to the sources of waste generation, poor planning of waste treatment facilities, and lack of incentives, which have reduced the demand for recycle rates and the interest in developing business from the recycling sector [6, 10, 14].

The reuse of C&DW materials reduces the use of natural resources, and avoids the landfill of inert materials coming from the construction industry [27]. Unlike recycling, materials reuse involves the use of the materials with little or no alteration to its physical state, and without any change to its chemical constituents. In the construction industry, material re-use has been adopted as a means of diverting own waste as well as domestic and other industrial waste from landfill. Construction demolition materials have been widely reused for land reclamation, road surfacing, and as constituents of concrete aggregates [14].

The other important aspects in order to properly manage C&DW are the classification and quantification processes, for example, concretes, bricks, tiles or ceramics are the most representative components and should be properly classified and quantified before they are reused or recycled [34]. Quantifying C&DW generation is regarded as a prerequisite for the implementation of successful waste management, and key to precisely determine the type and amount of C&DW waste to be expected from the various construction processes. Quantification helps to forecast the C&DW production in a particular project. It can help to adjust the material purchase schedule, to arrange the stockpiling on-site and to determine the potential waste recycling benefit and disposal cost. Quantification and classification information can assist decision-makers in making more realistic policies and efficient integrated management solutions [29, 35].

3.6 Recycled Aggregates

The use of RA from treated C&DW as a replacement of NA has been considered one of the most efficient methods to add value to these materials and provides an alternative mean to the dependence of construction industry on NA sources. The production of RA from C&DW is a common practice for several European countries including the USA, Australia, and Japan. RA applications are also creating new market opportunities which are favourable to the environment. For instance, Germany, UK, Netherlands, France, and USA produced approximately 286 Mt RA in total in 2010 [36-38]. RA is generated from demolished buildings, airport runways, bridge supports, and even concrete roadbeds. Depending on their original waste material, RA may contain concrete, ceramic, bricks, tiles, metals and other miscellaneous materials such as glass, wood, paper, and plastics [39-41].

Recycled aggregates are mainly limited to low-value added applications such as roadbed materials because of their inferior qualities compared with NA. This is because of a layer of residual cement mortar coated on the surface of the RA. The porous nature of this residual mortar introduces undesirable properties including higher water absorption, lower strength, lower specific gravity, lower density and higher crushing value. The porosity of RA is also much higher than those of NA. This negatively affects the workability and mechanical properties of the concrete made from RA, resulting in higher creep and shrinkage than those of concrete using NA (see Table 3.2) [20, 37, 39, 41, 42]. However, it is still difficult to overcome the barriers that prevent the wider use of RA in construction due to technical limitations related

to their applications and properties. Acceptability of RA is also hampered due to a poor image associated with recycling activity, cost of recycling operations, and lack of confidence in a finished product made from recycled material. The solution should be to impose fee charges on landfill to encourage constructors to divert more waste into recycling and reuse [7, 16, 25].

3.7 Recycled aggregates demand

The global demand for construction of quality aggregates is expected to be more than 51 billion metric tons by 2019. The mining, processing, and transport operations for such a large quantity of aggregates will consume a huge amount of energy and adversely affect the landscape, environment and ecology. Though the demand for aggregates is entirely based upon region and economic growth, the availability of good aggregates is getting scarce as the demand is increasing. For example, in Tanzania, the aggregate demand is approximated to be 2 tons per capita annually, 11 tonnes per capita in New Zealand, 5 tonnes per capita in the UK and 8 tonnes per capita in the US. China with the largest population in the world needs more construction activities and requires the corresponding infrastructure to supplement its rapid economic development, urbanization and rising standards of living. All these factors imply a growing demand for aggregates, leading to the risk on the environment, economics, human health impact and therefore increasing the attractiveness of turning C&DW into recycled aggregate [1, 15, 43].

3.8 Recycled aggregates use in construction

Leivaet et al. [35] analyzed the possibility of recycling C&DW as RA into building materials with fire and sound absorption resistance. The new construction material developed by C&DW showed low toxicity level, high fire resistance, good heat insulation, and acoustic insulation properties with respect to standard concrete similar to that of other construction materials. The blocks manufactured showed no significant problems regarding leaching and were in accordance with general and specific regulations from waste recycling in construction materials. Sabalet et al. [43] investigated the possibility of recycling C&DW collected at different construction sites into building material to produce a concrete block. The results showed that the blocks produced with 100% RA were weaker than those with NA. However, the results also showed that there is a possibility of recycling the C&DW into building material because 85% of the tested concrete block specimens from recycled aggregates achieved a

compressive strength of 7 N/mm², which is defined as the minimum required load bearing capacity in Tanzania.

Table 3.2. Comparison between RA and NA [5]

Property	NA	RA	RA versus NA
Size	Depends on the crushing process. Breakage may occur for softer rocks. Fines may be generated by friction between rough grains.	Depends on the crushing process. Breakage and fines generation are expected during compaction<comma> disaggregating the grains.	Higher breakage is expected for RA.
Shape and roughness	Depends on the type of rock and its cleavage plans.	Depends on the original material and crushing process. Less adhered old mortar helps to create smoother surfaces.	Depends on the crushing process and type of materials. May be more difficult to attain homogeneity for RA.
Particle density and porosity	Depends on the type of rock	Depends on size and materials and their proportions present in the particles	Larger density expected for NA. Larger porosity expected for RA<comma> but not homogeneous.
Particle crushing strength	Depends on size and type of rock	Depends on size and materials and their proportions present in the particles.	Smaller strength is expected for RA<comma> but is not homogeneous. Smaller strength for masonry fragments than for concrete particles. Lower resistance is expected when adhered cement paste is present.
Particle stiffness	Depends on size and on the type of rock.	Depends on size and on the materials and their proportions present in the particles.	High stiffness is expected for RCA aggregates of structural concrete. Smaller stiffness is expected in masonry particles than for concrete fragments
Water retention properties	Depends on the type of rock and amount of accessible pores.	Depends on the materials and their proportions present in the particles.	Larger water absorption is expected for RA due to the presence of adhered cement paste but the value decreases significantly for bituminous<comma> glass or vitrified masonry.
Frost resistance<comma> soundness and toughness	Depends on the type of rock.	Depends on the materials and their proportions present in the particles.	Toughness depends mainly on the number of cracks and defects in the grains. They are present in both types of aggregates but more in large fragments of rocks. Freeze–thaw resistance and soundness depend on the accessible porosity and size of pores.

Contreras et al. [44] reused construction and demolition waste as substitute of natural aggregate to produce bricks incooperating lime and cement as binding agent. The study found that the C&DW composition (50% ceramic, 20% concrete and 30% mortar) is a good

proportion to produce bricks with better mechanical properties which are established by standards. The results showed that it is possible to produce low-cost bricks with excellent physical properties using C&DW as aggregate and lime or cement as additive. Mataret et al. [45] determined the properties of concrete building blocks manufactured using recycled aggregates from concrete recycling. The results showed that application of recycled aggregates with addition of cement allowed the production of concrete blocks with compressive strengths comparable to those obtained on concrete blocks made exclusively of natural aggregates. The authors concluded that using recycled aggregates without natural aggregates in the manufacture of concrete blocks is not economical due to the necessity of a high rate of cement addition in order to obtain the required compressive strength. Arenas et al. [34] developed fly ash-based geopolymeric concrete with construction and demolition wastes as aggregates in acoustic barriers using sodium silicate and sodium hydroxide as alkali activators. The C&DW used as aggregate in geopolymeric porous concretes presented better mechanical and acoustic properties than the crushed-granite aggregates in geopolymeric concretes when the size distribution of both aggregates were similar. The study results allowed the reuse of any type of C&DW as aggregate, regardless of their variety of chemical composition, but always maintaining the particle size distribution in order to keep the sound absorbing properties.

Brandes et al. [46] studied the effects of recycled concrete aggregates (RCA) in precast/prestressed concrete applications. The results showed that RCA from precast concrete performed better than RCA from returned ready-mix concrete. The usage of RCA did not have a significant effect on the rate of concrete compression strength gain with time; however, the stiffness gain of concrete with time were somewhat more varied than the results for the strength gain. Bravo et al. [47] investigated the durability performance of concrete with recycled aggregates from construction and demolition waste plants from various locations in Portugal. Different concrete mixed with RA were evaluated to understand the influence of RA composition on the characteristics of the concrete produced. The durability performance of the study showed that the use of RA is highly detrimental in terms of its durability, especially when fine RA are used. The authors concluded that the use of fine RA causes a significant drop in concrete quality for all properties analyzed, relative to the use of coarse RA. Güneyisi et al. [38] investigated the rheological properties of self-compacting concrete (SCC) using RCA as both coarse and fine aggregates. The self-compactability characteristics of the concretes are remarkably improved by the replacement levels of coarse and fine aggregates used in SCC

mixtures. The results demonstrated that the shear thickening behavior of SCC was reduced by the use of RCA compared to the NA. The specific gravity values of RCA were lower than the natural aggregates due to the porous old cement mortar adhered to RCA. The 50% coarse aggregates replacement level increased the slump flow diameters whereas the higher utilization provided less increase in the flowability due to the more angular shape of coarse RCA.

Shahidan et al. [40] investigated the influence of aggregates of varying sizes on the compressive strength, split tensile and water absorption of concrete materials treated with epoxy resin to reduce the water absorption. The results showed that RA had comparable tensile strength and compressive strength with normal concrete material. The optimum results for the tensile test, compressive strength test and water absorption test were obtained for the aggregates measuring 10mm, as compared to larger size aggregates. Pedro et al. [48] evaluated the capacity of producing concrete with a pre-established performance incorporating RCA from different sources. The results showed that there were no significant differences between aggregates from controlled sources and those from precast in mechanical and durability terms. Kabir et al. [8] explored the potential usage of construction waste for the development of sustainable construction materials from various sources: lab-tested concrete, reclaimed C&DW concrete waste, and regular aggregate from the market. The bulk density of the C&DW concrete was higher than the market product, whereas the number of voids was less. The absorption value for the recycled aggregate was much higher than that of the similar virgin aggregate, most likely due to the cement mortar attached to the particles. The results confirmed potential usage of construction waste for the development of sustainable construction materials. Ossa et al. [49] recycled construction and demolition waste aggregates to create hot asphalt mixtures for urban paved roads which can be an alternative to mitigate the environmental problems derived from the inadequate administration and disposal of this type of waste. The results indicated that the use of C&DW aggregates in percentages of up to 20% for paving urban roads is feasible. Therefore, the results obtained suggested that the incorporation of recycled C&DW aggregate in asphalt concrete is a feasible alternative for the construction of urban paved roads, which contributed to the sustainable development and reduction natural resources.

3.9 Conclusion

Construction and demolition waste is a major problem in both developing and developed countries, and a key generator of total solid waste production in the world. The quantity of this waste has caused serious environmental, economic and ecological concerns due to rapid urbanization, industrial growth, construction booms, and unsustainable raw materials consumption. Significant efforts have been made to the management and utilisation of C&DW to prevent the adverse effects of the materials consumption and waste generation by promoting the reuse and recycle of materials, instead of conventional dumping and landfilling. There is however a critical shortage and great demand for good quality natural aggregates worldwide mainly due to a boom in construction activities.

Recycled aggregates can be used as a replacement of natural aggregates in concrete production despite having lower density and higher water absorption than natural aggregates. They can be used to manufacture conventional concretes and building materials with good performance if they are added in the proper amounts and properly managed. The quality of recycled aggregates is strictly related to their content of porous and low strength phases, and specifically to the patches of cement that remain attached to the surface of natural aggregates. Use of recycled aggregates in concrete provides a promising solution to the problem of C&DW management and constitutes a significant step towards a more sustainable and environmentally friendly society.

Therefore, effective C&DW management is crucial for achieving the visions of landfill space conservation, environmental impact awareness, job opportunity creation, and to develop sustainable integrated management solutions. All the stakeholders involved in construction should implement all necessary legislations and policies to efficiently manage C&DW. Waste reduction, reuse and recycling which are the key elements in waste management resulting in natural resources conservation and landfill space reduction should be prioritised. In addition, classification and quantification processes of C&DW management should be strongly monitored and implemented in most countries due to lack of data on solid waste generation.

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CHAPTER FOUR:

THE APPLICATION OF FLY ASH AS INDUSTRIAL WASTE MATERIAL IN BUILDING CONSTRUCTION INDUSTRIES

(Book Chapter in “Waste-to-Profit” (W-T-P), *Value added products to generate wealth for a sustainable economy Volume 1*, edited by Linda Zikhona Liganiso (**2018**) Chapter 9, 147-160; New York, Nova Science Publishers).

THE APPLICATION OF FLY ASH AS INDUSTRIAL WASTE MATERIAL IN BUILDING CONSTRUCTION INDUSTRIES

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Abstract

The increasing interest in sustainable awareness has created the need for the construction industry to develop construction materials with the appropriate utilization of wastes in a manner that meets our economic, social and cultural needs. The interest is also due to ever increasing scarcity of landfill space, accumulation of unmanaged wastes and awareness to protect the environment. The use of wastes as brick material is a sustainable solution to solid waste management and provides alternative raw materials and an additional source of revenue. The application of industrial wastes such as fly ash to develop construction bricks offers an attractive alternative to its disposal, and has a number of advantages including low cost, abundant raw material availability and lower degree of industrialization. Fly ash is a by-product of the combustion of pulverized coal in thermal power plants gathered by electrostatic precipitators from the combustion gases before they are discharged into the atmosphere. This waste is a potential source of material with pozzolanic reactivity and its application in brick manufacturing will minimize the volume of waste in the landfill sites. For these reasons, this chapter will focus on the utilization of fly ash on developing environmentally friendly, low-cost and lightweight bricks as a response to environmental and economic concerns. The current worldwide production of construction bricks is about 1.391 trillion units per year, and the demand for bricks is constantly rising.

Keywords: Fly Ash; Construction Materials; Waste and Bricks

4.1 Introduction

The promotion of sustainable developments has pressured industries, including the construction sector to develop products and materials that are environmentally friendly. This interest is due to current global environmental concerns for sustainable development, impoverishment of natural resources and the rapid pace of technological advancement within the building sector. The construction building process requires high energy input and causes a wide range of quantifiable environmental side effects including greenhouse gas emissions, large amounts of water use, as well as solid and liquid waste production [1, 2]. In addition, the cost of conventional building materials keeps increasing because of the energy that is required for production, and high transportation cost from the factories to the construction sites. These environmental and economic concerns have generated interest in construction techniques that are more sustainable while maintaining the material requirements affirmed in the standards [3, 4].

Bricks have been a major construction and building material for a long time. The dried-clay bricks were first used in 8000 BC and the fired clay bricks used as early as 4500 BC. The current worldwide production of construction bricks is about 1.391 trillion units per year, and the demand for bricks is constantly rising. Various types of bricks are used in construction. The most common are conventional firing, and cementing [5-7]. The geopolymers bricks are also used as an alternative bricks due to their low calcination temperatures needed, eco-friendliness, and low cost [8, 9]. Other types of bricks are mostly “unburnt” building bricks that are made from industrial or agricultural by-products stabilized with cement or lime and then forming the bricks by compaction. These types are also referred as CEBs and have gained popularity in recent times due to various reasons such as high cost of conventional bricks and willingness to promote sustainable construction materials [10].

The current annual production of FA worldwide, a by-product from coal based thermal power plant is about 500 million tons. Thus, the disposal of this large amount of FA has become a serious environmental and ecological concern due to large area of land required and toxicity associated with heavy metal leached to groundwater [11-13]. Because of these ecological challenges and the high costs of management associated with disposal of these materials, significant research has been devoted to find beneficial uses for this waste in the construction field. FA utilization as main raw material in the manufacture of bricks will not only create

economical opportunities for its utilization but will also help in environmental pollution control. These bricks can be extensively used in all building constructional activities similar to that of common fired clay bricks [14, 15].

4.2 Construction bricks

Construction bricks are an important and prevalent building material that is used in a wide range of construction projects. The current world-wide production of construction bricks is about 1,391 trillion units per year, and the demand for bricks continues to rise. The conventional bricks are either produced from natural clay cured by high-temperature kiln firing or produced from OPC using the cementing method [7, 16, 17]. Bricks are also manufactured by alternative method known as geopolymerization. Other types of bricks are mostly “unburnt” building bricks commonly known as compressed earth bricks which are made from industrial by-products or solid waste materials and not fired at high temperatures [5, 8].

The brick industry is the most indicated technological activity sector to absorb solid waste due to the large quantity of raw material used by the sector as well as by the large volume of final products in construction. Hence, recycling the wastes in the bricks production appears to be a viable solution not only to environmental pollution but also economical option to manufacture green bricks [9, 17, 18]. Attempts have been made to incorporate waste in the production of bricks; for instance, the use of industrial waste such as silica fume [2], granite fines [19], billet scale [20], cigarette butts [21], waste marble powder [22], crumbed rubber [23], briquette ash [24], and ceramic waste [25] to develop environmentally friendly building materials have been utilized. Agricultural wastes such as sugarcane bagasse [3], palm oil fuel ash [26], rice husk [27], barley straw [28], wheat straw [29], sunflower seed [30], cassava peels [31], and coconut fiber [32] have also been used. The cementitious binder fly ash [13] and lime [33] also find extensive application in the manufacturing of construction bricks. In this respect, for the development of bricks with waste materials, further research and development is needed not only on the technical, economic and environmental features but also on standardization, government policy and public education related to waste reusing [22].

4.2.1 Fired clay bricks

One of the most used construction materials are fired clay bricks which are manufactured from clay with high temperature kiln firing [27]. Worldwide, approximately 1500 billion bricks valued at approximately US\$ 70.8 billion are produced every year which involves more than 4000 million tons of clay extraction processed by more than 100,000 large-scale kilns with fixed chimneys [16, 34]. In Pakistan, being one of the country commonly using clay bricks in construction activities, approximately 12,000 brick kilns are present with yearly production of 59 billion [7]. These bricks are associated with ecological concerns related to their manufacturing process. Quarrying operations for obtaining the clay are energy intensive, adversely affect the landscape, environmentally harmful and generate high level of wastes. The high temperature kiln firing not only consumes significant amount of energy, but releases large quantity of greenhouse gases which are a key contributing factor in global warming and climate change [5]. It is also noted that there is a shortage of clay in many parts of the world. To protect clay resource and the environment, some countries such as China have started to limit the use of bricks made from clay [6]. However, the utilisation of waste materials in clay bricks usually has a positive effect on the resulting properties; such as lightweight bricks with improved shrinkage, porosity, thermal properties, and strength [21].

4.2.2 Cementing bricks

OPC concrete brick is the most commonly used material in the construction industry and its global demand is projected to increase steeply until 2050 due to its mechanical performance, durability, shape adaptability and availability of raw precursors [35, 36]. The method for producing bricks through OPC cementing is based on hydration reactions to form mainly C-S-H and C-A-H phases contributing to strength [17, 26]. The manufacturing process of this method is energy intensive, and results in the emission of greenhouse gases. However, the production of OPC brick cementing does not need kiln firing since it relies on cementing material from OPC or other added cementing materials [9, 37]. The production of 1 kg of OPC consumes approximately 1.5 kWh of energy and releases about 1 kg of CO₂ to the atmosphere and worldwide production of OPC is responsible for about 7% of all CO₂ generated. In addition, quarrying operations for producing the aggregates are energy intensive, adversely affect the landscape, and release high level of waste materials [5, 6].

4.2.3 Geopolymer bricks

Geopolymerization is a technology that relies on the chemical reaction of amorphous silica and alumina rich solids with alkaline solution to form amorphous to semi-crystalline aluminosilicate inorganic polymer or geopolymers. Compared to OPC, they exhibit some superior engineering properties, low emission of CO₂ and widen the possibilities to recycle waste to useful products, especially building materials that can contribute to environmental benefits [9, 38]. The use of alkali silicate in addition to alkali hydroxide is known to accelerate the activation of aluminosilicates and improve physicochemical properties but makes the material more expensive than cementitious ones. Given the cost of alkali silicate and energy, as well as the negative impact of high temperature, it would be advantageous to have access to a local source of amorphous silica that could replace alkali silicate in the synthesis of geopolymer, followed by heat treatment at moderate temperatures [8]. Furthermore, application of geopolymer technology provides a new green solution to the utilization of FA, avoiding its negative impact on the environment and ecology. The alumina and silica in FA can be activated with alkali to form geopolymer. Moreover, the toxic trace metal elements can be trapped and fixed in the geopolymer structure [39].

4.2.4 Unfired bricks

Over the past seventy years, the use of unfired bricks has developed and has been increasingly used by following existing masonry practices, especially in developing countries including China, India and a number of African and South American countries [10, 40]. The chemical admixtures such as lime, cement, and/or fly ash are widely used as a mean of chemically transforming unstable soils into structurally sound construction foundation. In clay-bearing soils, those stabilizers induce a textural change in greater ease of compaction and handling as well as moderate improvements in the resulting strength [2, 41, 42]. The application of unfired bricks represents sustainable environmentally-friendly materials alternative to conventional bricks due to low usage of energy, and lack of specialized labour in manufacturing processes [43]. There is also no need for high curing temperatures as it is required for fired clay bricks, and the release of carbon dioxide into the atmosphere is 80% less. The optimum degree of compaction or compression level can be achieved with hydraulic equipment or hand levers [14]. Furthermore, the government of Vietnam is currently promoting the gradual replacement of conventionally fired clay bricks supplies with unfired bricks as a measure to reduce the

mining of clay, which is considered a non-renewable natural resource. The government now officially encourages the use of unfired bricks in all types of construction projects regardless of funding source, urban/rural setting, or number of stories [5].

4.3 Construction bricks demand

Since a high demand has been placed on building bricks especially in the last decade owing to the increasing population, urbanisation, and industrialization, there is generally a mismatch between demand and supply management of these materials in both the developed and developing countries [44, 45]. The construction sector remains one of the largest employment generating industries in most developing countries. However, the overall brick productivity of developing countries in Asia is far behind than that of most developed countries. With China's rapid construction development, there is a large demand for building materials, which brings about serious environmental problems simultaneously. In China, there are about 110,000 factories with an annual output of about 1000 billion pieces, consuming up to 60 million tons of coal and destroying more than 1.5 million (247,105 acres) of farmland (see Table 4.1) [10, 46]. In India, the country is currently on the verge of large-scale urbanization hence facing a huge demand for building houses and thus for the materials to build them. The Indian brick industry stands the second largest producer in the world, next to China with more than 100,000 operating units producing about 200 billion bricks annually [34, 46, 47]. In Vietnam, there are about 1,300 brick industries that are owned by both private and public sectors with an annual production of about 25 billion pieces. According to official government estimates, the demand in Vietnam for bricks is expected to be 42 billion units in 2020. On the other hand, there are about 10,000 brick manufacturing units in Sri Lanka with ranging capacities of 15,000 to 24,000 bricks per kiln. This sector employs about 60,000 people producing over 800 million brick per annum [5, 46].

4.4 Fly ash

4.4.1 Chemical composition and physical properties

FA is a by-product of the combustion of pulverized coal in thermal power plants and gathered by electrostatic precipitators from the combustion gases before they are discharged into the atmosphere. FA contain significant amounts of silicon dioxide (SiO_2), aluminium oxide

(Al₂O₃), iron oxide (Fe₂O₃), calcium oxide (CaO), and magnesium oxide (MgO), which exist in the form of amorphous and crystalline oxides or various minerals. FA also contains many other trace metal elements, such as Ti, V, Cr, Mn, Co, As, Sr, Mo, Pb and Hg. However, the actual composition varies from plant to plant depending on the coal burned and the type of burner employed [49-51]. FA can be classified as Class C and Class F types based on their calcium oxide contents. Class C fly ash has high calcium content, and is mainly generated from the burning of lignite coal sources. Class C FA has a total SiO₂, Al₂O₃ and Fe₂O₃ content between 50 wt.% and 70 wt.% and CaO content more than 20 wt.% respectively. Class F FA has low calcium content, and is generated from burning anthracite or bituminous coal. Class F FA has a total SiO₂, Al₂O₃ and Fe₂O₃ content over 70 wt.% and CaO content less than 10% [2, 39]. Physical properties of FA are summarized in Table 2.

Table 4.1. Global brick production [48]

Country	Production	Billion Per annum
China	66.6%	1000
India	13.33%	200
Pakistan	3.00%	45
Vietnam	0.40%	25
Bangladesh	1.13%	17
Nepal	0.40%	7
Rest of Asia	0.47%	6
Total Asia	86.67%	13,00
UK	53.00%	8
US	37.00%	4
Australia	13.00%	2
Rest of World	12.40%	186
Total	100.00%	1,500

4.4.2 Fly ash utilization: management of waste

The present day utilization of FA on worldwide basis varied widely due to substantial amount of FA that is still disposed of in landfills and/or lagoons at a significant cost to the utilizing companies [11]. The pozzolanic properties of the FA, including its lime binding capacity makes it useful for the manufacture of cement, building materials concrete and concrete-admixed products in many developed countries. The chemical composition of FA like

high percentage of silica (60–65%), alumina (25–30%), magnetite (6–15%) enables its use for the synthesis of zeolite, alum, and precipitated silica. The other important physicochemical characteristics of FA, such as bulk density, particle size, porosity, water holding capacity, and surface area makes it suitable for low-cost adsorbent for gas and water treatment and is used as filler in polymers [13]. In future, large-scale application of this waste product may be possible for recovery of heavy metals, reclamation of wasteland, and floriculture. This waste has found application in ceramic, paint and enamel manufacturing. However, these applications are not sufficient for the complete utilization of the fly ash generated. The remainder is waste, and has to be discharged into ash ponds, lagoons or landfills.

Table 4.2. Physical properties of FA [52]

Parameters	Fly Ash
Density	2.17 g/cm ³
Bulk density	1.26 g/cm ³
Moisture content	2%
Particle shape	Spherical/Irregular
Colour	Grey
pH	6.0-10.0
Specific gravity	1.66-2.55
Grain size distribution	Sandy silt to loam
Porosity	45%-55%
Water holding capacity	45%-60%
Electrical conductivity (dS/m)	(dS/m) 0.15-0.45

In India, about 10% ash is currently utilized in various segments include cement, asbestos-cement products and concrete manufacturing industries, land development, road embankment, reclamation of coal mine, ash dyke construction, soil amender and as source of micro and macro nutrients in agriculture and only about 3% ash is utilised in other construction industry [13, 49, 52]. The ash is further used for the manufacture of bricks, cellular concrete blocks, insulating bricks, and road and dam constructions. In South Africa, approximately 1.2 million tons of ash per year is sold to, amongst others, the cement industry where the ash is used as a cement extender and to enhance the quality and economy of concrete. Approximately 250 000

tons of ash from Lethabo Power Station, for instance, was exported to Lesotho for the Katse Dam project [53].

4.4.3 Fly ash utilization in brick manufacturing

FA utilization as main raw material in the manufacture of bricks will not only create opportunities for its useful disposal but also help in environmental pollution control. FA bricks are typically made of FA, lime, cement, waste materials, aggregates and sand amongst other materials. These bricks can be extensively used in all building constructional activities similar to that of common burnt clay bricks. They are comparatively lighter in weight and stronger than common clay bricks [15, 45]. FA bricks exhibits excellent compressive and flexural strength including low density, low water absorption, negligible shrinkage, and thermal stability (see Table 4.3) [54]. In some countries, the use of FA has been promoted and even regulated by the governments through legislations. For example, the clay brick industry has to incorporate at least 25% FA in the brick making mixture if the clay brick facility is within 100 km from a coal power generation plant in India. The use of FA in construction materials and concrete production is relatively high in countries such as Germany, the Netherlands, United Kingdom, United States and China [55].

In the manufacture of bricks, FA can be used as an alternative material to clay. This is due to the fact that both clay and FA are not much different in respect of their chemical composition. FA can be used either with clay as part replacement or in combination with other materials like sand, lime, gypsum and cement to produce a substitute to conventional clay bricks. Shetkar et al.[12] addressed the technology of making compressed bricks with low-calcium FA as the base material. The FaL-G bricks were mixed with quarry dust and sand as fine aggregates, and prepared without the use of conventional cement. The experimental results revealed that the FaL-G bricks are suitable to be used for the construction of masonry structures. The bricks produced were economical and having higher strength than conventional burnt clay bricks in structural, and functional aspects. Rajkumar et al. [47] performed a feasibility study on using FaL-G bricks mixed with quarry dust as an alternative building material. The results showed that the compressive strength of FaL-G bricks was much higher than the conventional burnt clay bricks. The water absorption property of FaL-G brick was reduced compared to the water absorption of burnt clay bricks (20%). The bricks were economically viable and can be used to solve unmanaged FA and quarry dust quantity. Another investigation on FaL-G bricks was

conducted by Kumar et al. [56]. The results they obtained showed that the FaL-G hollow blocks prepared have a potential as a replacement for conventional hollow burnt clay bricks and hollow concrete blocks due to their mechanical strength [56]. The cementitious binder with FA content in between 20% and 40% showed low water absorption and better compressive strength. The FaL-G brick produced will reduce the dead weight and material handling cost in multi-storied constructions and impart thermal insulation to the buildings.

The bricks of high strength possessing good quality can be produced from FA using lime as a binder. The FA lime building bricks can be used in all types of brick masonry. Chindaprarsit et al. [57] prepared fly ash–lime granule unfired bricks from a mixture of FA and lime with hydrothermal treatment at temperature of $130 \pm 5^\circ\text{C}$ and pressure of 0.14 MPa. The results revealed that the strengths of unfired bricks increase in fineness of FA due to the formation of new hydrated phases. The main advantage of utilization of granule was the ability to increase the pozzolanic reaction of FA through moisture retention in the granule. The results thus indicated that fly ash–lime granule offers a good alternative in using fly ash for making environmental friendly unfired brick. Turgut [58] utilized LP waste and class-C FA to produce a composite brick material without the addition of ordinary Portland cement. LP was mixed with the FA at levels of 10, 20 and 30% by volume in the samples, wetted and compressed under high pressure in a steel mould. The test results satisfied the requirements in the standards for load-bearing and non-loadbearing concrete masonry units. The thermal conductivities results were lower than those obtained for granite, marble and sandstone. The results further showed that the utilization of LP and FA may be used for the production of a new type of economical masonry block. In another study by the same author, Turgut [2] manufactured masonry building bricks using limestone powder, class C fly ash, and silica fume without Portland cement. The compressive and flexural strengths, density, water absorption, porosity and thermal conductivity of the bricks produced were comparable to that of clay bricks. The estimated production cost of the brick was also cheaper than that of traditional fired clay brick. Cicek et al. [55, 59] examined the production of light-weight and high thermal insulating bricks made out of the FA and lime produced through steam curing in an autoclave to determine the optimum conditions for mechanically sound bricks. The optimum raw material composition was found to be a mixture of 68% FA, 20% sand and 12% hydrated lime. The findings obtained suggested that FA/lime bricks produced can be an alternative product to aerated cellular concrete, with heat conductivity superior to that of clay bricks. The suggested production route

of FA bricks would be capable to compete with aerated cellular concrete process due to its relatively low cost of raw materials and production process.

The utilization of both agricultural and industrial waste as additives in the production of construction quality bricks is also a common practise in FA bricks manufacturing. Shakir et al. [20] produced the bricks using FA, QD, and billet scale (BS) along with cement and water, and then forming the bricks within moulds without applying pressure over them. The approach utilized neither uses clay nor shale nor requires high pressure on mould or high temperature kiln firing. The mechanical properties and durability results obtained showed the best performance indicating that the bricks developed can be used as an alternative to conventional bricks in the building sector. Koseuglu et al. [50] utilized FA and a liquid waste as additives in the production of construction bricks in order to eliminate these wastes by permanently fixing the heavy metals in the structure of the fired bricks. The results showed that simultaneous addition of FA and acidic waste into clay increases the mechanical strength of the fired bricks while lowering the water retention capacity compared to those observed with the standard bricks which contained no additives. Sivagnanaprakash et al. [54] developed the fly ash brick composed of FA, QD, and cement. The results showed that the compressive and flexural strength of brick were higher than that of clay bricks. The brick also possessed high impact resistance, durability and low water absorption. The brick was found to be an eco-friendly material protecting the environment through conservation of topsoil, reduction in carbon emissions, and utilization of waste products like FA and QD. Yilmaz et al. [60] evaluated the feasibility of utilizing FA and rubber waste with Portland cement as a composite material for masonry applications. The results showed that composite materials containing 10% Portland cement, 70% and 60% FA and 20% and 30% tire rubber particles have sufficient strength for masonry applications. The authors concluded that utilization of FA and rubber tire wastes in the construction industry may provide an opportunity to recycle these wastes and achieve a solution to environmental and economic problems. Lingling et al. [61] manufactured fired clay bricks by replacing clay with FA in high volume ratio. The results obtained indicated that the properties of fired bricks improved by using pulverized FA. The fired bricks with high volume ratio of FA were of high compressive strength, low water absorption, no cracking due to lime, no frost and high resistance to frost-melting. The study concluded that FA used as raw material replacement of clay to make fired bricks is an effectively measure of saving land and decreasing pollution.

Table 4.3. Comparison of FA/Lime bricks produced by various researchers

Properties	[2]	[14]	[57]	[58]	[59]	[62]
Composition	FA, LP, SF	FA, LP, SCFBCA,C	FA, LP, OPC	FA, LP	FA,LP, Sand	FA, LP Gypsum
Compressive strength (MPa)	26.5	34.6	62.5	14.7	10.25	44
Flexural strength (MPa)	4.1	n/a	n/a	1.07	n/a	10.5
Water absorption (%)	16.5	31.3	18.5	19.35	40.5	9
Density (g/cm ³)	1.78	2.44	1.66	1.79	1.14	1.45
Compaction (MPa)	20	55.2	26	20	20	n/a

FA= Fly ash, LP= Lime powder, SF= Silica fume, C= Clay, S= Sand, QD=quarry dust, SCFBCA = Stockpiled circulating fluidized bed combustion ashes

4.5 Sustainable development in the construction industry

Large quantities of unmanaged solid wastes are generated every year by industrial and agricultural production that leads to environmental and health concerns such as flooding, air pollution and other public health scarce. In addition, the growth of population, increasing urbanization, rising standards of living due to technological innovations are also contributing to an increase in the quantity of solid wastes generated [4, 63]. These increased accumulations of unmanaged waste emphasize the need for the construction industry to develop environmentally friendly materials in a sustainable manner. It is estimated that construction sector contribution accounts for 30% of raw material extraction, 25% of solid waste, 25% of water use and 12% of land exploitation [16]. Thus, for achieving the goal of sustainable development in the construction industry, alternative building materials such as demolition waste, municipal solid waste, agricultural waste and industrial waste (i.e., FA) should be practised in building materials [64, 65]. The utilization of these wastes presents advantages from an economic and ecological point of view. i.e., the reduction of costs related to use of alternative raw materials; the reduction in consumption of virgin raw materials; reduction on transport and production energy costs [66]. Governments worldwide have responded to the need to reduce waste with regulation and legislation that respond to the challenges of environmental sustainability, and resource depletion. These legislations based on waste management and recycling are adopted by many countries and presents an opportunity to save resources, reduce the amount of waste disposed at landfills, and create employment opportunities. Waste management services rely heavily on landfills for the disposal of waste,

as over 90% of all South Africa's waste is disposed of at landfill sites [67-69]. The best way to tackle waste-related problems is to prevent waste generation, and to favour waste minimization, recovery, recycling and reuse as discussed in waste management hierarchy [70].

4.5.1 Waste management hierarchy

The waste management hierarchy provides a technical approach to the understanding of waste and is South Africa's adopted approach to waste management. Management of waste through the hierarchy approach is a recognised model for the prioritisation of waste management options, throughout the world. It offers a holistic approach to management of waste materials, and provides a systematic method for waste management during the potential waste product lifecycle addressing in turn waste avoidance, reduction, re-use, recycling, recovery, treatment, and safe disposal as a last resort. The model is further entrenched in the legal framework governing waste in the country and linked to national policy action plans on waste management. The global trend in the economic transition taking place in the waste sector is a shift from a collection and disposal dominated waste hierarchy to a waste minimisation and recycling dominated hierarchy as illustrated in Figure 4.1.

This approach towards waste management emphasizes the following key elements:

- **Avoidance and Reduction:** Products and materials must be designed in a manner that minimizes their waste components or in a manner that reduces the natural material quantities used and potential toxicity of waste generated during the production, and after use;
- **Re-use:** Materials can be used for similar or different purposes without changing form or properties. This approach seeks to re-use a product when it reaches the end of its life span. In this way, it becomes input for new products and materials;
- **Recycle:** This involves separating materials from the waste stream and processing them as products or raw materials. The first elements of the waste management hierarchy are the foundation of the cradle-to-cradle waste management approach;
- **Recovery:** Reclaiming particular components or materials or using the waste as a fuel; where the quantity of waste cannot be further reduced, they will be discharged to landfill. Landfill is presently considered the most affordable way to manage the final stage of waste.

- **Treatment and disposal:** This is a ‘last resort’ within the waste hierarchy. Treatment refers to any process that is designed to minimize the environmental impact of waste by changing the physical properties of waste or separating out and destroying toxic components of waste. Disposal refers specifically to the depositing or burial of waste onto, or into land; and,
- **Legal:** Processing, treatment, and disposal of waste must take place in accordance with the principles of environmental justice and equitable access to environmental services [67, 70, 71].

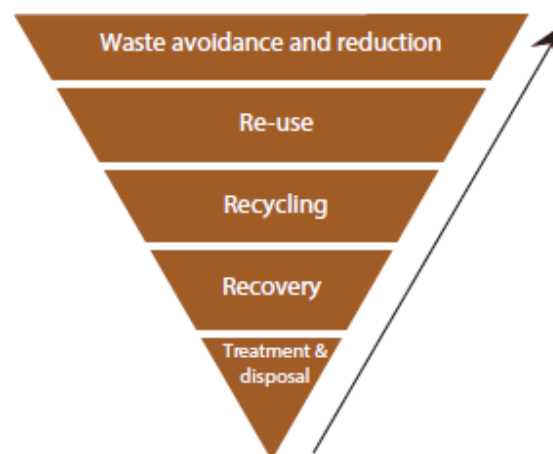


Figure 4.1. Waste hierarchy [71].

4.6 Conclusion

The disposal, management and proper utilization of FA has become a major concern for the scientists and environmentalists due to the promotion of sustainable development in the construction sector. This concern is due to current global environmental concerns for sustainable development, impoverishment of natural resources and the rapid pace of technological advancement within the building sector. FA is one of the coal combustion products of coal burning power plants and it contains substantial amounts of potentially harmful constituents to the environment. Large quantities of unmanaged FA waste are still landfilled and disposed in lagoon/ditches affecting water, soil, and air because of the mineral composition and morphology of the material, a practise that need to be discouraged. The conventional method of bricks making has caused serious environmental contamination represented by the enormous emissions of greenhouse gases and drastic economical expenditures. Recycling of FA into the bricks production remain a viable solution not only to

environmental pollution to unmanaged waste but also economical option to manufacture green bricks

FA utilization as main raw material in the manufacture of bricks will not only create economic opportunities for its utilization but also help in environmental pollution control. FA bricks have shown the potential to develop energy efficient and cost effective sustainable construction materials along with enhanced thermomechanical behaviour compared to conventional clay bricks. The main advantage of these bricks is that they can be extensively used in all building constructional activities similar to that of common fired clay bricks. The ultimate goal to tackle waste-related problems is to prevent waste generation, and to favour waste minimization, recovery, recycling and reuse as depicted in waste management hierarchy. Thus, for achieving the goal of sustainable development in the construction industry, alternative building materials such as demolition waste, municipal solid waste, agricultural waste and industrial waste should be practised in building materials.

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CHAPTER FIVE:

RECYCLED CEMENT AND MASONRY

(Book Chapter in “Waste-to-Profit” (W-T-P), *Circular economy in the construction industry for a sustainable future. Volume 2*, edited by L.Z. Linganiso and T.E. Motaung (2019) Chapter 2, 33-49; New York, Nova Science Publishers).

RECYCLED CEMENT AND MASONRY

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Abstract

The emerging sustainable development in the construction industry requires the recycling of waste materials to reduce the negative environmental impact of construction activities. Accumulation and management of construction and demolition waste (C&DW) is also becoming a major environmental and economical concern in many developing countries. Huge volumes of waste generated end up piled on landfill sites or illegally dumped, posing serious health and ecological problems. In the construction industry, recycling of waste concrete and masonry as recycled concrete aggregates (RCA) has become an important aspect due to the continued increase of construction wastes and depletion of natural aggregates. The application of RCA in new concrete mixes will conserve the natural resources and reduce the environment impact of concrete manufacturing. The utilization of recycled masonry and concrete from C&DW will also be an economical option in designing green buildings. These materials will further solve the problematic issues of waste disposal, land filling and illegal dumping.

Keywords: Sustainable Development, Construction and Demolition waste (C&DW), Recycled masonry

5.1 Introduction

Sustainable development and environmental awareness are emerging rapidly as key global indicators as climate change becomes an increasingly serious concern for the future [1]. Sustainable development is defined as a development that meets the needs of the present without compromising the ability of future generations to meet their own needs. The reduction of pollution, conservation of natural resource, and savings of energy have also generated an interest within the construction industry, while not compromising the needs of the future generations [2].

With the rapid urbanization and industrialization in major cities around the world, the huge volumes of C&DW are continuously rising. These generated waste constitute a major portion of total solid waste production worldwide, and raises concerns on sustainable environment [3–5]. According to the Eurostat, the total amount of waste generated in the EU in 2012, was over 2.5 billion tonnes, 34% of which resulting from construction and demolition activities. The problem is also widespread throughout the United States, with C&DW accounting for an estimated value of 35 to 40 percent of the total municipal solid waste (MSW) generated [6].

The usual method of C&DW management in the recent past was dumping it illegally or dispose it in landfills, since most countries have no specific treatment plan for these materials. In this treatment, wide, landfill sites of C&DW were made, consuming space that is becoming increasingly scarce, and posing environmental problems [2, 7, 8]. Recently, waste management is the main principle of every government through different policies and frameworks to promote environmental awareness and sustainable development. The main priority of waste management is in finding ways to recycle, reduce and reuse existing materials. Waste management is also aimed at preserving the environment, reduce expenses related to waste management and protect the natural resources [1, 5, 9].

5.2 Concrete and masonry

Concrete is the most consumed construction materials in the world. As the population around the world continues to grow, so does the demand for concrete material. The primary ingredients of a concrete mixture are sand, cement, aggregates, and water [10, 11]. Concrete production is energy intensive, contribute to all environmental impacts, mainly because of

cement production. Manufacturing of cement is responsible for 5–7% of total global CO₂ generated causing about 80% of energy consumption and about 90% of global warming. This is a result of high energy consumption and calcination of limestone during the clinker production [2, 12, 13].

Masonry are considered the second most widely used material after concrete. Masonry blocks are widely used in the developing world for urban development as countries industrialize. They are the most popular building materials for construction due to their wide availability, cost effectiveness, durability, thermal comfort and adequate resistance to weathering [1, 14]. Developing masonry products that use alternative binders could produce a significant savings in cement, reducing carbon emissions and sustainable construction activities [12].

The consumption of concrete in the world is around three tons per capita per year, which is equivalent to 17.5 billion tons for seven billion populations in the world. To make this huge volumes of concrete, 10 billion tons of sand and rocks, 2.62 billion tons of cement, 13.12 billion tons of aggregate, 1.75 billion tons of water are necessary [2, 15]. This implies high usage of raw resources, significant emissions of CO₂ due to the aggregate manufacturing process, high-energy consumption of cement manufacturing, and the creation of large volumes of concrete wastes. Despite this, the use of concrete will continue to grow in the coming decades, mostly in developing countries [16, 17].

5.3 C&DW

The Construction industries generate a large amount of waste, in quantities that are increasing with economic and social development. Construction waste is defined as the “by product generated and removed from construction, renovation and demolition sites of buildings and civil engineering structures”. The waste produced predominantly comprises of concrete and brick masonry waste. For example, in the Netherlands, almost 90% of C&DW materials consist of masonry and concrete [16, 18]. The Australian state of South Australia generated 1.8 million tons of C&DW in 2011, of that 89% was masonry and concrete materials. C&DW generation is perceived as one of the main worrisome negative effects of the construction industry together with natural resources depletion, high-energy consumption, and emissions of greenhouses gases [19, 20].

It is estimated that over 11 billion tons of C&DW are produced annually worldwide, in which concrete and masonry waste accounts for about 50-70% [21, 22]. In Europe, the quantity of waste produced annually is estimated at 180 million tons of which 40% comes from C&DW dominated by concrete and masonry waste [2, 23]. In the US, the construction waste produced from building demolition alone is estimated to be 170 million tons per year and about 77 million tons for Japan was reported. Given that China and India are now producing and using over 50% of the world's concrete, their waste generation will also be significant as development continues [10, 24, 25].

Lately, the use and application of C&DW as aggregates have been recognized as an attractive approach to reduce the environmental impact and economic cost of operations for sustainable construction practices [26, 27]. C&DW have been applied as road base material due to the potential to consume much more demolition waste and prevent landfills or separately reused to produce new building materials. Currently, in the Netherlands and China, over 80% of the material used for road bases is recycled C&DW, which mainly composed of recycled masonry and concrete [18, 28]. Therefore, the recycling of C&DW is important, because it minimizes the consumption of natural resources, which require considerable energy in their extraction and grinding processes, and is an eco-friendly alternative source of aggregates for the production of concrete [13].

5.4 Recycling of concrete and masonry

Recently, environmental awareness, conservation of natural resources and sustainable development have become significant factors towards sustainability in the construction industry [3, 21]. On the other hand, production and utilization of concrete is rapidly increasing, which results in increased consumption of natural aggregate as the largest concrete component. For example, two billion tons of aggregates are produced and consumed each year in the United States. Production is expected to increase to more than 2.5 billion tons per year by the year 2020 [24]. Recycling of waste concrete and masonry has become an important issue worldwide due to the continued increase of construction wastes and natural aggregates depletion. Also, the growing global construction activities urge to find sustainable resources to replace natural materials for the production of concrete [29].

Concrete as a widely used building material produces a large amount of waste, which has the potential for recycling and reuse. Recycling and crushing of waste concrete to produce RCA for the production of new concrete is one of the common methods to achieve an environmentally-friendly concrete. This reduces the consumption of natural resources as well as the disposal of waste concrete in landfills, and presents a sustainable solution to the problems of the depletion of natural aggregate deposits [30-32]. By recycling of demolished concrete, 20% of normal aggregates can be saved. It is also estimated that in the next 10 years, the amount of demolished concrete will be increased to 7.5–12.5 billion tons [15].

As economical sources of natural aggregates become scarce and sustainable construction practices become increasingly popular, the recycling of masonry have become a viable solution in sustainable construction initiatives. The general practice of recycling masonry waste is to crush and use them as aggregates in the manufacture of RCA [8, 13]. The study of these aggregates is not recent, after Second World War in England and Germany, rubble from damaged brick buildings or destroyed by bombs was crushed and recycled for use in new concrete construction. The utilization of masonry waste as an aggregate in concrete would have a positive effect on preservation of natural resources and sustainable building that would be cost effective [5, 17, 26].

5.4.1 Environmental benefits of RCA

The recycling and reuse of concrete and masonry wastes as RCA is trending due to its outstanding potential to significantly reduce construction waste landfill volume and pollution, as well as many advantages. Recycling of RCA minimise the consumption of natural aggregates, which then leads to reduction in energy and pollution with considerable advantages to the environment. In addition, there is no need for opening of new mining areas for quarrying operations as well as the energy consumption associated with emissions of greenhouse gases [11, 21, 22]. Using waste concrete as RCA could save about 60% of limestone resources and reduce CO₂ emissions by about 15%-20%. Therefore, the utilization of RCA has a great significance in saving resources, protecting the environment and realizing the sustainable development of the construction industry [29].

5.4.2 Economic benefits of SCA

In addition to the environmental benefits, using RCA can also be economical, depending on the situation and local conditions. The cost of using C&DW or sending waste to landfill can often be greater than the cost of new material or sorting and selling concrete waste. Some US states have estimated savings of up to 50%-60% from using RCA compared to new materials. Recycling is also less costly than disposal in Germany, Holland and Denmark. In countries without recycling infrastructure and abundant natural resources, recycling can however be more expensive [10, 11]. In addition, government authorities in Europe, Japan and the U.S. have begun to encourage the usage of RCA either through direct demands or indirectly (e.g., increasing tipping fees for landfilling concrete wastes) [21].

5.4.3 Limitations of SCA

The idea of using recycled concrete aggregate in new concrete production appears to be an effective utilization of concrete waste. However, concrete recycling faces various difficulties such as the inferior quality of recycled aggregates, energy consumption and increased labour cost [21, 30]. RCA concrete is often associated with lower durability and compromised mechanical properties because the properties of RCA are normally different compared to natural aggregates and the source of old concrete is usually unknown [3, 27]. The use of RCAs in structural concrete is also limited due to inferior durability properties, which are attributed to high porosity, permeability, shrinkage and low mechanical properties [17, 33].



Figure 5.1. A pictorial example of recycled concrete aggregate sample with attached mortar paste [20].

RCA tends to have decreased specific gravity, and increased abrasion loss and greater water demand compared to natural aggregates (NA), since they contain the mortar paste from the original concrete. Generally, RCA has lower compressive strength, less stiffness, increased creep, and increased shrinkage as compared to NA concrete [12, 32]. Recycled masonry aggregates are lighter than normal aggregates, and use of concrete that incorporates brick aggregates can significantly reduce the self-weight of a structure. This aggregates have the potential to enhance the fire performance of concrete due to their thermal expansion and conductivity properties. Recycled masonry aggregates have characteristics, such as high absorption and angular particle shapes that are often seen as undesirable. Inclusion of the mortar fraction with recycled brick masonry brings about concerns with absorption and inclusion of impurities, as well as abrasion resistance and weak zones due to adhered mortar. These characteristics must be considered in the development of concrete mixture designs [26].

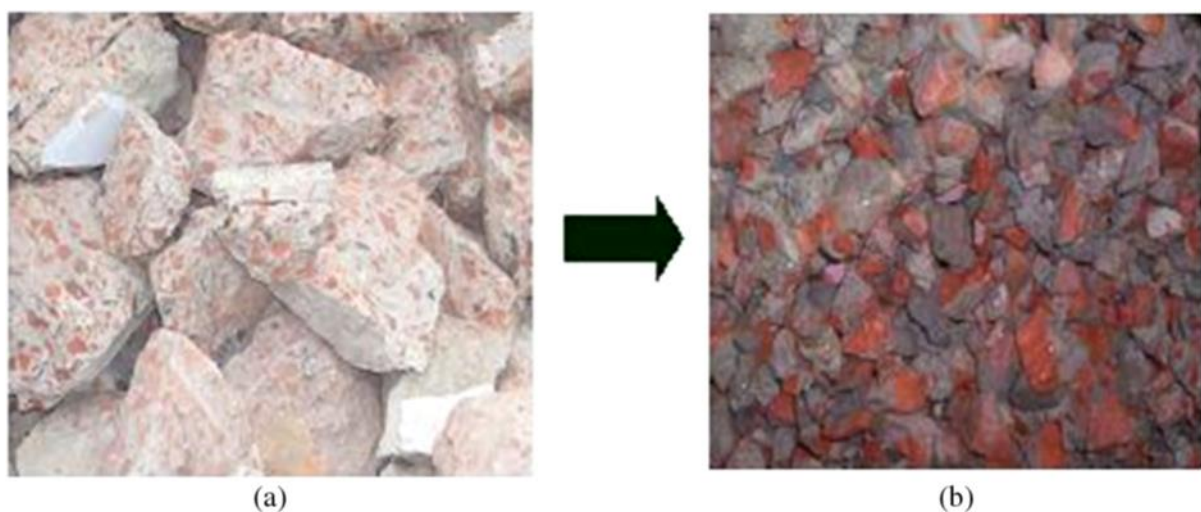


Figure 5.2. Demolished concrete block and recycled aggregates [15].

5.4.4 Applications of RCA

The application of RCA in construction works has become a subject of priority throughout many places around the world. Aggregates produced using recycled masonry have been used in new construction applications in several locations worldwide, but often in non-structural or non-critical applications [8, 10]. Even though RCA has significant economic and environmental benefits, its use has so far been limited in construction industry because of the concerns regarding the inferior quality of recycled aggregate compared to that of natural

aggregate. In the US, application of RCA has been limited to non-structural applications such as sidewalks and road base even though the quality of the material is significantly higher than what is required in these applications [16]. US estimates for concrete recycling indicate that 50% of the material is recycled for raw materials. Of the recycled product, 68% is used as road aggregate and the remainder is used for new concrete, asphalt hot mixes and low value products like general filling. In Canada, RCA is mainly used to produce more concrete, but often applied as a road base. In 2007, 13 million tons of recycled concrete aggregate was used in the construction of buildings, roads, sewers, and water mains [10, 32].

5.4.5 RCA utilization per country

With the generation of huge amounts of masonry and concrete waste and the depletion of natural aggregate resources, the use of RCA as a renewable resource in concrete has been promoted and applied widely in many countries [33]. In Europe, RCA accounts for an estimated 6-8% of aggregate use, with substantial differences between countries. The greatest users are the United Kingdom, the Netherlands, Belgium, Switzerland and Germany. In 2000 an estimated 5% of aggregate in the US was recycled. In Australia, RCA has been the most common C&DW used in concrete production. About five million tons of recycled concrete and masonry are available in Australian markets, principally in Melbourne and Sydney, of which 500,000 tonnes is RCA [10]. In the US, nearly 100 highway paving projects by the mid-1990s had incorporated RCA in concrete for pavements [11].

5.4.6 RCA and masonry studies

Significant research on recycling concrete that have been made to date demonstrated that RAC can be a feasible and environmentally friendly alternative to conventional natural aggregate concrete for the use in construction applications. Mechanical properties and durability of recycled aggregates concrete were investigated by Radonjanin et al. [2] and Debieb et al. [23] who showed lower strength and durability of recycled aggregates concrete than that of natural aggregates concrete. The reduction in strength and durability depended mainly on the quantity of recycled aggregates, the strength of the original concrete composition and types of mineral admixtures previously used. However, physical and mechanical properties of these materials can be improved by applying and adding chemical admixtures and relatively small amount of highly reactive mineral supplements. In another study by Silva et al. [13], the

mechanical properties of concrete were reduced with the incorporation of the recycled coarse aggregate due to the poor adhesion between the old mortar and aggregate; however, the results fall within acceptable mechanical values.

Several experimental studies have also found comparable mechanical and physical properties between RCA and conventional materials. Jayasinghe et al. [1] experimentally found that the compressive and flexural strength of the RCA composite material was comparable with that of conventional counterpart. A mix proportion was selected based on the standard testing for grading of aggregate mixed with cement stabilized rammed earth. The load bearing properties of the composite material was satisfactory for general masonry applications involving single and two storey houses. Matara and El Dalati [34] showed that using recycled aggregates with the addition of cement allows the production of concrete blocks with compressive strengths comparable to those obtained on concrete blocks made exclusively of natural aggregates. Seara-Paz et al. [35] recommended that recycled concretes are able to fulfil strength and serviceability requirements similarly to conventional reinforced concrete. However, in order to encourage its use as structural concrete, it is important to be able to use existing design methods. In another study by Gholampour and Ozbakkaloglu [16], the RCA prepared with full replacement of natural aggregates with recycled concrete aggregates having a higher parent concrete strength, exhibited time-dependent and long-term mechanical properties that were similar than those of companion natural aggregate concretes.

Some studies showed the production and application of RCA in new construction materials follows the idea of sustainable development in protecting the environment by reduction of CO₂ emissions, depletion of natural resources and consumption of energy. A study by Verian et al. [11] revealed that the use of coarse RA obtained from the C&DW reduced the greenhouse gases footprints up to 65% and saved up to 58% of the energy consumption. The greenhouse gases assessment in a study by Yap et al. [3] showed that the CO₂ emission of 100% RCA mix was lower than the control mix. A significant CO₂ emission reduction of 24% was achieved in the 100% RCA mix with considerably high waste content of 87% by weight and 73% by volume. The authors concluded that when RCA are crushed and re-used in the construction, CO₂ emissions resulting from transportation to/from a recycling plant will be minimized. Experimental studies are also outlined in the literature with respect to recycling of masonry waste. These studies are oriented towards the production of concrete mixes with brick masonry waste being used as partial replacement for aggregates and cement. Tara et al. [26] developed

recycled brick masonry aggregate concrete mixtures using crushed recycled brick masonry from a demolition site as a replacement for conventional coarse aggregate. The results showed that concrete mixtures exhibited acceptable workability and exhibited mechanical properties comparable to that of structural and pavement-grade containing conventional coarse aggregates. Recycled brick masonry aggregate (RBMA) can be used as a 100% replacement for conventional coarse aggregate in concrete that exhibits acceptable mechanical properties for use in structural and pavement elements. Mueller et al. [36] manufactured lightweight aggregates from recycled masonry rubble in their studies. The results indicated that these concrete achieved a comparable performance to lightweight concretes produced with conventional expanded clay. The authors concluded that industrial production of lightweight aggregates from recycled masonry rubble could provide the opportunity to replace natural pumice and expanded clays and reduce the use of natural resources.



Figure 5.3. Residue of masonry [13].

Kumar et al. [14] evaluated the strength and water absorption characteristics of cement stabilized masonry block (CSMB) units made with brick powder (BP) and fine recycled concrete aggregate (FRCA). The average values of wet compressive strength of CSMB units at 28 days were found to meet the minimum requirement of 3.5MPa. The percentage of water absorption was found to be higher, but, still within permissible limit of 18% by weight. The average dry density also met the minimum requirement of 1750kg/m³. Jiménez et al. [37] evaluated the performance of fresh and hardened masonry mortar manufactured using fine recycled aggregate from ceramic partition wall rubble. The results showed that replacement ratios of up to 40% by volume did not significantly affected the properties of fresh and hardened mortar, with the exception of density and workability. Therefore, they concluded that the use of fine recycled aggregates in masonry mortar manufacturing could be a viable alternative that

would help increase the recycling rate of C&DW and support sustainable development in the building sector.

Dahmen et al. [12] evaluated the environmental impacts of two emergent masonry blocks designed to serve as sustainable replacements for conventional masonry blocks. The results showed that these blocks offered the same strength and durability as conventional structural concrete blocks. The two emergent masonry blocks offered 42-46% less embodied carbon than conventional concrete block dependent on stabilisation. In another study by Schwerin et al. [8], an application of recycled masonry in construction materials concrete resulted to recycled brick masonry aggregate which can be used as a 100% replacement for conventional coarse aggregate in concrete that exhibits acceptable mechanical properties for use in structural and pavement elements, including satisfactory performance in some durability tests.

5.5 Legislation, waste management and challenges

Governments worldwide have responded to the need to reduce waste with regulation and legislation that respond to the challenges of environmental sustainability, greenhouse gas emissions, natural resource depletion, and a market for building materials and products derived from the C&DW [38]. Successful C&DW management can only take place if the appropriate policy and framework conditions are in place. To achieve this, a dialogue between public and private sectors in the field of C&DW management is of the greatest importance [39].

5.5.1 Legislation

In Australia, they have adopted the “*The National Waste Policy: less waste, more resources*” which is a collaborative approach that aims to avoid the generation of waste, reduce the amount of waste for disposal, manage waste as a resource and ensure that waste treatment, disposal, recovery and re-use is undertaken in a safe, scientific and environmentally-sound manner [38]. In the US, much of the recycling activity has been driven by the Federal Highway Administration’s endorsement of recycled concrete as aggregate in road sub-base and base. The American Society for Testing and Materials (ASTM) and the American Association of State Highway and Transportation Officials have accepted recycled concrete as a source of aggregate in new concrete. Some elements of state policy include, for example, allowing higher material costs if recycled materials are used in government contracts [40]. In Europe, waste

policy is aimed at waste recovery. Landfill is increasingly discouraged and some countries have banned C&DW from landfill. As part of a Strategy on the Prevention and Recycling of Waste, a Revised Waste Framework Directive has been adopted. The European Union is also pursuing a sustainable use of natural resources strategy through Construction & Demolition Waste Management Protocol. In the UK, an Aggregates Levy and landfill tax is used to encourage use of recycled aggregate and includes grants for recycling infrastructure projects, investigates ways to reduce regulatory barriers and undertakes research [39-40]. In South Africa, the focus of waste management is changing. The emphasis is no longer on the disposal of waste, but rather on avoiding its generation and minimising the waste stream wherever possible. South Africa has a policy on Integrated Pollution and Waste Management in place and a comprehensive National Waste Management Strategy and Action Plans to implement that Policy [41]. Many other developing countries in Africa, South America and Asia are also actively pursuing alternative waste management options, which are focussed on increased materials and energy recovery through increased recycling and recovery. China is also driving this trend towards increased recycling and recovery [42].

5.5.2 Waste management

Waste reduction and recycling are very important elements in a waste management framework and are becoming industry standard practise. Waste management principle is finding ways to recycle and reuse existing materials, and safe and ecologically acceptable depositing of unused waste through the waste management hierarchy [5, 38, 43]. Waste management hierarchy is a model that aims to prevent, reduce and manage waste through encouraging waste avoidance first and then the reduction, reuse, recycling and disposal of waste. If the hierarchy is implemented, it will assist in the prevention of greenhouse gas emissions, reduces pollutants, saves energy, conserves resources, creates jobs and stimulates the development of green technologies [44]. A wide range of waste processing and treatment options exist, and these are commonly known as reuse, recycling and energy recovery. Preparing for reuse is to be promoted as it involves application with little or no processing. In theory, reuse offers even greater environmental advantages than recycling since environmental impacts associated with reprocessing do not arise. C&DW recycling needs to be promoted particularly in densely populated areas, where supply and demand are geographically close, resulting in shorter transport distances than for the supply of materials [39]. However, regulation and legislation alone will never be enough to achieve the required amounts of

C&DW recovery; other initiatives are required to drive innovation and industry-led activities [42].

5.5.3 C&DW challenges

One of the common challenges to recycling and reusing C&DW in the EU is the lack of confidence in the quality of C&DW recycled materials. There is also uncertainty about the potential health risk for workers using recycled C&DW materials. This lack of confidence reduces and restricts the demand for C&D recycled materials, which inhibits the development of C&DW management and recycling infrastructures in the EU. The EU Waste Framework Directive target of 70% of C&DW being recycled by 2020 need to be implemented, in order to close the loop of product lifecycles through greater recycling and re-use and bring benefits for both the environment and the economy [20, 39]. Even though the European policies and strategies encourage the use of C&DW for the production of new RCA, most standards do not consider the replacement of RCA from C&DW to be acceptable due to the observation that it reduces the new concrete's compressive strength and increases its shrinkage [22, 37]. RCA material has also proven more difficult to incorporate into concrete or mortar, mainly due to a large water demand and fresh mixture workability problems. In the production of coarse recycled aggregates, the fine fraction is involuntarily produced and it represents a large amount of the weight of the crushed C&DW [4].

In South Africa, there is currently no legislation making recycling a legal requirement. Recycling is at this stage voluntary and not associated with any incentives or rewards from the government [43]. However, future recycling targets need to be regulated by law. Such targets must set realistic levels of recycling within achievable timeframes and be agreed in consultation with the key role-players in the recycling chain. A phased approach should be adopted to achieve targets such as: i) inclusion of recycling options in Integrated Waste Management Plans which should be an element of an Integrated Development Plan, required of every municipality by law. ii) requiring business and industry to produce recycling plans as part of their broader environmental strategy iii) municipalities and other government departments adopting a procurement (purchasing) policy that requires a certain proportion of the products they purchase to contain recycled material [41].

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CHAPTER SIX:

SUSTAINABLE GREEN BRICK USING SUGARCANE BAGASSE ASH WASTE

(Conference paper in SASUF 2019 Sustainable Urbanisation Symposium, Paper 032)

SUSTAINABLE CONSTRUCTION BRICK USING SUGARCANE BAGASSE ASH

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Abstract

There are emerging sustainable development practices in various sectors as global climate change becomes a serious concern. The construction sector is one of the principal component of anthropogenic activities and a major contributor of greenhouse gases (GHGs) emissions. The manufacturing process of conventional construction materials such as cement and bricks is energy intensive and generates quantifiable amounts of GHGs emissions. Therefore, different stakeholders including researchers need to develop effective measures on how to mitigate GHGs emissions. The concerns have generated interest in developing construction materials that are more sustainable, while maintaining structural integrity as required by national regulating bodies. In this study, various factors that can mitigate GHGs reduction in the construction industry and application of sugarcane bagasse (SBA) waste in development of green bricks were reviewed. The utilization of wastes offers an attractive alternative to a disposal and contributes towards sustainable environment. SBA brick is presumed to be economically and ecologically advantageous over conventional bricks. Furthermore, the brick physical and mechanical properties such as compressive strength, and water absorption are discussed.

Key words: Sustainable Development, Greenhouse Gases, Sugarcane Bagasse Ash.

6.1 Introduction

Sustainable development is emerging as a key challenge all over the world, as global climate change becomes an increasingly serious concern for the future [1, 2]. According to *World Commission on Environment and Development* [3], “sustainable development is a development that meets the present needs and preserve an opportunity for future generations”. The idea of sustainability involves improving social, economic and environmental conditions [4]. It is reported that the current global climate change is mainly caused by anthropogenic emissions of GHGs. This situation is expected to have negative impact on both natural and socio-economic systems even in the next century, if not properly attended. Therefore, different stakeholders including politicians, economists and environmental scientists need to develop effective measures on how to reduce GHGs emissions [5-7]. Globally, construction sector is the largest consumer of raw materials, requires high energy input and causes a wide range of quantifiable environmental effects [8-12]. These environmental concerns have generated an interest in developing construction materials that are more sustainable [13-15]. Hence, it is important to develop alternative building materials such as bricks that can give comparable properties with conventional materials, while strictly and effectively controlling the emission of GHGs [1]. This short study review factors that are behind global carbon emissions in the construction industry, and investigate the potential of sugarcane bagasse ash (SBA) as an industrial waste material in the development of a brick.

6.2 Literature review

Recently, there is an interest among economists, environmentalists and policy makers in studying the relationship between economic and carbon growth factors, in order to mitigate high emissions of GHGs. Majority of the research conducted was based on the mechanism of carbon emissions, the relationship between carbon emissions, economic growth, and energy consumption [5, 6]. In another study [16] investigating the decoupling relationship between economic growth and carbon emissions from the construction industry of China. The authors further noted that the economic development and high energy efficiency levels as key factors correlated with construction industry carbon emissions. The study findings were consistent with the results obtained by Chang et al. [6] investigating the driving forces of global carbon

emissions. In this study, the authors mentioned economic development, carbon emission intensity and population increase amongst other factors accelerating global carbon emissions.

Factors such as low-carbon materials, waste management and construction optimization strategies are also highlighted by various researches as key strategies to mitigate high emissions of GHGs [17-20]. In the case study conducted by Huang et al. [5], they recommended that there would be an energy saving and low carbon emission for urban buildings with the implementation of positive low-carbon development policies. The construction industry still plays a significant role in the economic growth and waste management alleviation, despite associated with high emissions of GHGs [4, 21]. In China, for example, the construction industry contributed approximately 7% of the country GDP in 2012, making it a pillar of the [national economy](#). In South Africa, the economic growth is however still facing a host of development challenges impaired by the legacy of apartheid, gap between rich and poor, and high levels of unemployment [22, 23].

6.3 Construction materials

Cement and bricks are important construction materials used around the world due to their continuous demand, population increase and infrastructure development. When mixed with water, cement forms a paste that sets and hardens due to the formation of C-S-H and C-A-H [24]. Over 3 billion metric tons of cement is produced globally every year, with volume predicted to rise to more than 4-5 billion metric tons by 2050 [25]. However, the manufacturing process of cement is energy intensive and generates 5–7% of total global CO₂ emissions (see Figure 6.1) [2, 4, 11]. The current worldwide production of construction bricks is about 1.391 trillion units per year, and demand for bricks is constantly rising [26-28]. The production of bricks is mainly based on conventional firing using clay [29-31] or cementing methods [32-34]. These conventional methods are energy intensive, adversely affect the landscape, and generate large quantity of greenhouse gases [27, 35]. Other alternative type of brick is made from industrial or agricultural by-products stabilized with cement or lime and then forming the bricks by compaction [10, 36]. This alternative type has gained popularity in recent times due to various reasons such as high cost of conventional bricks and willingness to adopt and promote sustainable construction materials [26, 37].

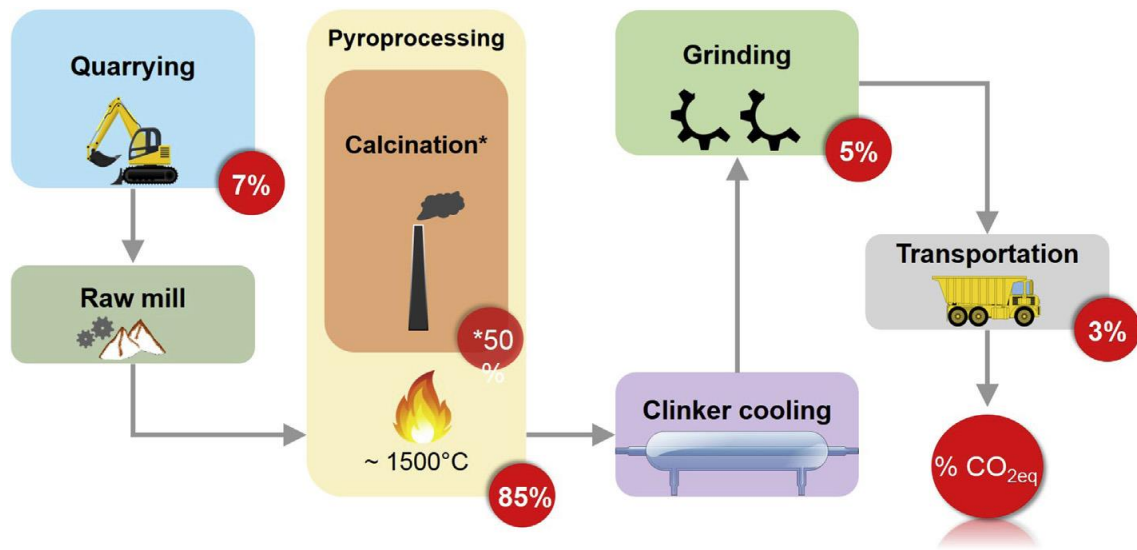


Figure 6.1: Simplified diagram of the cement production process [25].

6.4 Sustainable construction

Sustainable construction is defined as "the creation and responsible management of a healthy built environment based on resource efficient and ecological principles" [38]. This practice requires the use of alternative methods including conserving natural resources, and reusing of alternative materials such as agricultural and industrial waste materials [39-42]. Sustainable construction requires a shift in industrial policy, and provision for sectors to be sensitive to changes in energy prices. Moreover, economic developments, a growing population and increasing rates of urbanization have also resulted in increased waste generation which requires establishing and implementing effective waste management policies [22]. Hence, numerous directives and regulations have now been introduced with the aim of minimizing the consumption of raw materials and energy, saving earth from pollution and maximizing the re-use of materials. For the construction industry, this resulted in a social contract for sustainable methods and utilization of waste materials in order to conserve the natural resources and to reduce the quantities waste deposited in landfills [22, 43].

6.5 Industrial and agricultural waste

The large volume of solid waste generated by industrial and agricultural sectors has created an interest to incorporate this waste in developing alternative construction materials. The interest is also due to ever increasing scarcity of landfill space, accumulation of unmanaged waste and awareness to protect the environment [44-46]. The use of industrial and agricultural waste as brick material provides solution to solid waste management and offers an alternative raw material. Otherwise, waste is land filled and thus, add to ever escalating cost of disposal [47-49]. Both industrial and agricultural wastes present advantages from an economic and ecological point of view i.e., the reduction of costs related to use of alternative raw materials; the reduction in consumption of virgin raw materials; reduction on transport and production energy costs [50-52]. According to the World Bank statistics on solid waste management, the world cities are currently generating about 1.3 billion tons of solid waste per year and this volume is expected to increase to 2.2 billion tons by the year 2025 [53]. These unmanaged solid wastes generated every year by may leads to environmental and health concerns such as flooding, air pollution and other public health scarce. In addition, the growth of population, increasing urbanization, rising standards of living due to technological innovations are also contributing to an increase in the quantity of solid wastes generated [54-56].

The building construction industry which is a major sector when it comes to environmental control, continue to be a viable option for waste disposal and land filling due to its high volume of consumption of waste material [15, 54, 57]. For these reasons, industrial and academic researchers are developing environment friendly construction materials from waste material that offers an attractive alternative to their disposal, and a viable solution in [58, 59]. Amongst the waste generated in the agricultural and industrial sectors which have potential to be used in the construction industry, the following are discussed:

6.5.1 Lime

Lime is a by-product of stone crushing operations in limestone quarries and normally presents a serious problem in terms of disposal, pollution, and health hazards because of its fine powder. This white alkaline material consists of calcium oxide, which is obtained by heating limestone and used in the production of hydrated lime. Lime performs better with very fine particles and can reduce the amount of water entrapped in the system to form a stable pozzolanic material [60-62]. Lime typically produce a more compact structure by pore-filling effect when it reacts, leading to improvement of the strength and durability. Lime reacts with

cement by binding carbon hydroxide (Ca(OH)_2) with free silica by a pozzolanic reaction forming a non-soluble calcium silicate hydrate. Lime can form several chemical reactions including pozzolanic reactions that are similar to the mechanisms of cement, leading to the formation of C-S-H and C-A-H [18, 63, 64].

6.5.2 Sugarcane bagasse ash

SCBA is the waste generated by the combustion of bagasse in boilers of the sugar and alcohol industries. SCBA is generally used as a fertilizer or is disposed of in landfills, which generate environmental related concerns. It is considered an important raw material for application in construction materials due to its high amorphous silica content, which provides hardness, durability, and prevents [65-68]. It typically forms pozzolanic reactions when reacting with calcium hydroxide due to its high amorphous silica content, leading to the formation of the C-S-H [69]. The pozzolanic reactivity of SCBA depends significantly on factors such as its fineness, high temperatures and incomplete combustion that take place in the boilers rather than the chemical composition [70, 71]. SCBA utilization in brick production can save the sugarcane industry disposal costs, leading to the manufacturing of 'greener' bricks [72, 73].

6.6 Discussion

A lot of studies related to solid waste management and environmental awareness reported the brick industry as the relevant technological sector to absorb solid waste, due to the large quantity of raw material that can be absorbed [46, 47]. The bricks made from SCBA waste represent an alternative future to conventional bricks because of abundant availability of raw materials, low usage of energy, and lack of specialized labour in manufacturing processes. The advantage of the brick is that there is no need for high curing temperatures as it is required for clay brick, and the release of GHGs into the atmosphere is 80% less. In addition, the finished bricks are very accurate and uniform, and have lower embodied energy than cement and clay bricks [74, 75]. In one study, it is reported that manufacturing of SCBA bricks reduce energy consumption by 50-60 % over the commercially available clay and cement building bricks. The SCBA bricks are energy-efficient, lightweight and contributes towards sustainable construction practices [7]. Similar sentiments were also shared by Alavez-Ramarez et al [70] who observed reduction of 38%, 40% and 21% for energy, CO_2 emissions and energy

consumption respectively, in the manufacture of SCBA bricks compared with conventional bricks. In another study, the embodied energy of the commercially available burnt clay brick and fly ash brick were 47 % and 5% lower than SCBA bricks respectively. Moreover, the cost analysis showed that SCBA bricks are economically (9% cheaper) as compared with commercially available clay bricks [78].

Green bricks made from SCBA are produced by a simple manual press which can manufacture around 1000-1500 bricks per day. However, for large scale production and more consistent quality, motorized or hydraulic machines are preferred [76, 77]. When a brick is compressed it loses nearly 30% of its volume due to the mechanical compression of the press driving out air pockets, improving the compressive strength and water resistance [72]. In a study by Filho et al. [7], the SCBA bricks mixed with lime and quarry dust exhibited a compressive strength of 6.59 MPa, which was double that of the conventional clay bricks. The brick also met the minimum requirement of Class II bricks (70 kg/cm^2) for flexural strength according to IS 4860:1996. Patel et al. [79], reported that compressive strength normally increases the strength of concrete with the use of SCBA, while reducing the consumption of cement. This sentiment was supported by Sajjard et al. [80] who observed compressive strength increase of 12% with a cement replacement by 5% SCBA. In another study by Noorwardawati et al [81], replacement of cement with 20% SCBA enhanced the compressive strength of bricks, without any loss of workability and strength properties. Modani et al. [82] and Alavez-Ramarez et al. [70] also observed a significant improvement in compressive strength with the addition of 10% and 20% SCBA in combination with lime. Another major factor that is key to durability of SCBA bricks is water absorption. The less infiltration of water in the brick, the more durable is the brick, hence the internal structure of brick must be intensive enough to prevent the intrusion of water. This factor typically decreases with an increase in SCBA content [72]. It is normally recommended that up to 20 to 25 % SCBA can replace cement in concrete bricks in order for the bricks to have permissible water absorption values [10].

6.7 Recommendations and conclusion

In this paper, we discussed factors that are behind global carbon emissions, relationship between economic and carbon growth, and investigated the application of SCBA in the development of green brick. Reduction of GHGs and embodied carbon is one of the practical mitigation options for the building sector by utilizing agricultural and industrial waste in

construction materials. In such cases, low carbon building materials including SBA should be used as alternative materials to manufacture construction materials such as bricks that are not compromising on structural strength. Many policies and legislatures available in many countries including waste management policies, should be strictly implemented and monitored to mitigate a decrease of carbon emissions.

The main advantages of SCBA bricks discussed is that they do not need high curing temperature in their production, and the release of greenhouse gases is less compared to conventional bricks. Therefore, the application of SCBA in the development of green bricks will mitigate a balance between economic, social and environmental challenges related to GHGs emissions. The SCBA bricks can achieve acceptable masonry properties such as compressive strength, water absorption, permeability and durability to be accepted by the public and construction industry. However, further research and development is needed to develop guidelines for masonry bricks incorporating different waste material.

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CHAPTER SEVEN:

PHYSICAL AND MECHANICAL PROPERTIES OF SUGARCANE BAGASSE ASH (SCBA) GREEN BRICKS STABILIZED WITH LIME POWDER

PHYSICAL AND MECHANICAL PROPERTIES OF SUGARCANE BAGASSE ASH (SCBA) GREEN BRICKS STABILIZED WITH LIME POWDER

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Abstract

The demand for sustainable construction materials have led researchers on finding ways of utilizing either industrial or agricultural wastes as supplementary cementitious materials. Sugarcane bagasse ash (SCBA) is an industrial waste material obtained from sugar milling industry used as a pozzolanic material. In this study, SCBA and lime powder were used to develop the bricks. The pozzolanic reactivity and formation of cementitious bonds between SCBA and lime were investigated by Fourier-transform infrared (FTIR) spectroscopy (FTIR) and X-ray Diffactogram (XRD). The mechanical properties of SCBA bricks tested include compressive strength, water absorption and density parameters. The bricks manufactured with 10 % lime were found to have have higher compressive strength, lesser water absorption rate and lower density than bricks containing 5 % lime. The usage of SCBA to manufacture bricks could alleviate both environmental and health concerns associated with waste mismanagement and emission of greenhouse gases (GHGs).

Keywords: Waste Material; Sugarcane Bagasse Ash; Lime; Greenbricks.

7.1 Introduction

OPC is the most utilized construction material in the world, and will probably remain so in the near future. This is due to its exponential demand as a result of population increase, rapid urbanization and infrastructural development [1-3]. It is reported that over 3 billion tons of cement was manufactured in 2012, and the demand will reach at least 5 billion tons in 2050 [4-5]. The production of 1 tonne of cement requires about 2.8 tonnes of raw materials, and releases almost 0.9 ton of carbon dioxide. Worldwide, cement production generates almost 2.8 billion tons of anthropogenic greenhouse gas annually [6-7]. Hence, researchers are finding alternative ways of replacing cement by other lower carbon materials with cementitious properties to reduce CO₂ emissions. Industrial waste such as blast furnace slag, fly ash and silica fume, and agricultural waste including rice husk ash, wheat straw ash, and sugarcane bagasse ash are amongst some cementitious materials used to replace cement [8-10]. These materials are predominantly composed of silica and alumina, and possess little or no cementitious properties. Nevertheless, they can react with lime or cement in finely divided form in the presence of moist to form compounds with cementitious properties [11-14].

Sugarcane or *Saccharum officinarum* L. is major food crop grown in over 110 countries with a total production in excess of 1500 million tonnes per annum. The processing of sugarcane in sugar milling industries generate SCBA as a waste product. It is reported that one tonne of sugarcane generates approximately 0.62 % of bagasse ash [15-17]. The ash produced generally originates from two sources: bottom ash that settles at the bottom of the boilers, and fly ash which is obtained from the washing of the chimney gases [12, 18]. Lately, the generation of SCBA have substantially increased due to the demand for sugar and ethanol. However, most of the SCBA generated is however used as a fertilizer in the agricultural fields or disposed of in landfill (approximately 70 %) which have led to environmental concerns [19-21]. In recent years, SCBA has been used in construction materials as a pozzolanic material to reduce waste landfilling and alleviate environmental concerns caused by cement production [22-24].

SCBA contains silica in amorphous or crystalline phase that influences its pozzolanic activity. Reactive amorphous silica comes from groundwater when sugarcane absorbs silicic acid and polymerizes into amorphous silica in sugar cane cells. The crystalline silica comes from two sources: the uncontrolled incineration process and the sand in the soil [10]. SCBA also contains minor components of alumina (Al₂O₃), ferric oxide (Fe₂O₃), calcium oxide (CaO),

magnesium oxide (MgO), and sulphur trioxide (SO₃) [25]. Both the amorphous and crystalline forms of silica are controlled by the temperature and time of combustion of bagasse ash. De Soares et al. [26], Tantawy et al. [27] and Sultana et al. [28] reported that SCBA calcinated around 500-700 °C transforms silica content of the ash into amorphous silica with high pozzolanic activity. However, the ash burnt above 700 °C transform amorphous silica into crystalline silica polymorphs such as quartz, cristobalite and tridymite with low pozzolanic activity. The pozzolanic activity and the composition of SCBA also depends on factors such as surrounding environment, nature of soil, and ash fineness amongst others [29-30]. In studies conducted by Zareei et al. [31] and Bahurudeen et al. [32], they reported that the particle size had a significant effect on the pozzolanic activity of the ash, rather than the chemical composition. Hence, the ashes used must pulverized or ground to required fineness to achieve maximum pozzolanic activity. Alavez-Ramirez et al. [33] related low pozzolanic activity of SCBA with the presence of impurities such as carbon and unburned material. These impurities limit the contact between calcium hydroxide and reactive silica by preventing the formation of stable compounds.

There is a constant demand for bricks due to rapid population growth and infrastructure development. The conventional methods of bricks production include fired clay and cement bricks because of their economic and performance competitiveness. These methods consume huge amounts of raw materials, adversely affect the landscape, and generate large quantity of greenhouse gases [34-35]. Hence, researchers are developing alternative bricks by utilizing waste products not only to reduce the environmental challenges but also to meet economical and sustainable solution. Various studies conducted have been directed towards partial or total substitution of OPC by pozzolanic binders such as lime, fly ash, and SCBA in the development of compressed or stabilized bricks. These bricks are reported to have numerous advantages over conventional bricks such as low cost, fire resistance and easy processing. In addition, they have comparable performance in terms of appearance, durability and structural properties such as density, water absorption and compressive strength [36, 37].

A few studies on development of bricks have been conducted in the literature using SCBA obtained directly from the sugar milling industries. James et al. [36] investigated the mechanical properties of lime stabilized soil blocks amended with bagasse ash. The results showed the addition of SCBA to lime stabilization resulted in an increase in compressive strength and water absorption properties of the brick. The strength of the brick increased from

1.687 MPa to 1.87 MPa with the introduction of 6 % lime and 8 % SCBA, while the water absorption of the blocks increased from 7.46 to 8.38 %. Alavez-Ramirez et al. [33] investigated the use of lime and SCBA as chemical stabilizers in compacted soil blocks. The blocks manufactured with 10 % of lime in combination with 10 % of SCBA showed better performance than those containing only lime. Nevertheless, the addition of lime improved the strength of the blocks when compared with blocks manufactured with plain soil. Madurwar et al. [38] developed SCBA-lime bricks using quarry dust (QD) as a replacement to natural river sand. The bricks developed with 20 % addition of lime exhibited a compressive strength of up to 6.59 MPa, which was double of the conventional clay bricks (3.5 MPa). In addition, the manufacturing process of bricks resulted in 50 % and 6 % reduction in energy consumption over the commercially available burnt clay and fly ash–cement building bricks. In other studies, Amaral et al. [25] and Singh et al. [39] investigated the usage of SCBA as an alternative raw material in soil-cement brick. These studies found that the replacement of OPC with SCBA in the range up to 15-30 wt.% allowed for the production of bricks with technical properties comparable with those specified in the standards. SCBA has been utilized in other different applications such as ceramic, cement paste, mortar and concrete as a cementitious replacement material. The usage of ash was reported to improve compressive strength, water absorption, chemical attack, abrasion and durability while reducing the shrinkage and permeability [9, 14, 19, 40]. This study investigates the physical and mechanical properties of SCBA bricks enhanced with lime stabilizer. The bricks of size (220 x 100 x 85) mm were developed using different compositions of SCBA and lime. The test conducted include water absorption, compressive strength and density parameters. Fourier-transform infrared and X-ray diffraction analysis were conducted to study the pozzolanic reactivity and hydration products formed during the reaction of SCBA and lime.

7.2 Materials and equipments

7.2.1 Sugarcane bagasse

SCBA was collected from a local sugarcane milling industry (Hulleets, Tongaat) in Felixton near Empangeni, South Africa. The ash was taken during the cleaning operation of the boiler. SCBA particles were very coarse, larger in size and possess significant amount of unburnt carbon. Before SCBA was used, it was ground and sieved off 45 μm to disposed of any large particles.

7.2.2 Lime (Cape hydrated lime)

Cape hydrated lime was purchased from local retailer shop. The appearance of lime was white crystalline powder substance containing calcium hydroxide, $\text{Ca}(\text{OH})_2$. The Melting point of lime was 580 °C, pH: 11,8 (saturated aqueous solution 0,15%), solubility (water): 0,8 g/l at 0 °C, density: 2,5 g/cm³ and bulk density 0.55g/cm³. This white alkaline material was used as obtained without any further process.

7.2.3 Water

Water is an important ingredient used for binding raw materials and curing. Water used was free from impurities. In this study, laboratory tap water was used without any further purification.

7.2.4 Equipments

Manually-operated laboratory mould presser that produces (220 x 100 x 85) mm blocks was used (see Figure 7.1). The presser was moderately light in weight and easy to handle.

7.3 Experimental methodology

The manufacturing process of bricks consist of three operations namely; mixing the raw materials, pressing the mix in the mould and curing the bricks.

7.3.1 Mixing the raw materials

The raw materials used were weighed according to the ratios displayed in Table 7.1, before being transferred into the mixer. The dry materials were hand mixed for approximately 5 minutes to ensure that they are homogeneous mixed. After that, water was then added and the mixture was further processed for additional 5 minutes before transferred into the mould.

Table 7.1: Various SCBA ash composition mixtures

Composition	SCBA %	Lime %	Cement %	Water %
1	95	5	-	5
2	90	10	-	5

7.3.2 Pressing the mixture in the mould

The mixture was transferred into the mould presser, and hand pressed for approximately a minute using laboratory mould presser to allow for sufficient compaction.

7.3.3 Curing of the bricks

The brick samples were water cured for 7 days to develop sufficient strength. After sufficient strength was gained, the bricks were kept for air drying in laboratory environment for 28 days before any testing commenced.

7.4 Characterization techniques

7.4.1 Physical properties of SCBA

Physical properties such as fineness, moisture absorption, density and other properties of ash sample were determined in accordance with ASTM C 311 [41].

7.4.2 Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) analysis was performed with Bruker Tensor 27 FT-IR spectrometer utilizing a standard ATR cell. The samples were scanned over the mid-IR region ($4000 - 600 \text{ cm}^{-1}$) at a resolution of 4 cm^{-1} .



Figure 7.1: Laboratory mould presser and SCBA bricks developed

7.4.3 Powder X-ray diffraction

Powder X-ray diffraction (XRD) analysis was carried out using Bruker AXS Advance D8 diffractometer model with monochromatic Cu K α ($\lambda = 1.5406 \text{ \AA}$) incident radiation at 40 kV and 40 mA, at room temperature.

7.4.4 Water absorption

Water absorption test was conducted based on South African National Standards (SANS) 1058:2007 [42]. In brief, five bricks were first dried in an oven at a constant temperature of 105 °C and weighed until constant mass was obtained. After that, the bricks were submerged in water at room temperature for 24 hrs, 72 hrs and 168 hrs. Finally, bricks were removed from water and weighed after wiping off the excess water from the surface, and the saturated mass determined. The difference between the saturated mass and oven dry mass expressed as a fractional percentage of oven dry mass gives the water absorption.

7.4.5 Compression strength

The compressive strength was determined using compression testing machine based on SANS 1215-2008 [43] for concrete masonry units. For each composition, five samples were tested and the average values obtained reported.

7.4.6 Apparent density

Apparent density was conducted based on International Standards (IS) 2185-1 (2005) [44] for concrete masonry units. In brief, five bricks were dried to constant mass in an oven heated to constant temperature of 105 °C. After cooling the bricks to room temperature, the dimensions of each bricks were measured and the overall volume calculated in meters. The bricks were weighted in kilograms to the nearest 10 g. Finally, the density of the bricks was calculated.

7.5 Results and discussion

7.5.1 Physical characterization of SCBA

The physical properties results of SCBA are summarized in Table 7.4.2. SCBA collected from the sugar milling industry were coarse and possess significant amount of unburnt carbon. The ash was greyish in colour. However, some black particles were observed which might indicate incomplete combustion. The specific gravity and moisture content of the ash were 2.29 and 1.3 % respectively. The density of SCBA obtained was influenced by the presence of unburnt carbon.

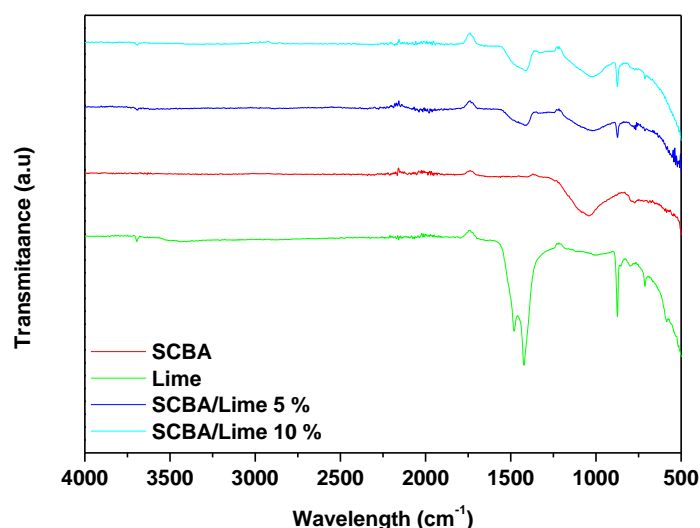
7.5.2 FTIR analysis

FTIR spectroscopy was used to identify different functional groups by measuring the absorption at characteristic wavelengths of bonds that vibrate independently of one another [38]. The spectra of raw SCBA, lime and various composition are shown in Figure 7.2. The main dominant peak of SCBA was observed at 1045 cm⁻¹ related to asymmetric stretching vibration of the Si(Al)–O–Si bonds.

Table 7.2: Physical properties of SCBA

Physical properties	Result
Colour	Grey
Appearance	Coarse
Specific gravity	2.29
Density	2.4 g/cm ³
Fineness	45 μm = 13.3 %
Moisture content	1.3 %

The peak corresponding with the presence of crystalline quartz was observed at 772 cm^{-1} , while there was also an appearance of minor peak at 1740 cm^{-1} related to hydroxyl bending mode of the adsorbed water [4, 14]. Furthermore, there was a new band at 1423 cm^{-1} observed for raw lime assigned with asymmetric stretching vibration of carbonate [25, 38]. The intensity of this absorption band decreased in the composition mixtures, probably due to pozzolan reactions between SCBA and lime [8, 25]. For both SCBA compositions at 5 and 10% lime loading respectively, there was a decrease of intensities seen for the band at 1045 cm^{-1} which is an indication of lowering the degree of polymerization of silica network due to formation of hydration product (C-S-H) [26]. This cementitious bond was reported by Govindarajan et al. [16] and Amaral et al. [25] as the main product developed from the reaction between SCBA and lime.

**Figure 7.2: FTIR spectra of SCBA, lime and various SCBA composition mixtures**

7.5.3 XRD analysis

Figure 7.3 shows the X-ray diffraction patterns of SCBA, lime and various compositions mixtures used in the study. The SCBA peaks observed at 21.2° , 26.9° , 36.8° , 39.8° , 40.7° , 42.7° , 46.1° , 50.7° and 69.7° are typical peaks of quartz in the crystalline phase of silica [4, 14, 45, 46]. According to Joshaghani et al. [9], and Jayasinghe et al. [37], the quartz peaks are characterized by sharp and narrow peaks, and are attributed to sand adhering to the sugarcane and uncontrolled incineration. According to literature, the silica in the ash is predominantly amorphous at temperatures of $500\text{--}700^{\circ}\text{C}$. However, at temperatures greater than 700°C , the amorphous silica present in sugarcane is converted in crystalline silica polymorphs, such as quartz, cristobalite, and tridymite [15, 28]. With the introduction of lime content in SCBA composition, typical peaks corresponding to calcium hydroxide are observed at 18.5° and 47.5° . In addition, the composition mixture revealed the presence of a peak at 29.5° attributed to the formation of C-S-H in the mixtures [26]. The intensity of this peak and calcium hydroxide peaks seemed to change with an increase in lime content, which might signal that pozzolanic reactions between lime and SCBA took place.

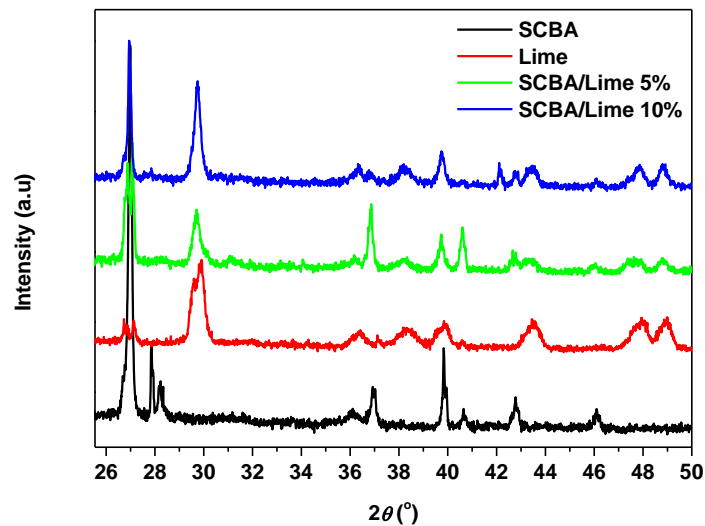


Figure 7.3: XRD patterns of SCBA, lime and various SCBA composition mixtures

7.5.4 Water absorption

Water absorption results of SCBA developed bricks are shown in Figure 7.3. Water absorption is related to the volume of open pores, and is an effective physical property in evaluating the technical quality of bricks used in construction [25]. According to NBR 10834 [45], water absorption in bricks should not be more than 17 % for severe weathering resistance and 22 % for moderate weathering resistance at 28 days of age. It could be seen that water absorption results of both brick compositions increase with an increase in time submerged in water. For the composition mixture of 10 % lime, there was an increase from 19.4 % to 20.5 % and 21.2 % at 3 and 7 days respectively. In addition, the brick composition mixture containing 5% lime absorbed more than the 10 % composition at different time interval. The higher rate in water absorption may be due to an increase of open pore volume in the bricks, since raw SCBA contains coarser and unburnt particles which are porous [18]. The water absorption results were between 19 and 22 %, and satisfactory for both compositions. Hence, these bricks could be used in moderate weather regions.

Table 7.3: Water absorption of various SCBA composition mixtures

Composition	24 hrs (%)	72 hrs (%)	146 hrs (%)
1	21.2	22.2	22.6
2	19.4	20.5	21.2

7.5.5 Compression strength

The compressive strength results of SCBA developed bricks are summarized in Table 7.4. It is noted that the average compressive strength values of the bricks containing 10 % lime were higher than the bricks developed with 5 % lime. In other words, compressive strength of the bricks increased with lime increase and SCBA reduction content. Similar increase in strength were also reported in the studies of Zareei et al. [31] and Govindarajan et al. [16] who observed an increase of the compressive strength with a decrease of SCB content in their brick composition mixtures. However, the content of other raw materials in both studies were constant, only SCBA was varied unlike in our study. Moreover, the compressive strength values obtained were significantly higher than those obtained by Madurwar et al. [38], which was 6.59 MPa for brick developed with SCBA, quarry dust and lime composition mixture. The

formation of C-S-H phase due to the reaction between SCBA and lime might be responsible for the mechanical strength development in both compositions. The compressive strength results are found to be within specified limits as indicated in Table 7.5 based on SANS 1215-2008.

Table 7.4: Results of the compressive strength testing

Composition	Load at failure (kN)	Average compressive strength (MPa)
1	22.5	10.245
2	28.3	12.873

Table 7.5: SANS 1215-2008 compressive strength of masonry units

1	2	3
Nominal compressive strength MPa	Compressive strength MPa. min Average (for 5* units)	Individual units
3.5	4.0	3.0
7	8.0	5.5
10.5	11.5	8.5
14	15.5	11.0
21	23.5	17.0

7.5.6 Apparent density

Summary of the results obtained from dry density test are presented in Table 7.6. The results show that the average dry density of the SCBA bricks containing 10 % lime content was lower than bricks containing 5 % lime content. This was expected as lime has a low density, and therefore increase of its content with the reduction of the SCBA content which has high porosity will decrease the density of the bricks. A similar trend was also obtained by Ali et al. [48] where the density of CEBs decreased as the percentage of SCBA was reduced. However, the values reported were between 1690.73 and 1718.03 kg/m³ higher than the values obtained in our study. Both the lowest and highest values of density of the SCBA bricks are higher than

1100 kg/m³ and lower than 1500 1100 kg/m³ which are the range of density values required for load bearing blocks as recommended in IS 2185 (Part 1): 2005.

Table 7.6: Results of the dry density testing

Composition	Average dry density (kg.m ³)
1	1336.9
2	1330.5

7.5.7 Micromorphology images

Figure 7.4 shows the fracture surface images for various compositions of SCBA bricks. Both composition mixtures exhibited a dense microstructure of the cured cementitious matrix.

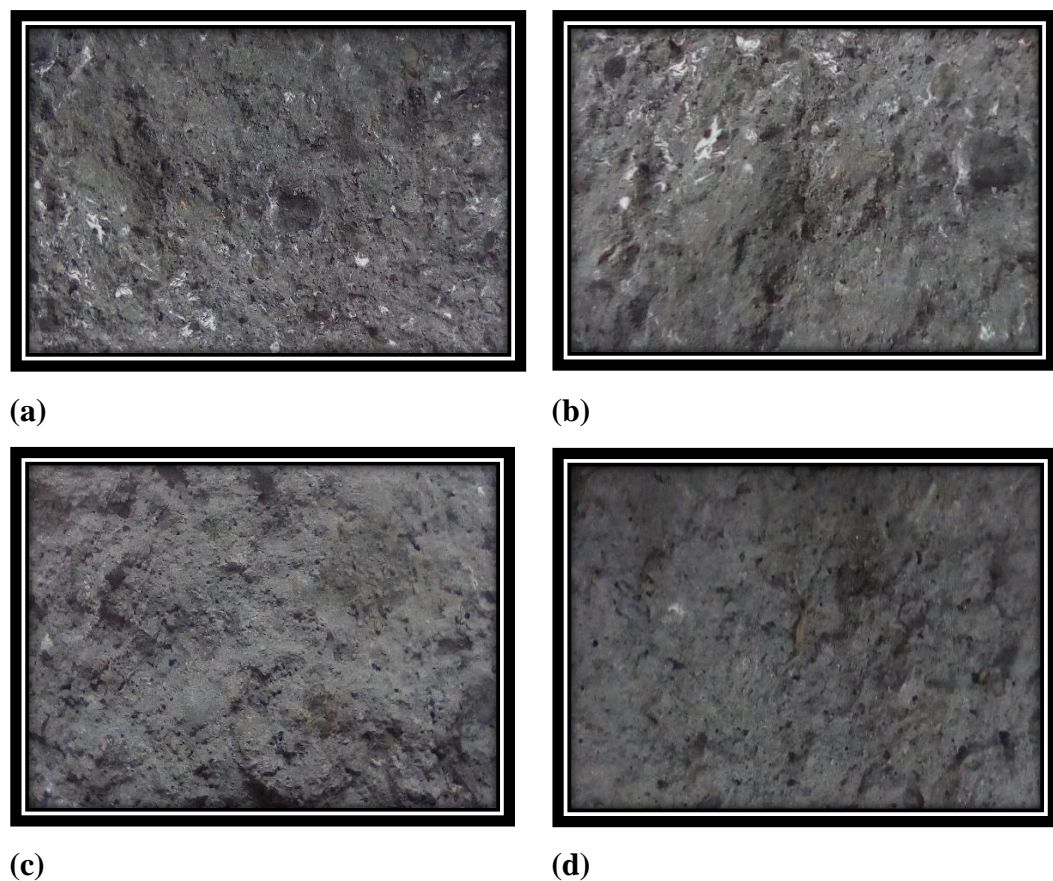


Figure 7.4: Micrographs of various SCBA composition mixtures (a, b) SCB/Lime 5% and (c, d) SCB/Lime 10%.

However, the composition mixture using 10 % lime was more homogeneous with a finer microstructure compared with the 5 % composition. The composition of 5 % lime display some porous structure embedded in the gel matrix, due to the presence of unreacted SCBA particles which are unburned. Some particles are coarse and rough with unique microstructure.

7.6 Conclusion

In this study, SCBA was used in combination with lime to develop sustainable green bricks. The results obtained showed that SCBA sample is chemically rich in crystalline silica, and has moderate pozzolanic activity as shown by predominant quartz peaks in the XRD patterns. The pozzolanic activity and the formation of C-S-H bond between SCBA and lime powder were confirmed by FTIR and XRD analyses. The compressive strength of SCBA bricks containing both 5 % with 10 % lime content were within the values specified in SANS 1215-2008 standards, with the 10% composition exhibiting slightly higher values than 5% composition. The water absorption values obtained for both compositions were within the values reported in the standards and the bricks could be used in moderate weather according to NBR 10834. The results showed significant potential for utilizing SCBA for manufacturing of bricks that are light and sustainable. The densities of the SCBA bricks were in the range of values required for load bearing blocks as recommended in IS 2185 (Part 1): 2005.

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CHAPTER EIGHT:

THERMAL DEGRADATION KINETICS OF SUGARCANE BAGASSE CELLULOSE AND SOFT WOOD CELLULOSE

(Article in *Materials* 2017, 10, 1246; doi:[10.3390/ma10111246](https://doi.org/10.3390/ma10111246)).

THERMAL DEGRADATION KINETICS OF SUGARCANE BAGASSE CELLULOSE AND SOFT WOOD CELLULOSE

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Abstract

The properties of untreated sugarcane bagasse (SCB) and soft wood (SW) and their respective celluloses were investigated. The celluloses indicated improved crystallinity index values and decreased concentration of lignin and hemicellulose compared to their untreated counterparts. Three degradation models, Kissinger-Akahira-Sunose (KAS), Flynn-Wall-Ozawa (OFW), and Kissinger (KGR) methods were employed to determine apparent activation energy values. Generally, the thermal degradation processes of both sugarcane bagasse and soft wood included dehydration, degradation of hemicellulose and cellulose, whereas the lignin degraded from the degradation temperature of hemicellulose to the end of the cellulose. The apparent activation energy values obtained from OFW and KAS models vary with the degree of conversion, and showed similar trends. The activation energies obtained by KGR were relatively lower than those obtained from KAS and OFW methods.

Keywords: Lignocellulosic waste, Kinetics modelling, Apparent activation energy, Thermogravimetric analysis

8.1 Introduction

Recently a considerable interest has been shown in the utilization of natural fibers as reinforcing fillers in thermoplastic composite materials. The unique properties of natural fibres include low density, good specific modulus values, considerable toughness, flexibility, easy processing, non-toxicity, non-abrasion during processing, recyclability, and resistance to corrosion. Lignocellulosic fibers from agricultural residues/biomass mainly consist of natural composites of polymers (cellulose, hemicellulose, and lignin) [1, 2]. Sugarcane is one of the most abundant biomass in the tropical countries such as Brazil and India, creating about 54 million dry tons of residue bagasse per year. SCB typically contains approximately 26.6–54.3% cellulose, 22–32% hemicelluloses, and about 14–25% lignin, as well as small proportions of ash (2–4%) and waxes [3–5]. A handful of farmers around “uMhlathuze” municipality in South Africa also produce sugar cane, which is mainly used as an energy source, though the surplus of SCB is way far higher than demands. The case of wood chips around the municipality is worse. Industries around, which process wood, face a surplus of chips that end up abandoned in the environment. Wood chips are complex biomass material composed of polysaccharide cellulose, hemicellulose, lignin and small proportions of extractives. SW is widely used in buildings, furniture, and paper pulp production [6–8]. Since the common practise is to burn the biomasses, it would be worthwhile to get more insight into thermal degradation kinetics of the biomass. Knowledge of kinetic parameters, such as the reaction rate and activation energy, is one of the keys to determining reaction mechanisms in solid phases. Solid state kinetic data are of major and growing interest in many technological processes. These processes include, for instance, thermal decomposition of crystalline solids and energetic materials, thermal oxidation and decomposition of polymers and coal, crystallization of glasses and polymers, and pyrolysis and combustion of biomass resources [9, 10].

The thermal degradation kinetics of SCB and SW fibers have been investigated using thermogravimetric analysis TGA at various heating rates. Detailed kinetic analysis of the degradation process were performed using model based isoconversional methods to predict the kinetic parameters, i.e. pre exponential factor, A and activation energy, E_a . Motaung et al. [11] and Edries et al. [12] investigated the thermal degradation kinetics of alkali treated SCB and SCB chars, respectively. The alkali treated sample showed the highest values of activation energy in all the investigated degree of conversions, as compared to sulphuric acid treated SCB. The authors observed that the peak of weight loss rate in the differential thermogravimetry

(DTG) curves shifted to a higher temperature with increasing the heating rate. Ramajo-Escalera et al. [10] applied Vyazovkin's model-free kinetics to determine conversion, isoconversion and apparent activation energy of SCB and detected three steps. The apparent activation energy values were $76.1 \pm 1.7 \text{ kJ.mol}^{-1}$, $333.3 \pm 15.0 \text{ kJ.mol}^{-1}$ and $220.1 \pm 4.0 \text{ kJ.mol}^{-1}$ in the conversion range of 2–5%, 15–60% and 70–90%, respectively.

Thermal degradation kinetics of wood was also given attention by many researches using Kissinger-Akahira-Sunose, Flynn-Wall-Ozawa, and Coats-Redfern methods [13-18]. The results showed that the whole course of pyrolysis of wood can be divided into three phases and the activation energy results of Kissinger method are higher than Kissinger-Akahira-Sunose. The objective of this paper is to systematically investigate and compare the thermal degradation kinetics of SCB and SW celluloses under similar preparation conditions. Various degradation models including the Kissinger-Akahira-Sunose, Flynn-Wall-Ozawa, and Coats-Redfern methods were used to determine the apparent activation energy values.

8.2 Experimental

8.2.1 Materials

Sugar cane bagasse and soft wood were collected from industries respectively located near Empangeni, South Africa. Sodium hydroxide pellets (99.9%) were supplied by Merck, Mumbai, India, Sodium perchlorite by Capital lab Suppliers CC, New Germany, Durban, South Africa. Glacial acetic acid was supplied by Minema Chemicals, Roodepoort, South Africa. All chemicals were used as received without further purification.

8.2.2 Chemical composition

The untreated SCB and SW raw samples were used to determine their respective chemical composition. The lignin content was analysed according to a standard method recommended in TAPPI-T222 om-88 [19] and the cellulose content obtained as described in TAPPI T19m-54 standards [19].

8.2.3 Extraction of SCB and SW cellulose

The SCB and SW raw samples were washed and immersed in water bath for 24 hrs at room temperature before drying at 60 °C overnight. Then SCB and SW were treated with an alkali solution (2 wt% NaOH) at 100 °C for 4 hours. The solid precipitates were then filtered and washed several times using distilled water. This treatment was performed four times. The same treatment was performed using 1.7 wt% sodium perchlorite buffered with acetic acid. Finally, the suspension was allowed to cool and rinsed using deionized water to neutral pH.

8.3 Characterization methods

8.3.1 Fourier Transform Infrared

The FTIR spectra were collected by using a Perkin Elmer FTIR spectrometer (Stillwater, GA, USA) in the diffuse reflectance mode. The samples were analyzed in the spectral region between 4000 and 400 cm^{-1} with a 4 cm^{-1} resolution.

8.3.2 X-ray Diffraction

Powder X-ray diffraction (XRD, (Bruker AXS D8 Advance X-Ray diffractometer) equipped with Cu K α generator ($\lambda=0.154$ nm) as X-ray source, operating (40 kV, 40 mA) was used to examine the crystal structure of SCB, SW and extracted celluloses.

8.3.3 Thermogravimetric analysis

Thermogravimetric analyses were performed using TGA analyser unit (Perkin Elmer, Foster City, CA, USA), under flowing nitrogen atmosphere at flow rate of 20 $\text{ML}\cdot\text{min}^{-1}$. Approximately 10 mg of sample was heated from 25 °C to 600 °C, at different heating rates rate of 3 °C min^{-1} , 7 °C min^{-1} , 11 °C min^{-1} , and 15 °C min^{-1} . The sample weight loss and rate of weight loss were recorded continuously as functions of temperature.

8.4 Degradation kinetics

Different kinetic models are proposed to understand degradation mechanisms through prediction of the kinetic parameters based on the data obtained from TGA curves. The kinetic parameters (i.e., A, n and E) can be calculated from TGA data by using the following rate equation [20-23]:

$$d\alpha/dt = k(T) f(\alpha) \quad (1)$$

where α represents the extent of reaction, which is determined from the TGA data (fractional mass loss), t is time, $k(T)$ represents the temperature dependent rate constant expressed by an Arrhenius type expression and $f(\alpha)$ denotes the particular reaction model, which determines the dependence of the reaction rate on the extent of reaction. In this study, the conversion rate is defined as:

$$\alpha = (W_o - W_t)/(W_o - W_f) \quad (2)$$

where W_t , W_o , and W_f are time t , initial and final weights of the sample, respectively. The temperature dependence of the rate constant can be expressed by Arrhenius equation:

$$k = A \exp((-E)/RT) \quad (3)$$

where A and E are pre-exponential factor and activation energy, respectively. Equation (1) can be written as

$$d\alpha/dt = A \exp((-E)/RT) f(\alpha) \quad (4)$$

In order to determine the kinetic triplet (A, E and $f(\alpha)$), various methods have been developed. They are classified as isoconversional and model fitting methods. In this study Kissinger-Akahira-Sunose, Flynn-Wall-Ozawa, and Kissinger models are considered for determining the kinetics of thermal degradation of SCB and SW celluloses.

8.4.1 Flynn Wall Ozawa (OFW) model

OFW model is an integral isoconversional method derived by using Doyle's approximation using multiple heating rates TGA data. The model expression is given by

$$\ln \beta = \ln AE/g(\alpha)R - 2.315 - 0.4567 E/RT \quad (5)$$

The plot of $\ln \beta$ vs. $1/T$ gives a straight line whose slope is equal to $-0.4567E/RT$ from which activation energy can be calculated. Pre exponential factor is calculated from the intercept of the resulting straight line by assuming a reaction model.

8.4.2 Kissinger Akahira Sunose (KAS) model

KAS is an isoconversional model based on the numerical approximations of the Arrhenius integral over a wide range of thermal history. The model expression is written as

$$\ln (\beta/T^2) = \ln (AR/(Eg(\alpha))) - E/RT \quad (6)$$

The Plot of $\ln (\beta/T^2)$ vs. $1/T$ yields a straight line. The values of E and A can be calculated from slope and intercept for a particular reaction model.

8.4.3 Kissinger (KGR) model

This is a maximum rate method and applicable only to the multiple heating rate TGA or DTG data. The temperatures (T_m or T_p) at which the rates reach maximum weight loss are used to predict the single values of E_a and A . In the Kissinger method, $\ln(\beta/T_m^2)$ is plotted against $1/T_m$ for a series of experiments at different heating rates with the maximum peak temperature, T_m , obtained from the DTG curve.

The expression for this model is

$$\ln (\beta/T_m^2) = -(E/(RT_m)) + \ln (AR/E) \quad (7)$$

8.5 Results and Discussion

8.5.1 Chemical compositions of SCB and SW

The chemical composition of sugarcane bagasse and soft wood content are shown in Table 10.1. As expected, the cellulose content in both untreated sugar cane bagasse and the wood was the highest. However, the wood revealed an uncommon behaviour in which hemicelluloses was dominated by lignin content. There are lot of factors involved for the results including the method used to measure chemical compositions and the origin of the cell wall structure [3-5, 10].

Table 8.1: Fractions of principal constituents of SCB and SW

Sample	Lignin (%)	Cellulose (%)	Hemicellulose (%)
SCB	18.8 ± 0.1	42.9 ± 0.99	38.2 ± 1.08
SW	37.2 ± 0.01	39.2 ± 0.01	23.6 ± 0.01

8.5.2 FTIR

FTIR spectra of SCB, SCB cellulose, SW, and SW cellulose are shown in Figure 8.1. The untreated SCB and SW materials showed similar patterns with the dominant peaks observed at approximately 3340 cm^{-1} (O–H stretch), 2892 cm^{-1} (C–H vibrations), 1730 cm^{-1} (C=O stretching), 1627 cm^{-1} and 1513 cm^{-1} (C=C aromatic), 1245 cm^{-1} (O–H vibration of phenolic group), 1110 cm^{-1} (C–O–C stretching), 1051 cm^{-1} (O–H stretching) and 897 cm^{-1} (β -glycosidic linkage). These peaks are typical for lignocellulosic materials and are known for sugar cane bagasse and soft wood [6, 7, 24-26]. However, in this study the wood has blunt peaks between 1000 and 2000 cm^{-1} , which may explain difference in chemical compositions. The peaks at 1241 cm^{-1} and 1722 cm^{-1} in the celluloses, normally linked to aromatic skeletal vibrations of lignin and hemicelluloses, were reduced and others are almost invisible as compared to untreated counterparts [8]. This indicates removal of lignin and hemicelluloses, as well as an exposure of cellulose [28].

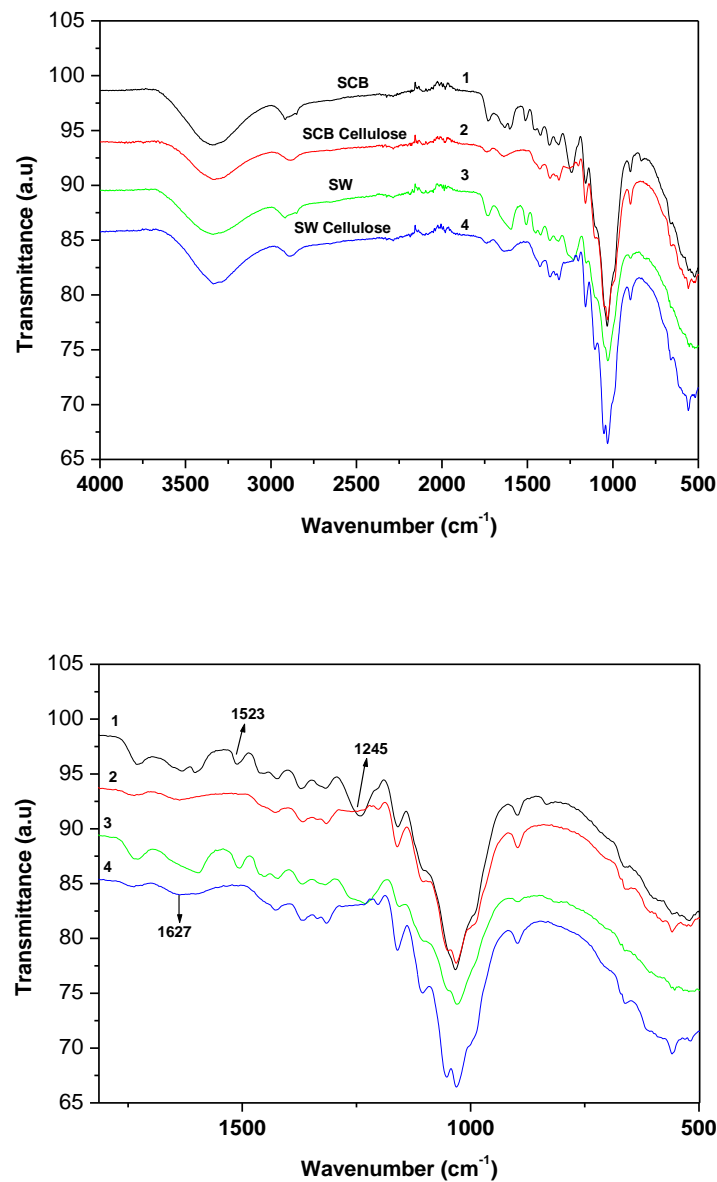


Figure 8.1: FTIR spectra of untreated SCB, SCB cellulose, untreated SW, and SW cellulose

8.5.3 XRD

Figure 8.2 and Table 8.2 shows the XRD analysis to evaluate the crystallinity of SCB and SW materials. The diffraction pattern of untreated SCB and SW indicated typical behavior of cellulose I type, which showed major intensity peaks related to their crystalline structure at 2θ values of around 15.5° and 22.5° [4, 8, 21]. The Segal and deconvolution methods were used to calculate crystallinity index values of the samples respectively. For the first method crystallinity index (CI) was obtained from the ratio of the maximum peak intensity 002 (I_{002} ,

$2\theta = 22.5$) and halo depression ($I_{am} 2\theta = 18.5$) between peaks 001 and 002 according to Equation (8).

$$CI (\%) = \frac{I_{002} - I_{am}}{I_{am}} \times 100 \quad (8)$$

where I_{002} is the maximum intensity of the 002 peak and I_{am} the minimal depression of the amorphous structure.

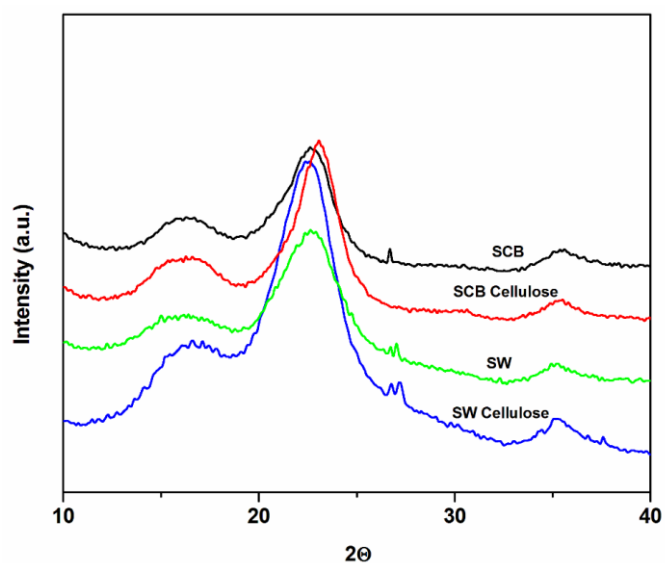


Figure 8.2: XRD analysis of untreated SCB, untreated SW, SCB cellulose and SW cellulose.

Table 8.2: Crystallinity index of SCB raw, SW raw, SCB cellulose and SW cellulose.

Samples	Segal Method	Deconvolution Method
SCB raw	53.9	33.5
SW raw	52.8	32.3
SCB cellulose	61.3	43.9
SW cellulose	88.7	57.3

For the second method, individual peaks were fitted by Gaussian functions to predict areas according to the following Equation (9).

$$Cl (\%) = \frac{\sum A_{cryst}}{\sum A_{cryst} + \sum A_{amorp}} \times 100 \quad (9)$$

where A_{cryst} and A_{amorp} are the fitted areas of the crystal and amorphous domains, respectively.

The untreated materials presented the lowest relative crystallinity, because of higher content of hemicellulose and lignin. The treatment of NaOH and bleaching agents removed the lignin and hemicellulose content and increased the degree of crystallinity by almost 20%. The effect is well known in the literature [29,30]. In this study, the effect corresponded to the chemical compositions. This is underlined by the fact that the highest containing cellulose of untreated material has the highest crystallinity compared to the untreated counterparts. However, after the treatment SW cellulose surpassed of SCB cellulose by 30%. This confirms the removal of lignin and hemicelluloses as alluded to by FTIR. Nonetheless, the difference in crystallinity index values obviously arose from the difference in compactness of the cell walls [3–5], which responded differently to cellulose extractions.

8.5.4 TGA

Figure 8.3 represented the TGA and DTG curves of untreated SCB, untreated SW, SCB cellulose and SW cellulose at $11^{\circ}\text{Cmin}^{-1}$. The untreated materials display three degradation stages as confirmed by DTG, and SW is thermally more stable than SCB with higher char content than the rest. On the other hand, both celluloses display two degradation stages with virtually similar higher thermal stability than untreated counterparts. The celluloses generally have lower char contents than untreated materials; however SW cellulose dominates SCB cellulose content. The first degradation stage is normally attributed to a release of moisture, while the second and the third stage, in the case of untreated materials, are attributed to degradation of lignin, hemicelluloses and cellulose [31–35]. The removal of lignin and hemicelluloses as confirmed in FTIR and XRD results rendered both celluloses two stages for water release and cellulose scission. As for the different in char content, Moniruzzaman et al. [8] and Shen et al. [14] related the similar observation to both removal of cellulose, origin of lignin and cell wall. In this study, the reactive hypochlorite treatment, which seemed to have

altered the chemistry of the both celluloses to form derivatives could also be responsible for the difference in char content.

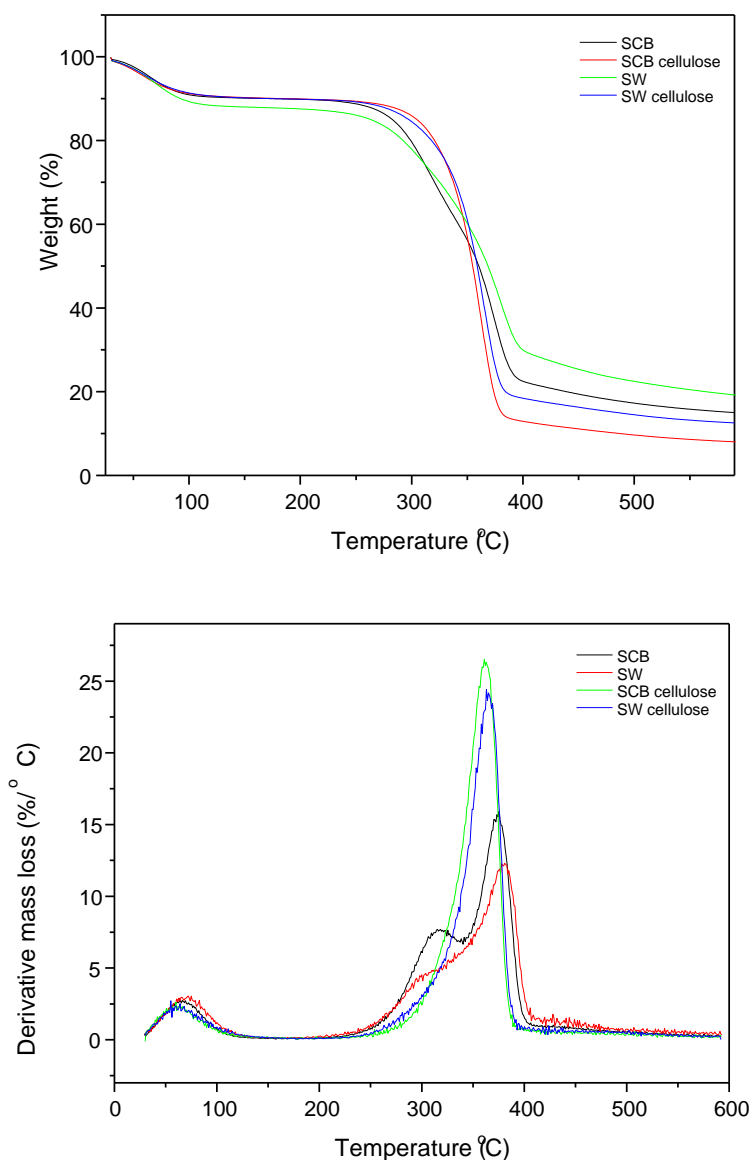


Figure 8.3: TGA and DTG graphs of untreated SCB, untreated SW, SCB cellulose and SW cellulose at 11°Cmin⁻¹

To obtain more information into thermal degradations, kinetics studies were undertaken using KAS, OFW and KGR models. Because KGR depends on T_m , KAS and OFW were compared first, followed by comparison of all models. The models require different heating

rates which are known to display increased thermal stability due to time temperature disposition principle and the particle thermal gradient theory of lignocellulosic materials [14, 36]. All the current results obeyed the principle within experimental uncertainty as shown by exemplary graphs of untreated SCB and SW (See Figure 8.4).

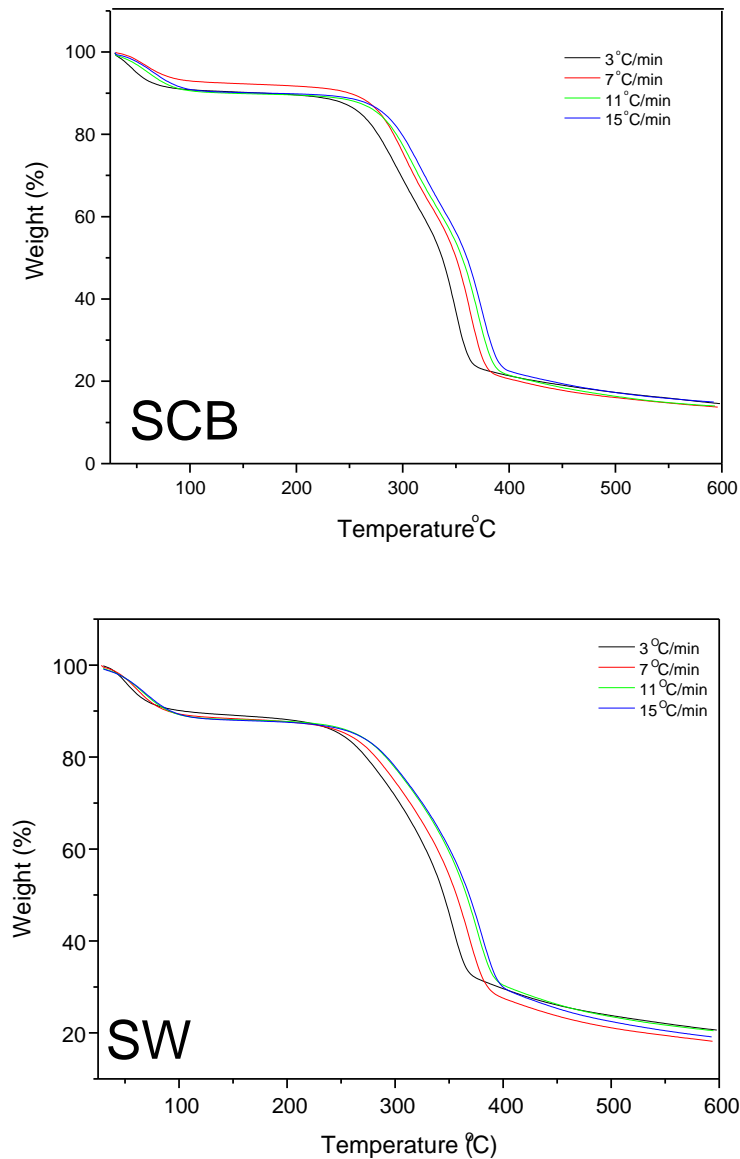
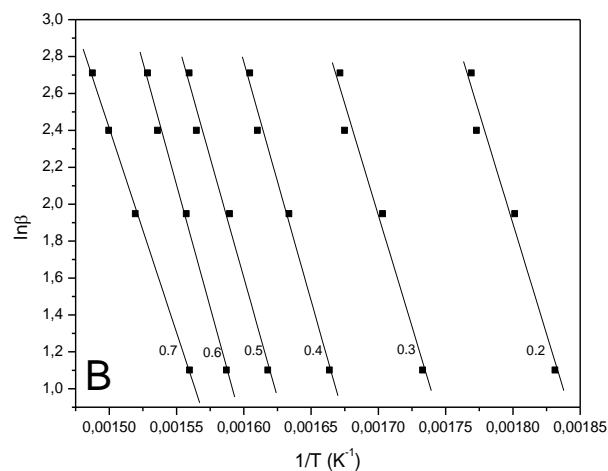
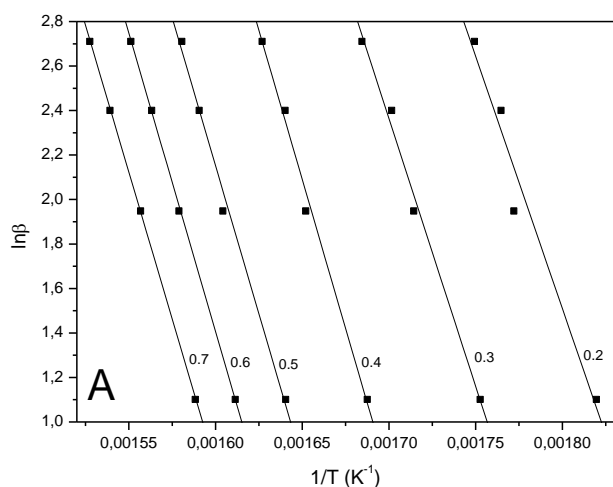


Figure 8.4: TGA graphs of SCB raw and SW raw at different rates

8.6 Kinetics degradation

The plots of $\ln \beta$ and $\ln (\beta/T^2)$ against $1/T$ corresponding to the several conversion degrees are shown in Figure 8.5-8.7 for FWO, KAS and KGR respectively. The Kissinger model unaided was also employed as presented in Figure 8, which showed linear plots of $\ln (\beta/T_m^2)$

versus $1/T_m$. The activation energy values were calculated from the slopes of the isoconversional plots. It can be observed in all cases that the lines become nearly parallel indicating the possibility of a simple reaction mechanism (Figure 8.6 and 8.7 for all a,b,c and d). Similar observations were also reported in the literature and our activation energy values were within the range of reported values ($110\text{--}300\text{ kJ.mol}^{-1}$) [1, 10, 20]. However, in this study it is worth noting that the gap between the lines is generally wider for untreated materials compared to cellulose (Figure 8.6 a,b and 8.7 a,b). Furthermore, the slopes are generally steeper for all untreated materials compared to celluloses. This might probably relate to the accelerated decomposition process of main degradation stage in the untreated materials as compared to delayed process in celluloses. Figure 8.9 showed the relationship between activation energy (E_a) values calculated from the corresponding slopes of the degree of conversions. The overall trend of E_a was relatively similar for both SCB and SW materials, from which there was an increase in the degree of conversion from 20%-50% followed by a gentle reduction up to 70% mass loss. The SCB celluloses revealed a slight decrease in activation energy values while SW showed a linear proportional relationship with the increase in the degree of conversion.



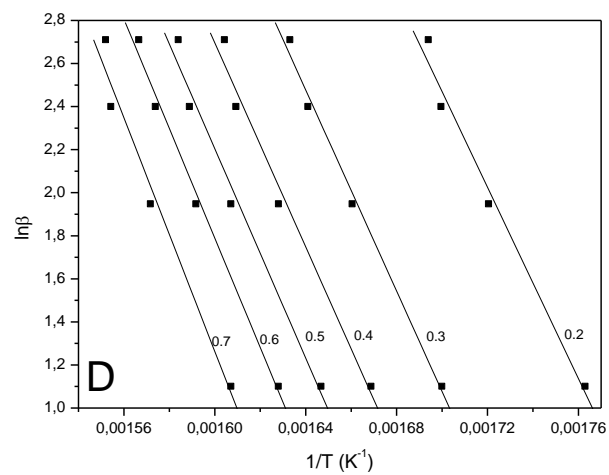
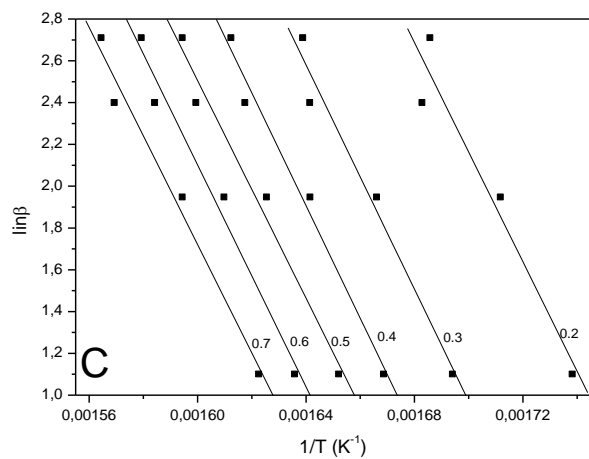
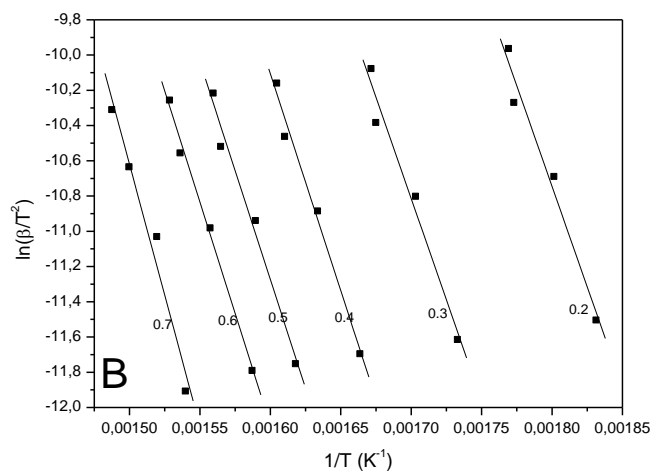
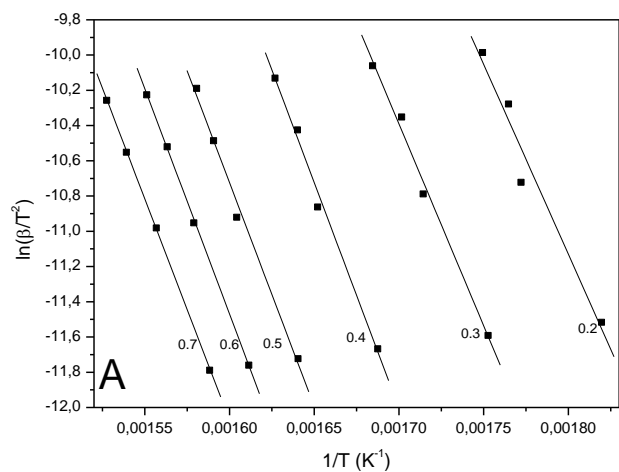


Figure 8.5: (A) FWO of untreated SBA, (B) FWO of untreated SW, (C) FWO of SBC cellulose, (D) FWO of SW cellulose



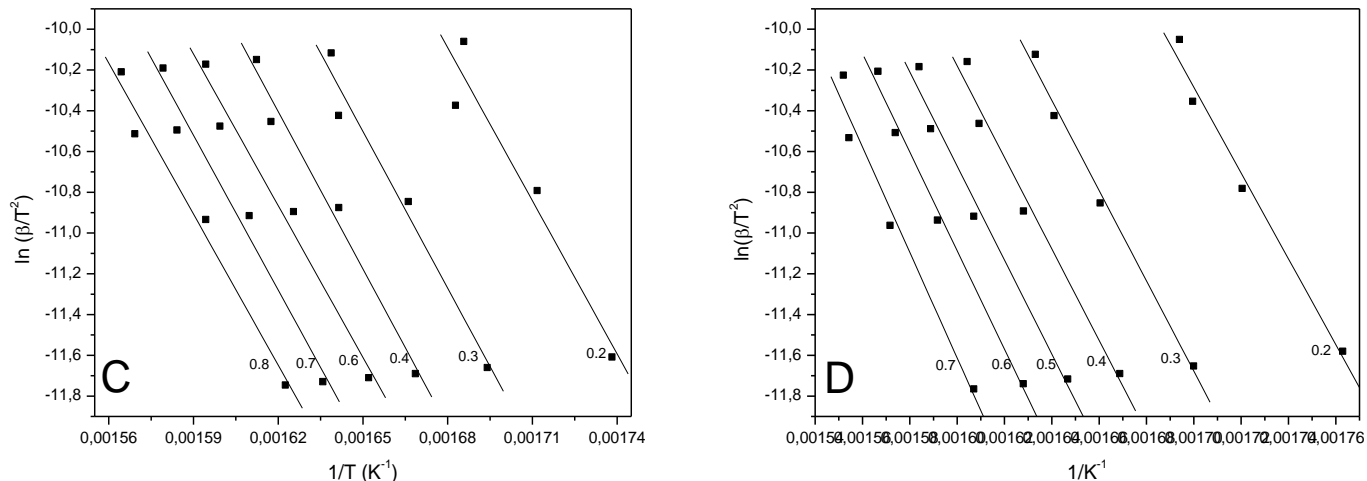


Figure 8.6: (A) KAS of untreated SBA, (B) KAS of untreated SW, (C) KAS of SBC cellulose, (D) KAS of SW cellulose

In the reported trends in previous research, hemicellulose and cellulose of lignocellulosic materials degrade at lower and higher temperatures respectively, while lignin degrades across the temperature ranges [37, 38]. This suggests in our case that the most char for untreated materials formed at 70%. The cellulose apparently decomposes into volatile levoglucosan and glycolaldehyde which then interact exothermically to form a char. Shen et al. [14] proposed the pathways as indicated in Figure 8.10.

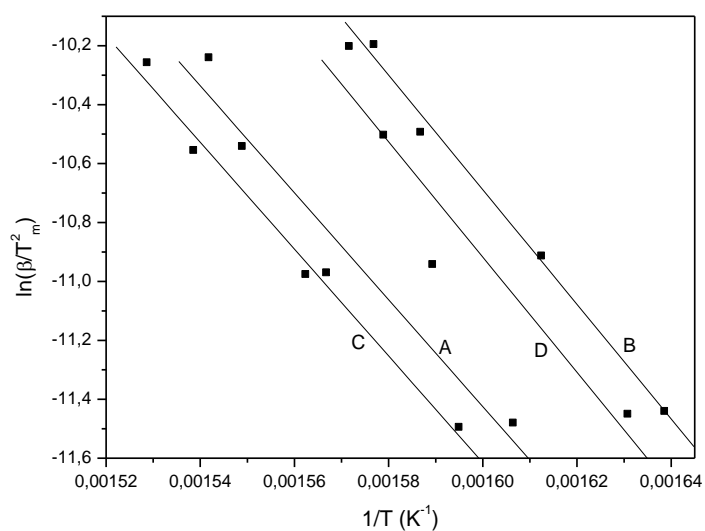


Figure 8.7: (A) Kissinger of untreated SCB raw, (B) Kissinger of SBC cellulose, (C) Kissinger of untreated SW, and (D) Kissinger of SW cellulose

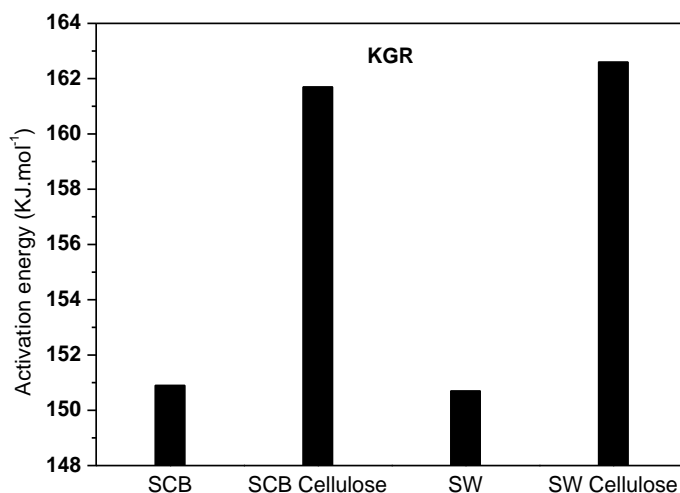


Figure 8.8: Activation energy values as a function of degrees of conversion obtained by KGR

The initial thermal degradation of cellulose is the depolymerization of the cellulose polymer to form various anhydrosugar derivatives including levoglucosan as the most prevalent. It can be seen from the mechanism that levoglucosan (LG) is reduced at higher temperature, in contrast to other products which implies a complex and competitive mechanism between the LG and other products (such as HAA, HA, and 5-HMF). In our case it is clear that initially treatments led to completely different cellulose derivatives which rendered a higher activation value for SCB cellulose than SW cellulose at 20% mass loss. However, at 70% mass loss SW cellulose has the highest activation value that corresponds to its char content which is twice that of SCB cellulose. This seems to agree with Pathway 5 which indicated formation of 5-hydroxymethyl-furfural which can form a crosslinked structure to increase char content once polymerized. This in fact could explain the different behaviors of activation energy values for the celluloses. The Kissinger model indicated that both celluloses displayed higher activation energy values than their corresponding untreated counterparts, even though the SW surpassed that of SCB cellulose (Figure 10.8).

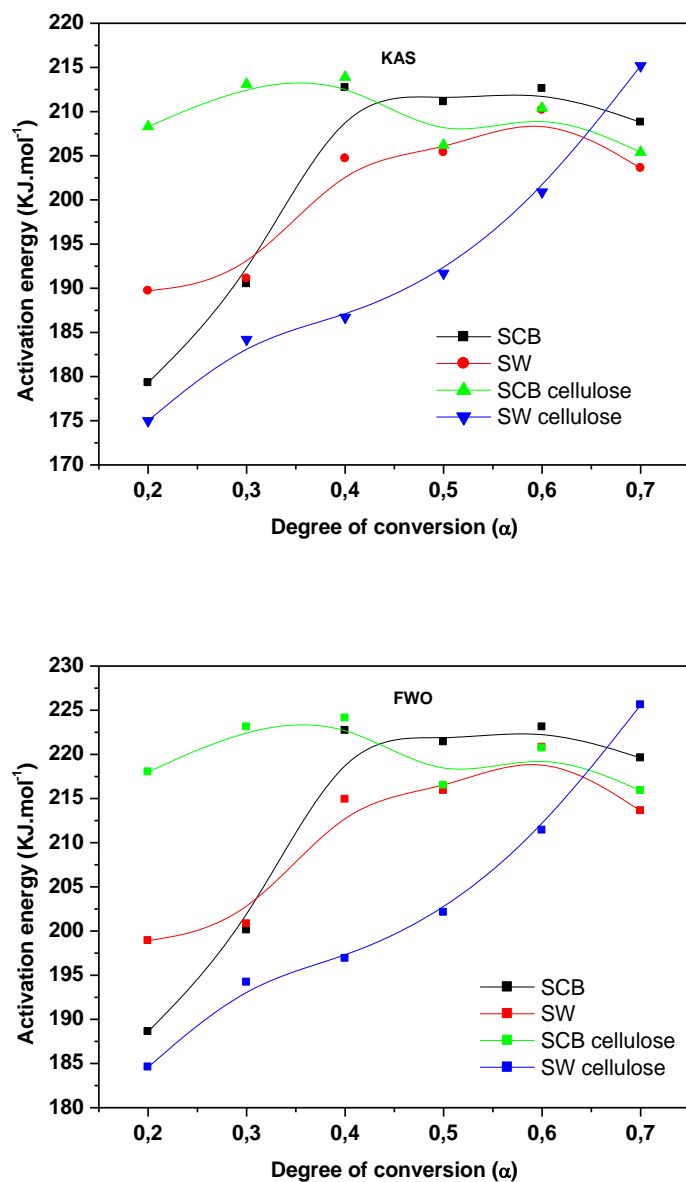


Figure 8.9: Activation energies ($\text{kJ}\cdot\text{mol}^{-1}$) obtained by KAS and FWO methods.

This clarifies the observed increased in thermal stability of celluloses and is in line with the increased crystallinity index values of celluloses.

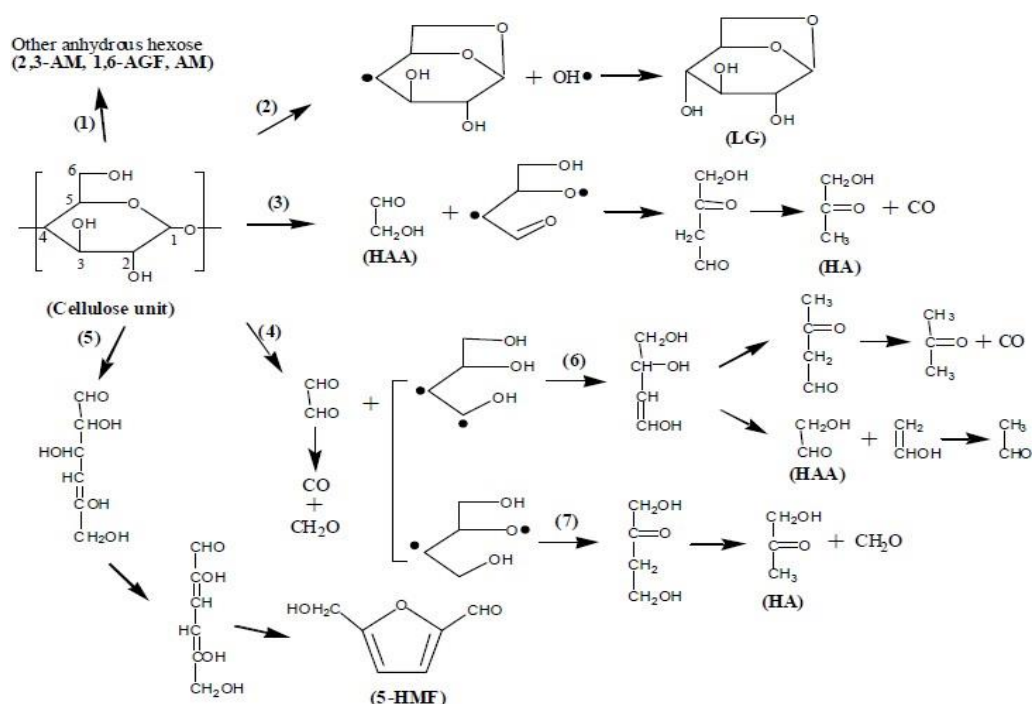


Figure 8.10. The speculative chemical pathways for the direct conversion of the cellulose molecules. levoglucosan (LG), hydroxyacetaldehyde (HAA), hydroxyactone (HA), pyruvic aldehyde (pa), glyceraldehyde (GA), 5-hydroxymethyl-furfural (5-HMF), furfural (FF), and 1,6-anhydroglucofuranose (AGF).

8.7 Conclusion

Thermal degradation of SCB and SW was investigated using TGA at different heating rates of 3 °C.min⁻¹, 7 °C.min⁻¹, 11 °C.min⁻¹ and 15 °C.min⁻¹. The thermal degradation of SCB and SW raw materials displays a three stage weight loss, which correspond to three peaks on the DTG curves: moisture evaporation, decomposition of hemicellulose and cellulose, and decomposition of lignin content. Increasing heating rate resulted in increasing mass loss rates, but the start of the thermal decomposition was delayed to higher temperatures. The thermal stability of extracted cellulose increased and high content of lignin produces more char residue for the untreated counterparts. Kinetic parameter in terms of the apparent activation energy were determined and compared using the FWO, KAS and KGR methods. The apparent activation energy of both FWO and KAS methods varied with conversion fractions, and showed similar trends. The FWO method provided higher activation energy values than those

from the KAS method. The Kissinger model resulted in lower apparent activation energy than was obtained using the other kinetic models.

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CHAPTER NINE:

THE EFFECT OF EXTRACTION PERIOD ON PROPERTIES OF SUGARCANE BAGASSE AND SOFTWOOD CHIPS CELLULOSE

(Article in *Wood research* **2017**, 62(6), 931-938; doi:[10.3390/ma10111246](https://doi.org/10.3390/ma10111246))

THE EFFECT OF EXTRACTION PERIOD ON PROPERTIES OF SUGARCANE BAGASSE AND SOFTWOOD CHIPS CELLULOSE

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Abstract

This work evaluates the extraction of sugarcane bagasse (SCB) and soft wood (SW) celluloses with alkali treatment followed by bleaching process using sodium chlorite at different time. The influence of extraction time (2 hrs and 4 hrs) on the thermal, crystallinity and morphological properties of the extracted celluloses was investigated. The extracted celluloses were analysed by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transmission infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). The aromatic skeletal vibrations of lignin and hemicellulose confirmed the extraction of cellulose and varied with extraction time. TGA analysis shows that the untreated SCB degrade earlier than their respective celluloses and the prolonged treatment affects the onset of main degradation. XRD results of SCB showed that extracted celluloses had greater crystallinity index, and was affected at prolonged time due to long range destruction of cellulose crystals. The SW revealed a complex behaviour due to the dominated lignin content as revealed from chemical composition analyses.

Keywords: Sugarcane bagasse, Soft wood, Cellulose, Extraction time

9.1 Introduction

There has been an increasing interest towards more sustainable usage of lignocellulosic biomass such as sugarcane bagasse and softwood as raw materials for industrial applications [1-3]. SCB is a by-product of cane from the alcohol and sugar industries that is mainly used in pulp and electricity generation. Chemically, sugarcane bagasse contains approximately cellulose (46.0%), hemicellulose (24.5%), lignin (19.95%), fat, waxes (3.5%), ash (2.4%), silica (2.0%) and other trace elements (1.7%) [4-6]. SW is increasingly becoming a renewable alternative to fossil fuels due to the high abundance, particularly in areas, such as uMhlathuze in South Africa, where industries abandon soft wood dust in an open space as a waste. SW has a wide range of applications in fibre, pulp, and polymer industries. Structurally, this complex biomass material constitutes mainly of cellulose (40-50%), hemicelluloses (15-25%), lignin (20-30%) and variable amounts of extractives. SW is characteristically known for its high lignin content, which results in its reluctances to chemical treatment [7].

The process of pure cellulose isolation has become the subject of extensive research work for many decades due to the cell wall structure complexity. Cellulose is the main constituent of biomass, forming approximately 40% to 45% of the dry substance in most lignocellulosic materials. Cellulose is a linear, unbranched homopolysaccharide composed of anhydroglucose units which are linked together by β -1,4-glycosidic bonds to form a crystalline material [8-9]. This is confirmed by the presence of three hydroxyl groups (secondary OH at the C-2, and at the C-3 and primary OH at the C-6 position) with different reactivities. These hydroxyl groups and their ability to form hydrogen bonds play a major role in directing the crystal packing and also governing the physical properties of cellulose [7, 10].

Alkaline treatment or mercerization is one of the most used chemical methods for isolation of cellulose in natural fibers as well as agro-waste. The important modification achieved with alkaline treatment is the disruption of the hydrogen bonding in the network structure [11-15]. This treatment is generally followed by delignification process, since alkali treatment may not completely remove lignin contents. Acidified- NaClO_2 is an established laboratory method for lignin removal. In the presence of acetic acid, aqueous sodium chlorite solutions dissociate into highly reactive chlorine anion (ClO^{2-}) and chloride anion (Cl^-) to destroy lignin to simpler compounds, which are dissolved and washed out, resulting in permanent whiteness [8, 16]. There is a little information or no information in literature which test the same treatment against

time. In most studies concentration of chemicals was varied. The aim of this study was to investigate the influence of extraction time (2 hrs and 4 hrs) on the morphology, crystallinity and thermal stability of the resulting cellulose extracted from SCB and SW.

9.2 Materials and methods

9.2.1 Materials

Sugarcane bagasse and soft wood were obtained from local sugar and wood factories (Empangeni, South Africa). Sodium hydroxide pellets (99.9%) were supplied by Merck, India, Sodium perchlorite by Capital lab Suppliers CC, Germany. All chemicals were used as received without further purification.

9.2.2 Methods

The washed and room temperature dried SCB and SW were initially treated with 2% (w/v) NaOH for 2 and 4 hours respectively and washed with deionised water to expel excess chemicals in order to obtain a neutral pH fiber. This process was repeated 4 times. Secondly, the alkali treated SCB and SW were further subjected to treatment of 2% (w/v) NaClO₂ treatment for a further 2 and 4 hours and washed to obtain neutral pH and dried. This process was also repeated 4 times.

9.2.3 Chemical composition

The untreated SCB and SW raw samples were used to determine their respective chemical composition. The lignin, cellulose and hemicellulose of the untreated materials SCB and SW were determined according to the TAPPI Standard T222 om-88, and TAPPI T19m-54 standards.

9.3 Characterization techniques

9.3.1 Scanning electron microscopy

The scanning electron microscopy (SEM) and EDX measurements of the as-deposited thin films were performed on a Philips XL 30 FEG (at 10 kV) and DX4 detector (at 20 kV), respectively. The films were carbon-coated by using Edward's E306A coating system, prior to the analyses.

9.3.2 Fourier transmission infrared spectroscopy

FT-IR spectroscopy analysis was carried out on a Bruker Tensor 27 FT-IR spectrometer using a standard ATR cell; the catalysts were analysed as-synthesised with no prior preparation required. The force was adjusted to 90 gauge for sufficient contact between the surfaces. The catalysts were scanned over the mid-IR region (450 cm^{-1} - 4000 cm^{-1}).

9.3.3 Powder X-ray diffraction

The XRD characterization of all samples was performed on Powder X-Ray Diffraction spectroscopy (Bruker AXS Advance D8 diffractometer) with monochromatic Cu K α ($\lambda = 1.5406\text{ \AA}$) incident radiation at 40 kV and 40 mA at room temperature. The samples were scanned within the high angle 2θ range to get all characteristic diffractions of the materials at 0.5 scan speed and 0.01314 increments. The crystallinity index (CI) was obtained from:

The height peak method

The CI was calculated from the ratio of the maximum peak intensity 002 (I_{002} , $2\theta = 22.5$) and minimal depression (I_{am} $2\theta = 18.5$) between peaks 001 and 002 according to Equation 1.

$$CI = (I_{002} - I_{am})/I_{am} \times 100 \quad (1)$$

where: I_{002} - maximum intensity of the 002 peak,
 I_{am} - minimal depression of the amorphous structure.

The CI was determined using Equation 2, by comparing the corresponding areas of the crystalline and amorphous fractions, obtained by deconvolution of the diffractogram, where A_a is the area of the amorphous phase and A_t the total area of the diffractogram.

$$CI = (1 - A_a/A_t) \times 100 \quad (2)$$

9.3.4 Thermal gravimetric analysis

Thermogravimetric analyses were performed using TGA analyser unit (Perkin Elmer), under flowing nitrogen atmosphere at flow rate of 20 mLmin⁻¹. Approximately 10-15 mg of sample was heated from 25 °C to 600 °C at a heating rates rate of 10 °C.min⁻¹. The sample weight loss and rate of weight loss were recorded continuously as functions of temperature. The analysis was only started when isothermal condition had been obtained.

9.4 Results and discussion

9.4.1 Chemical composition

Chemical composition analysis was conducted to ascertain various contents of biopolymers from untreated SCB and SW in Table 9.1. The cellulose content is highest in both materials than hemicellulose and lignin. There is no common trend exhibited by hemicellulose and lignin in both materials, however a first trend shown by SCB, in which hemicellulose is more than lignin in a natural fibre, is abundant in literature and appeared acceptable. However, in this study a second trend by SW showed the opposites. The phenomenon which is infrequent in literature but not ruled and/or impossible due to various factors affecting the contents of the components such as the origin and a part in a plant [7].

Table 9.1: Chemical composition of SCB and SW fibres

Sample	Cellulose (%)	Hemicellulose (%)	Lignin (%)
SCB	39.75 ± 0.7	38.03± 0.1	22.01± 0.6
SW	40.00 ± 0.5	24.00 ± 0.1	37.00 ± 0.5

9.4.2 Surface analysis

Figure 9.1 represents the SEM images of extracted cellulose from SCB and SW. It is clear that the untreated SB and SW (Figures 9.1a, and b, respectively) have particles, probably waxes and pectin, on the surfaces which were removed after treatments to obtain cellulose. In fact, the removal of particles for SCB Cell 2 and SW cell 2 was accompanied by a decrease in diameter from approximately 45 to 10 and 60 to 20 μm respectively (Figures 9.1 c, and e). The SCB Cell 4 and SW Cell 4 revealed even smaller average diameter, which is approximately smaller than 5 μm and 10 μm respectively, than both Cell 2 samples. This suggests that further defibrillation occurred during 4 hours treatment and it seems as though SCB has a weak cell wall which rendered little resistance to defibrillation. This also explains why SCB Cell 4 contained what arguably looked like nanofibrils compared to SW Cell 4, which contained almost none.

9.4.3 Spectral analysis

FTIR spectra of untreated SCB and SW and their corresponding celluloses are shown in Figure 9.2. The FTIR spectra of SCB showed more intense peaks than SW. Both spectra showed similar patterns with the dominant peaks observed around 3336 cm^{-1} (O–H stretch), 2901 cm^{-1} (C–H vibrations), 1593 cm^{-1} (C=C aromatic), 1319 cm^{-1} (O–H vibration of phenolic group), 1028 cm^{-1} (O–H stretching), 897 cm^{-1} (β -glycosidic linkage), and 558 cm^{-1} related to C–OH out-of-plane bending. These peaks are typical for lignocellulosic materials and in agreement with those reported in the literature for both untreated SCB and SW [7, 8, 10]. But after the chemical treatment, the peaks observed in the range 1750 and 1250 cm^{-1} linked to aromatic skeletal vibrations of lignin and hemicelluloses were reduced and others are almost diminished as compared to untreated materials. This indicates removal of lignin and hemicelluloses, as well as an exposure of cellulose [17, 18]. The intensity of most peaks for SCB cell 2 was reduced, while an aromatic peak at 1503 cm^{-1} almost disappeared. The same applied for SCB cell 4 except the intensity which was not that much affected in most peaks. Surprisingly for SW cell 2 and 4, a peak which seems to disappear is at 1732 1391 cm^{-1} with no much change with time. This might be associated to removal of the aromatic structure of lignin which seems to differ with that of SCB.

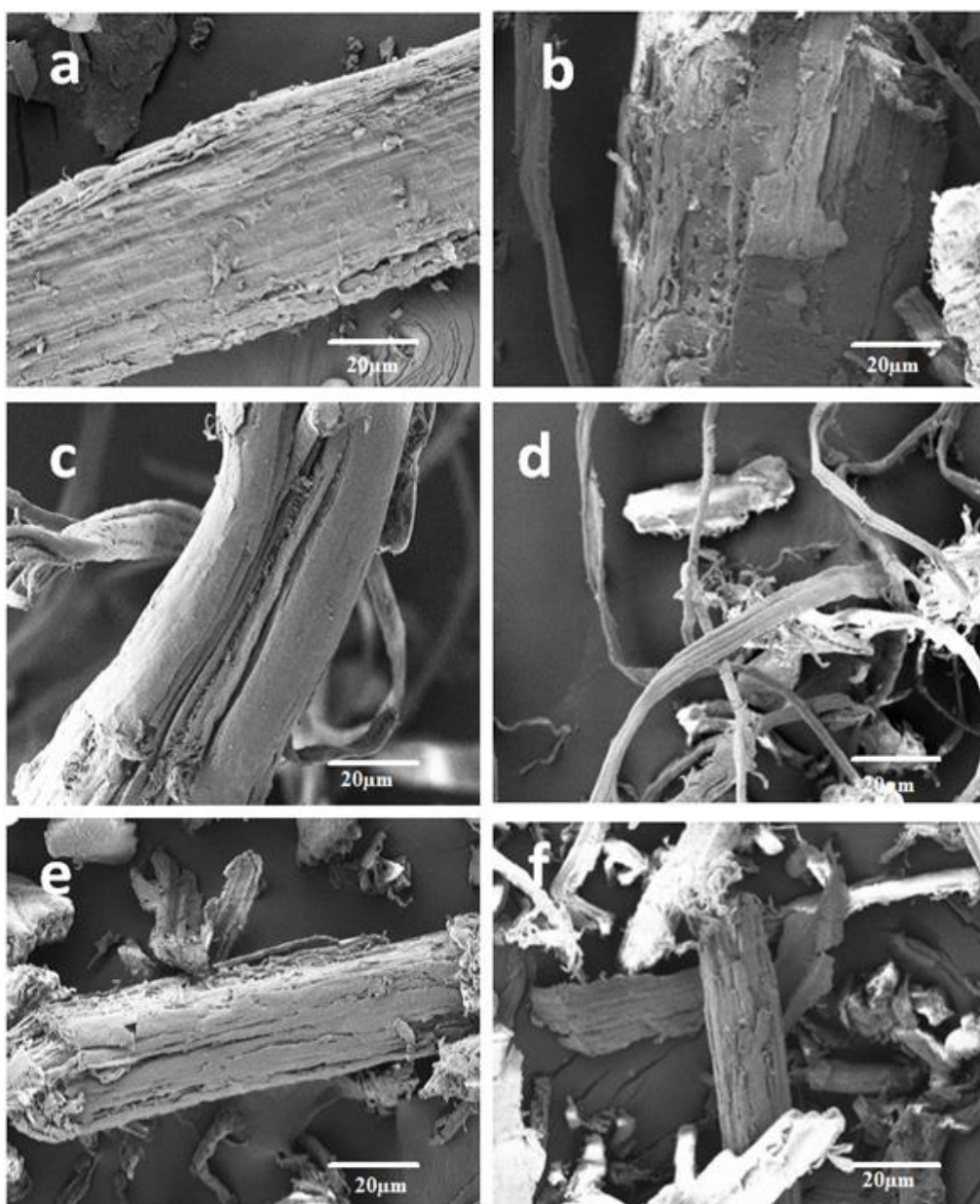


Figure 9.1: SEM images of untreated SCB (a), SW (b), SBC Cell 2 (c), SW Cell 4 (d), SW Cell 2 (e) and SW Cell 4(f).

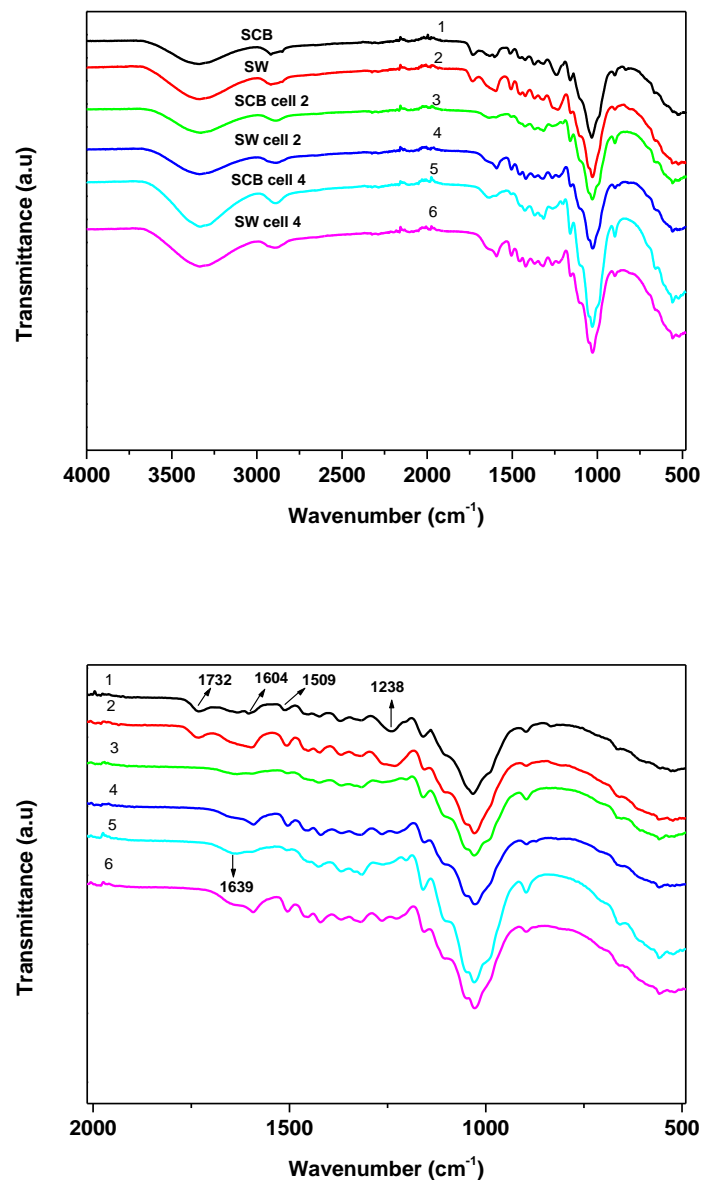


Figure 9.2: FTIR spectra of untreated SCB and SW, and extracted SCB and SW cellulose at 2 and 4 hrs

9.4.4 X-ray diffraction

The X-ray diffraction patterns of untreated SCB and SW and their corresponding celluloses are shown in Figure 9.3 and the crystallinity index values presented in Table 9.2. The diffractogram of SCB and SW materials display dominant peaks at 2θ values corresponding with 15.5° and 22.5° of the polymorphs of cellulose I of natural fibers [19, 20]. The crystallinity results showed that both the untreated SCB and SW presented the lower crystallinity when compared to celluloses. Similar results were also reported by Candido et al.,

[21] who observed an increase in crystallinity index after extraction of cellulose from SCB. They ascribed the higher crystallinity index to a larger exposure of cellulose in SCB cellulose than in untreated SCB. The SCB cell 4 and SW cell 4 presented a reduced crystallinity index as compared SCB cell 2 and SW cell 2. This observation suggests that time of 4 hrs was too severe to not only remove the amorphous phase, but also destroyed part of the cellulose. Wang et al., [22] explained the similar observation to broken. This reduction at broken intermolecular and intra-molecular hydrogen bonds of cellulose which apparently cause the disintegrate of crystal structure. This is highly possible in this study when considering disappearance and intensity change of some peaks in the FTIR results, which reflected change in crystal structure.

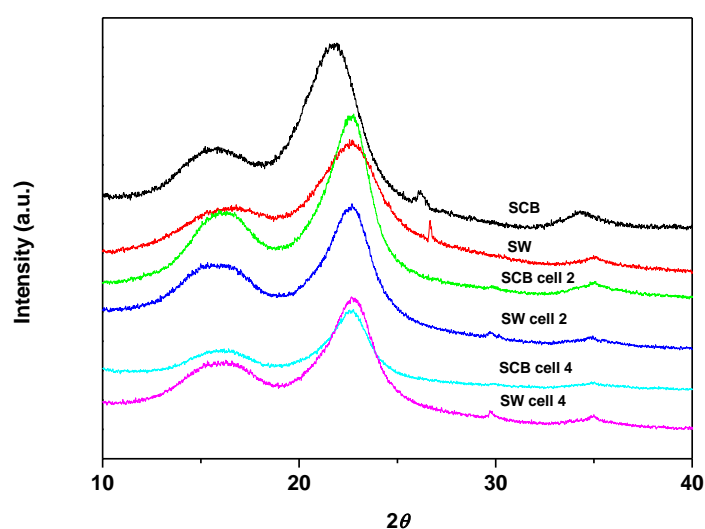


Figure 9.3: XRD analysis of untreated SCB and SW, and extracted SCB and SW cellulose at 2 and 4 hrs

Table 9.2: Crystalline index of untreated SCB, SW and extracted SCB and SW celluloses

Sample	Peak height method	Deconvolution method
SW	51.0	56.9
SW Cell 2	71.9	75.8
SW Cell 4	62.9	67.4
SCB	62.4	66.4
SCB Cell 2	78.3	80.3
SCB Cell 4	64.2	76.3

9.4.5 Thermal properties

The TGA curves for untreated SCB and SW and their respective celluloses are shown in Figure 9.4. The untreated materials exhibited three degradation steps known for moisture, hemicellulose, cellulose, and lignin that cuts across the thermal region of cellulose and hemicellulose [7, 16, 20]. The SW was thermally stable than the untreated SCB and presented the higher char content than SCB. As expected, the onset of main degradation shifted towards a higher temperature for all celluloses and SCB Cell 2 and SW Cell 2 presented the higher thermal stability than SCB Cell 4 and SW Cell 4. This clarifies the observations of XRD and FTIR that prolonged period, in fact, depolymerized cellulose to give the reduced crystallinity index values and ultimately lowered thermal stability. Interestingly, SCB cell 2 and cell 4 in char content while the opposites occurred for SW cell 2 and cell 4. The observation is embedded in the thermal degradation mechanism which is informed by morphology observed from FTIR and XRD.

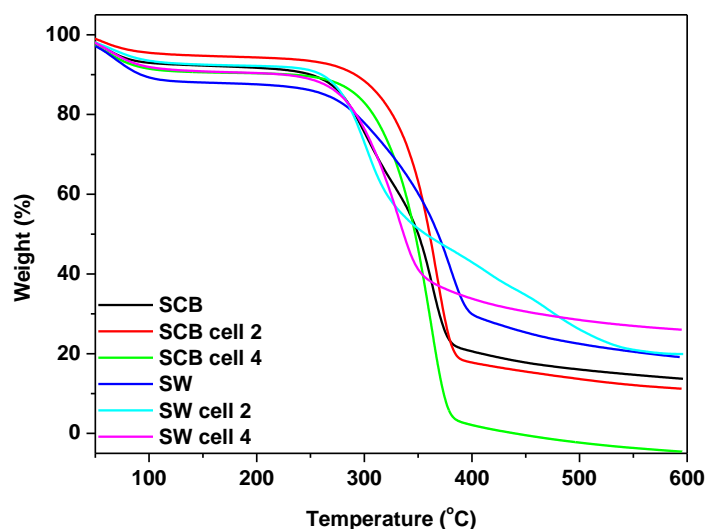


Figure 9.4: TGA graphs of untreated SCB and SW, and extracted SCB and SW cellulose at 2 and 4 hrs

9.5 Conclusion

Cellulose materials were successfully extracted from SCB and SW lignocellulosic materials through alkali treatment and delignification using NaClO_2 bleaching agent. The chemical composition results showed that SCB had higher hemicellulose content than cellulose, and SW presents the highest lignin content. The results obtained from FTIR

confirmed that both lignin and hemicellulose were removed during the chemical process with complete removal obtained at 2 hrs. The crystallinity index results showed that the crystallinity was increased with chemical treatment, with the highest crystallinity values obtained at 2 hrs for treated SCB and SW respectively. The TGA further results revealed that the untreated SCB and SW materials analysed at 2 hrs were thermally stable than their untreated and 4 hrs treated counterparts.

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CHAPTER TEN:

COMPARISON OF ALKALI TREATED SUGARCANE BAGASSE AND SOFTWOOD CELLULOSE/POLYPROPYLENE COMPOSITES

(Article in *Plastics, Rubber and Composites* **2019**, 62(6), 931-938; doi:[10.3390/ma10111246](https://doi.org/10.3390/ma10111246))

COMPARISON OF ALKALI TREATED SUGARCANE BAGASSE AND SOFTWOOD CELLULOSE/POLYPROPYLENE COMPOSITES

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Abstract

In this study, composite materials from agricultural biomass and polypropylene (PP) thermoplastic were produced by melt compounding using a melt mixer. The chemical interaction of sugarcane bagasse (SCB)-PP and soft wood (SW)-PP composites and corresponding cellulose were verified by Fourier-transform infrared spectroscopy (FTIR) analysis, X-ray diffraction (XRD) and Scanning electron microscopy (SEM). The cellulose composites were more crystalline than PP, trailed by PP/SCB and PP/SW composites. It was found that among composite materials, PP/SCB were least thermally stable compared to PP/SW. The addition of extracted cellulose decreased the thermal stability of PP/SCB composites at higher filler content due to poor interfacial bonding as compared to PP/SW composites. SEM results confirmed a rough morphology and the presence of many voids resulting from fibre pull-out in composites, especially for the ones with higher fibre content. Dynamic mechanical analysis (DMA) of both PP/SCB and PP/SW composites indicated improvement in the storage modulus compared with neat PP.

Key words: Polypropylene; Sugarcane bagasse; Soft wood; Cellulose; Composites

10.1 Introduction

Recent growth in environmental awareness, government legislation and landfills challenges have led to the development of green and smart materials by using agricultural wastes. The waste is abundantly available and has potential to substitute conventional fibre such as aramid, glass, and carbon fibres [1–3]. In addition, agricultural waste is less harmful, nonabrasive, biodegradable, easily processed and environmentally friendly [4–6]. However, agricultural waste is easily degradable by UV radiation, hydrophilic in nature and has tendency to form aggregates during polymer composites processing [6–8]. There are studies on the development of thermoplastic composites using agricultural waste (sugar cane bagasse, rice hulls, wood flour) and thermoplastics such as PP, PE, and PVC reported in the literature [9–11]. These composite materials are widely used in industries such as construction, automotive, and packaging because of their superior mechanical properties and lower cost compared to synthesis of new polymers [12–14]. Their main drawbacks include poor adhesion and incompatibility due to fibre hydrophilicity. Chemical treatments such as maleic anhydride and alkaline treatment among others have been reported to increase the surface roughness of the fibres for an improved adhesion with polymeric matrices [15–17].

Kim et al. [4] compared the mechanical properties of cotton and wood fibre (WF)/PP composites. The tensile and flexural strength of the PP/WF composites decreased with increasing amount of WF. However, the opposite occurred for PP/cotton fibre composites. This behaviour was explained by the entanglement of the cotton fibre when its content was above 10 wt-%. The difference in the tensile strength was also attributed to various factors such as the fibre length, hydrophilicity as well as the difference in the chemical nature of the fibres. In another study, Yuang et al. [18] investigated WF/PP composites materials using twin-screw extruder techniques. The authors reported higher tensile and flexural modulus of WF/PP composites at higher filler content (50%) WP content compared to neat PP. Furthermore, the tensile and impact strength of WF/PP at 50 wt-% wood fibre content were reduced due to increasing melt viscosity of the polymer. SEM analysis indicated that the polymer molecules penetrated into the vessels and cracks of the cellulose fibre, the addition

of maleic anhydride-grafted polyolefin as a compatibiliser improved the level of adhesion between the WF and the PP.

El-Fattah et al. [11] investigated the effects of sugarcane bagasse fibres content on the recycled high-density polyethylene/sugarcane bagasse fibre composites. The tensile modulus and strength of the composites increased and decreased respectively with the addition of bagasse fibre. The decrease was attributed to lack of interfacial adhesion between the fibre and the polymer which apparently resulted in poor stress transfer from the polymer to the reinforcing filler. The SEM analysis indicated that the fibres were agglomerated, and appeared to be free of any matrix interactions. Similar observations of bagasse reinforced thermoplastic were also reported by Subramonia et al. [19]. They observed that an increase in bagasse content reduces the tensile strength of polypropylene composite material, which resulted in brittle and less ductile material. The results further showed that flexural strength and modulus increased with the addition of bagasse fibre at lower filler content and decreased at higher content. SEM investigations revealed a porous structure and fibre fracture on a composite specimen which was apparently an indication of uneven mixing of the fibre and PP.

Mulinari et al. [3, 20] investigated mechanical property and morphology of composite materials developed from sugarcane bagasse cellulose and high-density polyethylene. The composite materials presented lower average values for tensile strength, elongation at break and significant improvement in the Young and flexural modulus compared to neat HDPE. The addition of cellulose fibres decreased the thermal stability of the HDPE resulting composite. SEM analysis showed that the cellulose fibres increased defects and voids, which apparently emanated from poor interaction and agglomeration between fibres and matrix. Similar results were also reported by Moubarik et al. [8] investigating the reinforcing capability of cellulose fibres extracted from SCB and LDPE as matrix. In another study, Luz et al. [21] developed PP composites reinforced with SCB cellulose. The cellulose/PP composites presented the highest flexural and tensile strength values compared to neat PP. The tensile and flexural moduli for cellulose/PP composites were also higher as compared to the neat PP. In addition, the presence of fibres decreased the thermal stability of the composite. This was explained by the nucleating ability of untreated cellulose fibre on the crystallisation of PP. The study observations were in line with the results of Ashori et al. [22]. The later reported that the performance properties of microcrystalline cellulose (MCC) as a reinforcing agent in wood plastic composites.

There is a limited information about systematic and direct comparison of cellulose from different biomasses. In this work, PP/SCB and PP/SW thermoplastic composites were prepared by melt mixing using the brabender mixer. A comparative study on the effects of untreated SCB and SW, and their respective celluloses on the resulting PP composites was conducted and analysed.

10.2 Materials

PP was supplied by Sasol Polymers (Johannesburg, South Africa), it has a density of 0.90 g cm^{-3} , a melting point of 165°C , and an MFI of 12 g.10 min^{-1} . SCB and SW were collected from Tongaat Hullet and Mondi in Empangeni, South Africa respectively. SCB and SW celluloses were extracted and chemical composition was estimated according to a method reported in the literature [23]. Dry SCB and SW were treated with an alkali solution (2 wt-% NaOH) at 100°C for 4 h. The solid white precipitates were filtered and washed several times with distilled water. The same treatment was performed using 1.7 wt-% sodium perchlorite buffered with acetic acid. Finally, the white suspension (cellulose) was allowed to cool and filtered using deionised water in order to attain a neutral pH.

10.3 Preparation of composites

The composites materials were weighed according to ratios and formulation as indicated in Table 10.1, and thoroughly mixed in the Brabender Plastograph internal mixer. Mixing of the samples was done at 190°C and a mixing speed of 30 rev min^{-1} for 15 min. The samples were then melt pressed at 200°C and 100 bar for 3 min and allowed to cool at room temperature for 10 minutes.

Table 10.1. Sample composition of PP, PP/SCB and PP/SW composites

Abbreviations	Fibre (wt-%)	PP (wt-%)
PP	-	100
PP/SCB untreated 5 wt-%	5	95

PP/SCB cellulose 5 wt-%	5	95
PP/SCB cellulose 10 wt-%	10	90
PP/SW untreated 5 wt-%	5	95
PP/SW cellulose 5% wt-%	5	95
PP/SW cellulose 10 wt-%	10	90

10.4 Characterization methods

10.4.1 Chemical composition

Untreated SCB and SW untreated samples were used to determine their respective chemical composition. The quantification of lignin, cellulose and hemicellulose were estimated according to the TAPPI Standard T222 om-88, and TAPPI T19m-54 standards.

10.4.2 Fourier transmission infrared spectroscopy

The FTIR spectra were collected by using a Perkin Elmer FTIR in the diffuse reflectance mode; the samples were analysed in the spectral region between 4000 to 400 cm⁻¹ resolution.

10.4.3 Powder X-ray diffraction

Powder X-Ray Diffraction (Bruker AXS Advance D8 X-Ray diffractometer) equipped with Cu K α generator ($\lambda = 1.5406 \text{ \AA}$) as X-ray source, operating (40 kV and 40 mA) was used to examine the crystal structure of the samples.

10.4.4 Thermal gravimetric analysis

Thermogravimetric analyses were performed using TGA analyser unit (Perkin Elmer), under flowing nitrogen atmosphere at flow rate of 20 ml.min⁻¹. Approximately 10-15 mg of sample was heated from 30°C to 700°C at a heating rates rate of 10°C.min⁻¹.

10.4.5 Digital scanning calorimetry

Digital scanning calorimetry (DSC) was performed using a DSC analyser unit (Perkin Elmer), under flowing nitrogen atmosphere at flow rate of 20 ml min⁻¹. Around 10-15 mg of the sample were heated from room temperature to 200 °C at a heating rate of 10 °C.min⁻¹. Fractional crystallinity was calculated using Equation (1).

$$X_{dsc} = \left(\frac{\Delta H}{\Delta H_m} \right) \times 100\% \quad (1)$$

Where ΔH is the heat of fusion of the sample, ΔH_m is the heat of fusion of a 100% crystalline PP = 209 J.g⁻¹ and w is the mass fraction of PP in composites [7].

10.4.6 Scanning Electron Microscopy

The SEM micrographs were taken at an accelerating voltage of 15 kV. All samples were fractured in liquid nitrogen, sputter-coated with gold and allowed to dry before taking images.

10.4.7 Dynamic Mechanical Analyzer

The dynamic mechanical analyser (DMA, Q800 instrument) of the PP and composites were investigated from 40 °C to 180 °C by 3 point bending mode with 15mm sample size at a heating rate of 5°C min⁻¹ and a frequency of 1 Hz.

10.5 Results and discussion

10.5.1 Chemical composition

Table 10.2 represents the chemical compositions of both SCB and SW. In both samples, the cellulose content is dominating followed by hemicellulose and lignin respectively. The observation is common in literature but not generic [23]. Apparently, factors such as the origin of the natural fibre and a harvest season have the potential to affect the chemical compositions [24, 25].

Table 10.2. Chemical constituents of SCB and SW

Sample	Lignin (%)	Cellulose (%)	Hemicellulose (%)
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SCB	18.8 ± 0.1	42.9 ± 0.99	38.2 ± 1.08
SW	37.2 ± 0.01	39.2 ± 0.01	23.6 ± 0.01

10.5.2 Scanning electron microscope

The SEM micrographs of PP/SW and PP/SCB untreated fibre and cellulose composites are shown in Figure 10.1. A rough morphology with the presence of voids resulting from fibre pull-out was observed in Figure 10.1(a,b) (see arrows). Figures 10.1(c,d) shows agglomerates and fibre pulled out from the polymer matrix, as well as uneven filler distribution. Those may be an indication of poor interfacial adhesion and incompatibility between untreated fibre and hydrophobic PP matrix [20]. Islam et al. [3] related this phenomenon to the difference in polarity between the fibres and the matrix that result in fibre agglomeration and uneven distribution throughout the matrix. However, the SEM micrograph of PP/SCB cellulose 5% composites revealed a penetration of PP into agglomerated fibres as shown by arrows. The SEM micrograph of PP/SW cellulose 5% showed cellulose fibrils and entanglement with very minor pulls and voids, indicating that the cellulose was fairly covered by the polymer matrix to a large extent [8]. Figure 10.1(e,f) shows virtually loose fibres untangled from the matrix. That suggested the reduced adhesion between the fibre and the matrix with the increase in cellulose content.

10.5.3 Fourier transform infrared

FTIR results of PP composites are shown in Figure 10.2. The PP and composites generally displayed main peaks around 2900, 1456, and 1200 cm^{-1} which are attributed to C-H stretching vibrations, $-\text{CH}_2$ to $-\text{CH}_3$ bending vibration, and symmetric deformation vibration. In addition, there are other observable peaks around 3340, 2137, and 899 cm^{-1} which are typical for PP material [26]. The presence of both SW and SCB fibre seemed to intensify the peak around 3400 cm^{-1} which corresponds to O-H stretching vibration as well as intramolecular and intermolecular hydrogen bonds. This may be due to the reduction in hydrogen bonding in cellulosic O-H groups, thereby increasing $-\text{OH}$ concentration due to high energy of O-H bonds [7]. The peak is even more pronounced in the presence of the highest cellulose containing composites. Nonetheless, peaks around 1700 cm^{-1} were suppressed in the presence of untreated fibres, yet there appeared to be a development of peak in the presence of the

highest cellulose containing composites. These may be due to interaction between $-C=O$ stretching in the acetyl groups of PP and $-OH$ groups in cellulose, probably due to reduction of OH bonds [25].

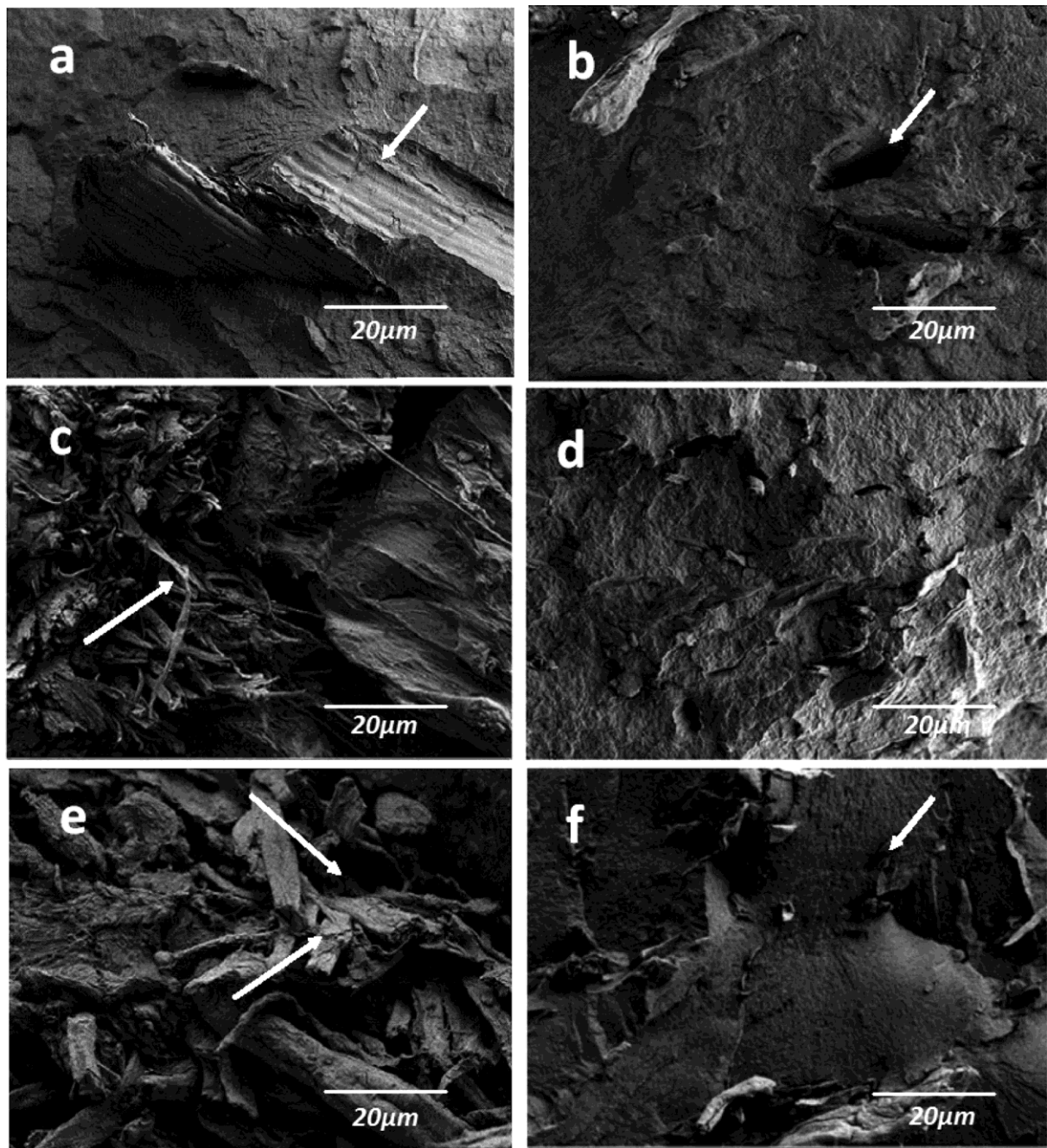


Figure 10.1. SEM micrograph of PP/SCB and PP/SW untreated fibre and cellulose composites. (a) PP/SW untreated 5%, (b) PP/SBC untreated 5%, (c) PP/SW cellulose 5%, (d) PP/SBC cellulose 5%, (e) PP/SW cellulose 10%, and (f) PP/SBC cellulose 10%

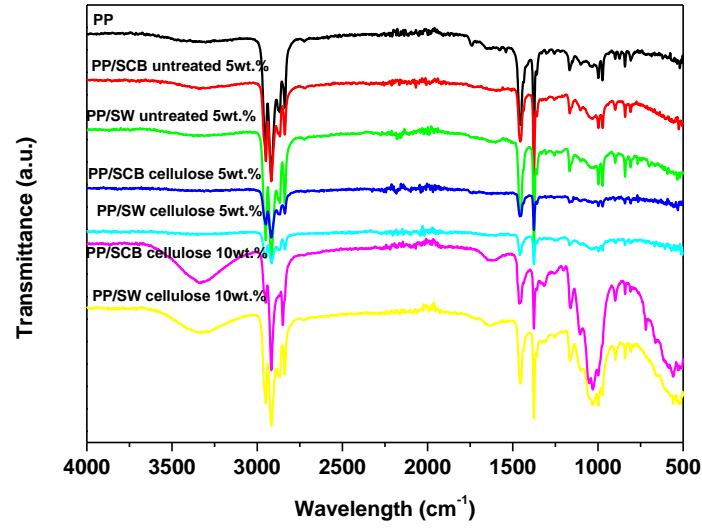


Figure 10.2. FTIR spectrum of PP, PP/SCB and PP/SW composites

10.5.4 Powder X-ray diffraction

XRD patterns of PP, SW and SCB polypropylene composites are shown in Figure 10.3, and Table 10.3 summarizes crystallinity index and crystalline sizes. The crystallinity index (CI) of PP/SCB and PP/SW composites was determined by using the deconvolution and peak height method using equation 2 and 3 respectively.

$$CI = (1 - A_a/A_t) \times 100 \quad (2)$$

where A_a is the area of the amorphous phase and A_t the total area of the diffractogram.

$$CI = (I_{002} - I_{am})/I_{am} \times 100 \quad (3)$$

where I_{002} is the maximum intensity of the 002 peak, and I_{am} is minimal depression of the amorphous structure.

The crystalline sizes of PP composites were obtained by using the Scherer's equation (4) based on full width at half maximum (FWHM).

$$CS = K\lambda / B \cos \theta \quad (4)$$

where, CS= crystalline size

K = constant (0.89)

λ = wavelength (0.154 nm)

B = (FWHM) in (rad.)

$\cos \theta = 2 \theta_{\text{peak}}$

The PP indicated well known crystalline lattice at 14.3° (110), 17.2° (040), 19.00° (130), and 22.2° (041) as well as halo humps at 26 and 29° [27]. The presence of both untreated fibres and cellulose generally resulted into more crystalline peaks, except for PP/SW cellulose 5% which generally displayed halo peaks with smaller crystalline size than the rest. In fact, PP/SW cellulose 5% did not display a peak whereas all untreated materials and PP/SCB cellulose 5% has shouldered peak at 22°. This suggests that treatment of fibre may have destroyed some crystalline regions of cellulose, thereby increasing the interlayer spacing between crystalline lattices and collapsing the peak [28]. Two different methods were used to estimate the crystallinity index as summarised in Table 3. There was no clear trend for the deconvolution method. However, the peak height method of all composites displayed diminishing crystallinity in the presence of untreated fibre and an increase of cellulose content. Interestingly, the untreated composites materials had higher crystallinity than their corresponding extracted celluloses composites. The reduction in crystallinity may be associated with the disruption of the chains of the crystalline structure of PP probably due to bonding with untreated fibre and cellulose, giving rise to the formation of amorphous regions [29]. The observations are further verified by crystalline sizes that have shown smaller crystallites for the alleged halo peaks and the opposites for the sharper peaks.

10.5.5 Thermogravimetric analysis

The thermal stability results of the PP composites are shown in Figure 10.4. Table 10.4 summarizes the decomposition temperatures at 10% and 40% mass loss. The PP displayed one degradation step at around 446.95 °C, but decomposition of fibre and polymer respectively led to two stages of degradation [11]. It is clear that all the composites are more thermally stable than the pristine PP. In fact, lowest cellulose containing composites appeared to be more stable than the rest. Similar results were reported by Islam et al. [7], who obtained improved thermal stability investigating alkali-treated kenaf fibre and PP composites. They

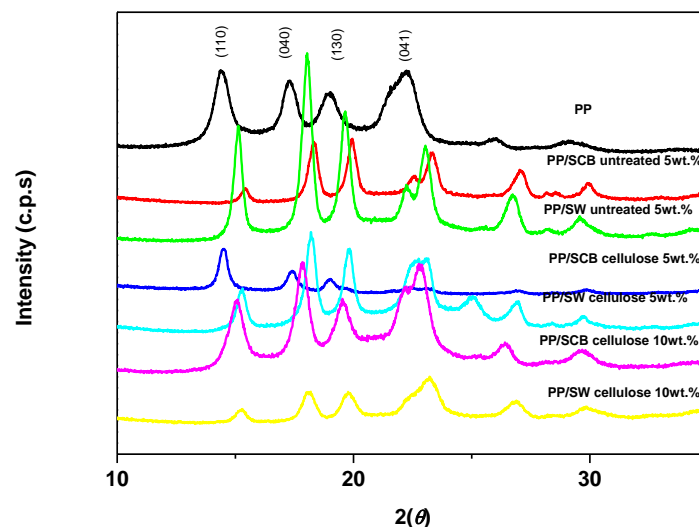


Figure 10.3. XRD patterns of PP, PP/SCB and PP/SW composites

Table 10.3: Crystallinity index (CI) of and crystalline sizes (CS) of composites materials

Sample	Deconvolution	Peak height	CS (nm)
	CI%	CI%	
PP	26.29	35.45 ± 4.35	14.19 ± 1.84
PP/SCB untreated 5 wt-%	26.72	26.89 ± 2.54	24.09 ± 5.3
PP/SCB cellulose 5 wt-%	31.34	25.87 ± 2.95	19.99 ± 2.5
PP/SCB cellulose 10 wt-%	29.01	14.01 ± 3.66	18.02 ± 3.5
PP/SW untreated 5 wt-%	14.98	26.28 ± 6.77	27.92 ± 4.3
PP/SW cellulose 5 wt-%	22.93	18.17 ± 2.22	16.95 ± 1.4
PP/SW cellulose 10 wt-%	25.76	15.84 ± 6.77	19.93 ± 2.5

attributed the higher thermal stability of the composites to interfacial interaction and bonding between fibre and matrix. Even though, in this study there was no coupling agents, but it is clear from SEM that there is a fair interfacial bonding, particularly for 5 wt-% cellulose composites, which could explain improved thermal stability SCB composites. The thermal decomposition results in Table 10.4 indicated that the PP/SCB composites are thermally stable than PP/SCB composites. That means PP/SCB composites leads to a better hindering of diffusion for the volatile decomposition products [29–32].

Table 10.4. Thermal degradation temperature of PP, PP/SCB, PP/SW untreated and celluloses composites at 10 % and 40% mass loss.

Sample	10% Mass loss	40% Mass loss
PP	-	446.95
PP/SCB untreated 5 wt-%	357.07	459.14
PP/SW untreated 5 wt-%	366.22	448.16
PP/SCB cellulose 5 wt-%	344.80	460.29
PP/SW cellulose 5 wt-%	344.82	460.99
PP/SCB cellulose 10 wt-%	343.17	461.67
PP/SW cellulose 10 wt-%	350.86	460.90

10.5.6 Differential scanning calorimetry (DSC)

The DSC crystallization and melting curves are shown in Figure 10.5. Crystallization, T_c (°C), and melting temperature, T_m (°C), as well as observed and calculated enthalpy of melting (ΔH_m) are summarised in Table 10.5. The DSC curves in Figure 10.5 displayed a single melting peak for all composites materials including PP. This is a well-known characteristic PP for a dominance of α -crystalline [33]. The T_m decreased in all composites materials, and the greatest decline was for PP/SW untreated composites with almost 5 °C lesser than PP. That is normally attributed to a formation of smaller crystallites in the presence of the fibre [34, 35]. The same seems to be the point in this study considering the nano-range crystallites size (14–25 nm) as anticipated by XRD. Nonetheless, Dikobe et al. [25] and Luz et al. [21] attributed the reduced melting temperature to a change in crystallisation of PP. The reason is highly possible as well considering our SEM. The micrographs revealed different size of agglomerates and more cellulose of PP/SW cellulose 5% was covered by polymer than PP/SCB cellulose 5%. Therefore, in this study, it is worth noting that the increase in SCB cellulose seems to further reduce T_m of the composites and the opposite is correct for SW composites. Therefore, it means any form of crystallisation formed around fibres is diminished in sizes for SCB and opposites for SW. This is confirmed by XRD results which indicated the presence of both untreated fibres and cellulose generally resulted into different crystalline peaks with some having shoulders and others with smaller crystalline size than the rest. In addition, the different crystallisation in PP showed little or no changes on the T_c of composites.

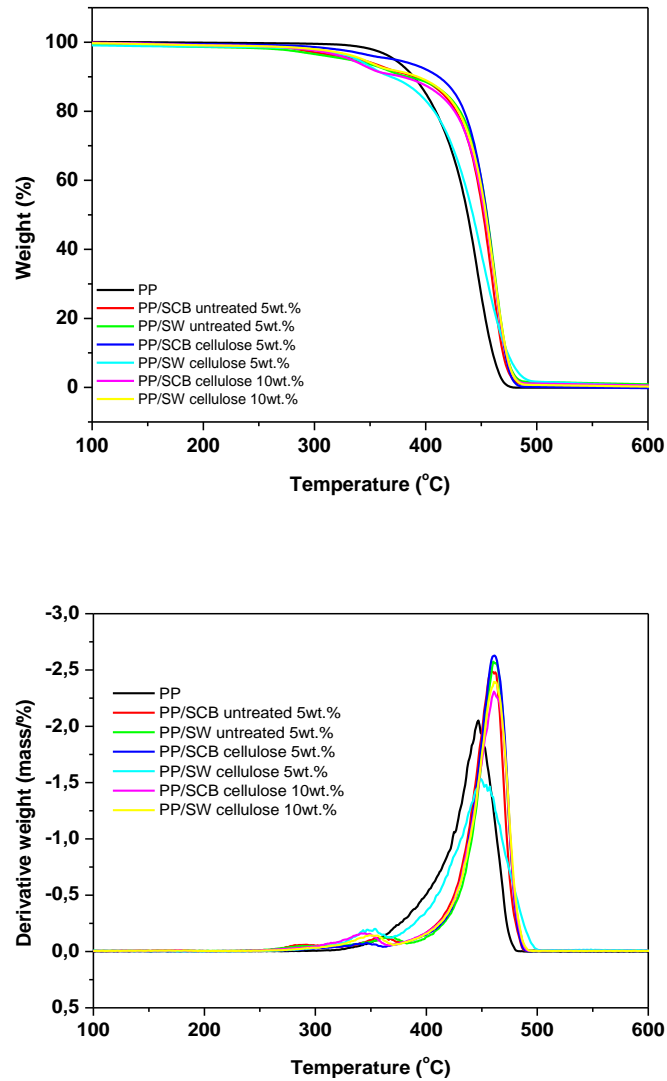


Figure 10.4. TGA and DTGA graphs of PP, PP/SCB, PP/SW untreated and celluloses composites

10.5.7 Dynamic mechanical analysis

Dynamic mechanical analysis was used to characterise the mechanical behaviour of PP/SCB and PP/SW untreated fibre and cellulose composites in terms of storage modulus (G) and loss factor ($\tan \delta$). The results in Figure 10.6 showed that the incorporation of fibres resulted in an increase in the storage modulus over the range of temperature investigated. The strong interfacial interaction and bonding between fibre and matrix from SEM, FTIR and TGA could be responsible for the observation. Furthermore, the results showed that the storage modulus of PP/SCB untreated is higher than PP/SW, and seem to decrease with the substitution of fibre with cellulose at higher filler content.

Table 10.5: DSC analysis of PP, PP/SCB composites and PP/SW composites

Samples	T_c (°C)	T_m (°C)	ΔH_m^{obs} (J.g ⁻¹)	ΔH_m^{calc}	X_c
PP	118.20 ± 0.11	164.98 ± 3.11	71.50 ± 1.01	-	34.21
PP/SCB untreated 5 wt-%	120.40 ± 0.30	162.06 ± 2.11	54.48 ± 1.11	51.76	26.07
PP/SCB cellulose 5 wt-%	119.63 ± 1.12	160.79 ± 0.18	50.37 ± 1.41	47.85	24.10
PP/SCB cellulose 10 wt-%	119.26 ± 1.12	161.65 ± 1.14	49.93 ± 1.22	44.94	23.89
PP/SW untreated 5 wt-%	118.25 ± 1.23	159.09 ± 0.11	51.19 ± 0.21	48.63	24.49
PP/SW cellulose 5 wt-%	120.36 ± 2.10	161.79 ± 0.31	50.17 ± 0.41	47.66	24.01
PP/SW cellulose 10 wt-%	118.34 ± 1.31	162.07 ± 2.11	44.49 ± 0.61	40.04	21.27

For both PP/SCB and PP/SW at 5%, the composites have higher modulus than the rest. Figure 12.6 shows the effect of SCB and SW untreated fibres and extracted celluloses on the loss factor ($\tan \delta$) for PP composites. It could be observed that graphs showed three zones, which appears to increase with an increase in temperature. At lower temperature, there is an observable shift of the glass transition temperature with the introduction of both SCB and SW fibre and cellulose. At higher temperature, composites materials seem to be having lower $\tan \delta$ as compared to pure PP. The observations are in line with the results reported by da Luz et al. [36] investigating PP composites reinforced with bagasse fibres. Furthermore, PP/SCB cell 5% cellulose and PP/SW cell 5% were having the lowest $\tan \delta$ respectively, which might indicate that these formulations exhibited more elasticity than viscous material, when compared with pure PP.

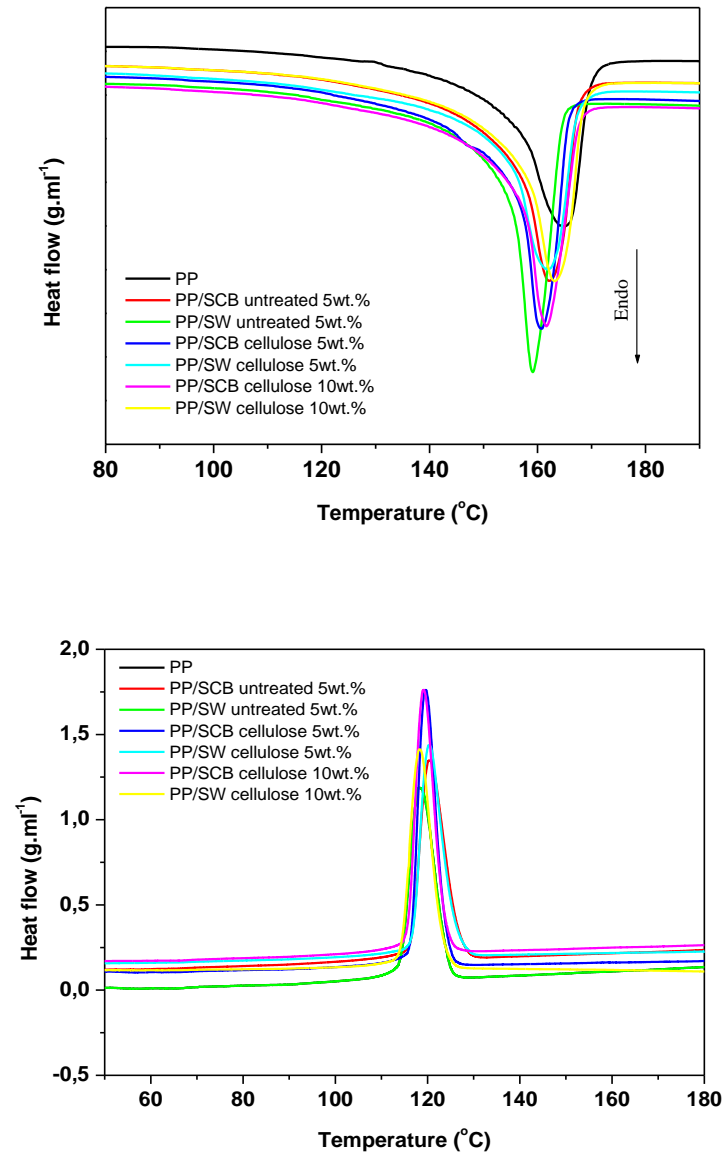


Figure 10.5: DSC melting and crystallization of PP, PP/SCB, PP/SW and celluloses composites.

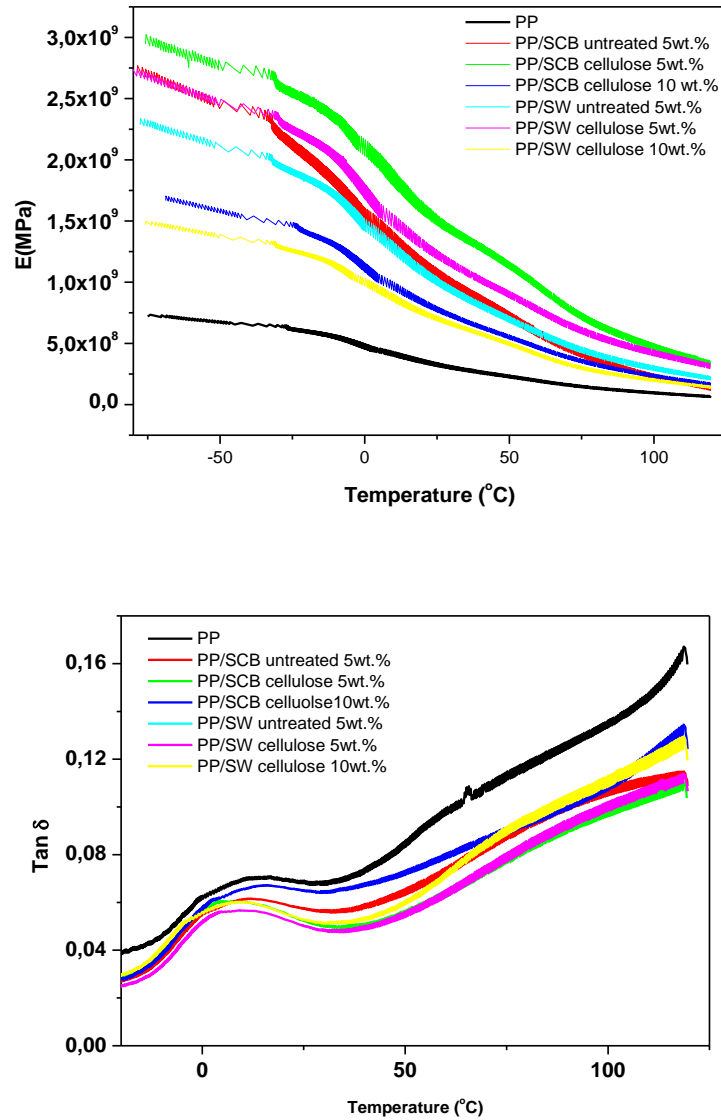


Figure 10.6: Storage modulus and Tan delta peaks of PP/SCB and PP/SW and cellulose composites

10.6 Conclusion

The comparative study on the effects of agricultural waste fibre and extracted cellulose from sugarcane bagasse and softwood on the properties of PP composites were investigated. The effect of agricultural waste fibre and extracted cellulose on PP interaction was confirmed by FTIR analysis and XRD. The modification on cellulose fibres surfaces and composition affected the thermal stability and crystallinity index of the composites. The TGA results indicated that PP/SW was more thermally stable than PP/SCB composites, however, PP/SCB cellulose composite were more thermally stable than PP/SW cellulose at both lower and higher

filler content. From the XRD analysis, it can be observed PP/SW composites shows higher crystallinity values than the PP/SCB composites. This was confirmed by DMA which displayed higher storage modulus as the result of enhanced interfacial bonding.

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CHAPTER ELEVEN:

THE EFFECT OF BAGASSE AND SOFT-WOOD ON MECHANICAL AND THERMAL PROPERTIES OF PP/PE BLEND COMPOSITES

(Article submitted in Journal of Reinforced Plastics and Composites)

THE EFFECT OF BAGASSE AND SOFT-WOOD ON MECHANICAL AND THERMAL PROPERTIES OF PP/PE BLEND COMPOSITES

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Abstract

This article investigates the effect of sugarcane bagasse (SCB) and soft wood (SW) on the mechanical, thermal and morphological properties of polypropylene/polyethylene (PP/PE) blend. The blend and its corresponding cellulose and untreated fibre composite materials were prepared using the Brabender Plastograph internal mixer, with the ratio of PP and PE fixed at 90 and 10 respectively. The Scanning electron microscope (SEM) analysis suggested a stronger interaction between PP/PE/SW as compared to PP/PE/SCB took place. The highest crystallite size and lowest crystallinity were observed for PP/PE/SW cellulose 5% and PP/PE/SCB cellulose 5% as compared to their fibre counterparts. Thermogravimetric analysis (TGA) results showed that the cellulose containing blend composites are thermally stable compared to untreated fibre, and both are less stable compared to neat PP/PE blend. Differential scanning calorimetry (DSC) analysis reveals that the introduction of SCB or SW did not significantly change the melting and crystallization behaviour of both the PE and PP. The storage modulus values of all blend composites materials were higher compared to PP/PE blend, with the cellulose containing blend composites displaying higher values than untreated fibre.

Key words: Sugarcane bagasse, Soft wood, Cellulose, Polypropylene, Polyethylene

11.1 Introduction

The use of cellulosic fibres as fillers in thermoplastics have attracted scientific interest lately due to a growing environmental awareness, combined with new government regulations on sustainable development. These fibres enjoy many benefits and are abundantly available, biodegradable, non-toxic, and environmental friendly [1-5]. Polymer blending is a convenient method for formulating of novel polymeric materials with superior properties than individual polymers. Polypropylene and Polyethylene are among the most commonly used thermoplastics due to their excellent properties such as processability, high strength, recyclability and low costs [6-9]. These thermoplastics find different applications in various industries including automotive, medical, packaging, construction and building amongst others. The thermoplastics blends offer many intermediate desirable properties even if they are immiscible in one another. Furthermore, the addition of cellulosic fibres positively impact on thermoplastics blends morphology, thermal and mechanical properties [10-13].

Various PP/PE blends composites have been studied in the literature over the years to fully understand their morphology, thermal stability, crystallization/melting behaviour, and mechanical properties compared with those of the neat PP/PE blend. Gao et al. [14] investigated the mechanical and rheological properties of PP/PE blends grafted with maleic anhydride on the resulting wood/thermoplastics composites. They found that maleic anhydride grafting result in an increase in the tensile and flexural strength of the resulting PP/PE/wood composites when compared to the non-grafted samples. The introduction of anhydride groups grafted onto PP/PE blend enhanced the dispersion and interfacial bonding of wood particles in the blend matrix, as supported by SEM and rheological analyses. In another study, Dikobe et al. [15] investigated thermal and mechanical properties of PP/HDPE/wood blend composites with wood powder (WP). The results showed an improvement in mechanical properties due to stronger interaction between MAPP and WP. The Young's modulus and the stress at break increased and decreased respectively with an increase WP content in the composites. The introduction of WP increased the thermal stability of PP/HDPE blend, and SEM analysis revealed an enhanced dispersion of WP in the PP/HDPE blend. Taufiq et al. [16] developed wood plastic composite from recycled PP/PE (r-PP/PE) blend reinforced with kenaf fibre. The results confirmed improvement in flexural strength and modulus with the introduction of kenaf fibre, with maximum improvements obtained at 30% weight loading. The results further

showed that there was reduction in the melting point and degree of crystallinity of r-PP/PE with an increase of kenaf fibre beyond 30 % loading.

There are also various studies on PP/PE blend composites reported in the literature, investigating mechanical and morphological properties using different fillers and compatibilizers [17-19]. But there was never a systematic comparison of PP/PE/SCB and PP/PE/SW blend composites to best of our knowledge. This study establishes a potential to use the biomasses to compensate for the environment.

11.2 Experimental

11.2.1 Materials

PP was supplied by Sasol Polymers (Johannesburg, South Africa), it has a density of 0.90 g cm^{-3} , a melting point of $165 \text{ }^{\circ}\text{C}$, and an MFI of 12 g/10 min . Low density polyethylene was supplied by Sasol Polymers (Johannesburg, South Africa), it has a density of 0.956 g cm^{-3} , a melting point of $136 \text{ }^{\circ}\text{C}$, and an MFI of 2.0 g/10 min . Sodium hydroxide (NaOH) pellets (99.9%) were supplied by Merck (India), and Sodium chlorite by Capital lab Suppliers CC (Germany). SCB and SW were collected from sugar milling and wood industries respectively in Empangeni, South Africa.

11.2.2 Extraction of cellulose from SCB and SW

SCB and SW celluloses were extracted from their respective fibres according to a method reported in the literature [20]. Briefly, the SCB and SW samples were washed and immersed in water bath for 24 h at room temperature before drying at $60 \text{ }^{\circ}\text{C}$ overnight. Then SCB and SW were treated with an alkali solution (2 wt % NaOH) at $100 \text{ }^{\circ}\text{C}$ for 4 h. The cellulose was then filtered and washed several times using distilled water to pH neutral. This treatment was performed four times. The same treatment was performed using 1.7 wt % sodium hypochlorite buffered with acetic acid. Finally, the suspension was allowed to cool and rinsed using deionized water to neutral pH.

11.2.3 Chemical composition of SCB and SW

The cellulose and lignin content was analysed by a reaction with sulphuric acid according to a standard method recommended in TAPPI-T222 om-88 and the hemicellulose content was obtained as described in TAPPI T19m-54 standards.

11.2.4 Preparation of blend composites

The blend composites were prepared according to the ratios as indicated in Table 11.1, and mixed in the Brabender Plastograph internal mixer. Mixing of the samples was done at 190 °C and a mixing speed of 30 rate per minutes (rpm) for 15 min. The samples were then melt pressed at 200 °C and 100 bar for 3 min and allowed to cool at room temperature for 10 minutes.

Table 11.1. Sample composition of PP/PE, PP/PESCB and PP/PE/SW composites

Formulation	Fibre type	Fibre content	Blend content
PP/PE (90/10)	-	-	100
PP/PE/SCB untreated	SCB untreated	5	95
PP/PE/SCB cell	SCB cellulose	5	95
PP/PE/SW untreated	SW untreated	5	95
PP/PE/SW cell 5%	SW cellulose	5	95

11.3 Characterization

11.3.1 Fourier-transform infrared spectroscopy

The FTIR spectra were collected by using a Perkin Elmer FTIR spectrometer (Stillwater, GA, USA) in the diffuse reflectance mode. The samples were analysed as-synthesised with no prior preparation required. The force was adjusted to 90 gauges for sufficient contact between the surfaces. The samples were scanned over the mid-IR region (450- 4000 cm⁻¹).

11.3.2 X-ray diffraction

Powder X-Ray Diffraction spectroscopy (Bruker AXS Advance X-Ray diffractometer, Karlsruhe, Germany) with monochromatic Cu K α ($\lambda = 1.5406 \text{ \AA}$) incident radiation at 40 kV and 40 mA was used to examine the crystal structure of all samples.

The crystallinity index (CI) was determined by using the deconvolution method and peak height method (see Equation 1 and 2) respectively.

$$CI = (1 - A_a/A_t) \times 100 (\%) \quad (1)$$

where A_a is the area of the amorphous phase and A_t the total area of the diffractogram

$$CI = (I_{002} - I_{am})/I_{am} \times 100 \quad (2)$$

where I_{002} is the maximum intensity of the 002 peak, and I_{am} is minimal depression of the amorphous structure.

The crystalline sizes of PP composites were obtained by using the Scherer's equation (3) based on FWHM.

$$CS = K\lambda/\beta\cos\theta \quad (3)$$

where, CS= crystalline size

K = constant (0.89)

λ = wavelength (0.154 nm)

B = FWHM in (radians)

$\cos \theta = 2 \theta$ peak

11.3.3 Thermogravimetric Analysis

Thermal degradation of the PP/PE blend and its corresponding blend composites were performed using TGA analyser unit (Perkin Elmer), under flowing nitrogen atmosphere at flow rate of 20 ml min⁻¹. Approximately 10-15 mg of sample was heated from 30 °C to 700 °C at a heating rates rate of 10°C.min⁻¹. The sample weight loss and rate of weight loss were recorded continuously as functions of temperature. The analysis was only started when isothermal condition had been obtained.

11.3.4 Differential Scanning Calorimetry

DSC analysis was performed out using a Perkin Elmer, DSC analyser unit under flowing nitrogen atmosphere at flow rate of 20 ml min⁻¹. Around 10-15 mg of the sample were heated from room temperature to 200 °C at a heating rate of 10 °C.min⁻¹. Fractional crystallinity was calculated using Equation (4).

$$X_{dsc} = \left(\frac{\Delta H}{\Delta H_m \cdot w} \right) \times 100\% \quad (4)$$

Where ΔH is the heat of fusion of the sample, w is the weight fraction of blend and the heats of fusion (ΔH_m) for crystalline PP and PE correspond with 209 and 293 Jg⁻¹ respectively [21].

11.3.5 Scanning electron microscopy

The surface morphologies of composites materials were analysed by a SEM (model-ZEISS). Prior to analysis, samples were coated with gold by means of a sputter-coater for ease conduction.

11.3.6 Dynamic mechanical analysis

The DMA tests were performed on DMA Q800 (TA Instruments, USA) machine using the following parameters: Frequency: 1 Hz; temperature range: -100 to 70 °C; heating rate: 5 °C.min⁻¹.

11.4 Results

11.4.1 Chemical composition of SCB and SW

The chemical composition of SCB and SW are shown in Table 11.2. The composition of both fibres are dominated by cellulose as compared to lignin and hemicellulose. Moreover, SCB fibre seemed to have more hemicellulose and less lignin compared to SW (with about 20% difference observed for each). This trend of SCB composition is within the reported literature in other studies [23-24]. As for SW, it is known that the origin of a plant, harvesting period, a domain of the plant and the aging thereof are amongst the reasons that alter its chemical compositions [1].

Table 11.2: Chemical compositions of SCB and SW fibres

Sample	Cellulose (%)	Hemicellulose (%)	Lignin (%)
SCB	39.75 \pm 0.7	38.03 \pm 0.1	22.01 \pm 0.6
SW	40.00 \pm 0.5	24.00 \pm 0.1	37.00 \pm 0.5

11.4.2 Scanning electron microscopy

Figure 11.1 (a,b,c and d) represents the SEM microstructure of fractured surfaces of PP/PE blend composites. In all the images, fibre pull outs and vacant spaces left by PE phase are visible. Figure 11.1 a (See arrows) contained more vacant spaces than the rest, arguably followed by Figure 11.1 b (See arrows). The phase separation seemed suppressed for Figure 11.1 (c and d). Loose and hanging fibres are clear in Figure 11.1c (See arrows) while clear and big pull outs are also visible in Figure 11.1 d (See arrows). Similar observations were also reported in other studies investigating the fracture surfaces of the PP/PE composites. The fibre pull outs and phase separation were related to poor interfacial interaction between the blend and fibre, in the absence of the compatibilizer [14-15]. It is therefore clear that the current results may further suggest poor adhesion between the fibre particles and the matrix blend. However, the lack of surface separation in the case of Figure 11.1 (c and d) may suggest stronger interaction than in Figure 11.1 (a and b).

11.4.3 Fourier-transform infrared spectroscopy

The spectra of PP/PE and all blend composites show main absorbance peaks at around 2915 cm^{-1} , 1716 cm^{-1} and 1469 cm^{-1} which are associated with the $-\text{CH}$ asymmetric, $-\text{CH}_3$

symmetric and the scissor modes of the -CH stretching of both PP and PE. Moreover, there are other small bands observed at around 1158 cm^{-1} and 718 cm^{-1} which are associated with -CH_3 symmetric deformation and -CH_2 rocking vibration [15, 21]. The peak attributed to -OH group from fibre materials as well as intramolecular and intermolecular hydrogen bonds at 3340 cm^{-1} is more pronounced in the blend containing cellulose [25-26]. This might be due to the element of interfacial interaction or migration of cellulose into more compatible phase of the matrix. The peaks at 1716 cm^{-1} and 1046 cm^{-1} are completely not observed with the addition of SCB and SW fibre or cellulose, which could be attributed with the interaction between the blend and fibres. Furthermore, the PP/PE blends spectra have -CH_2 rocking vibrations around 718 cm^{-1} , which is not present in the cellulose containing blend composites [27]. This disappearance was caused by the decrease in the intermolecular hydrogen bonding of the treated fibre and PP/PE.

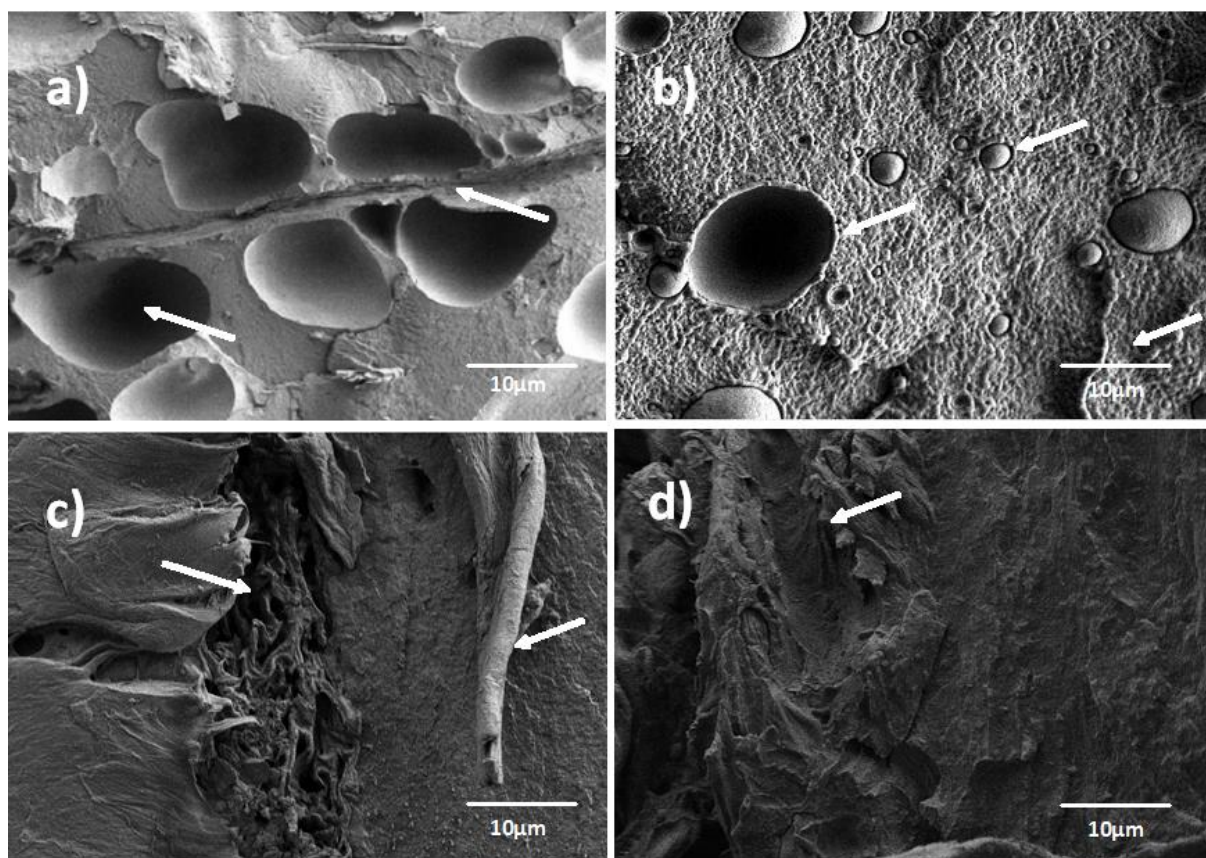


Figure 11.1. SEM images of (a) PP/PE/SCB untreated 5%, (b) PP/PE/SCB cellulose 5%, (c) PP/PE/SW untreated 5% and (d) PP/PE/SW cellulose 5% blend composites

11.4.4 X-ray powder diffraction

The XRD patterns of PP/PE, PP/PE/SCB and PP/PE/SW blend composites are displayed in Figure 11.3. The crystalline sizes obtained by the Scherer's equation and crystallinity index are summarized in Table 11.3. The PP/PE blend patterns consist of crystalline peaks at 14.4° (110), 17.3° (040), 18.9° (130) and 22.2° (041) which are typical crystal lattices of α PP [28]. Furthermore, there are also peaks at 21.6° (110) and 23.4° (200) which correspond with orthorhombic PE lattices, and halo bumps peaks at 26.01° and 29.09° [8,21]. The introduction of both untreated fibres and cellulose generally reduced the intensities of crystalline peaks, except for PP/PE/SCB cellulose 5%. This is normally attributed to swelling of amorphous domain due to the defects created by fibre [11, 16, 17].

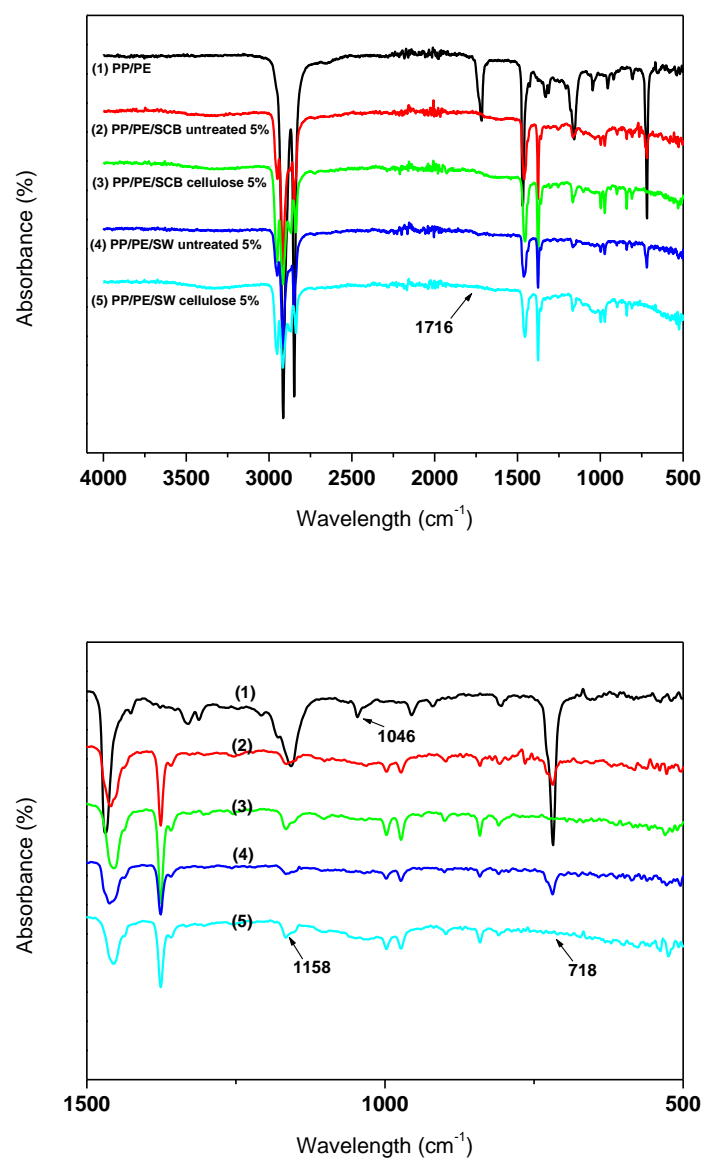


Figure 11.2. FTIR spectra of PP/PE, PP/PE/SCB and PP/PE/SW blend composites

Nonetheless, in the case of PP/PE/SCB cellulose 5%, it seems cellulose derivative formed has favoured more of crystal lattices of PP. These observations are verified by crystalline sizes that have shown to increase with disruption of crystalline lattices (Table 11.3). Moreover, the PP/PE/SW cellulose 5% and PP/PE/SCB cellulose 5% displayed the highest crystallite size and lowest crystallinity as compared to their fibre counterparts. The reason might be due to an increase in PP/PE crystalline inter-planar distance as a result of strong cellulose interaction caused by decrease in the intermolecular hydrogen bonding as discussed in the FTIR results.

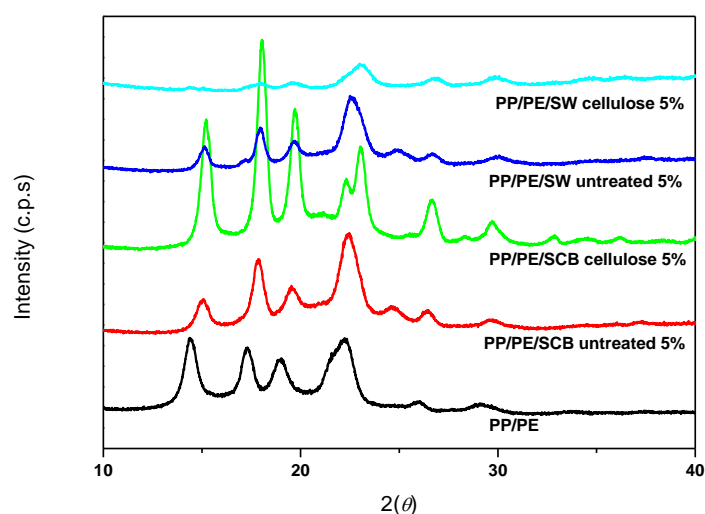


Figure 11.3. XRD spectra of PP/PE/SCB and PP/PE/SW blend composites

Table 11.3: Crystallinity index of materials

Sample	Deconvolution CI (%)	Peak height CI (%)	CS (nm)
PP/PE	61.2	27.30	14.64
PP/PE/SCB untreated 5%	32.6	24.79	22.27
PP/PE/SCB cellulose 5%	24.9	21.94	23.27
PP/PE/SW untreated 5%	27.9	23.80	30.60
PP/PE/SW cellulose 5%	21.8	17.07	34.7

11.4.5 Thermogravimetric analysis

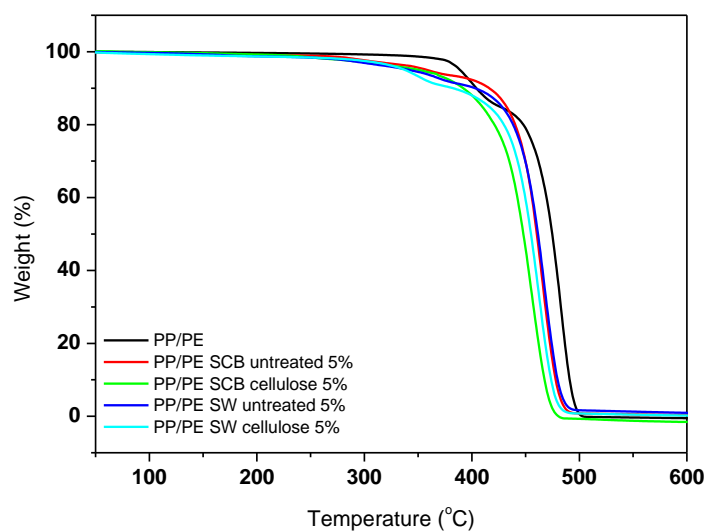
Figure 11.4 represents the weight loss and derivative of weight loss of PP/PE, PP/PE/SCB and PP/PE/SW blends composites. The PP/PE blend showed two stage decomposition which are related to the degradation of the neat PP and PE respectively in the blend [15]. Furthermore, the PP/PE/SCB and PP/PE/SW blend composites further displayed two degradation steps. In this case, the first step shifted towards lower temperatures as compared to the pristine blend. It is known that a low thermal stability of fibre/cellulose has a potential to lower degradation temperatures of polymer composites [2, 13]. However, in this case the fibre seems to have intermediate degradation temperature with the PP. The thermal decomposition results in Table 13.4 indicated that all the blend composites are thermally less stable compared to neat PP/PE blend. None, except poor interfacial interactions can explain this better as seen from SEM images. In fact, cellulose containing blend composites appeared to be least thermally stable compared to untreated fibre. While cellulose derivatives and thermal degradation mechanisms are possible reasons [20], but vacant space and poor distribution of fibre as witnessed in SEM and resulting crystallinity could account for the observations. On the contrary, Dikobe *et al* [15] observed an increase in the thermal stability of PP/PE blends composites with the introduction of wood powder (WP). They related the improved thermal stability with WP char decomposition that acted as a barrier that delayed the heat transfer to the polymer matrices. In this study, that is not the case because the introduction of untreated filler and cellulose appeared to have accelerated degradation of the PP/PE.

Table 11.4: DTG peaks temperatures of all the investigated samples.

Sample	Peak 1 (°C)	Peak 2 (°C)
PP/PE	402.79	483.79
PP/PE/SCB untreated 5%	358.54	466.88
PP/PE/SCB cellulose 5%	347.89	456.86
PP/PE/SW untreated 5%	367.68	466.76
PP/PE/SW cellulose 5%	350.86	461.99

11.4.6 Differential scanning calorimetry

The DSC melting and crystallization curves are shown in Figure 11.5 and 11.6 respectively. It could be clearly observed that two well separated melting peaks of LDPE and PP component at low and high temperature respectively are developed [17, 19]. This phenomenon might indicate that both polymers are immiscible in one another. The DSC data summarized in Table 11.5 indicated that the introduction of untreated fibre and cellulose did not significantly change the melting and crystallization behaviour of both the PE and PP. Similar observation was also reported by Khanam et al. [2] investigating recycled polymer based date-pal fibre reinforced composites. However, in our case, there was a delayed crystallization for blend composites. According to Dikobe et al. [22] a small variation in the crystallization temperature of the PE influences the fibre to locate in PE which led to the crystallization route of the blend composites. The rational is highly possible in the current study, however it seems as though the sugar cane bagasse cellulose was dispersed almost homogeneously on both phases since its crystallization appeared more stable than of the blend composites containing SW cellulose. Perhaps it is for that reason it has shown exceptional crystallinity in XRD.



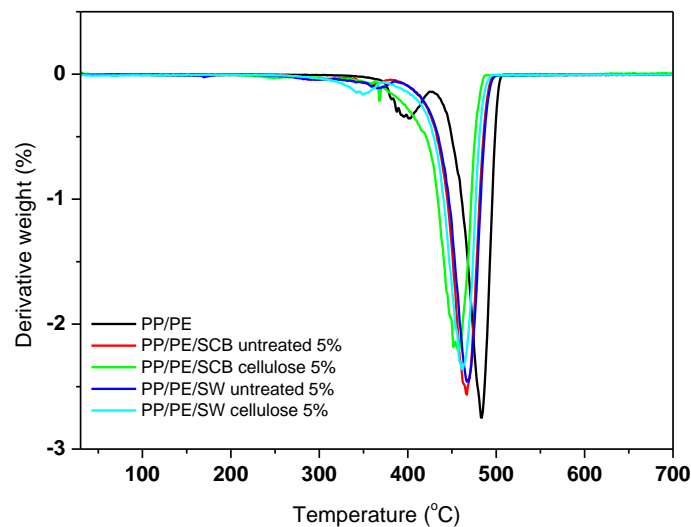


Figure 11.4. TGA and DTGA graphs of PP/PE/SCB and PP/PE/SW blend composites

As expected, the melting enthalpy (ΔH_m) of PP and PE decreased with introduction of fibre and cellulose due to the decrease in polymer matrix quality [24]. The results are signalled by the decrease in crystallinity, which indicated that lower crystallinity developed for the two components [8]. This decreasing trend of crystallinity was also reported in the XRD investigation. There is also a huge difference in the observed enthalpy (ΔH^{obs}) values and calculated (ΔH^{calc}) values of PE as compared with PP. This might indicate that the crystallization behaviour of PE is probably influenced by the presence of fibre and cellulose in the blend.

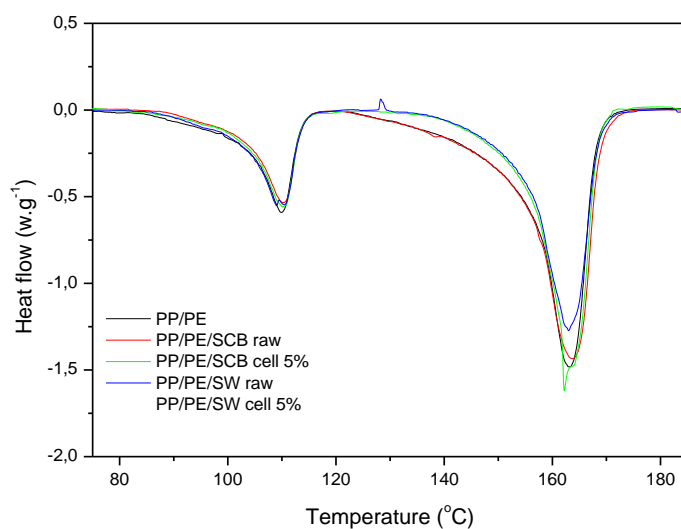


Figure 11.5. DSC melting graphs of PP/PE blend, PP/PE/SCB and PP/PE/SW blend composites

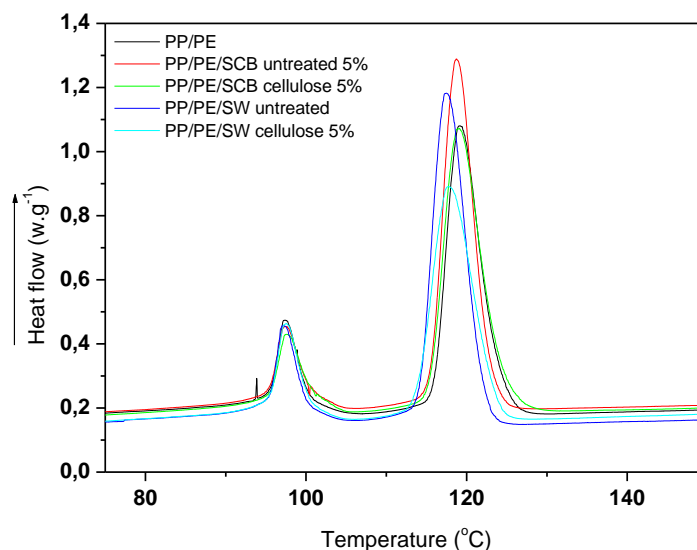


Figure 11.6. DSC crystallization graphs of PP/PE blend, PP/PE/SCB and PP/PE/SW blend composites

Table 11.5: DSC analysis of PP/PE blend, PP/PE/SCB and PP/PE/SW blend composites

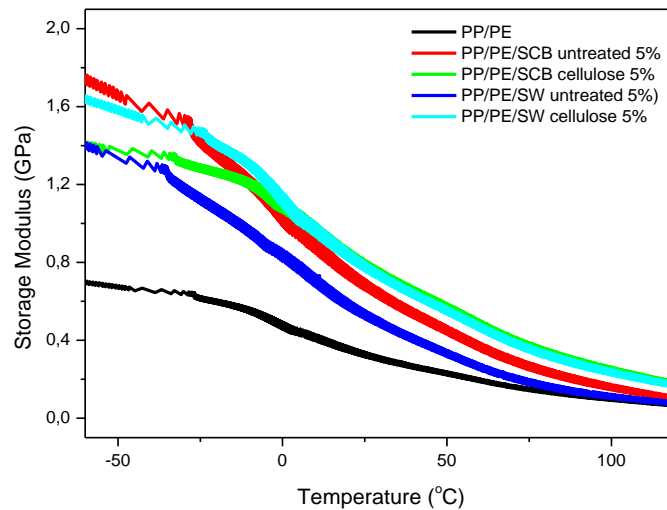
Composition	Crystallization		Melting		$\Delta H^{obs}/(J/g)$		(ΔH^{calc})		$X_c/\%$
	PE	PP	PE	PP	PE	PP	PE	PP	PP/PE
PP/PE	119.18	97.39	109.92	163.16	22.54	74.14	2.25	66.73	44.47
PP/PE/SCB untreated 5%	118.71	97.49	109.83	162.43	16.37	66.57	1.23	58.25	40.36
PP/PE/SCB cellulose 5%	119.10	97.55	110.27	163.67	19.79	68.31	1.48	59.77	42.87
PP/PE/SW untreated 5%	117.47	97.18	110.12	162.21	16.48	66.89	1.24	58.53	40.57
PP/PE/SW cellulose 5%	117.67	97.54	110.46	163.02	17.3	67.9	1.29	59.41	41.46

11.4.7 Dynamic Mechanical Analysis

The storage modulus and Tan δ curves of PP/PE/SCB and PP/PE/SW blend composites are presented in Figure 11.7. In general, the storage moduli decreased with an increase in temperature, with a sharp drop around the glass transition temperature (T_g) related to enhanced mobility of the polymer chains [23]. Most significantly, all blend composites materials have higher storage modulus compared to PP/PE blend. This increase cannot be attributed to a rise in crystallinity, since the DSC results indicated a reduction in crystallinity as fibres was

introduced. This behaviour might rather be related to effective stress transfer from matrix to fibres and interfacial interaction [36]. Moreover, the storage modulus of the blend composites displays no general pattern with the introduction of fibre/cellulose at lower temperature. However, the cellulose blends seemed to have higher storage modulus around the T_g , before the occurrence of viscoelastic deformation of polymer [24-25].

The $\tan \delta$ values increase with an increase in temperature before and after the glass transition temperature of the blend. The untreated SCB and SW blend composites seem to be having higher $\tan \delta$ as compared to cellulose counterparts, probably due to strong restriction on mobility of their polymer chains [25]. Furthermore, both the untreated and cellulose in-cooperation did not cause a significant shift in T_g of the blend, except a small variation and broadening of peak in blends filled with cellulose. The T_g shift in in this case might be related to better interfacial interaction between the celluloses and PP/PE blend as highlighted in FTIR results. The broadening of peak may be explained by an increase in the segmental relaxation time of the polymer matrix caused by polymer–filler interaction [38].



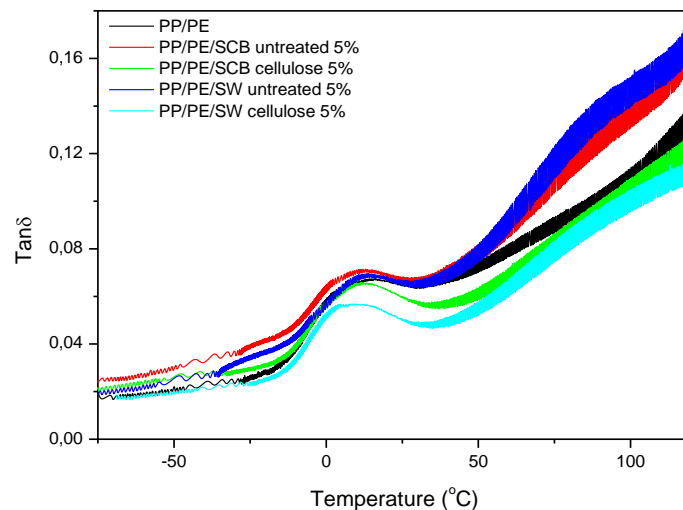


Figure 11.7. Storage modulus and Tan δ graph of PP/PE, PP/PE/SCB and PP/PE/SW blend composites

11.5 Conclusion

The effect of sugarcane bagasse, softwood and their extracted cellulose on the mechanical, thermal and morphological properties of polypropylene/polyethylene (PP/PE) blends was investigated. The crystallinity index and size results generally showed a decreasing and increasing trend respectively with the introduction of cellulose and untreated fibre. TGA results indicate that cellulose blend composites were the least thermally stable sample, and further confirm immiscibility between PP and PE. This results were further supported by DSC analysis, revealing that the introduction of SCB or SW untreated fibre and extracted celluloses did not change the melting and crystallization behaviour of both the PP/PE blend. The crystallinity index decreased with introduction of fibre and cellulose, as confirmed by DSC and XRD results. The blend composites materials were having the higher storage modulus compared to PP/PE blend, with PP/PE/SCB untreated blend displaying the highest. FTIR analysis and SEM analysis revealed interaction and poor dispersion of SCB and SW filler with PP/PE blend. The fractured surfaces showed that the interfacial adhesion between the PP and PE was poor, signalling immiscibility and poor interaction.

11.6 References

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CHAPTER TWELVE:

INFLUENCE OF EXTRACTION METHODS ON THE PROPERTIES OF POLYPROPYLENE SUGARCANE BAGASSE CELLULOSE-PP COMPOSITES

(Article submitted in **Polymer and Polymer Composites Journal**)

INFLUENCE OF EXTRACTION METHODS ON THE PROPERTIES OF POLYPROPYLENE SUGARCANE BAGASSE (SCB) CELLULOSE-PP COMPOSITES

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Abstract

In this study, cellulose was extracted from sugarcane bagasse (SCB) using five different alkali treatments, and compounded with polypropylene (PP) to develop thermoplastics composites. The influence of various alkali treatment on the resulting PP/SCB cellulose composites were investigated using Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Differential scanning calorimetry (DSC), and Thermogravimetric analysis (TGA). FTIR results confirms possible interaction between various alkali treated SCB cellulose with PP. XRD patterns of PP/SCB composites revealed dominant structure of α -monoclinic crystalline PP, with featureless crystalline peaks of SCB cellulose, and traces of celluloses derivatives. TGA, crystallization and melting temperature results revealed that the presence of various cellulose had a little impact on the behaviour of PP. XRD and DSC analysis showed similar declining patterns of crystallinity with the introduction of various celluloses.

Keywords: Polypropylene, Sugarcane bagasse, Cellulose, Alkali treatment

12.1 Introduction

Recent research towards utilization of cellulosic materials in production of polymeric composites has increased due to the demand for renewable resources, and growing environmental awareness [1-4]. The demand is also perpetuated by continuous problem of solid waste generation, high energy consumption and pollution as a result of non-degradability of petroleum polymers [5-7]. There are many studies in the literature on the use of lignocellulosic materials derived from agricultural wastes such as coffee husk, rice straw, corn stover to obtain value-added products which can be applied in diverse industrial products [8-10]. Lignocellulosic materials possess several advantages compared to synthetic fillers, such as non-toxicity, biodegradability and recyclability. Additionally, these materials have potential to replace conventional fillers and petroleum products due to their excellent benefits [11-13]. The main disadvantage of lignocellulosic reinforced polymer composites is their inherent incompatibility between the hydrophilic cellulosic fibres, and hydrophobic polymeric matrix such as polypropylene [14-17].

Amongst the agricultural wastes, sugarcane bagasse is a residue widely generated in high amounts in sugar milling and alcohol industries that can be used a source of lignocellulose material. SCB contains cellulose (40%-50 %), hemicellulose (25%-35%), lignin (10%-15%) and other extractive elements in minor constituents [18-20]. Cellulose is hydrophobic, fibrous and physically tough with different degrees of polymerization depending on the source of lignocellulosic material. Structurally, it consists of linear homopolysaccharide chain of β -1,4-linked anhydro-D-glucose units comprising of both crystallites ordered and amorphous disordered domains (see Figure 12.1) [21-23]. In the natural plant cell wall including SCB, crystalline cellulose is normally embedded with hemicellulose and lignin substances, which make it difficult to isolate pure cellulose [24-26].

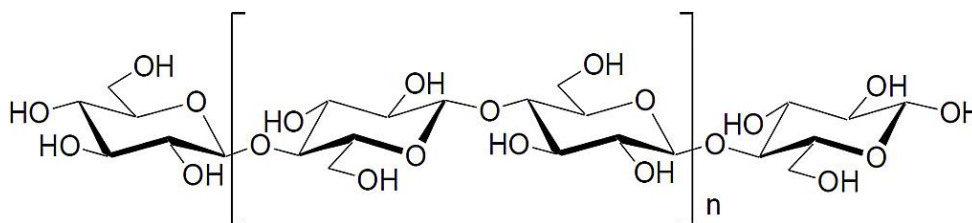


Figure 12.1. General chemical structure of cellulose [24].

There is a wide range of publications reported on the extraction of cellulose from natural fibres using different procedures and reagents [27-30]. Amongst them, alkaline treatment or mercerization is known to eliminate lignin and hemicellulose through breaking them into soluble units of low molecular weight. This treatment is usually followed by delignification/bleaching process using chemicals such as sodium chlorite to completely remove any traces of lignin and hemicellulose present [31-39]. However, only a handful of publication investigated the influence of alkali treatment on the resulting thermoplastic composites, especially when PP was used as a matrix. Amongst other studies, Khalid et al. [11] extracted cellulose from oil palm empty fruit bunch fibre (EFBF) through alkalization method before incorporating it with PP to develop composites. The mechanical properties of PP/EFBF cellulose composites revealed improvement in the tensile strength, impact strength and flexural modulus as compared to PP/EFBF fibre composites. The improvements were related to complete removal of lignin and hemicellulose, which makes the cellulose fibrils more capable of rearranging themselves in the direction of tensile deformation. Ummartyotin et al. [13] developed PP cellulose composite using cotton as a source of cellulose, and maleic anhydride as a coupling agent. They observed superior mechanical and thermal properties in the presence of a coupling agent. The reason was related to chemical bonding formation between the anhydride group and OH group from the cellulose. Interestingly, the 20 wt% content of cellulose reinforced in PP matrix exhibited strong influence of composite properties as compared to 5 and 10 wt%. Their observations were in line with the results obtained by Moubarik *et al* [23] who also achieved maximum improvements in the mechanical properties of low density polyethylene (LDPE)/SCB cellulose composites at 20 wt% optimum. In other studies, modification of cellulose with chemical treatment also had opposing results on the resulting PP composites. Mulinari et al. [40] reported improved thermal and mechanical properties for composites reinforced with modified cellulose (zinc oxide) when compared to the non-modified cellulose fibres. In contrast, Luz et al. [41] reported reduction of mechanical properties of developed PP composites reinforced with acetylated cellulose fibres attained from sugarcane bagasse. The decrease was mainly related to change in fibre morphology due acetylation process. The aim of the study is to prepare and characterise PP/SCB cellulose composites, using celluloses extracted by five different alkali treatment. The objectives are to investigate the effect of various alkali treatment on thermal stability, crystallization/melting behaviour, and morphology of the resulting composites.

12.2 Experimental

12.2.1 Materials

PP was obtained from Sasol Polymers (Johannesburg, South Africa). It has a density of 0.90 g cm^{-3} , a melting point of 165°C , and an MFI of 12 g/10 min (230°C , 2.16 kg). SCB was collected from Tongaat-Hulett Sugar Ltd - Felixton Mill (Felixton, South Africa). Acetic acid was obtained from Laboratory Consumables and Chemical Suppliers (Durban, South Africa). Sodium sulphite and sodium hydroxide pellets (99,9%) were obtained from Merck Chemicals (India). Sodium chlorite was obtained from Capital lab Suppliers CC (Germany), and commercial sodium hypochlorite was obtained from a local supermarket. All chemicals were used without further purification, but were prepared to the desired concentrations.

12.2.2 Extraction of cellulose from sugarcane bagasse

The extraction methods used were adopted from a study comparing cellulose extraction from sugarcane bagasse through various alkali treatments by Mzimela et al. [42].

12.2.2.1 Method 1 (M1)

Sugarcane bagasse was boiled in water (4hrs). Soaked in 4% sodium hydroxide (4hrs), followed by treating with 4 % sodium hypochlorite and 2% sodium hydroxide (4hrs) at 100°C before washing with distilled water to pH neutral. The final product was dried at room temperature for 2 days.

12.2.2.2 Method 2 (M2)

From the method 1, 4 % of sodium hypochlorite was acidified with acetic acid to pH 4.

12.2.2.3 Method 3 (M3)

From the method 1, 2 and 1% of NaOH was used in the second and last step respectively, 0.7 % sodium chlorite acidified with acetic acid to PH4 was used instead of 4 % sodium hypochlorite.

12.2.2.4 Method 4 (M4)

From the method 3, the last step was eliminated.

12.2.2.5 Method 5 (M5)

From the method 3, the additional step was added after sodium chlorite step, in which sample was treated with 5% sodium sulphite at 100 °C for three hours.

12.2.3 Preparation of composites

The composites materials were weighed according to the required ratio (90/5 w/w) as indicated in Table 12.1, and thoroughly mixed in the Brabender Plastograph internal mixer. Mixing of the samples was done at 190 °C and a mixing speed of 30 rpm for 15 min. The samples were then melt pressed at 200 °C and 100 bar for 3 min and allowed to cool at room temperature for 10 minutes.

Table 12.1. Sample composition of PP, and PP/SCB cellulose composites

Formulation	Extraction method	Cellulose content	PP content
PP	-	-	100
SCB/M1	M1	5	95
SCB/M2	M2	5	95
SCB/M3	M3	5	90
SCB/M4	M4	5	95
SCB/M5	M5	5	95

12.3 Characterization methods

Fourier transform infrared spectroscopy

FTIR spectra of PP and SCB celluloses composites were analysed using a Perkin Elmer, 2000 FT. The spectra were scanned over the mid-IR region (500- 4000 cm⁻¹), with a resolution

of 4 cm⁻¹. The FTIR spectroscopy of PP and its composites were also recorded to detect the chemical changes after modifications.

Powder X-ray diffraction

The XRD characterization of all samples was performed on Powder X-Ray Diffraction spectroscopy (Bruker AXS Advance D8 diffractometer) with monochromatic Cu K α (λ = 1.5406 Å) incident radiation at 40 kV and 40 mA at room temperature. The samples were scanned within the high angle 2 θ range to get all characteristic diffractions of the materials at 0.5 scan speed and 0.01314 increments.

The crystallinity index of PP/SCB and PP/SW composites was determined by using the deconvolution and peak height method using equation 1 and 2 respectively.

$$CI = (1 - A_a/A_t) \times 100 \quad (1)$$

where A_a is the area of the amorphous phase and A_t the total area of the diffractogram.

$$CI = (I_{002} - I_{am})/I_{am} \times 100 \quad (2)$$

where I_{002} is the maximum intensity of the 002 peak, and I_{am} is minimal depression of the amorphous structure.

The crystalline sizes of PP composites were obtained by using the Scherer's equation (3) based on full width at half maximum (FWHM).

$$CS = K\lambda/B\cos\theta \quad (3)$$

where, CS= crystalline size

K = constant (0.89)

λ = wavelength (0.154 nm)

B = FWHM in (radians)

$\cos \theta = 2 \theta$ peak

Thermal gravimetric analysis

Thermal stability of PP and PP/SCB composites were determined using TGA analyser unit (Perkin Elmer), under flowing nitrogen atmosphere at flow rate of 20 ml min⁻¹. Approximately 10-15 mg of sample was heated from 30°C to 700°C at a heating rates rate of 10°C.min⁻¹ and flow rate of 30mL/min.

Differential scanning calorimetry

DSC was performed out using a DSC analyser unit (Perkin Elmer), under flowing nitrogen atmosphere at flow rate of 20 ml min⁻¹. Around 10-15 mg of the sample were heated from room temperature to 200 °C at a heating rate of 10 °C/min. Fractional crystallinity was calculated using Equation (4).

$$X_{dsc} = \left(\frac{\Delta H}{\Delta H_m \times w} \right) \times 100\% \quad (4)$$

Where ΔH is the heat of fusion of the sample, ΔH_m is the heat of fusion of a 100% crystalline PP = 209 J/g and w is the mass fraction of PP in composites.

12.4 Results

12.4.1 FTIR

FTIR spectroscopy method was used to obtain the information on chemical changes of PP, before and after the introduction of various SCB celluloses. Figure 12.2 shows the FTIR spectra of PP and PP/SCB cellulose composites, and Table 12.2 summarized the chemical functional groups changes of PP. The spectra of neat PP displayed main bands at 2917 cm⁻¹ (–CH₂ stretching vibrations), 1456 cm⁻¹ (–CH₃ symmetrical bending), and 1376 cm⁻¹ (–CH₃ symmetric bending) as supported by the literature [4, 31]. The individual spectra of various SCB celluloses were previously reported by Mzimela et al. in their investigation [42]. With the introduction of various cellulose in PP matrix, the cellulosic characteristic peak typically observed around 3300 cm⁻¹ (–OH stretching vibration [42]) and 1054 cm⁻¹ (C-O-C pyranose ring stretching

vibration [31]) were completely not observed in PP/SCB cellulose composites spectra, possibly due to some interaction between celluloses and PP.

For all PP/SCB cellulose composites, the absorption bands at around 2949, 2917 and 2839 cm^{-1} were observed in all spectra, with minor shift of vibrations detected (see Table 12.2). There was also a notable increase in intensity of peak at 1741 cm^{-1} attributed to esterified carboxylic groups [28], and appearance of a new peak at 1217 cm^{-1} which correspond with aliphatic –C-O vibration. Moreover, the absorption bands at around 1456, 1376 and 1167 cm^{-1} were also observed in all PP/SCB cellulose composites spectra, with their intensities almost reduced. Interestingly, the overall intensity of PP/M3 spectrum was drastically reduced as compared to other composites, probably due to improved interaction or complete removal of non-cellulosic material during SCB extraction.

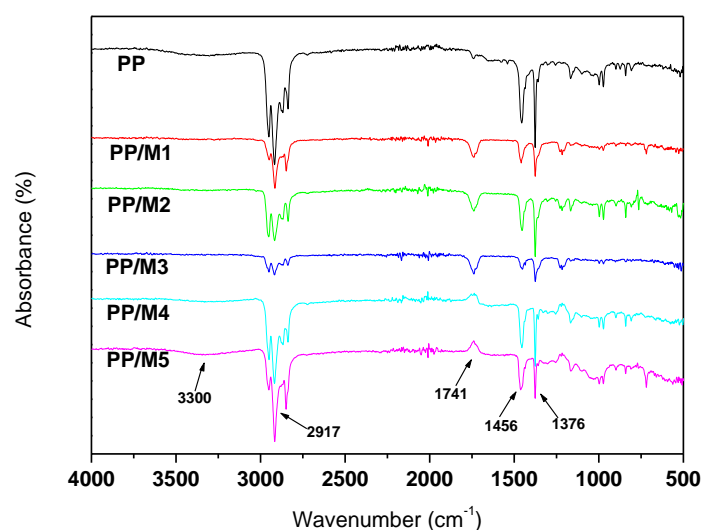
Table 12.2: Summarized chemical functional groups changes of PP

Wave number (cm^{-1})						Functional group
PP	PP/M1	PP/M2	PP/M3	PP/M4	PP/M5	
801	801	807	801	808	801	C-C s tretching
841	841	841	840	841	841	C-H rocking
899	899	898	894	899	898	Glycosidic linkage rocking
973	974	973	973	973	973	C-C rocking
998	996	995	998	998	998	CH ₃ rocking
1037	1037	1038	1038	1048	1044	Si-O-Si stretching
1167	166	1167	1166	1167	1166	C-H Wwagging
1376	1376	1376	1376	1376	1376	CH ₃ bending
1456	1459	1454	1453	1455	1463	CH ₃ bending
1741	1739	1739	1739	1739	1739	C=O vibration
2839	2848	2837	2839	2838	2849	C-H wagging

2871	-	2871	2871	2867	-	CH ₃ stretching
2917	2915	2917	2918	2918	2916	CH stretching
2949	2950	2952	2952	2950	2951	-CH stretching

12.4.2 XRD

Figure 12.4 shows the XRD patterns of PP and various PP/SCB cellulose composites. The results summarizing the crystallinity index and sizes of PP crystals are presented in Table 12.2. The crystalline peaks of neat PP were observed at 14.4° (110), 17.3° (040), 19.0° (130) and 22.3° (041) and some weak peaks at 26.0° and 29.7° which might indicate the presence of α -monoclinic crystalline PP as reported by other researchers [5, 13, 43]. With the introduction of various SCB cellulose, the composites material spectra revealed a dominant structure of α -monoclinic crystalline PP, with featureless crystalline peaks of SCB cellulose. However, various composites spectra exhibited some impurities, which might be associated with the presence of cellulose derivatives.



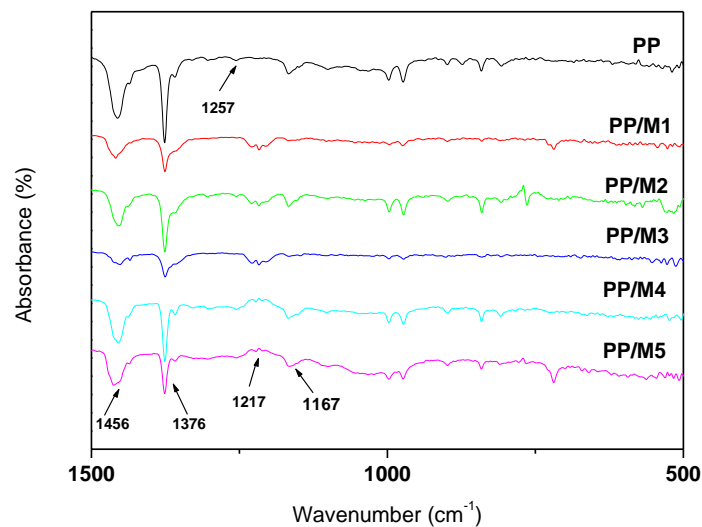


Figure 12.2. FTIR spectra of PP and PP/SCB cellulose composites

The PP/M1, PP/M2 and PP/M3 patterns showed improved intensity, exhibits bigger crystallite size and reduced crystallinity in comparison with neat PP. In addition, there was the presence of double-headed peak noticed for PP/M1 and PP/M2 at around 22° . The sharp and high peak intensity observed for PP/M3 composites may be associated with substitution of sodium hypochlorite with acidified sodium chlorite. This may have attributed to the growth of large PP crystallites, which correspond with crystallinity reduction. The composites PP/M4 and PP/M5 displayed minimal intensity as compared with other samples. Both composites revealed minimum impact on the crystallite size and crystallinity of PP. This might be due to lack of interaction between cellulose and matrix, or the formation of agglomerates preventing segmental mobility of PP [43].

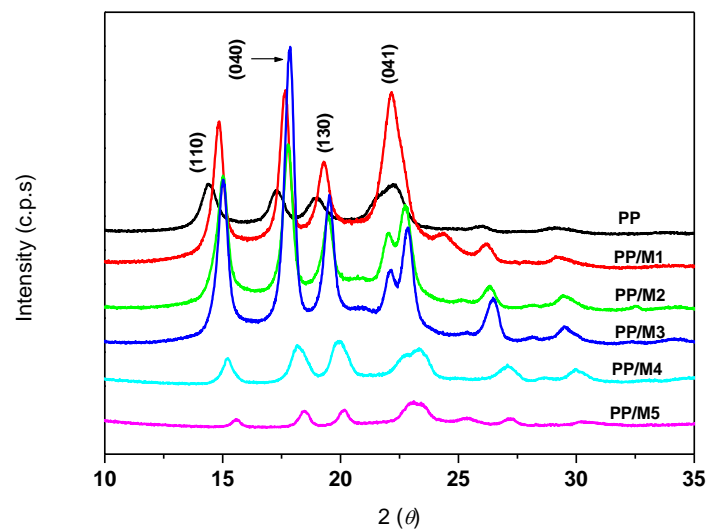


Figure 12.3. XRD patterns of PP and PP/SCB cellulose composites

12.4.3 TGA

Figure 12.4 shows the TGA and DTGA graphs of PP and various PP/SCB cellulose composites. The graph of PP degrades in a single step, starting from 300 °C, and decomposing at 447 °C where substantial mass loss is observed [31, 44]. The PP/SCB cellulose composite materials degrade in two stages related to degradation of cellulose and PP at low and high temperature respectively [30, 38]. Above 500 °C, all the samples appear to decompose at a similar rate with the amount of residual mass almost identical.

Table 12.3: Crystallinity index (CI) and crystalline sizes (CS) of composite materials

Sample	Deconvolution CI%	Peak height CI%	CS (nm)
PP	62.77	32.99	14.276
PP/M1	52.88	27.17	18.622

PP/M2	56.11	24.85	19.071
PP/M3	35.01	20.18	22.710
PP/M4	59.57	31.26	14.542
PP/M5	58.41	30.37	14.633

The decomposition temperatures at 10% and 40% mass loss ($T_{10\%}$ and $T_{40\%}$) as well as peak temperature at maximum loss rate (T_{\max}) of composites samples are summarized in Table 12.4. It could be seen that with the introduction of various celluloses to PP, temperature at T_{\max} shifted marginally to lower values, with more pronounciation for PP/M3 composite. It could be said that the presence of various cellulose had a little impact on the decomposition of PP. For the decomposition at $T_{10\%}$, the decomposition shift towards lower temperature was more noticeable for PP/M1 and PP/M3 composites probably due to complete removal of the hemicelluloses and lignin as a result of bleaching treatment, which allow the cellulose to degrade earlier [22]. In addition, both the PP/M5 and PP/M2 composites at $T_{40\%}$, shifted the onset to higher temperature as compared to other composites. Higher onset temperature can be attributed to partial existence of lignin or hemicellulose in the lignocellulose fibre.

Table 12.4: Thermal decomposition temperatures at 10%, 40% and maximum (max) mass loss of PP and PP/SCB celluloses composites

Composition	$T_{10\%}$ (°C)	$T_{40\%}$ (°C)	T_{\max} (°C)
PP	387.95	430.95	446.95
PP/M1	372.78	435.78	445.78
PP/M2	378.86	430.86	446.86
PP/M3	373.96	427.96	445.75
PP/M4	384.96	432.96	446.96
PP/M5	358.04	439.04	455.24

12.4.4 DSC

The melting and crystallisation graphs of PP and PP/SCB cellulose composites are shown in Figure 12.5 and 12.6 respectively. The values obtained for crystallization temperature (T_c), melting temperature (T_m), melting enthalpy (ΔH_m) and fractional crystallinity (X_c) are summarized in Table 12.5. The neat PP display a single melting and crystallisation peak temperatures at 164.98 °C and 118 °C, respectively, which may suggest the presence of α -monoclinic crystalline PP.

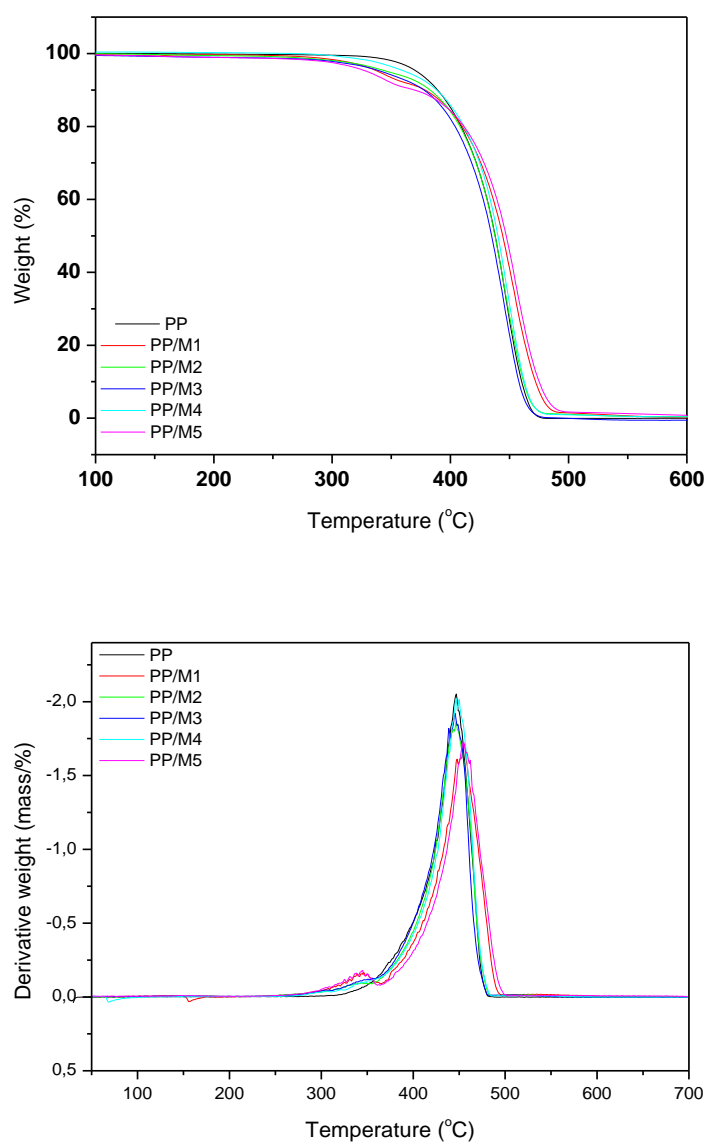


Figure 12.4. TGA and DTGA graphs of PP and PP/SCB celluloses composites

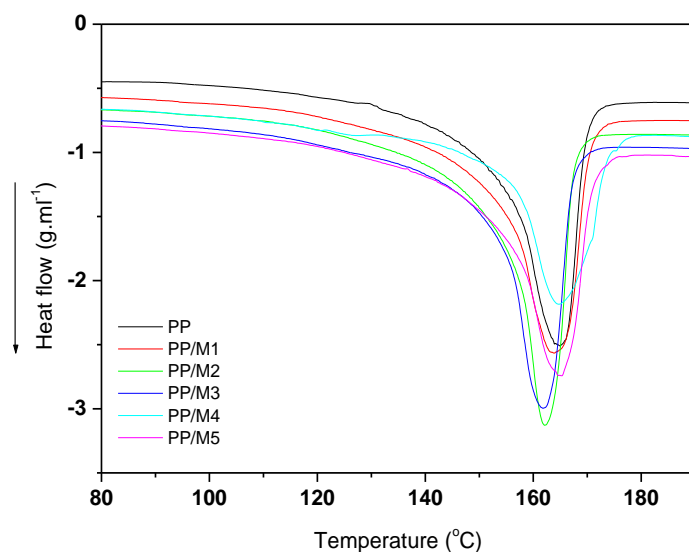


Figure 12.5: DSC melting of PP and PP/SCB celluloses composites

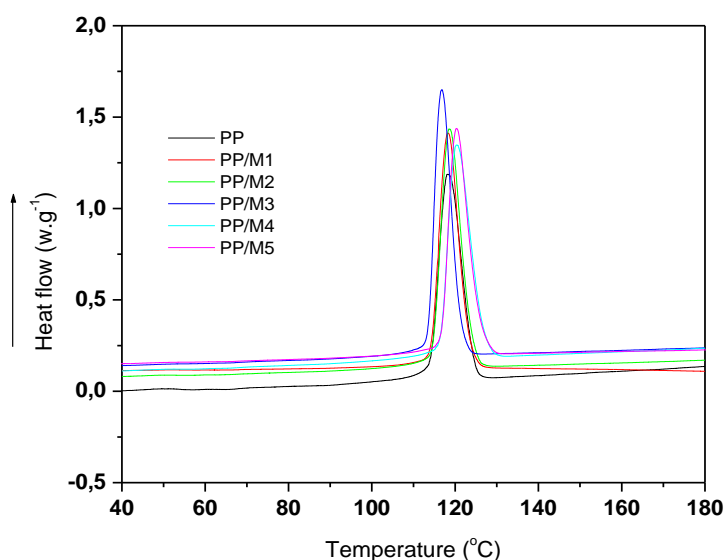


Figure 12.6: DSC crystallization of PP and PP/SCB celluloses composites

The T_c values of various PP/SCB celluloses showed marginally changes towards higher values as compared to PP. The results suggest that the lower content of cellulose nor the alkali treatment had little impact on the crystallization of PP. Hence, cellulose could not have acted as nucleating agent due to lesser content or interaction. However, the main increment observed for PP/M3 composite might indicate that cellulose treatment using sodium chlorite promoted

PP to crystallize at higher temperature. The trend of T_m showed little and minimal shifts on the melting behaviour of PP similarly to the T_c values except for PP/M3 composites, which was drastically reduced. As expected, the melting enthalpy (ΔH_m^{obs}) and (ΔH_m^{calc}) decreased with the addition of SCB cellulose, due to a decrease in polymer matrix quantity. The similarities in ΔH_m^{obs} and ΔH_m^{calc} trends might be due to assumptions that the presence of cellulose have no effect on the crystallization behaviour of PP. Table 12.5 revealed a decrease in X_c on all PP/SCB cellulose composites compared to PP, similarly to the trend obtained for crystallinity of XRD. The difference in crystallinity was due to alkali treatment and the potential of chlorites salts. For instance, the substitution of sodium hypochlorite with chlorite slightly increase the crystallinity of the composite while the opposite was obtained for PP/M4 and PP/M5 composites.

Table 12.5: DSC analysis of PP and PP/SCB celluloses composites

Composition	T_c (°C)	T_m (°C)	ΔH_m^{obs} (J.g ⁻¹)	ΔH_m^{calc} (J.g ⁻¹)	X_c
PP	118.21	164.98	52.05	52.05	34.24
PP/M1	118.55	163.83	26.1	24.79	17.17
PP/M2	118.44	162.06	27.84	26.44	18.32
PP/M3	120.44	161.78	28.25	26.84	18.59
PP/M4	118.34	164.82	23.69	22.51	15.59
PP/M5	116.79	165.21	20.12	19.55	13.24

12.5 Conclusion

The influence of various alkali treatment on thermal stability, crystallization/melting behaviour, and morphology of the resulting PP/SCB cellulose composites were investigated. FTIR spectroscopy revealed better interaction for acidified sodium hypochlorite than its non-acidified counterpart. The crystallinity index and crystalline sizes of PP decreased and increased respectively with the introduction of various celluloses. The introduction of various celluloses had a minimum impact on the thermal stability of PP, with noticeable shift observed for PP/M3. The crystallization and melting values were marginally changed with addition of various alkali treated SCB celluloses, with sodium chlorite imparting greater nucleation

efficiency. The usage of sodium chlorite as a bleaching agent (PP/M3) proved more efficient in influencing the properties of PP, in comparison with other composites.

12.6 References

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CHAPTER THIRTEEN:

CONCLUSION AND RECOMMENDATION

13.1 Summary and conclusion

The main objective of this study was to investigate the physical, mechanical and durability properties of sugarcane bagasse ash enhanced bricks stabilized with lime powder. XRD analysis revealed that SCBA is chemically rich in crystalline silica, and thus possess moderate pozzolanic activity. The pozzolanic activity and the formation of C-S-H bond between SCBA and lime powder were confirmed by FTIR and XRD analyses. The physical properties of SCBA showed that it possesses significant amount of unburnt carbon due to incomplete combustion. The composition mixtures of SCBA and lime (SCBA 95/ lime 5) and (SCBA 90/ 10) were optimized before the bricks were manufactured, while the water ratio was maintained at 5 % ratio per volume in both compositions. The compressive strength of both bricks compositions were within the values specified in SANS 1215-2008 standards. However, the bricks developed with 10% lime content revealed slightly higher values than 5% composition. The micromorphology images of these bricks revealed less porous surface and smooth microstructure. Water absorption and density values obtained were within the values reported in the standards (NBR 10834 and IS 2185 (Part 1): 2005).

Based on the results obtained in this study, it can be concluded that SCBA can be utilized in combination with lime to develop bricks that are sustainable. The bricks meet the strength and workability requirement for load bearing bricks that can be used in moderate weather regions. The bricks have acceptable masonry properties such as compressive strength, water absorption, and durability as described in various standards. The manufacturing of this bricks will contribute towards reduction of GHGs and practical mitigation options for the building sector by utilizing agricultural and industrial waste materials. The SCBA bricks developed do not need high curing temperature in their production, and OPC as a raw material. An overview on the mechanical and durability properties of compressed bricks using agricultural waste stabilized with fly ash and lime further suggested that sustainable bricks utilizing waste materials can be produced with replacement of cement with pozzolan materials. The brick properties are influenced by type of raw materials used, methods and period of curing and the degree of compaction. Construction and demolition wastes such as recycled cement, and masonry can be used as a replacement of natural aggregates in concrete production despite

having lower density and higher water absorption than natural aggregates. They can be used to manufacture conventional concretes and building materials with good performance if they are added in the proper amounts and are properly managed. Finally, the usage industrial and agricultural waste materials in concrete and brick production provides a solution to the problem of waste management and constitutes a significant step towards a more sustainable and environmentally friendly society.

The other objective of the study was to investigate cellulose chemistry and its applications in the development of composites and blends materials. The results showed that cellulose can be extracted from agricultural waste materials including SCB and SW through alkali treatment and delignification processes. Cellulose generally had the greatest enhancement on the mechanical properties and decrease the moisture sensitivity of the composites compared to the untreated fibre. TGA analyses showed that the thermal decomposition of SCB and SW was delayed to higher temperatures with increasing the heating rate. In addition, cellulose materials are less stable than untreated fiber and had minimum impact on the thermal stability of PP composites and PP/PE blend. XRD analyses showed that the crystallinity index increased with chemical treatment, and decrease with prolong alkali treatment and cellulose introduction in composites and blends composition. FTIR and SEM analysis further revealed poor interaction and dispersion of raw fiber with PP/PE blend and/or PP composites as compared to cellulose materials.

15.1 Recommendations for future work

From this study, the following recommendations for further research into the development of SCBA-lime bricks are suggested:

- The chemical, physical and mineralogical properties of SCBA had significant effects on performance of the bricks. Therefore, it is necessary to control the combustion of SCBA in order to harvest SCBA with improved pozzolanic activities.
- Mechanical and durability properties of CEBs are directly linked with compaction pressure, curing method and period employed. Hence, it is critical to use hydraulic compressor and prolong the curing period of the bricks in order to achieve improved properties.
- Industrial waste materials such as fly ash and recycled concrete are potential raw materials to be utilized in various construction works. However, various tests need to

be carried out to ensure that these waste materials have physical and mineralogical properties to be incorporated in the brick composition.

- Commercial production and application of bricks incorporating waste is still limited due to lack of standards guiding waste incorporation. Hence further research and development is needed to develop guidelines for incorporating various waste material.

In addition, the following recommendations for cellulose chemistry and its applications are suggested as follows:

- Cellulose has shown to have numerous advantages such as biodegradability, renewability, and low density even at high filling levels. However, these materials are still characterized by poor compatibility and adhesion due to their hydrophilic structure. Hence, research on environmentally friendly treatment methods to improve the fiber–matrix adhesion need to be addressed.
- The progress should be made on the development of maize fiber, sorghum, rice husk and sugar cane bagasse green composites as compared to other natural fibers such as such as flax, agave, kenaf and sisal fibers.
- Additional research focused on the biodegradability and renewability of agricultural waste and their respective composites and blend materials need to be conducted.
- A research on “green” composite based agricultural fillers should not only be driven by their biodegradability and environmental awareness but also by their commercial applications.

