Phosphate Bonded Wood and Fibre Composites

by

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Declaration

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Abstract

In a world constantly driven by change, developing new composite products requires moving beyond the traditional approach to more environmentally benign processes and products. This study investigates the application of magnesium-based phosphate cement and calcium-based phosphate cement in the development of natural fibre composite products. The magnesium phosphate cement was prepared from a heavy magnesium oxide (MgO) and monopotassium phosphate (KH_2PO_4), while the calcium phosphate cement was prepared from unslaked lime (CaO), calcium silicate ($CaSiO_3$) and monopotassium phosphate (KH_2PO_4). These phosphate cements were used to produce composite panels using bio-based industrial residues. The residues utilized include sugarcane bagasse (*Saccharum officinarum*), hemp hurds (*Cannabis sativa*), pine sawdust (*Pinus elliottii*), paper mill sludge and waste paper. Additionally, forest biomass waste from the clearing of locally occurring invasive alien species including Black wattle (*Acacia mearnsii*), Long-leaved wattle (*A. longifolia*), Port Jackson (*A. saligna*), Rooikrans (*A. cyclops*), Blue gum (*Eucalyptus globulus*), Sekelbos (*Dichrostachys cinerea*) and Deurmekaarbos (*Ehretia rigida*) were used.

The study utilized a central composite statistical design, whereupon the following factors were considered i.e. KH_2PO_4: MgO ratio, KH_2PO_4: CaO + $CaSiO_3$ ratio, CaO: $CaSiO_3$ ratio and the amount of wood/fibre as a ratio of wood/fibre to the total inorganic content. Additionally, the use of coal fly ash as a complementary material in the composite was investigated. Fitted response surface methodology plots were used to show the relationship between the variable factors on the desired responses. The effect of the main factors and their interactions on the measured board properties were evaluated using Pareto analysis of variance. Response surface models were developed to predict the parameters yielding the optimum board properties. While the physical properties of the panels met the minimum requirements for cement bonded particleboard (EN 634-2:2007) and LD-1 grade particle board (ANSI A208.1:1999), the strength properties needed to be improved to offer more flexibility in terms of application.

Three biomass materials were selected for further study aimed at enhancing the properties of the boards. These materials were subjected to three different treatments, namely alkalization, acetylation and hot water extraction. The effect of each of the treatments on the fibre materials was evaluated using HPLC, SEM and FTIR. These materials were used to manufacture composite panels and µCT was used to characterize the microstructure of the composite samples. A numerical technique was used to quantify the phases in the composites, namely cement matrix, filler and void spaces. All treatments improved the fibre characteristics and did not significantly reduce the fibre yield. In magnesium phosphate bonded panels, the mean modulus of rupture was 0.74 MPa for untreated, 1.03 MPa for hot water extracted, 1.20 MPa for acetylated and 1.66 MPa for alkalized black wattle panels. In calcium phosphate bonded panels, the mean modulus of rupture was 0.88 MPa for untreated, 0.83 MPa for hot water extracted,

0.73 MPa for acetylated and 1.18 MPa for alkalized black wattle panels. Boards made with alkali treated fibres had the best properties. The study concluded that bio-based residues can be incorporated into formulated phosphate cement binders to produce durable products that are comparable to current cement bonded products.

Opsomming

In 'n wêreld voortdurend gedryf deur verandering, vereis die ontwikkeling van nuwe saamgestelde produkte ‘n buite die tradisionele benadering tot meer omgewingsvriendelike prosesse en produkte. Hierdie studie ondersoek die toepassing van magnesium-gebaseerde fosfaat sement en kalsium-gebaseerde fosfaat sement in die ontwikkeling van natuurlike vesel saamgestelde produkte. Die magnesium fosfaat sement is bereid van 'n swaar magnesiumoksied (MgO) en monokaliumfosfaat (KH_2PO_4), terwyl die kalsiumfosfaat sement is bereid om van ongebluste kalk (CaO), kalsium silikaat ($CaSiO_3$) en monokaliumfosfaat (KH_2PO_4). Hierdie fosfaat sement is gebruik om saamgestelde panele met behulp van bio-gebaseerde industriële oorblyfsels te produseer. Die oorblyfsels sluit in Suikerriet bagasse (*Saccharum officinarum*), Hennep hurds (*Cannabis sativa*), Denne saagsels (*Pinus elliottii*), papierfabriek slyk en afval papier. Daarbenewens is bos afval van plaaslike uitheemse spesies, insluitend Swartwattel (*Acacia mearnsii*), Lang-blaar wattel (*A. longifolia*), Port Jackson (*A. saligna*), Rooikrans (*A. cyclops*) en Bloekomhout (*Eucalyptus globulus*), Sekelbos (*Dichrostachys cinerea*) en Deurmekaarbos (*Ehretia rigida*) gebruik.

Die studie benut n sentrale saamgestelde statistiese ontwerp, waarin die volgende faktore in ag geneem was; KH_2PO_4: MgO verhouding, KH_2PO_4: CaO + $CaSiO_3$ verhouding, CaO: $CaSiO_3$ verhouding en die hoeveelheid van hout / vesel as 'n verhouding van hout / vesel tot die totale anorganiese inhoud. Daarbenewens was die gebruik van steenkool vliegas as 'n aanvullende materiaal in die saamgestelde produk ondersoek. Gepasde reaksie oppervlak metode areas is gebruik om die verhouding tussen die veranderlikes en die verlangde reaskies te toon. Die effek van die belangrikste faktore en hul interaksies op die gemete bord eienskappe is geëvalueer met behulp van die Pareto ontleding van variansie. Reaksie oppervlak modelle is ontwikkel om parameters te voorspel wat optimum bord eienskappe lewer. Terwyl die fisiese eienskappe van die panele aan die minimum vereistes vir sement gebinde spaanderbord (EN 634: 2007) en LD-1 graad spaanderbord (ANSI 208,1: 1999) voldoen, sal die sterkte eienskappe moet verbeter om meer buigsaamheid te bied in terme van toepassing .

Drie biomassa materiale is gekies vir verdere ondersoek met die doel om die bord eienskappe te verbeter. Hierdie materiaal is onderwerp aan drie verskillende behandelings, naamlik alkalisasie, asetilering en warm water onttrekking. Die effek van elk van die behandelings op die vesel materiaal is geëvalueer met behulp van HPLC, SEM en FTIR. Hierdie materiaal is gebruik om saamgestelde panele te vervaardig en µCT is gebruik om die mikrostruktuur van die saamgestelde monsters te kenmerk. 'n Numeriese tegniek is gebruik om die fases te kwantifiseer in die samestellings, naamlik sement matriks, toevoeger en leë ruimtes. Alle behandelings het die vesel eienskappe verbeter en het nie die vesel opbrengs aansienlik verminder nie. In magnesium fosfaat gebinde panele, was die gemiddelde modulus van breking 0,74 MPa vir onbehandelde, 1.03 MPa vir warm water onttreking, 1.20 MPa vir asetilering en 1,66 MPa vir alkaliseerde swartwattel panele. In kalsiumfosfaat gebinde panele, was die gemiddelde

modulus van breking 0,88 MPa vir onbehandelde, 0.83 MPa vir warm water onttreking, 0.73 MPa vir asetilering en 1.18 MPa vir alkaliseerde swartwattel panele. Borde gemaak van alkali behandelde vesel het die beste eienskappe. Die studie het bevind dat bio-gebaseerde oorblyfsels geïnkorporeer kan word in geformuleerde fosfaat sement binders om duursame produkte te produseer wat vergelykbaar is met die huidige sement gebinde produkte.

Acknowledgements

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To my blessed family, my dad Mr Sylvester Amiandamhen and my siblings Mrs Adeyeye, Mr Elvis, Mrs Sokunbi, Mark and Martha, I thank you for your prayers, support and encouragement to carry on despite all odds. I love you all. Everywhere and always, I thank God for the spirit to carry on this far. Where would I have been Lord, if not for your light in my academic path. For the invaluable knowledge acquired so far, I give you thanks and praises.

Newton's second law of graduation

The age, *a*, of a doctoral process is directly proportional to the flexibility, *f*, given by the advisor and inversely proportional to the student's motivation, *m*

$$Age\ (PhD) = \frac{flexibility}{motivation}$$

$$a = f/m$$

As motivation goes to zero, the duration of the PhD goes to infinity.

Dedication

To the glory of God, this work is dedicated to my mother of blessed memory, Mrs Patricia Eduzala Amiandamhen.

List of Publications

This dissertation is based on the following publications which in the text are referred to by their Roman numerals and appended within the dissertation.

Journal articles

1. **Publication I**

Inorganic bonded natural fibre composites: Opportunities and state of the art in phosphate based cement

Amiandamhen SO, Meincken M, Tyhoda L

Springer Science Reviews (under review)

2. **Publication II**

Magnesium based phosphate cement binder for composite panels: A response surface methodology for optimization of processing variables in boards produced from agricultural and wood processing industrial residues.

Amiandamhen SO, Meincken M, Tyhoda L

Industrial Crops and Products 94 (2016): 746-754

3. **Publication III**

Phosphate bonded wood composite products from invasive Acacia trees occurring on the Cape Coastal plains of South Africa.

Amiandamhen SO, Montecuccoli Z, Meincken M, Barbu MC, Tyhoda L

European Journal of Wood and Wood Products (revised version submitted)

4. **Publication IV**

Calcium phosphate bonded wood and fibre composite panels: Optimization of panel properties using response surface methodology.

Amiandamhen SO, Meincken M, Tyhoda L

Holzforschung (revised version submitted)

5. **Publication V**

Surface treatments of natural fibres and their effects on the properties of phosphate bonded composite products

Amiandamhen SO, Meincken M, Tyhoda L

(in preparation)

Articles in conference proceedings

6. **Conference presentation I**

Phosphate bonded natural fibre composites.

Amiandamhen SO, Gonya S, Meincken M, Tyhoda L

Proceedings of the 2nd International Conference on Composites, Bio-composites and Nano-composites, In: Kanny MK, Adali S (Eds), Advances in Composites, Bio-composites and Nano-composites, Vol. 2, 161-177, October 28-30, 2015, Durban, South Africa.

7. **Conference presentation II**

Effect of Bark on the Physical and Mechanical Properties of Phosphate Bonded Wood Composites of Black Wattle (*Acacia mearnsii* De Wild)

Amiandamhen SO, Meincken M, Tyhoda L

Proceedings of the 59th International Convention of Society of Wood Science and Technology, Susan LG (Ed), Forest Resource and Products: Moving toward a Sustainable Future, 165-173, March 6-10, 2016, Curitiba, Brazil.

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CHAPTER ONE

1. Introduction

1.1 Background and motivation

Against the backdrop of a competitive building materials market and the current production status of several key wood composite panels, this study investigated the emerging opportunities of phosphate binders in the manufacturing of value-added wood and fibre composite products from various biomass sources including industrial residues and forest waste. The phosphate binder originally developed to encapsulate harmful substances in nuclear waste streams presents many advantages and has found increasing interest in other fields of application including civil and architectural engineering (Jeong and Wagh, 2002). The phosphate binder which is formulated at room temperature from an acid-base reaction sets rapidly into a solid mass like ceramics (Wagh and Jeong, 2003; Wagh, 2004). This study is focussed on magnesium and calcium based phosphate binders that were formulated to develop bio-based composite products. The solution chemistry of the binders is reported in chapter two of this dissertation. Details of the stoichiometry and thermodynamics of different metallic phosphate compounds are beyond the scope of this dissertation but can be found in the book of Wagh (2004, 2016).

Different inorganic binders have been used with wood and other lignocellulosic fibres to produce durable composite panels for many decades (Youngquist, 1999; Stark *et al*., 2010; Irle *et al.*, 2013). Portland cement boards are highly durable and resistant to moisture. Fibre reinforced cement composites have been developed for high performance applications (Parra-Montesinos, 2005; Kuder and Shah, 2010) and improved acoustic performance and damping properties (Neithalath *et al*., 2004). However, the natural incompatibility between wood fibres and cement is a major limitation. Further details about wood-cement compatibility are available in chapter two of this dissertation. The production of 1 kg of Portland cement releases 1 kg of carbon dioxide (CO_2), which adds to global warming (EPA, 2005, 2010). Mankind in its effort to provide environmentally-friendly alternatives for traditional composite products continue to find new ways of harnessing novel materials in green composite manufacturing.

The substitution of phosphate binders for cement promises to reduce the overall consumption of energy and curtail the environmental effect of processing, production and disposal (Laufenberg and Aro, 2004). The production of phosphate binder consumes only about 41% of the total energy used in cement production and requires only a fraction of the total energy used in traditional wood composite binders such as the polymeric resins (Donahue and Aro, 2010). According to Wagh (2013), the processing and production of phosphate binder emit 20% less greenhouse gases compared to Portland cement. Most of

the research on inorganic phosphate bound biocomposites is based on the use of acid phosphate fertilizers, commercially available as monopotassium phosphate. It is interesting to note that since this material consists principally of the elements potassium (K) and phosphorus (P), debris from disposed products may enrich soil nutrients (Laufenberg and Aro, 2004). Although, the presence of phosphates in aquatic streams can be a problem by producing unwanted algae growth, product leaching tests showed that the products release phosphates slowly into ground water (Singh *et al.*, 1996; Wagh, 2013). The slow release of phosphates from disposed products may be beneficial to plants and should not affect the environment.

The development of phosphate bonded wood and fibre composite products utilizing wood-based industrial residues and forest waste comes as a logical choice to harness the high volume of waste generated globally. According to Hoornweg and Bhada-Tata (2012), the current global waste generation is about 1.3 billion ton per year, and is expected to increase to about 2.2 billion ton per year by 2025. About 46% of this is organic waste which consists of wood and other industrial residues. This figure shows that there is a huge material availability and utilization potential for wood processing industrial waste. Apart from the availability of valuable raw materials for biocomposite production, the industrial exploitation of the waste contributes to the protection of the environment (absorption of CO_2) and gives economic potential to developing countries (Papadopoulou *et al.*, 2015). In addition, waste utilization reduces the energy cost of disposal and the environmental impacts on human health and safety (McDougall and Hruska, 2000).

1.2 Research aim

The general aim of this study was to investigate the prospects of phosphate bonded natural fibre composite panels utilizing agricultural residues, wood processing industrial residues and forest waste from alien invasive tree species occurring in Southern Africa. The technology utilized a phosphate binder which is an environmentally friendly binder with a low carbon footprint. Early studies revealed that the physical properties of phosphate bonded composite boards met the minimum requirements for cement bonded particleboards according to EN 634-2 (2007). However, some properties such as the bending strength could still be improved to offer more flexibility in terms of application of the products. As with other natural fibre-based cementitious composites, property improvement of the composites is usually directed toward the modification of the fibre surface. The surface treatments of natural fibres have been the subject of extensive research on fibre-based composites and it has been reported that fibre modification improves the bonding with the inorganic matrix and enhances the composite durability (Bledzki *et al*., 2004; Li *et al*., 2007; Sgriccia *et al*., 2008; Enriquez *et al*., 2016). In view of the foregoing, this study was conducted to improve the properties of the composite products.

1.3 Objectives of the study

The following objectives were identified and addressed to accomplish the general aim of the study:

Objective 1

To investigate and characterize phosphate bonded wood and fibre composite panels from wood-based industrial residues

To address this objective, different lignocellulosic residues, including Slash pine (*Pinus elliottii*), crushed Sugarcane bagasse (*Saccharum officinarum*), Hemp hurds (*Cannabis sativa*), Papermill sludge and waste paper were selectively screened. Magnesium potassium phosphate cement was developed from an acid-base reaction, which was then applied to bind the residues. The composite panel production parameters including acid: base ratio, fly ash content and wood/fibre content were optimised using a response surface methodology. The physical and mechanical properties of the composite panels were evaluated and the results are presented in the appended publication (**II**).

Objective 2

To investigate and characterize phosphate bonded wood composite panels from alien invasive tree species

This objective was addressed by selecting wood residues of some invasive alien Acacia species including Black wattle (*Acacia mearnsii*), Long-leaved wattle (*A. longifolia*), Port Jackson willow (*A. saligna*) and Rooikrans (*A. cyclops*) occurring in the Cape coastal plains of South Africa. Based on the methodology developed in objective 1, magnesium potassium phosphate cement was prepared to develop composite panels from these species. The production process was optimized and the properties of the panels were evaluated. The results are presented in the appended publication **(III)**. From the results of the experiment, the optimum conditions were used to develop composite panels from two invasive alien species occurring in the northern parts of Southern Africa. These species include Sekelbos (*Dichrostachys cinerea*) and Deurmekaarbos (*Ehretia rigida*). The properties were evaluated and the results are presented in the appendix. The effect of bark content on the properties of the panels were also evaluated and discussed. The results are presented in the appended conference presentation **(II)**.

Objective 3

To investigate and characterize calcium-based phosphate bonded wood and fibre composite panels

Calcium hydrogen phosphate cement was developed and optimised to accomplish this objective. The binder was formulated from a low cost unslaked lime, silicate powder, fly ash and monopotassium

phosphate. The residues utilized to achieve this objective were selected to cover grasses, hardwood, softwood as well as industrial residues from pulp and paper production. These raw materials included Black wattle, Blue gum, Slash pine, Bagasse, Hemp hurds, Papermill sludge and waste paper. The composite panel manufacturing process was optimized and the panel properties were evaluated. The results are presented in the appended publication (**IV**).

Objective 4

To treat the lignocellulosic biomaterials with alkali, acetic anhydride and hot water and evaluate the effect of surface treatments on the fibre and composite properties

To accomplish this objective, three lignocellulosic biomaterials were selected from hard wood (black wattle), soft wood (slash pine) and grass fibres (bagasse). The fibres were subjected to three treatments, namely alkali, acetic anhydride and hot water treatment, and were thereafter characterised. The effects of the fibre treatments were evaluated using advanced surface characterization techniques such as FTIR, SEM, HPLC and µCT. The untreated and treated fibres were used to produce the composite panels bonded with magnesium phosphate and calcium phosphate cement. The results are presented in the appended publication (**V**).

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CHAPTER TWO

Paper I

Inorganic bonded natural fibre composites: Opportunities and state of the art in phosphate based cement

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Abstract

Over the last few decades, inorganic bonded composites have been developed for high performance applications using conventional cement and concrete. The demands for wood based composites along with increasing economic and environmental concerns on conventional wood products necessitate moving beyond the traditional processing methods to more cost-effective and environmentally friendly approaches. In the wake of the 21st century, a fast-setting phosphate binder with a low carbon footprint was developed which can alternatively be utilized in wood composite development. This paper reviews the recent progress in phosphate bonded composite products based on published literature from the last two decades. A brief background on natural fibre composites is presented. The main interest of this review is the utilization of lignocellulosic fibres in phosphate binders, with special emphasis on fibre treatments and interfacial adhesion in inorganic bonded composites. In addition, the bonding mechanism of the phosphate binders and the environmental benefits accruable to such materials are discussed.

Keywords: Composites, environmental benefits, lignocellulosic fibres, phosphate binder

1. Background to natural fibre composites

The term wood composite is used to describe any wood-based material that is bonded with an adhesive, although binderless particleboards have also been developed. Wood-based composites can be classified into veneer-based material such as plywood and laminated veneer; laminates; composites such as fibreboard, particleboard, flake board, wafer board, oriented strand board; components such as beams and stress skin panels; and wood-non wood composites such as wood plastics and inorganic bonded composites (Youngquist 1999; Stark et al. 2010; Irle et al. 2013). The improvements and innovations both in raw materials and processing standards have opened new channels for the development of value-added composite products with improved properties and aesthetic appeal.

1.1 Materials

1.1.1 Lignocellulosic fibres

The most popular raw material for particleboard production is mill residues such as sawdust, planer shavings and chips. In South Africa, some companies including PG Bison produce wood composite materials from virgin fibres. Particleboard is also readily made from a variety of agricultural residues including wheat straw, rice husk, jute and cotton stalk. Low-density insulating or sound absorbing particleboard can be made from kenaf core or jute stick. Low, medium, and high-density panels can be produced with cereal straw and rice husks (Stark et al. 2010). Raw materials for oriented strand board (OSB), wafer board and fibre board are obtained from wood flakes or chips. However, in the production of fibre board, the chips are reduced to wood fibres using refiners. Wood flour and wood fibre are the primary lignocellulosic materials used in the production of wood plastic composites. Wood flour is processed commercially, often from mill waste and is used as filler in thermoplastic composites while wood fibres act more as reinforcement and lead to superior composite properties. Usually, several additives are used to enhance the performance of wood thermoplastic composites. These materials are known as compatibilizers and can improve bonding between the thermoplastic and wood component (Bhaskar et al. 2012; Effah et al. 2015). Others can be added to improve product performance (impact modifiers, UV light stabilizers, flame retardants) and process-ability (lubricants) (Youngquist 1999). The raw materials for wood cement composites are basically wood particles and fibre for high density products, while wood wool is used in the manufacture of low density wood cement composites. The use of pulp fibres offers numerous advantages when compared to other fibre reinforced cement composites (Mohr et al. 2004). Also, several research has demonstrated the suitability of different non-wood fibres in the production of fibre cement composites.

The advantages associated with lignocellulosic fibres include widespread availability, high stiffness and tensile strength, relatively low cost and well developed technology to extract fibres from renewable sources (Mohr et al. 2004). The addition of natural fibres to polymeric resins and cement presents certain difficulties owing to the natural incompatibility between the hydrophilic groups on the fibre and the hydrophobic groups on the matrix. The extent of this limitation depends on the type of fibre and nature of the matrix. In many cases, a prior knowledge of the chemical characteristics of the fibre gives an indication on the suitability of such fibre for wood composite production.

1.1.2 Adhesives and binders

The conventional wood-based composite products are typically made with a thermosetting or heat-curing resin or adhesive that binds the lignocellulosic fibres together, except for wood plastic and fibre cement composites which use polymer resin and cement binder respectively. These adhesives are chosen based upon their suitability for the product under consideration. Factors taken into account

include the materials to be bonded together, moisture content at time of bonding, mechanical property and durability requirements of the resultant composite products, and of course, resin system costs (Youngquist 1999). Commonly used thermosetting resin systems include phenol-formaldehyde, urea-formaldehyde, melamine-formaldehyde, and isocyanate. Phenol-formaldehyde (PF) resins are used in the manufacture of composite products that are durable in external conditions. Oriented strand board (OSB), softwood plywood, and siding are typical examples of these products. The drawback associated with this resin is the higher energy consumption due to the high press temperature and longer press time (Youngquist 1999). Urea formaldehyde on the other hand are more adapted to design specifications and are suitable for interior applications where dimensional stability is of utmost importance. Examples of products manufactured with urea resins are particleboard and medium density fibre board (MDF). Melamine-formaldehyde (MF) resins are used primarily for decorative laminates like the groups of melamine-faced boards, paper treating, and paper coating. MF resins may be blended with UF resins (melamine urea) for certain applications. Isocyanate as diphenylmethane di-isocyanate (MDI) is commonly used in the manufacture of composite wood products. MDI is used primarily in the manufacture of OSB.

Thermoplastics are a group of binders used in the production of wood plastic composites. Usually, thermoplastics selected for use with lignocellulosic materials melt at or below the thermal degradation temperature of the lignocellulosic component, normally 200°C to 220°C (392°F to 428°F) (Youngquist 1999). These thermoplastics include polypropylene (PP), polystyrene (PS), polyvinylchloride (PVC), and polyethylene (PE) (low and high density). PVC is a substantially harder material and is used as a green building material. It is also a proven polymer for use in the building industry. Inorganic binders used in the production of wood composites include gypsum, magnesia cement and Portland cement. Gypsum and magnesia cement are moisture sensitive, and their use in construction is generally restricted to interior applications. Composites bonded with Portland cement are more durable and are suitable for both interior and exterior applications. Portland cement reacts with water in a process called hydration and eventually solidifies into a stone-like mass (Stark et al. 2010). Portland cement is the most common type of cement in general use around the world as basic ingredient of concrete, mortar, stucco and most non-specialty grout. The low cost and widespread availability of the limestone, shale and other naturally occurring materials used in Portland cement make it one of the lowest-cost materials used throughout the world.

1.2 Processing technology

All the products in the family of particle and fibre composite materials are processed in similar ways. As described by Youngquist (1999), particleboard is produced by mechanically reducing the material into small particles, applying adhesive to the particles, and consolidating a loose mat of the particles with heat and pressure into a panel product. All particleboard is currently made using a dry process,

where air or mechanical formers are used to distribute the particles prior to pressing. Wood plastic composites are manufactured by a two-step process; compounding and forming. Compounding is the feeding and dispersing of the lignocellulosic component in a molten thermoplastic to produce a homogeneous material. The compounded material is then shaped into a product while still in its molten state or pelletized into small, regular pellets for future reheating and forming. Fibre cement boards are made using the Hatschek process. As described by Moslemi (2008), aqueous slurry of fibre and cement with some additives, about 7-10% solids by weight, is supplied to a holding tank which has a number of rotating screen cylinders. These cylinders pick up the solid matter removing some of the water in the operation. An endless felt band picks up a thin layer of fibre-cement formulation from each cylinder. The built-up laminated ply then travels over vacuum dewatering devices which remove most of the water. The sheet product thus formed subsequently wraps around an accumulation roll and continues to build additional thickness until the desired thickness is obtained.

1.3 Products and applications

Structural panels such as OSB and softwood plywood are used in light weight construction where they provide the rigid envelope that ties other structural elements of wood framed buildings together (Leland 2007). High strength, stiffness and resistance to moisture are the main performance criteria in such applications. MDF is used in the manufacture of furniture and cabinets. It is also used for interior door skins, mouldings, and interior trim components. The uses for hardboard can generally be grouped as construction, furniture and furnishings, cabinet and store work, appliances, automotive and rolling stock. Particleboard is used for furniture cores, where it is typically overlaid with other materials for decorative purposes. Particleboard can be used in flooring systems, in manufactured houses, for stair treads, and as underlayment. Fibre Cement Boards are applied in false ceilings, partitions, panelling, door shutters and flooring. Exteriorly, they can be applied as prefabricated structures, roof tiles substrate and skirting. Other applications include pelmets, blackboards, table tops, benches, beam or column encasing and under-decking structures. Wood Plastic Composites are applied in range of decking and floor tiles, railings, outdoor furniture, gates and fencing.

2. Inorganic bonded fibre composites

Inorganic bonded fibre composite consists of a discontinuous phase or reinforcing agent bonded with a continuous phase or matrix binder (Bledzki and Gassan 1999). Inorganic bonded composites contain 10% to 70% of fibre and conversely 90% to 30% of inorganic binder (Youngquist 1999). Inorganic bonded composites are made by blending wood or fibres with inorganic materials in the presence of water and allowing the resultant mixture to set into a rigid mass. Acceptable properties of inorganic bonded composites are obtained when the fibres are completely encased and the matrix is a continuous phase. The properties of inorganic bonded fibre composites are significantly influenced by the amount and type of the inorganic binder, the fibre element, as well as the target density of the composites (Stark

et al. 2010). As mentioned earlier, current inorganic bonded composites include gypsum bonded composites, Portland cement bonded composites and magnesia cement bonded composites.

A new class of inorganic bonded composites is in the infantile stage of development. This consists of non-sintered ceramic inorganic binder formed by acid-base aqueous reaction between a divalent or trivalent oxide and an acid phosphate or phosphoric acid (Jeong and Wagh 2003). The reaction slurry hardens quickly and can be used as inorganic binder to manufacture fibre composites named phosphate bonded composites. Phosphate bonded wood and fibre composites showed the potential to compete with cement bonded composites and met the minimum requirements for cement bonded composites (Amiandamhen et al. 2016). Magnesia and Portland cement composites are the most common cement bonded composites. However, gypsum and magnesia cement are sensitive to moisture and their use is restricted to interior applications. Detailed description of magnesia cement and gypsum bonded composites can be found in Youngquist (1999) and Stark et al. (2010). On the other hand, Portland cement bonded composites are more durable and are used in both interior and exterior applications. Our interest is to develop phosphate bonded composites that are durable and can be applied in both interior and exterior applications. A brief discussion of existing Portland cement bonded composites is presented in the next section.

2.1 Portland cement bonded composites

Portland cement is the most widely used material in wood-cement composites. Commercially available Portland cement composites consist of low density panels made with wood wool and high density panels made with particles and fibres (Stark et al. 2010). Low density panels are generally used for interior applications (Tittelein et al. 2012) while high density panels are used as flooring, load bearing walls and cement forms (Youngquist 1999). The most developed high density panels are those made with delignified wood fibres. Fibre cement composites have been manufactured for high performance applications (Parra-Montesinos 2005; Kuder and Shah 2010) and improved acoustic performance and damping properties (Neithalath et al. 2004). In housing construction, fibre cement composite products are used for non-structural components, including siding and roofing materials (Mohr et al. 2004). They offer good dimensional stability, high decay and fire resistance properties, and impart additional energy absorbing capacity to the composite material (Moslemi 1999). As a result, fibre cement composites show improved ductility, flexibility and crack resistance when compared to neat cement concrete (Mohr et al. 2004). The addition of fibres to Portland cement improves the fracture toughness of the composite by blocking crack propagation. This delayed multiple cracking reduces deformation at all stress levels and impacts a well-defined post-yield behaviour of the composite material (Wolfe and Gjinolli 1997).

The use of cement in wood composites is faced with many limitations. A major drawback is the vulnerability of natural fibres to decompose in the alkaline environment of cement. In addition, sugars, hemicelluloses and lignin present in wood affect the hydration characteristics of cement matrix (Karade

et al. 2003). Impermeable hydrates are formed around unhydrated cement grains, which delay the setting of the cement (Frybort et al. 2008) and affect the ultimate strength of the composites (Stark et al. 2010). These limitations have been addressed by several techniques. Hot water extraction and leaching in cold water have been effective in removing the detrimental components (Okino et al. 2005; Pelaez-Samaniego et al. 2014). Chemical extractions have also shown some positive effects (Alberto et al. 2000; Frybort et al. 2008). The use of cement curing accelerators like $CaCl_2$, $MgCl_2$ and $CaCO_3$ has been helpful in eliminating the need to pre-soak the wood particles (Youngquist 1999; Semple et al. 2002; Amiandamhen and Izekor 2013). Other methods that have been used to improve compatibility between wood and cement are fungi treatment of wood (Thygesen et al. 2006), application of blocking layers around wood particles (Jorge et al. 2004), CO_2 treatment (Qi et al. 2006; Soroushian et al. 2013) and the addition of pozzolans such as volcanic ash, fly ash, rice husk ash and condensed silica fume (Okino et al. 2005; Bezerra et al. 2006). The total amount of water available for bonding also affects the hydration of the cement paste, as too little or too much water in the paste affects the ultimate strength of the composites (Frybort et al. 2008).

Fast setting cement options are promising alternatives as it gives no time for extractives in wood to dissolve in the cement slurry (Frybort et al. 2008). In this regard, phosphate binder comes in as a logical choice. Phosphate binder is a fast setting binder formulated from an aqueous reaction between an acid phosphate and an alkali oxide or hydroxide (section 4). From the foregoing discussions, it can be concluded that although the incorporation of lignocellulosic fibres in cement matrix increase the flexibility and applicability of wood cement composites, poor interfacial adhesion between wood particles and cement can affect the composite properties, and hence composite durability (Karade et al. 2003). In view of the potentials to improve existing wood-cement composites by design approaches, it is imperative to have a closer look at the interfacial adhesion between natural fibres and cement matrix.

2.2 Fibre-matrix interface

The fibre-matrix interface is the diffusion zone in which the fibre and the matrix phases are connected either chemically or mechanically (Kabir et al. 2011). This region of connection influences the mechanical properties of the composites because the interfacial adhesion between fibres and matrix characterises many composite materials. The major problem between hydrophilic natural fibres and hydrophobic polymers is the presence of hydroxyl groups on the fibre surface. This hydroxyl groups are sensitive to moisture and makes the composite dimensionally unstable. The hydrophilic hydroxyl groups also hinder effective reaction with hydrophobic matrix. In addition, the presence of waxes and pectin in the cell wall prevents the interlocking with the matrix by covering the reactive functional groups of the fibres. The combined effect of this inaccessibility is a poor adhesion across the phase boundary and a resultant weak dispersion of force and poor strength properties (Kabir et al. 2011; Pickering et al. 2016). To optimize and maximize the interfacial bonding between fibre and matrix,

several fibre surface modification techniques have been addressed (section 2.3). Within a fibre-matrix system, it is also possible to tailor the interfacial bonding practically by developing interfaces from matrix-fibre reaction during fabrication and the coating of fibres before they are incorporated into the matrix (Daniel 1994).

As already mentioned, the interfacial bonding between fibre and matrix determines the mechanical properties of composites. During stress transfer between matrix and fibres, good interfacial bonding allows the composites to carry load to a higher strain limit, although strong interface enables crack propagation which ultimately reduces toughness and strength. Interfacial bonding usually occurs by mechanical interlocking, electrostatic bonding, chemical bonding and inter-diffusion bonding (Matthews and Rawlings 1999). Mechanical interlocking occurs when the fibre surface is rough. This increases the interfacial shear strength but has less influence on the transverse tensile strength (Pickering et al. 2016). The influence of electrostatic bonding is only significant and applicable in metallic interfaces. Chemical bonding occurs when there are chemical groups in the phase boundary that can react to form chemical bonds. In this instance, the resultant interfacial strength depends on the type and density of the bonds (Pickering et al. 2016). This type of bonding can be achieved when a coupling agent is used as a bridge between the fibre and matrix. Inter-diffusion bonding occurs when atoms and molecules of the fibre and matrix interact at the interface. However, it is possible for different types of bonding to occur at the same interface at the same time (Beckermann and Pickering 2008).

The essential interfacial properties required for developing tough composites are the debond fracture surface energy G_i and the interfacial shear sliding stress τ. The debond fracture surface energy must be considerably lower than the fibre fracture surface energy G_f for the composites to be non-brittle. If τ is too high, matrix micro cracking level may approach ultimate tensile strength. This shortens the fibre pull out lengths and the composite becomes brittle. If τ is too low, transferral of load from matrix to fibre will also be low. The result is a low micro cracking stress, low ultimate strength and less effort on fibre pull out (Daniel 1994). Several techniques have been used to study the interfacial micromechanical properties of fibre and matrix. For any technique to be successful in composite development, it must measure the interfacial frictional shear sliding stress τ, fibre-matrix interface fracture surface energy G_i and be applicable to a large range of fibre and matrix types with minimal, non-specialized specimen preparation (Daniel 1994). A number of the techniques rely on the tensile loading of a bar and measuring different parameters (Ramirez et al. 2009; Ding et al. 2014). Some techniques use small cut samples from actual components while others involve the pushing or pulling of individual fibres within the matrix and measuring the applied load and fibre displacement (Hsueh 1991; Yallee and Young 1998; Zhifei et al. 2005; Chi 2012). Recently, a new technique using a stress contour of composite matrix was reported (Budiman et al. 2014). The authors used a developed single-fibre fragmentation test model to simulate the stress contour and the interface was modelled as a cohesive zone model. However, many of the techniques are applied in high performance synthetic fibre-reinforced matrix composites,

probably owing to the low tensile modulus of some natural fibres in such applications and the weak interfacial bonding with the matrix. A major limitation is the difficulty in characterizing the wood-matrix interfacial property using the pull-out tests. This is most likely due to the small dimension of wood fibres.

In natural fibre composites, the distribution of adhesive in composites and the micromechanical properties of the fibre-matrix interface have been studied. Evans et al. (2010) used an X-ray micro-computed tomography (XCT) to examine changes in the distribution of melamine-urea-formaldehyde adhesive on wood flakes before and after pressing. The authors reported that resin accumulates in capillary channels within splintered ends of wood flakes and at the base of composite samples than the void space., thereby forming an anisotropic discontinuous network by aligning in the same *x-y* direction as wood flakes (Evans et al. 2010). Kamke et al. (2014) modelled the micromechanical behaviour of wood fibre-matrix interface, and integrated the microstructure of the interface region studied with the XCT. The model provided a 3D representation of equivalent strain and stress of the adhesive bond under an applied load and was validated using a lap-shear test (Kamke et al. 2014). Very recently, Joffre et al. (2017) proposed a method using acetylated wood fibres sticking out of the polylactic acid (PLA) matrix at the fracture surface. The length distribution of the fibres is approximated using XCT. This is then used to estimate the adhesion between the fibres and the matrix (Joffre et al. 2017). With the interfacial properties between fibres and matrix already discussed, it is important to discuss the different methods that have been adopted to modify natural fibre surface prior to composite development.

2.3 Modification of natural fibres for composite development

The production of inorganic bonded wood and fibre composite products present certain difficulties due to the inherent incompatibilities between lignocellulosic fibres and inorganic matrix. The use of methods that can alter the physical, chemical or morphological properties of the fibres is imperative to make hydrophilic natural fibres bond well to highly polar hydrophobic polymers (Bledzki et al. 2004). As with concrete and other cementitious materials, the major limitations to the use of natural fibres in composites include the sensitivity to moisture and variable fibre properties. The hydrophilicity of natural fibres results in high moisture absorption and weak adhesion with hydrophobic matrices. These limitations result in inadequate fibre distribution in the matrix and hence poor stress transfer from the matrix to the fibres (Li et al. 2007). Hence natural fibres have been treated to reduce the hydrophilic sites and improve the adhesion to matrix materials. Chemical treatments may activate hydroxyl functional groups and/or introduce new moieties that can bridge the fibre and the matrix. Ideally, the introduction of coupling agents such as in wood-polymer composites reacts with the hydroxyl group of the fibres and the functional groups of the matrix (Bledzki et al. 2004; Li et al. 2007). The result is the development of a highly cross-linked interphase region with an intermediate modulus between that of substrate and polymer and the formation of covalent bonds.

A better understanding of the chemical composition of natural fibres and its surface adhesive properties is important in order to develop any fibre-based inorganic composites (Li et al. 2007). Natural fibres contain cellulose, hemicellulose, lignin, pectin, waxes and other water soluble extractives. The holocellulose (cellulose and hemicellulose), sugars and lignin contents are of major considerations in wood based composites. Cellulose is made up of D-glucopyranose units linked together by β-(1-4)-glycosidic bonds. Due to the large proportion of hydroxyl groups within the cellulose structure, there is a high affinity for water, which generally affects the dimensional stability of fibre-matrix composites. Hemicellulose polymers are the most hydrophilic wood constituents and are partly soluble in water (Pelaez-Samaniego et al. 2013). They are fully amorphous and are strongly bound to cellulose fibrils presumably by hydrogen bonds (Li et al. 2007). Although, many treatments of natural fibres are directed toward removing much of the hemicelluloses, it has been found that hemicellulose removal also affect some wood properties (Sweet and Winandy 1999; Shi et al. 2007). Klüppel and Mai (2012) demonstrated that while hemicellulose improves wood strength in dry conditions, lignin maintains wood strength in wet conditions. Lignin is a highly complex and aromatic polymer of phenyl propane units. It is amorphous and binds the crystalline celluloses with the hemicelluloses within the cell wall (Li et al. 2007).

Several studies have been conducted on the modification of natural fibres for composite development. A few treatment methods have been applied in these studies. Physical methods do not change the structural composition of the fibres but modify the surface properties. This results in good mechanical bonding with the matrix and improved composite properties (Abdelmouleh et al. 2007). Some physical treatments include stretching, calendaring, cold plasma treatment, electric discharge and thermo-treatments. Chemical methods are the most widely developed and offers structural changes to fibres, enabling fibre-matrix interfacial bonding. Different chemical treatments have been reported in the literature. The most common is alkaline treatment using sodium hydroxide. This treatment alters the structural orientation of highly packed crystalline cellulose order and forms amorphous region by swelling the fibre cell wall (Kabir et al. 2011; Kumar et al. 2011). Alkaline treatment promotes the ionization of the hydroxyl group to the alkoxide as shown

$$\text{Fibre} - \text{OH} + \text{NaOH} \rightarrow \text{Fibre} - \text{O} - \text{Na} + \text{H}_2\text{O} \qquad [1]$$

Alkaline sensitive hydrogen bonds break down resulting in the formation of new hydrogen bonds between the cellulose molecular chains. This treatment also removes a certain amount of hemicellulose, lignin, wax and oil covering the external surface of the fibre cell wall (Abdelmouleh et al. 2007; Li et al. 2007). The factors affecting alkalization or alkaline treatment are the type and concentration of alkali, treatment time and temperature (Hajiha et al. 2014). Different conditions have been used by different authors, ranging from 0.5% to 29% NaOH; 20 min to 8 h and from room temperature to 120 ^{o}C (Sawpan

et al. 2011; Suardana et al. 2011). The concentration of the alkali should not be higher than the optimum condition; otherwise excess delignification will result in weaker and damaged fibres (Wang et al. 2007).

Another widely adopted fibre treatment is acetylation with acetic anhydride. This method introduces an acetyl functional group (CH_3COO^-) into the fibres by substituting the polymer hydroxyl groups of the cell wall, causing plasticization of cellulose (Li et al. 2007). The reaction of acetic anhydride with fibre is shown as

$$\text{Fibre} - OH + CH_3 - C(=O) - O - C(=O) - CH_3 \rightarrow \text{Fibre} - O - C(=O) - CH_3 + CH_3C(=O) - OH \quad [2]$$

Acetylation can be carried out with or without an acid catalyst. Usually, acetic anhydride and acetic acid individually do not react sufficiently with cellulosic fibres. As a result, the fibres are initially soaked in acetic acid before being treated with acetic anhydride between 1 to 3 h at slightly elevated temperatures (Kabir et al. 2011). Other authors use ratios of 1:1 or 1:1.5 of acetic anhydride to acetic acid. This treatment swells the fibre cell wall (Kabir et al. 2008) resulting in decreased hydrophilicity and improvement in dimensional stability of the composites (Hajiha et al. 2014; Haque et al. 2014). Acetylation provides a rough surface topography with fewer voids in the fibre cell walls, resulting in better mechanical interlocking with the matrix (Li et al. 2007).

Another chemical treatment of important consideration is hot water extraction. This method is the cheapest and oldest means of structurally modifying the composition of natural fibres. Hot water extraction is a thermochemical process for fractionation of soluble sugars (Amidon et al. 2008). During the hydrolysis, hemicelluloses are depolymerized into monomers and oligomers. Cellulose may be partially depolymerized while lignin may be subjected to plasticization, partial solubilisation, condensation or depolymerisation (Pelaez-Samaniego et al. 2014). The combined reactions change the composition and properties of the resultant fibres. By removing the hemicelluloses, the available hydroxyl groups in fibres are reduced, leading to increased resistance to moisture uptake, dimensional stability and durability of composites (Pelaez-Samaniego et al. 2013).

Other chemical treatments for modifying natural fibres have been reported elsewhere. Silane treatment stabilizes composite materials by incorporating silane coupling agents to modify the fibre surface. Silanols, formed in the presence of moisture from hydrolysable alkoxyl groups react with cellulose hydroxyl group to form stable covalent bonds to the cell wall (Li et al. 2007). Benzoylation improves fibre matrix adhesion, resulting in increased composite strength, improved thermal property and decreased moisture sensitivity. Benzoylation uses benzoyl chloride which includes benzoyl ($C_6H_5C=O$). Benzoyl is responsible for decreased hydrophilic nature of treated fibres and improved interaction with hydrophobic matrix (Li et al. 2007). Acrylic acid and Acrylonitrile can be used to modify fibres by graft polymerization. Maleic anhydride can also be used to modify natural fibre surface to achieve better interfacial bonding and mechanical properties in composites. Other treatments of natural fibre surfaces

involve the use of potassium permanganate ($KMnO_4$) solution in acetone, peroxides, isocyanate, stearic acid ($CH_3(CH_2)_{16}COOH$) in ethyl alcohol, sodium chlorite ($NaClO_2$) and triazine ($C_3H_3N_3$) (Li et al. 2007). Of interest is the sodium chlorite used in bleaching fibres. It was reported that the flexural strength of treated fibres increased owing to the lower stiffness and higher flexibility of fibres after delignification (Misra et al. 2002).

3. Phosphate binder for wood composites

Phosphates are naturally occurring rocks or ores containing phosphate ions and largely deposited in Florida in the United States, Kola in Russia, and in the disputed territories of the Western Sahara occupied by Morocco (Pearce 2011; Wagh 2004). Phosphates consist of minerals of calcium and aluminium phosphates mined to obtain phosphorus for agricultural and industrial use. A significant advantage of phosphate mining is the low energy consumption owing to the surface mining of phosphate rocks and the low temperature extraction of the Ortho-phosphoric acid (H_3PO_4) from the ore (Wagh 2004). Phosphate chemicals are used in large scale manufacturing of phosphate fertilizers and food ingredients. It is important to note that since the phosphate fertilizer will be used in product development, debris from disposed products may enrich soil nutrients (section 6).

A major theoretical problem faced with phosphate is the declining state of supply. A peak phosphate theory has been proposed where a catastrophic decline in production of phosphate fertilizer would result in a progressive decrease in human population (Dolan 2013). However, it is highly misleading to forecast a sharp peak of phosphate fertilizer production in the future, let alone to predict that mass starvation and population collapse would result. According to Dolan (2013), what is likely is a period of continued rising phosphate prices which will trigger three reactions; first, there will be economical processing of lower grades of phosphate rocks; second, there will be changes in farm management and development of improved crop varieties; and thirdly, there will be incentives for improved recycling of phosphorus from waste streams.

In wood composite development, phosphate binder can be formulated from acid-base reaction between an acid phosphate and an alkali mineral. The alkali suitable for this kind of reaction is usually an oxide or carbonate of divalent or transition metals while the acidic phosphate is usually a salt of phosphoric acid or a metallic phosphate (Wagh and Jeong 2003; Wagh 2004). Different alkali metals have been used in the formulation of phosphate binders such as calcium oxide CaO, magnesium oxide MgO, Aluminium oxide Al_2O_3, and Iron oxide Fe_2O_3. However, MgO has been found to be more effective because it has moderate solubility between CaO and Fe_2O_3 (Wagh 2004). Depending on the choice of components and the processing conditions, the reaction between the acid and the alkali can be highly exothermic and the resulting viscous fluid can bond to any earth metal (Wagh 2013). The fluid is thixotropic i.e. the viscous property is time-dependent and sets within minutes when left undisturbed into a highly crystalline and rigid product called chemically bonded phosphate ceramic (CBPC). Details

of the formulation processes are discussed in the next section. Full details on the thermodynamics and stoichiometry of the acid-base reactions can be found in Wagh (2004, 2016).

CBPC is a potential inorganic binder for developing wood composite products. It can also be used to develop other value-added products by recycling high volume industrial waste, such as wastepaper and pulp mill residues (Laufenberg and Aro 2004). Phosphate binder may be used in several ways either as adhesive, cement or surface material to manufacture wood and fibre based composites. An interesting advantage with the use of this binder is that it is not affected by the sugars and hemicelluloses in wood, thus providing a wider stream of utilization of wood species.

4. Formulation of chemically bonded phosphate ceramic (CBPC)

Chemically bonded phosphate ceramics (CBPCs) are formed by acid-base reactions between an acid phosphate (such as that of potassium, ammonium, or aluminium) and a metal oxide (such as that of magnesium, calcium, or zinc) (Jeong and Wagh 2002). Formulation of any given CBPC requires an in-depth understanding of solution chemistry. In this kind of ceramic product, the acid component is an acid phosphate while the alkaline component is a sparsely soluble oxide or an oxide mineral. When these compounds are mixed in an aqueous solution, the acid phosphate releases phosphate anions upon dissolution which decreases the pH of the solution. This low pH increases the solubility of the alkaline component, which dissolves slowly in the solvent and release cations in the acidic solution (Wagh 2004). The reaction of the alkaline cation and the phosphate anion results in the precipitation of a crystalline salt, otherwise called a neutral phosphate (Colorado et al. 2011a; Wagh 2013).

According to Wagh (2004), CBPC is formed as a result of three steps;

1. Dissolution of the acid phosphates in water, releasing phosphate anions and forming an acid-phosphate solution of low pH
2. Gradual dissolution of the oxides in the low pH solution releasing cations
3. Reaction between the phosphate anions and the cations forming CBPC

In conclusion, three parameters are important to determining the correct oxide or oxide mineral to be used in producing CBPC, and the physical conditions that can influence their formation. Wagh (2013) explained the cement chemistry notation using equation [3]

$$M_{2k}O_k + A_m(H_2P)_m + n\,H \rightarrow M_{2k}A_m(P)_m + (n+2m)\,H \qquad [3]$$

From the equation, M_{2k} is metal of valency $2k$, O is oxygen, A_m is alkali or a divalent metal of valency m, P is PO_4, and H is H_2O.

4.1 Magnesium phosphate

CBPCs are mainly magnesium and iron-phosphate ceramics, although specialty formulations have been developed for biomaterials applications using calcium-phosphate based ceramics (Wagh 2004). Magnesium oxide is the most common and widely used because of its moderate solubility in an acid-phosphate solution, when compared to calcium and iron oxides. To reduce the solubility of magnesium oxide in any acid-phosphate solution, it is calcined at 1300 ^{o}C so that its grains are well crystallized, and micropores from the grains are removed (Jeong and Wagh 2002). Reaction between hard burned magnesium oxide and phosphoric acid is highly exothermic resulting in difficulty of producing magnesium phosphate ceramics on a large scale (Wagh 2004).

In the reaction of magnesium oxide (MgO) and potassium dihydrogen phosphate (KH_2PO_4),Wagh (2013) describes the reaction process according to equations [4-8]

The release of anions in the solution is given by the reaction

$$KH_2PO_4 \rightarrow 2H^+ + KPO_4^{2-} \quad [4]$$

The release of hydrogen ions (H^+) facilitates the dissociation of the MgO. Thus, small parts of it dissociate in the solution as follows

$$MgO \rightarrow Mg\ (aq)^{2+} + O^{2-} \quad [5]$$

The cations and anions in the solution neutralize to form the neutral phosphate and water.

$$Mg\ (aq)^{2+} + KPO_4^{2-} \rightarrow MgKPO_4 \quad [6]$$

$$2H^+ + O^{2-} \rightarrow H_2O \quad [7]$$

The complete equation that forms this product is given by

$$MgO + KH_2PO_4 + 5H_2O \rightarrow MgKPO_4.6H_2O \quad [8]$$

This product is called magnesium potassium phosphate binder. The product has an orthorhombic colourless structure and is known as K-struvite in mineralogical literature (Wagh 2013). According to Wagh and Jeong (2003), the reaction products form crystals that can grow into insoluble solids, which form the CBPC. This makes the product highly crystalline when compared to Portland cement. Products that utilize the binding system in equation [8] are called Ceramicrete® and are common in civil and architectural engineering. Magnesium phosphates are applied in stabilization of hazardous and radioactive wastes, structural materials including road repair and architectural products (Jeong and Wagh 2002).

4.2 Calcium phosphate

The phosphate chemistry of calcium is quite complicated because of difficulties in identifying the reaction products using the X-ray diffractometry (XRD). Calcium forms a range of phosphate salts and these salts are often difficult to identify (Wagh 2016). In the reaction of calcium silicate ($CaSiO_3$), calcium oxide (CaO) and KH_2PO_4, the alkaline mineral dissociates as shown in equations [9] and [10] while equation [11] applies for the dissociation of the acid phosphate

$$CaSiO_3 \rightarrow Ca\ (aq)^{2+} + SiO_3^{2-} \quad [9]$$

$$CaO \rightarrow Ca\ (aq)^{2+} + O^{2-} \quad [10]$$

$$KH_2PO_4 \rightarrow 2H^+ + K^+ + PO_4^{2-} \quad [11]$$

The resulting equation of reactions between the anions and cations are given by

$$Ca\ (aq)^{2+} + PO_4^{2-} \rightarrow CaPO_4 \quad [12]$$

$$2H^+ + SiO_3^{2-} \rightarrow H_2SiO_3 \quad [13]$$

$$2K^+ + H_2SiO_3 \rightarrow K_2SiO_3 \quad [14]$$

The overall reaction is summarised as

$$CaSiO_3 + CaO + 2KH_2PO_4 + 2H_2O \rightarrow 2CaHPO_4.3H_2O + K_2SiO_3 \quad [15]$$

In this reaction, two products are formed, namely, calcium hydro-phosphate ($CaHPO_4.3H_2O$) and potassium silicate (K_2SiO_3). The K_2SiO_3 produces a glassy phase that fills the voids between particles of the bulk compound and produces a dense solidified non-porous ceramic product. It is believed that this alkali metal glass binds particles together within the product and increases the compression and flexural strength of the ceramic product (Wagh et al. 2003). Amiandamhen et al. (unpublished) observed that the addition of $CaSiO_3$ and KH_2PO_4 in an aqueous solution did not produce a precipitate. However, the addition of unslaked lime (CaO) to the solution initiated the reaction and increased the rate of precipitation. Wagh et al. (2003) reported that silicates and silicas, i.e. sand, are stable materials, and do not dissolve in acidic solutions, neither do they react in an aqueous environment. In a US patent, amorphous silica released from wollastonite ($CaSiO_3$) in an aqueous solution chemically reacted with phosphate anion from Ceramicrete® binder to produce a glassy phase within the structure of the ceramic (Wagh et al. 2003). Colorado et al. (2011b) fabricated a wollastonite-based CBPC (wo-CBPC) with wollastonite powders and a phosphoric acid formulation. The authors reported that when the phosphoric acid formulation and the wollastonite powder mixture are stirred, the sparsely alkaline oxide dissolves and an acid-base reaction is initiated. This hardens into a ceramic product because of gelation by salt

formation and the dissociation of the calcium cations from the calcium silicate. The molecules form an ordered structure which grows into crystals to form CBPC (Colorado et al. 2011b).

Several equations for the reaction of calcium silicate with phosphoric acid for molar ratios, r, of the acid to the alkali between 0.39 and 1.66, were proposed by Mosselmans et al. (2007). As reported by Colorado et al. (2011b), brushite, monetite and calcium dihydrogen phosphate monohydrate respectively can be formed depending on the molar ratio according to the equations below

$$CaSiO_3 + H_3PO_4 + (1+x)\ H_2O \rightarrow SiO_2.xH_2O + CaHPO_4.2H_2O \quad [16]$$

$$CaSiO_3 + H_3PO_4 \rightarrow SiO_2.yH_2O + CaHPO_4 + (1-y)\ H_2O \quad [17]$$

$$CaSiO_3 + 2H_3PO_4 + zH_2O \rightarrow SiO_2.zH_2O + Ca(H_2PO_4)_2.H_2O \quad [18]$$

4.3 Aggregates used in CBPCs

Aggregates are inert granular materials that are essential ingredients in concrete. They are used as fillers in inorganic matrix such as Portland cement to improve the properties of the base material. In CBPCs, aggregates can also be added to reduce the amount of the phosphate binder, thus reducing product cost. According to Donahue and Aro (2010), fly ash is the most beneficial filler in CBPC due to its spherical cenospheres (Fig. 1) which fills the voids of the CBPC paste and increases the compressive strength of the product. The increase in compressive strength is also thought to be a result of additional reactions between the acidic phosphates and amorphous silica from the ash, leading to the generation of more binder in the mix which produces a stronger product (Wagh 2013, 2016). Other studies reported a decrease in mechanical properties when fly ash was used as aggregate in CBPC. Ding et al. (2014) observed that the tensile strength of fibre sheets in magnesium phosphate cement (MPC) decreased by 15% when the ratio of fly ash to dead burnt magnesia increased from 0.4 to 1.0. However, the flexural and compressive strengths of the paste increased with increasing fly ash content up to 80% by weight of magnesia, and then decreased afterward (Ding et al. 2014). The authors also found that fly ash content has no significant effect on the pull out strength in a larger fly ash/magnesia ratio range which was probably due to the good fluidity of the paste attached to the mix proportion. Amiandamhen et al. (2016) observed decrease in flexural properties when fly ash was used in partial replacement of phosphate binder in wood composites. Such decrease may be attributed to the increase in fly ash and a corresponding decrease in the binder, which reduces the impregnation of the matrix into the fibres.

The presence of fly ash increases the heat capacity of the mixture which lowers the temperature rise of the product during its formation and slows down the setting process (Wagh 2013). In addition, there is evidence that Mg ions diffuse into the fly ash particle surface, while silicon and aluminium in fly ash disperse into the $MgKPO_4.6H_2O$ mineral and a non-crystalline layer is formed around the fly ash particles. This layer creates a strong bond between the fly ash particles and $MgKPO_4.6H_2O$ mineral

(Ding and Li 2005). Generally, the incorporation of fly ash into CBPC has multi-benefit objectives. For a given volume, the amount of binder used is small and less heat is generated, thereby reducing product cost, extending the working time and improving the properties of the product (Wagh 2013).

Other aggregates can also be incorporated into CBPC to improve the properties of the product. Regular sand can be used to increase toughness (Donahue and Aro 2010). The elongated (acicular structure) grains of wollastonite ($CaSiO_3$) serves as an advantage in enhancing the flexural strength of the product when the mineral is used as filler (Fig. 1). Also, whiskers of chopped glass fibres at a loading of 1-3% increased the flexural strength of CBPC ash composite from 900 psi to double its value (Wagh 2013). Finally, hammer milled flakes of aspen oriented strand board (OSB) resulted in increased bending strength of CBPC samples (Donahue and Aro 2010).

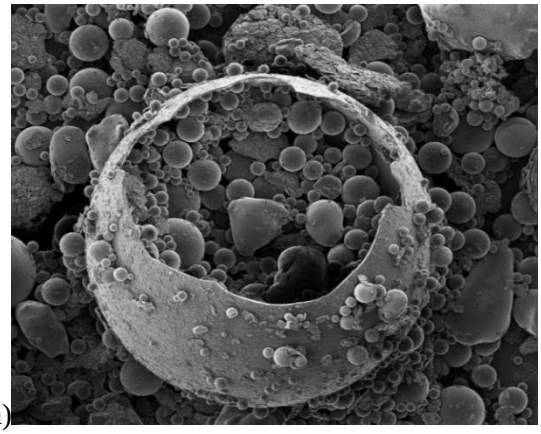
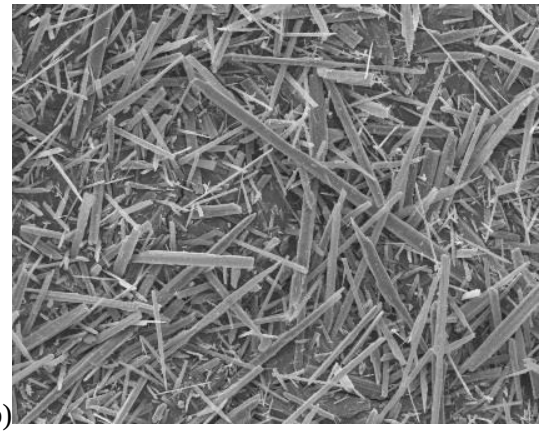
(a)  (b) 

Fig. 1: Scanning electron micrographs of CBPC aggregates (a) showing spherical cenospheres of fly ash (b) showing the acicular structure of wollastonite

Sources: (a) SACAA (b) IMERYS

5. Recent progress in CBPCs and utilization in wood composite products

In the 1st decade of its invention, the technology of CBPC was used to stabilize inorganic waste streams containing radioactive and chemically hazardous contaminants. The phosphate treatment of this waste streams results in chemical immobilization by converting them to insoluble compounds, thereby preventing leaching and nuclear contamination (Singh et al. 1996; Wagh et al. 2001; Wagh 2013). Following years of research in CBPC, this principle was adopted in products development by incorporating large volume industrial inorganic waste in the Ceramicrete® technology (Formosa et al. 2015; Gardner et al. 2015). According to Wagh (2004), any inorganic material can be added to CBPCs provided it has a low loss on ignition (LOI) value. High values of LOI (>8 wt. %) results in the evolution of gases such as CO_2 during the acid-base reaction. This however increases the porosity of the resultant material which invariably reduces the strength and integrity of the products. Originally developed to encapsulate low-level nuclear waste, CBPC has been used extensively as a shielding material against nuclear radiations such as alpha, beta, gamma rays and neutrons (Wagh 2013). In civil and structural

engineering, the technology of CBPC has gained increasing acceptance because of its superior properties over Portland cement and polymer products (Table 2). They are applied in road and concrete repairs, roof tiles and floor surfacing products. Their low water permeability and ability to bond to all earth materials including stones and concrete make them a 21st century material with diverse applications. Much of this detail can be found in Wagh (2016).

The development of fibre reinforced CBPC products is also on the horizon. As a result of the neutrality of the CBPC matrix and the low temperature processes involving the acid-base reactions of CBPC, natural fibres or polymer fibres may be added in the product (Wagh 2016). Jeong and Wagh (2003) incorporated chopped glass fibres of length 0.25 in. and 0.5 in. in ash-containing Ceramicrete®. They found that the fibres increased the flexural strength and fracture toughness of the product, and the increase was higher in the longer fibres. One advantage of glass fibre reinforcement in Ceramicrete® matrix is that corrosion of fibres does not occur because Ceramicrete® is neutral, unlike in highly alkaline cement matrix (Jeong and Wagh 2003). Ding et al. (2014) employed carbon fibre sheets in magnesium phosphate cement matrix to form fibre reinforced inorganic polymer composites. The authors reported that the improved fibre reinforced composite is a promising alternative for the strengthening of concrete structures. Other studies on polymer fibres in CBPC matrix have been reported. Colorado et al. (2011b) evaluated the mechanical properties of wollastonite-based (wo-based) CBPC. The authors reported that high performance composites were realized when glass and carbon fibres were used to reinforce CBPC. Wagh et al. (2003) studied the water permeability and mechanical properties of Mg-based CBPC with wollastonite and other fillers. The authors reported increased compressive and flexural strengths, fracture toughness and low porosity and permeability to water, when wollastonite is used as reinforcement. As reported elsewhere, the acicular (needle-like) crystals of wollastonite act like whiskers, which aid in increasing the flexural strength and fracture toughness of CBPCs (Wagh 2004).

Studies on scanning electron micrograph of these fibre reinforced composites showed that the CBPC matrix covered all around the fibres, which can be pulled out clean. This indicates that there is no clear adhesion between synthetic or polymer fibres and CBPC. However, CBPCs are dominated by ionic and covalent bonds, although van der Waals bonding is also present (Colorado et al. 2011a). According to Wagh (2004), a bond should form between natural fibre surface and the CBPC matrix unlike the case of polymer fibres such as glass. The formed bond should be able to produce superior fibre reinforced composites. A primary constituent of natural fibres is cellulose. Cellobiose, a repeating unit of cellulose contains six hydroxyl groups (OH) bonded by large number of intra and inter hydrogen bonds within a chain and between chains. It is well known that organic adhesives react with the hydroxyl groups of cellulose producing ethers, esters and new hydrogen bonds. These bonds form polymeric network that interconnects micro porous wood surfaces. It is therefore thought that similar bonds may be formed between wood and CBPC matrix.

Chi and Englund (2014) investigated the interfacial bonding properties between CBPC and sugar maple (*Acer saccharum*). The authors used mixture design analysis to evaluate the magnesium phosphate ceramic (MPC)/maple interfacial shear properties with different aggregate levels. Portland cement, wollastonite and vitrified calcium alumina-silicate (VCAS) were used as aggregates within the system. Binder level was the most influential determinant of the interfacial property while cement decreases the bond strength. However, wollastonite and VCAS mutually improved the interfacial properties. Based on fracture surface analysis, MPC block split failure and MPC/maple interfacial bond failure were identified and were correlated with the binder level and interfacial strength (Chi and Englund 2014). At the Forest Products Laboratory (FPL), pine planer shavings and sawdust were used as raw materials in CBPC matrix for a set of baseline experiments (Laufenberg and Aro 2004). The authors reported flexural stiffness and bending strength values comparable to existing cement bonded products. Subsequently, the National Resources Research Institute (NRRI) and the FPL conducted a preliminary study on the feasibility of producing composite building products utilizing waste pulp and paper mill residues and Ceramicrete®. They demonstrated that the residues can be incorporated in the CBPC binder to develop durable building materials and determined that the products have the potential to meet industry performance standards (Donahue and Aro 2010).

The exploitation of natural fibres in composite development has been a subject of intensive research. However, the application of natural fibres in CBPC technology is still at the infantile stage. Following earlier protocols conducted by the Argonne National Laboratory (ANL) and the National Resources Research Institute (NRRI) on the suitability of paper mill sludge in Ceramicrete®, there seems to be a literature gap on natural-fibre based CBPCs. Amiandamhen et al. (2016) demonstrated the feasibility of producing low and medium density composite panels utilizing agricultural and wood processing industrial residues. The authors investigated the effect of binder ratio, fibre content and fly ash as partial replacement of the phosphate binder. They reported that several strength properties are negatively affected when the proportion of fly ash exceeds a critical maximum. They showed the relationship between these variables on the panel properties using a response surface methodology. In another study, forest waste from the alien invasive tree species was used as baseline materials and the effect of bark on the properties of phosphate bonded wood products was investigated (Amiandamhen et al. 2016). Most of the work on CBPC reported in the literature and discussed in this section utilized Ceramicrete® technology, which is based on magnesium oxide. Due to the rapid exothermic reactivity of calcium oxide in the acid phosphate solution, it is practically impossible to produce calcium-based CBPC products on a large scale. In a similar way, calcium-based CBPC-natural fibre products are rare in literature. Wagh et al. (2003) demonstrated that calcium silicate with Ceramicrete® can be used to produce phospho-silicate ceramic, which has the potential to benefit the biomaterial industries. Recently, Amiandamhen et al. (unpublished) produced composite panels bonded with calcium silicate,

unslaked lime and fly ash. They observed that the fundamental properties of the composite products depend on the binder ratio and fibre content, and not the ratio of the alkaline minerals.

These investigations present a new dimension of interest for industrial partners and product developers in natural fibre composites. Preliminary market assessment showed that there are potentials for CBPC-waste pulp composite products to be utilized as interior door core, door stile and rail material (Donahue and Aro 2010). Phosphate bonded composite panels can be used in light weight construction such as applications with OSB which provides the rigid envelope that ties other elements of wood framed buildings together (Leland 2007). Phosphate bonded panels can be engineered for high strength, stiffness and moisture resistance applications (Wagh 2016). With a high binder level, the panels can be used in flooring systems and as underlayment. Like fibre cement boards, phosphate bonded panels can be applied in false ceilings and partitions. They can also be applied in roof tiles, prefabricated and under-decking structures.

6. Environmental benefits of CBPCs

As discussed in chapter one of this dissertation, CBPCs are low carbon content inorganic minerals that are environmentally friendly alternatives to conventional inorganic cement binders such as Portland cement and gypsum. Although the main environmental concerns about the use of the material still remains greenhouse gas emissions and fugitive particulates released in the atmosphere (Wagh 2013). The emission of greenhouse gases from inorganic phosphate ores is inevitable, careful process optimization would ensure that emissions are kept at a desirable minimum level. The other source of greenhouse gas emission in the manufacturing of phosphate minerals is in the total energy consumed from 'cradle to the gate'. While the carbon dioxide generated during the different phases of energy consumption may be reduced, the total greenhouse gases bound to the raw material which usually escapes during extraction and mining cannot be controlled. However, the fugitive particulates released into the atmosphere can be controlled with good work practices.

Wagh (2013) calculated the direct emissions of greenhouse gas from phosphate ore to Ceramicrete® manufacture as 40% less than in cement manufacture. The author further explained that the difference is due to the presence of fly ash, a coal-fired industrial plant by-product, which makes up about 60% of Ceramicrete®. When all possible sources of emissions are added for Ceramicrete® and Portland cement, Ceramicrete® emits 20% less greenhouse gases compared to Portland cement (Wagh 2013). The production of Ceramicrete® consumes only about 41% of total energy used in cement production and requires only a fraction of the total energy used in traditional wood composite binders such as the polymeric resins (Fig. 2).

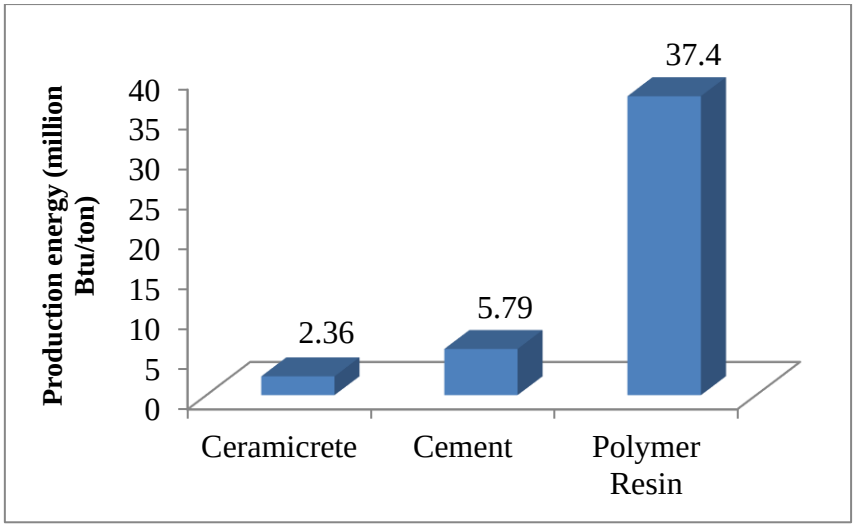


Fig. 2 Energy benefits of CBPCs

Source: NRRI (2008)

Another environmental consideration on the use of CBPCs is the leaching of nutrients and minerals from disposed products into soil and water streams. Since these materials contain active fertilizer ingredients, their presence in aquatic streams can be a problem. Excessive leaching of nutrients from the products may result in unwanted algae growth. The proliferation of algae on soil and water streams may choke aquatic life and plant growth (Wagh 2013). However, product consistency leaching test showed that CBPC products release phosphates extremely slowly into ground water (Singh et al. 1996; Wagh 2013). Therefore, when phosphate binder is used as adhesive, cement or coatings in manufactured products, the disposal of the products should not be a problem to the environment. The slow release of phosphates from disposed products may be beneficial to plants and aquatic life. Further information on the environmental impact factors of CBPC and polymeric coatings can be found in Wagh (2013).

7. Conclusions

Wood based composites encompass an array of products ranging from interior panels and furniture to exterior panels used for both structural and non-structural applications. Wood composites consist of conventional wood based composite panels, structural composite lumber and wood-matrix composites. Inorganic bonded composites have been designed to adapt to end of the cost and technology spectrum, facilitated by the low energy production profile of the composites. This adaptability makes inorganic bonded composites suited to many lignocellulosic materials. However, exceptions exist due to the inherent incompatibility between natural fibres and inorganic matrix, although this limitation can be avoided by careful design approach and fibre modifications. A new class of inorganic phosphate binders have been developed that can bond to many earth materials. This makes the phosphate binder a robust material of the 21st century with diverse applications. In wood and fibre composites, the phosphate binder is ideally suited because it is not affected by the sugars and hemicelluloses in natural fibres. Due

to this versatility, it is possible to incorporate lignocellulosic residues into the phosphate binder stream to produce value-added composites. The cost of the binder can be reduced by the addition of suitable aggregates in the matrix. With a small capital investment, satisfactory phosphate bonded composite materials can be produced on a small scale using mostly unskilled labour. However, technology can be introduced to increase the manufacturing output if the market for such composite materials increases.

Phosphate bonded wood and fibre products are light, durable and environmental friendly. They can be designed to meet moisture resistant requirements with high flexural and compressive strength properties. Ceramicrete®, a magnesium-based phosphate ceramic showed good mechanical properties and water absorption when compared to Portland cement and polymer resin (Table 2).

Table 2
Properties of Ceramicrete® as compared with cement and polymeric resin

Properties	Ceramicrete®	Cement	Polymer resin
Process Time	Short	Medium	Short
Mechanical Properties	Superior	Moderate	Poor
Water Absorption	Low	Low	High
Fire Resistance	Good	Good	Poor
Mildew Resistance	Good	Good	Poor

Source: Argonne National Laboratory (ANL)

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CHAPTER THREE

3. Materials and methods

3.1 Materials

3.1.1 Bio-based residues

The residues utilized in this project were Hemp hurds (*Cannabis sativa*) from Hemporium, a South African hemp processing company, Bagasse (*Saccharum officinarum*) from TSB Sugar Ltd, Slash pine (*Pinus elliottii*) from Cape Pine (a local subsidiary of the Global Environment Facility GEF), Papermill sludge from MPact Ltd (a Southern African paper and plastic packaging company) and office waste paper collected within the University of Stellenbosch. The selected invasive alien species used in this study were Black wattle (*Acacia mearnsii*), Long-leaved wattle (*A. longifolia*), Port Jackson (*A. saligna*), Rooikrans (*A. cyclops*) and Blue gum (*Eucalyptus globulus*). These species were supplied by EC Biomass Fuel Pellets (Pty) Ltd, Port Elizabeth, South Africa. The trees were harvested in the Green bushes area in Port Elizabeth, and the wood was supplied as wood waste from processed logs. The Black wattle was about 6 years old while the other acacia species were about 3 years old at the time of harvest. The study also utilized wood residues from other invasive species including Sekelbos (*Dichrostachys cinerea*) and Deurmekaarbos (*Ehretia rigida*). These species were supplied by a wood mill in Namibia.

3.1.2 Unslaked lime (Calcium oxide)

The metal oxide used was unslaked lime purchased from Bontebok Lime Works (Pty) Ltd, Bredasdorp, South Africa. It has the following composition; assay 70-88% Ca as CaO, CO_2 1.5%, phosphorus as P_2O_5 <0.01, specific gravity 3.37, pH 12.5, bulk density 1.1-1.3 g/cm^3 and vapour density of 1.9. It is typically used as a protective wall coating.

3.1.3 Calcium silicate

The calcium silicate used was Microcal ET purchased from PQ Corporation, Warrington, UK. It has the following composition: assay >87% SiO_2 basis, 12-22% CaO, <7.0% loss on drying, particle size 7.0-10.0 µm, pH 9.5-11.5, and density 2.9 g/ml. It is used as an absorbent, antacid, filter for paper and paper coatings, food additive (anticaking agents) and manufacturing of glass.

3.1.4 Magnesium oxide

The magnesium oxide used was MAGOXBPPO, a heavy magnesium oxide from Macco Organiques, Zahradnl, Czech Republic with the following composition: assay 96% min; calcium <1.1%; iron <0.05%; acid insoluble substances <0.1%; free alkali and soluble salts <2.0%, heavy metals <0.002%; arsenic <0.0003%; loss on ignition <10.0% and bulk density (loose) 400-600 g/l.

3.1.5 Monopotassium phosphate

Monopotassium phosphate is commonly used as plant fertilizer and as a food ingredient (salt). For this project, MKP 0-52-34, a white crystalline product was purchased from Shijiazhuang Lvhe Fertilizer Technologies Co. Ltd, China. It had the following composition: KH_2PO_4 >98%; P_2O_5 >51.2%; K_2O >33.5%; chloride <0.2%; water insoluble <0.2%; moisture <1.0% and pH 4.3-4.7. Wagh (2004) reports that acid phosphates with a P_2O_5 content of 50-60% may be suitable to produce chemically bonded phosphate ceramics.

3.1.6 Fly ash

The fly ash used in this study was supplied by Ulula Ash, South Africa. The product complies to the SANS 50450-1:2011 class S specification and is approved by South African Bureau of Standards (SABS). Class S fly ash (SFA) is an ultra-fine, powdery residue obtained from coal fired Ulula Ash Kriel power plant. It is of structural concrete grade, finer than cement and used as a partial replacement for cement (Katz, 2014). In this study, the fly ash was used as partial replacement for the phosphate binder. It had the following composition: SiO_2 <60%; Al_2O_3 <35%; CaO <10%; MgO <5%; Fe_2O_3 <5%; TiO_2 <5%.

3.1.7 Reagents

Analytical grade NaOH (98% purity), acetic anhydride (98% purity), acetic acid (99% purity) and sulphuric acid (72 and 98% purity) were used in the analysis and treatment of the fibres. These chemicals were supplied by Warren Chemical Specialities, Cape Town.

3.2 Methods

3.2.1 Bulk density calculation

The bulk density of the biomass was determined according to Miranda et al. (2012) using oven-dry samples in a 25-ml cylindrical container, and was calculated as the ratio of the sample mass in the container to the volume of the container. The measurement was made in triplicates.

3.2.2 Biomass sample preparations

The wood logs from the invasive trees were chipped in a wood chipper. The wood chips together with the pine flakes and shavings, hemp hurds and bagasse were thereafter hammer-milled and screened through a 1 mm sieving slice. The differences in the particle distribution were not considered in this study since the aim was to simulate an industrial wood milling process. The resultant particles were conditioned at 20 ^oC and 65% relative humidity (RH) for 96 h. The equilibrium moisture content of the material was found to be 7%. The papermill sludge was soaked in water for 1 h while the waste paper was soaked for 24 h. The wet papers were shredded in a laboratory sized pulper and dewatered using a spin dryer. The paper fibres were oven dried at 60 ^oC for 24 h and subsequently conditioned for 96 h at 20 ^oC and 65% RH.

3.2.3 Fibre treatments

The fibres were treated with hot water and solutions of NaOH and acetic anhydride using a solid/liquid ratio of 1/10 (g/mL). All the treatments were carried out in a 5 L stainless steel laboratory size pulp digester, and the predetermined temperature settings were controlled by a proportional integral derivative (PID) system (Beckermann and Pickering, 2008). Fibres treated with hot water were heated to a temperature of 100 ^{o}C for 1 h as described by Ferraz et al. (2016). Alkalization was carried out at 60 ^{o}C for 1 h according to a method described by Oladele et al. (2015). According to this method, a 0.25 M NaOH solution (1% wt.) was prepared to treat the fibres. The treatment was meant to be less severe than actual de-lignification in an alkaline pulping process. Fibres treated with acetic anhydride were heated to a maximum temperature of 90 ^{o}C for 1 h as described by Bledzki et al. (2008). Acetylation was carried out using a 1% wt. solution of acetic anhydride with 0.1% wt. sulphuric acid as buffer. The ester was prepared from a 1:1.5 ratio of acetic anhydride to acetic acid (Hajiha et al., 2014). After each treatment, the fibres were washed with distilled water until neutral pH was reached. Thereafter the treated fibres were dewatered using a spin dryer. The wet fibres were oven dried at 60 ^{o}C for 24 h and then conditioned at 20 ^{o}C and 65% relative humidity (RH) for 72 h. Subsequently, the fibres were weighed to determine the fibre yield from each treatment.

3.2.4 Chemical characterization

The chemical composition of the fibres was analysed to determine the acid-insoluble lignin, ash and sugar contents (glucose, cellobiose, xylose and arabinose), and to evaluate the effect of the treatment on the composition of the fibres. The ash content was determined according to TAPPI T211 (2004) by heating 2.0 g of oven-dried material at 575 ^{o}C for 3 h after which the residue was weighed. The acid-insoluble lignin was determined according to the National Renewable Energy Laboratory (NREL) Analytical Procedure (LAP 013) (Sluiter et al., 2012). According to this method, 3 ml of 72% sulphuric acid was added to 0.3 g of material in a test tube, stirred and placed in a water bath at 30 ^{o}C for 1 h. The material was washed with 84 ml distilled water into a flask to dilute the acid concentration to 4%. The solution was then heated in an autoclave for 90 minutes. The sample was transferred quantitatively on a crucible and was washed with 250 ml boiling water. Acid-insoluble lignin was determined as the mass of residue after drying at 105 ^{o}C and was based on the oven dry sample. The sugar composition i.e. glucose, cellobiose, xylose and arabinose were determined from the hydrolysate via high pressure liquid chromatography (HPLC). The HPLC system used for quantification comprised of a spectra system P2000 pump, an auto-sampler (AS3000), a UV1000 detector and a Shodex RI-101 refractive index detector. The sugars were measured with the RI detector and the column was operated at 65 ^{o}C with a mobile phase of 5mM H_2SO_4 and a flow rate of 0.6 mL min^{-1} (Vena et al., 2010).

3.2.5 Scanning Electron Microscopy (SEM)

SEM was performed to study the effect of the treatments on the morphological characteristics of the fibres at a magnification of 1000x. The samples were mounted on metal stubs with double-coated

carbon adhesive tape and sprayed with carbon using a high vacuum S150A sputter coater prior to the imaging. The micrographs of the treated and untreated fibres were examined using a LEO 1430VP MERLIN FE-SEM equipped with an energy dispersive X-ray spectrometer (EDS) GENESIS XM2.

3.2.6 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was performed to identify chemical changes in functional groups of the untreated and treated fibres. FTIR was conducted with a Thermo-Scientific Nicolet iS10 model consisting of an attenuated total reflectance unit and a transmission-FTIR unit. A minimum of 32 scans were acquired in the range of 500-4000 cm^{-1} and a resolution of 4 cm^{-1}.

3.2.7 Board formation

The fibres and the inorganic materials were measured according to the central composite design (CCD) to utilize more fibres and less binder, with partial replacement of the phosphate binder with fly ash. A pre-determined quantity of water (Equation 1) was added in each run and the mixture was stirred thoroughly. The paste was poured into a steel mould measuring 218 x 77 x 40 mm and a steel bar 27 mm thick was placed on the paste to fit into the mould. The purpose of the steel bar was to compress the composite in the mould to a final thickness of 13 mm, and squeeze out excess free water from the composite. This process removes entrapped air and minimizes the formation of voids in the panels. The set-up was transferred to the laboratory press and a pressure of 200 KPa was applied for 5 minutes at room temperature. Thereafter, the mould was removed from the press and the board was de-moulded. The formed boards were dried in ambient temperature for 24 h. Thereafter, they were conditioned at 20 ^{o}C and 65% RH for 96 h before testing.

The amount of water added was based upon formulation using;

$$W = B + (FSP - MC) \times F \quad [1]$$

W = Amount of water (ml)
B = Amount of inorganic components (g)
FSP = Fibre Saturation Point (%)
MC = Moisture content of fibre (%)
F = Amount of fibre (g)

3.2.8 Board testing

The properties of the formed panels were evaluated to investigate the effect of binder ratio, fibre content and fly ash content on the density, flexural strength and dimensional stability of the composites. Flexural test specimens were tested according to ASTM D1037 (2013) using an Instron testing machine fitted with a 5 kN load cell and operated at a rate of 5 mm/min. The specimens were tested to failure and the

modulus of rupture (MOR) and apparent modulus of elasticity (MOE) were calculated from the formula outlined in ASTM D1037 (2013).

Samples for dimensional stability were cut using an angle grinder with a concrete blade into dimensions of 75 x 50 mm. The thickness of all samples used in the test was 13 ± 1.2 mm based on the set-up configuration of the steel mould. Water absorption (WA) characteristics and thickness/volume swelling (TS/VS) tests were carried out according to ASTM D1037 (2013). Conditioned specimens were submerged horizontally in fresh water for 24 h. After submersion, the specimens were suspended to drain for 10 min and excess water was removed from the surface. The specimens were weighed and the thickness was determined as an average of four measurements. The WA of the specimen was calculated from the increase in weight and expressed as a percentage of the conditioned weight, while the TS/VS of the specimen were calculated as a percentage of the conditioned thickness/volume.

3.2.9 Micro computed tomography (µCT)

Based on the outcome of the composite tests, µCT was used to characterize the microstructure of the alkali treated and untreated composite samples. A numerical technique was used to quantify the cement matrix, fibre and void phases and their distribution in the samples. The composite samples were cut with a band saw into nominal dimensions of 10 x 10 x 13 mm^3. The samples were placed on the rotation stage and probed with a polychromatic X-ray beam using a General Electric Phoenix VTomeX L240 microCT scanner equipped with the Datos reconstruction software. The Volume Graphics VGStudio Max3 was used to construct 3-D images of the composite from stacks of 2-D images. The 3-D images were used to generate the actual phase distribution for void, fibre and cement matrix within the specimens. Two-phase segmentation steps were performed; between the matrix, fibre and voids, and between the voids, matrix and fibre. These two segmentations were combined to delineate the fibre phase. Data sets were visualized in 2 and 3-D using volume rendering in which a transfer function assigns each voxel a colour and transparency (Evans *et al.*, 2010). Volume rendering was performed using the VGStudio Max3. Numerical values were derived for the volumes of fibre, matrix and void across the thickness of a representative board sample using maximal sphere modelling. This defines for every point within the board, the diameter of the largest sphere which fully lies within the void, matrix or fibre phase and covers that point (Evans *et al.*, 2010).

3.2.10 Experimental design

The design of the experiments was based on the central composite design (CCD) with three factors at three levels. The factors considered represented as x_1, x_2 and x_3 were the binder ratio of KH_2PO_4: MgO, the fly ash content as partial replacement of the binder (in percentage) and the wood/fibre content as ratio of wood/fibre to the total inorganic content. The independent variables were coded at three levels -1, 0 and 1 representing the low, middle and high level. The selection of the variable levels was based on the results obtained from previous studies where the binder content was optimised in the

experimental design. In the treatment category, three fibre treatments, i.e. alkali, acetic anhydride and hot water, and untreated fibres (control experiment) were designated as independent variables in the design.

The number of experiments (N) required for the development of the CCD is defined by the relationship outlined by Ahmadi *et al.* (2005) as follows:

$$N = 2^{k-p} + 2k + C_p \quad [2]$$

(Where k is the number of factors, C_p is the number of centre points, and fractionalization element p = 0 for a full design).

3.2.11 Statistical analysis

The statistical analysis was performed using STATISTICA (version 13). The data was analysed through analysis of variance (ANOVA) to determine the variable(s) that were significant on the board properties. ANOVA was also used to evaluate the effects of fibre treatments on the physical and mechanical properties of the boards. Duncan's multi-stage range test was used in the separation of means for comparison. The overall contribution of each variable on the panel property was studied using the Pareto analysis. The response surface method (RSM) was used to establish a statistical model between experimental variables and responses. This was then used to predict the optimum experimental conditions to achieve optimum board performance. Regression analysis was used to test the adequacy and fitness of the developed polynomial models.

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CHAPTER FOUR

Paper II

Magnesium based phosphate cement binder for composite panels: A Response Surface Methodology for optimisation of processing variables in boards produced from agricultural and wood processing industrial residues

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Abstract

This study investigates the potential use of magnesium based phosphate cement prepared from a heavy magnesium oxide and monopotassium phosphate as a binder for the production of composite materials using bio-based industrial residues such as bagasse, hemp hurds, pine sawdust, paper mill sludge and wastepaper as raw materials. These residues were used to produce light-weight and durable materials that can compare with current cement based products. The development of phosphate bonded boards from bio-based residues promises to reduce the energy requirements from disposal of residues and provide environmentally friendly products. The phosphate binder is fast setting, cold curing and has a low carbon footprint. The board manufacturing process was laid out on a central composite design (CCD) to model the response variable, utilizing as much residues as technically feasible. The design allowed for the production of low and medium density boards that can be used for non-structural interior finishes and partition boards. Response surface methodology (RSM) was used to show the relationships between the production variables and predict the board property by variable optimisation. Tests of mechanical and physical properties were conducted on the boards. The density of hemp boards ranged from 0.59 – 0.83 g/cm^3, bagasse boards ranged from 0.54 – 0.78 g/cm^3, pine boards ranged from 0.58 – 0.84 g/cm^3, paper sludge boards ranged from 0.68 – 0.81 g/cm^3 and wastepaper boards ranged from 0.67 – 0.81 g/cm^3. The physical properties met the minimum requirements for cement bonded particleboard (EN 634:2007) and LD-1 grade particle board (ANSI 208.1:1999).

Keywords**:** Central composite design, industrial residues, phosphate bonded boards, response surface methodology

1. Introduction

This study describes the potential application and optimization of a magnesium phosphate cement binder in the development of wood composite panels. The phosphate binder, originally developed for the encapsulation of radioactive waste can be used as adhesive, cement or as coating for materials, therefore providing a wide range of applications (Laufenberg and Aro, 2004). The binder is produced at ambient conditions and set rapidly into a chemically bonded phosphate ceramic (CBPC) (Wagh, 2004). The magnesium phosphate cement, unlike Portland cement is not affected by the chemical composition of wood and other ligno-cellulosic fibres. Therefore, incorporating biological residues into the binding matrix to develop new products promises to bring significant advantage, compared to the current wood composite manufacturing process. Although the phosphate binder is more expensive compared to Portland cement, the chemical processing of the binder makes it inexpensive in high volume production (Colorado et al., 2011). In order to reduce binder cost and hence product cost, fly ash can be used as partial replacement for the binder. The addition of fly ash to CBPC has been reported to generate more binder, increase strength and improve the bonding between fly ash and phosphate binder (Zhu and Zongjin 2005; Wagh 2016). Since the phosphate binder is not cost-effective, only value-added products are commercially viable (Wagh, 2013). As a result, this study seeks to formulate and exploit the unique properties of CBPC to design composite products from agricultural and wood-based industrial residues.

Residues from industries, such as pulp mills, agricultural businesses and sawmills have been used in wood based panels to manufacture polymer and inorganic bonded wood and fibre composites (Wu 2003; Frybort et al. 2008; Kabir et al. 2012; Huang et al. 2012). In the wake of a novel phosphate binder made from an acid-base reaction, the applicability of these residues in the design and manufacturing has not yet been extensively studied. Preliminary investigations proved that wood and other ligno-cellulosic waste can be recycled to produce phosphate bonded composites (Laufenberg and Aro, 2004). Studies by Laufenberg and Aro (2004), Donahue and Aro (2010), Chi (2012) produced phosphate bonded fibre composites using magnesium phosphate cement as binder. In one report, pine shavings and sawdust were used as raw materials for a set of baseline experiments with one-third phosphate binder. Pressing to three densities (0.6-1.25 g/cc), the mechanical properties obtained compared well with those of other wood cement products (Laufenberg and Aro, 2004). In another study, waste paper sludge was bonded with phosphate binder using different ratios of waste fibre to binder (0.63-1.1) with the addition of fly ash as filler. All properties evaluated on the composites except the modulus of rupture (MOR) were comparable to those of low-density particle board (Donahue and Aro, 2010). Chi (2012) analysed the interfacial properties between sugar maple and magnesium phosphate cement. The author reported that using a phosphate/magnesium ratio of 3:1, maximum strength and initial crack stress

values can be maximized. None of the studies reported in the literature optimised the binder formulation process with binder ratio and fly ash content for wood composites.

In a world constantly driven by innovative technology to harness industrial residues into usable products, providing alternative means of industrial waste management come as a logical benefit. Land-filling has been a predominant means of waste disposal, however environmental regulation restricts new land-fills from being cited as quickly as existing ones are filled. Besides the environmental benefits of waste management, reduction in the energy cost of disposal, human health and safety are important considerations (McDougall and Hruska, 2000). According to the World Bank, the current global waste generation is about 1.3 billion tonnes per year, and is expected to increase to about 2.2 billion tonnes per year by 2025. In South Africa, over 42 million m^3 of waste is generated annually. Apart from the availability of valuable raw materials for bio composite production, the industrial exploitation of the materials contributes to the protection of the environment (absorption of CO_2) and gives economic potential to developing countries (Papadopoulou et al., 2015). This study utilized ligno-cellulosic residues from industrial processing plants to produce phosphate bonded composite boards. The rationale for the selection of the studied residues was in line with the substantial quantity generated by different industries, and the need to transfer these residues into usable products in the wood composite industry.

Bagasse is the residue from the sugar cane stalk (*Saccharum officinarum*) after the juice has been extracted. It is used to manufacture plastic and furniture (Hoareau et al. 2006), paper and fibre board (Agnihotri et al., 2010), insulating board and particleboard (Hossain et al., 2014). It has found increasing applications in the bio-energy industry (Diedericks, 2013). The South African sugar industry generates approximately 6 million tonnes of sugarcane bagasse annually (Vena, 2013) of which around 6 to 7% is used in the production of animal feed, paper and furfural products (www.namc.co.za). However, the sugar mills are energy self-sufficient, utilizing the bagasse as fuel in the cogeneration of steam and electricity in power plants.

Hemp hurds are the remnants of the stems and stalks of the hemp plants (*Cannabis sativa*) after the fibres have been removed. It has been used with lime to build Hempcrete walls and can also be used with gypsum and other binding agents to produce light panels that can compete with drywall (Small and Marcus, 2002). Hemp fibres can be used in fibre reinforced composites. Hemp fiber in combination with hurds as reinforcements increases the flexural properties of particleboards (Sam-Brew and Smith, 2015). Also, treated hemp fibres used as reinforcements improved the strength properties and thermal stability of polypropylene composites (Beckermann and Pickering 2008; Pickering et al. 2016). However, the production of hemp in South Africa has been unsteady over time as a result of delayed legalisation (DAFF, 2011).

Another waste material of interest is shavings and sawdust of slash pine (*Pinus elliottii*). The tree is planted mainly as a commercial tree and used for timber. South African wood processing mills generate

about 4-6 million tonnes of waste annually in the form of off-cuts, sawdust and shavings. Integrated mills utilize this waste as fuel to power steam boilers used in drying lumber. In many cases, the waste is supplied to industries for manufacturing particleboards. Several species of pines have been used in wood composites such as Monterey pine in particleboard (Garay et al., 2009), Jack pine in cement bonded board (Tittelein et al., 2012) and Scots pine in wood plastic composite (Ayrilmis et al., 2015).

Paper mill sludge and office waste represent an untapped feedstock in wood panel industry in South Africa. About 500 000 wet tons of paper sludge are generated annually by the pulp and paper industry (Boshoff, 2015). Although a fraction is recovered, the excess is usually landfilled. Paper mill sludge is increasingly being investigated for bioethanol production due to its fibre content (Wu and Zhou 2012; Boshoff 2015). It is also used in cement and polymer composite manufacturing (Bellamy 1995; Rahim et al. 2013; Soucy et al. 2014). Waste paper recycling has seen a gradual increase in the recycling rate since 2010. However, about 500 000 tons of office paper are produced annually, of which only about 60 000 tons are recovered (PRASA, 2015). This data suggests a substantial quantity of feedstock that could be channelled into wood composite manufacturing, without a significant interference with the conventional use of these residues.

The phosphate binder has a lower carbon footprint, low energy profile and is composed of common fertilizer ingredients, and therefore disposed products will enrich soil nutrients (Wagh, 2013). The proposed products promise to substantially reduce energy requirements in disposal of residues and reduce environmental impact and carbon footprint of current composites. The aim of this study is to investigate the feasibility of producing commercially-viable products utilizing the unique properties of the phosphate binder with those of industrial residues to develop durable composite building products.

2. Materials

2.1 Residues

The residues utilized in this research were hemp hurds (*Cannabis sativa*) from Hemporium, a South African hemp processing company, bagasse (*Saccharum officinarum*) from TSB Sugar Ltd, slash pine (*Pinus elliottii*) from Cape Pine; a local subsidiary of the Global Environment Facility (GEF), paper mill sludge from MPact Ltd; a Southern African paper and plastic packaging company, and office waste paper.

2.2 Magnesium oxide

The magnesium oxide used was MAGOXBPPO, a heavy magnesium oxide from Macco Organiques, Zahradnl, Czech Republic with the following composition: assay 96% min; calcium <1.1%; iron <0.05%; acid insoluble substances <0.1%; free alkali and soluble salts <2.0%, heavy metals <0.002%; arsenic <0.0003%; loss on ignition <10.0% and bulk density (loose) 400-600 g/l.

2.3 Monopotassium phosphate

Monopotassium phosphate is commonly used as plant fertilizer and as a food ingredient (salt). For this project, MKP 0-52-34, a white crystalline product was purchased from Shijiazhuang Lvhe Fertilizer Technologies Co. Ltd, China. It had the following composition: KH_2PO_4 >98%; P_2O_5 >51.2%; K_2O >33.5%; chloride <0.2%; water insoluble <0.2%; moisture <1.0% and pH 4.3-4.7. Wagh (2004) reports that acid phosphates with a P_2O_5 content of 50-60% may be suitable for the production of chemically bonded phosphate ceramics.

2.4 Fly ash

The fly ash used in this study was supplied by Ulula Ash, South Africa. The product complies to the SANS 50450-1:2011 class S specification and is approved by South African Bureau of Standards (SABS). Class S fly ash (SFA) is an ultra-fine, powdery residue obtained from coal fired Ulula Ash Kriel power plant. It is of structural concrete grade, finer than cement and used as a partial replacement for cement (www.ululaflyash.com). In this study, the fly ash was used as partial replacement for the phosphate binder. It had the following composition: SiO_2 <60%; Al_2O_3 <35%; CaO <10%; MgO <5%; Fe_2O_3 <5%; TiO_2 <5%.

3. Methods

3.1 Bulk density

Bulk density depends on material composition, particle size and shape, and specific density of individual particles resulting from the inherent physical structure of the raw material (Lam et al. 2008). Reducing biomass to fine particle size for particle board manufacturing presents difficulties in handling as a result of the low bulk densities of the materials (Miranda et al. 2012). Biomass with low bulk densities will need to be loaded in high quantity and compressed to increase the resultant density of the composite product. The bulk density of the biomass was determined using oven-dry samples in a 25 ml cylindrical container, and was calculated as the ratio of the sample mass in the container to the volume of the container. The measurement was made in triplicates.

3.2 Sample preparations

The pine sawdust, hemp hurds and bagasse were milled using a hammer mill fitted with a 1 mm sieving slice. The resultant particles were conditioned at 20 ^oC and 65% relative humidity (RH) for 96 h. The equilibrium moisture content of the materials was determined as 7%. The paper mill sludge was used in the fabrication as received, while the waste paper was soaked for 24 h, shredded in a Pulper and dewatered using a spin dryer. The paper fibres were oven dried at 60 ^oC for 24 h and subsequently conditioned for 96 h at 20 ^oC and 65% RH.

3.3 Board formation

The conditioned natural fibres were measured according to a design to utilize more of fibres and less binder content, with partial replacement of the phosphate binder with fly ash. A pre-determined quantity of water was added in each run and the mixture was stirred thoroughly in a planetary style. The paste was poured into a steel mould measuring 218 x 77 x 40 mm and a steel bar 27 mm thick was placed on the paste to fit into the mould. The purpose of the steel bar was to compress the composite in the mould to a final thickness of 13 mm, and squeeze out excess free water from the composite. This process removes entrapped air and minimizes the formation of voids in the panels. The set-up was transferred to the laboratory press and a pressure of 200 KPa was applied for 5 minutes at room temperature. Thereafter, the mould was removed from the press and the board was de-moulded. The formed boards were dried in ambient temperature for 24 h. Thereafter, they were conditioned at 20 ^{o}C and 65% RH for 96 h before testing.

3.4 Testing

The properties of the formed panels were evaluated to investigate the effect of binder ratio, fibre content and fly ash content on the density, flexural strength and dimensional stability of the composites. Flexural test specimens were tested according to ASTM D1037-06a standard using an Instron testing machine fitted with a 5 kN load cell, operated at a rate of 5 mm/min. The specimens were tested to failure and the modulus of rupture (MOR) and apparent modulus of elasticity (MOE) were calculated from the formula outlined in ASTM (2006).

Samples for dimensional stability were cut using an angle grinder with a concrete blade into dimensions of 75 x 50 mm. The thickness of all samples used in the test was 13 ± 1.2 mm based on the set-up configuration of the steel mould. Water absorption (WA) characteristics and thickness/volume swelling (TS/VS) tests were carried out by submerging conditioned specimens horizontally in fresh water for 24 h. After submersion, the specimens were suspended to drain for 10 min and excess water was removed from the surface. The specimens were weighed and the thickness was determined as an average of four measurements. The WA of the specimen was calculated from the increase in weight and expressed as a percentage of the conditioned weight, while the TS/VS of the specimen were calculated as a percentage of the conditioned thickness/volume.

3.5 Experimental design

The experiments were established based on a central composite design (CCD) with three factors at three levels. The factors considered represented as x_1, x_2 and $x_{3(i\text{-}iii)}$ were the binder ratio of KH_2PO_4: MgO, the fly ash content as partial replacement of the binder (in percentage) and the wood/fibre content as ratio of wood/fibre to the total inorganic content. The wood/fibre content was classified into x_{3i}- x_{3iii} to

provide for more fibres due to the different bulk densities of the materials. The independent variables were coded at three levels -1, 0 and 1 representing the low, middle and high level (Table 1). The selection of the variable levels was based on the results obtained from previous studies where the binder content was optimised at 80 g in the experimental design.

Table 1

Independent variables and their levels used for the CCD

Variable	Factors	Coded levels		
		Low (-1)	Medium (0)	High (1)
KH_2PO_4: MgO	x_1	2	3	4
Fly ash content	x_2	0	0.1	0.2
Wood	x_{3i}	0.63	0.75	0.88
Hemp/ bagasse	x_{3ii}	0.38	0.5	0.63
Paper sludge/ wastepaper	x_{3iii}	2	2.5	3

The number of experiments (N) required for the development of the CCD is defined by the relationship outlined by Ahmadi et al (2005) as

$$N = 2^{k-p} + 2k + C_p \quad (1)$$

(Where k is the number of factors, C_p is the number of centre points, and fractionalization element p=0 for a full design). In this study, the design included 16 experiments and 2 centre points (used to determine the experimental error). The response surface method (RSM) was used to establish a statistical relationship between experimental variables and responses. This could be used to predict the optimal experimental conditions for achieving optimum performance (Bloor and England, 1991). RSM can also be used to investigate the interaction effect of process variables and build a mathematical model needed to describe the overall process (Jin et al. 2012).

3.6 Statistical analysis

The statistical analysis was performed using the STATISTICA software (version 5). The data was analysed by the analysis of variance procedure (ANOVA) to determine the variable(s) that are significant on the board properties. The overall contribution of each variable on the panel property was analysed using the Pareto chart.

4. Results and discussion

4.1 Bulk density

The average bulk densities of the studied woody biomass materials were pine 171.6, hemp 104.1 and bagasse 84.9 kg/m^3.

4.2 Board properties

The density of the boards varied considerably, but was generally in the range of low and medium density boards as classified by ANSI (1999). Hemp boards ranged from 0.59 – 0.83 g/cm^3, bagasse boards ranged from 0.54 – 0.78 g/cm^3, pine boards ranged from 0.58 – 0.84 g/cm^3, paper sludge boards ranged from 0.68 – 0.81 g/cm^3 and wastepaper boards ranged from 0.67 – 0.81 g/cm^3. The results showed that density increases as the ash content decreases. High fly ash content increases the volume of the board without significantly adding to the mass, thereby lowering the density. Increase in density positively influenced all strength properties. The WA of the boards made from different residues was found to be higher than the maximum allowed value for particle board of 25% (EN-634). This is due to the fact that more wood/fibre was incorporated in this study, contrary to the conventional inorganic bonded wood composite which utilizes more binder and less of the wood component as reinforcement. This design was borne out of the need to utilize more residues as a disposal alternative in the management objectives of wood based industries. The response surface analysis showed that increasing binder and reducing fibre content results in decreased WA. Increased binder content will result in the generation of more bonding sites, better compaction and reduction of potential bonding sites for water on the fibres. TS and VS, which are changes in thickness and volume of the boards after 24 h submersion in water, met the minimum requirements for particle boards, which allow a maximum swelling of 15% (EN 634). TS values ranged from 0.78 – 12.97% and 0.15 – 14.25% for hemp and bagasse respectively.

The ability of a solid material to withstand bending stress or deformation is important in certain applications. MOR is the maximum strength that can be borne by a material before failure, and the MOE describes the stiffness or tensile elasticity. The strength properties of the boards vary accordingly. The MOE of hemp boards ranged from 1.37-11.22 MPa, bagasse boards ranged from 1.75-9.43 MPa, pine boards ranged from 38.15-464.36 MPa, paper sludge boards ranged from 67.02-196.48 MPa and wastepaper boards ranged from 31.99-150.86 MPa. The bending MOR and static MOE of existing wood-cement particle boards with a density of 1g/cm^3 is 9 MPa and 14.5 GPa respectively (EN 634-2). However, boards produced in this study are low and medium density boards (0.54-0.84 g/cm^3). This indicates that the boards are not ideal for general purpose applications and can only be used for sidings and partitioning where load bearing is not required. To produce boards of structural integrity, the binder content needs to be increased. It has been reported that the strength properties of composite boards depend on the amount of binder used (Moslemi 1999; Donahue and Aro 2010; Wagh 2013). High binder

content produces more $MgKPO_4.H_2O$ mineral during hydration resulting in better bonding between fibres (Donahue and Aro, 2010) and hence higher strength properties. The properties of the boards are summarised in Table 2.

Table 2

Board properties

Property	Hemp	Bagasse	Pine	Paper sludge	Wastepaper
Density (g/cm^3)	0.59 – 0.83	0.54 – 0.78	0.58 – 0.84	0.68 – 0.81	0.67 – 0.81
WA (%)	36.42 – 131.17	51.75 – 111.78	35 – 66.27	57.15 – 80.83	54.13 – 83.28
TS (%)	0.78 – 12.97	0.15 – 14.25	0.15 – 15.67	0.22 – 7.66	0.62 – 7.45
VS (%)	0.06 – 12.91	0.85 – 17.85	0.04 – 21.17	1.07 – 9.30	0.28 – 9.11
MOR (MPa)	0.08 – 0.73	0.11 – 0.65	0.17 – 1.2	0.61 – 1.44	0.45 – 1.21
MOE (MPa)	1.37 – 11.22	1.75 – 9.43	38.15 – 464.36	67.02 – 196.48	31.99 – 150.86

4.3 Relationship between production variables and their effects on panel properties

The composite boards were produced using different binder ratio, fly ash content and wood/fibre content. The effects of each variable and their interactions on the measured properties were studied using analysis of variance (ANOVA). Where there was a significant effect ($p<0.05$), RSM was used to show the relationship between the production variables on the measured property on a 3D response plot (Figs 1-5). The RSM plot shows the experimental units of two variables in two principal axes (x, y) and a fixed unit of the third variable on the surface plot. The RSM is a modelling technique used in evaluating the relationship between the experimental and the predicted results (Maran and Manikandan, 2012). From the legend on the plot, it is possible to predict a desired response by altering the experimental units. The Pareto analysis was used to show the contribution of each variable and their interactions on the measured property (Figs. 1-5). The variables were represented on the chart as binder ratio (1), fly ash content (2), and wood/fibre content (3) and were expressed in terms of both linear (L) and quadratic (Q) coefficients in the Pareto analysis. The interaction effect of the variables was also determined. The Pareto analysis is a statistical technique in decision-making used for the selection of a limited number of tasks that produce significant overall effect (Haughey, 2015). By such selection, it is possible to focus on such variable(s) that would produce more of the effect on any property.

Fig. 1 shows the relationship between the binder ratio, fly ash content and wood content (0.75) on the MOR of the pine boards. The interaction between the binder ratio and fly ash content was significant ($p < 0.05$) on the MOR of the boards. The interaction between the variables on the other properties was not significant ($p > 0.05$). The plot shows that the MOR increases with binder ratio at wood content of 0.75. The MOR increases as the binder ratio increases to about 4:1 at low ash content. High ash content

had a negative effect on the MOR. This suggests that increasing fly ash content while decreasing binder content does not improve the bending strength of phosphate bonded pine boards. The MOR of pine boards depends on the binder ratio as previously reported. Amiandamhen et al. (2015) found that high binder ratio (3:1) influenced the strength properties of phosphate bonded pine boards. The Pareto analysis shows that binder ratio and fly ash content had the most significant overall effect on the MOR of the pine boards (Fig. 1).

Fig. 2a shows the relationship between the binder ratio, fly ash content (10% replacement of binder) and fibre content on the MOR of the paper sludge panels. As binder content increases, the MOR increases with the fibre content at 10% replacement of binder with fly ash. This indicates that binder ratio and fibre content have a positive effect on the MOR of paper sludge boards. The MOR of panels depends on the binder ratio and ash content as previously reported. Donahue and Aro (2010) also observed positive correlation between high binder content and MOR in paper sludge composite boards. The authors suggested that a fly ash: binder ratio of 0.40-0.45 is beneficial to improve the MOR. From the Pareto analysis, the binder ratio was significant on the MOR of the paper sludge panels ($p < 0.05$) and had the most significant overall effect (Fig. 2a). The interaction between the binder ratio and fibre content was also significant. The variables and their interactions were not significant on the other properties ($p > 0.05$) and had insignificant overall contribution to the properties. The relationship between the binder ratio and fly ash content at a fibre loading of 2.5 times the total inorganic content is presented in Fig. 2b. The plot shows that VS decreases as ash content and binder ratio increase. This could be explained as a result of the cementing mechanism of fly ash which fills the void in the panels, and prevent the absorption of water at the edges. High binder ratio also generates more chemically bonded sites which reduces water movement in the panels. The Pareto analysis shows that the interaction between binder ratio and fly ash content had a significant effect on the TS/VS of paper sludge panels, and had the most significant overall effect (Fig. 2b).

In waste paper boards, the interaction between fibre and ash content on the MOE was significant ($p < 0.05$). At a binder ratio (KH_2PO_4/MgO) of 3:1, the MOE increases as the fibre and ash content increase, up to a point, and then decreases with more fibre and ash content (Fig. 3). This suggests that the stiffness of waste paper panels is a function of the amount of fibre and ash content. High binder content with less of the fly ash component results in better bonding between fibres (Donahue and Aro, 2010). The improved bonding results in higher strength and better compaction of the composite panels. Although, fibres play a significant role in increasing the specific gravity of composites and impart additional energy absorbing capacity to the product (Mohr et al., 2004), the stiffness of paper composites is affected. In waste paper panels, the fly ash content, the binder ratio and the interaction between ash and fibre content were significant on the MOE ($p < 0.05$). However, the ash content had the most significant overall effect on the MOE (Fig. 3).

Fig. 4 shows the interaction between the variables that was significant on the density of the bagasse board ($p < 0.05$). It was observed that density increased with ash content at a binder ratio of 3:1. The interaction between the other variables was not significant ($p > 0.05$) on the board properties. At low fibre content, density increases with ash content. This resulted in decreased strength properties. However, there was a gradual increase in strength properties as binder ratio increased. The Pareto analysis shows that fibre content had the most significant overall effect on the density, followed by the interaction between fly ash and fibre contents (Fig 4).

The effect of the interaction between ash and fibre contents was significant on the MOR of hemp boards. The interaction effect between binder ratio and fibre content was also significant on WA and VS of the hemp boards, while the interaction effect between binder ratio and ash content was significant on the TS (Fig. 5). By increasing binder ratio at low fibre content, the WA of hemp boards decreases. On the other hand, WA increases as the fibre content increases. Increased binder ratio increases the bonding between fibres, and since the hydrophilic fibres are low in the board, WA is reduced. However, MOR increases significantly as the fibre and ash contents increase at a binder ratio of 3:1. VS reduces as the binder ratio increases with fibre content while a high binder ratio and low ash content reduces the TS of the hemp composite boards. As seen in the Pareto analysis, fibre content had the most significant overall effect on the WA, TS and VS of the hemp boards (Fig. 5).

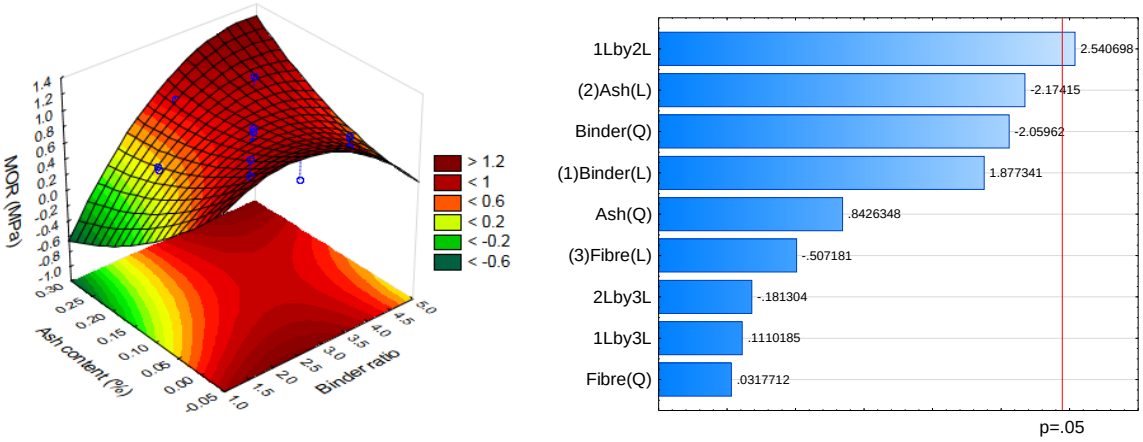


Fig. 1 Response surface plot and Pareto chart showing the effect of variables on the MOR of pine boards

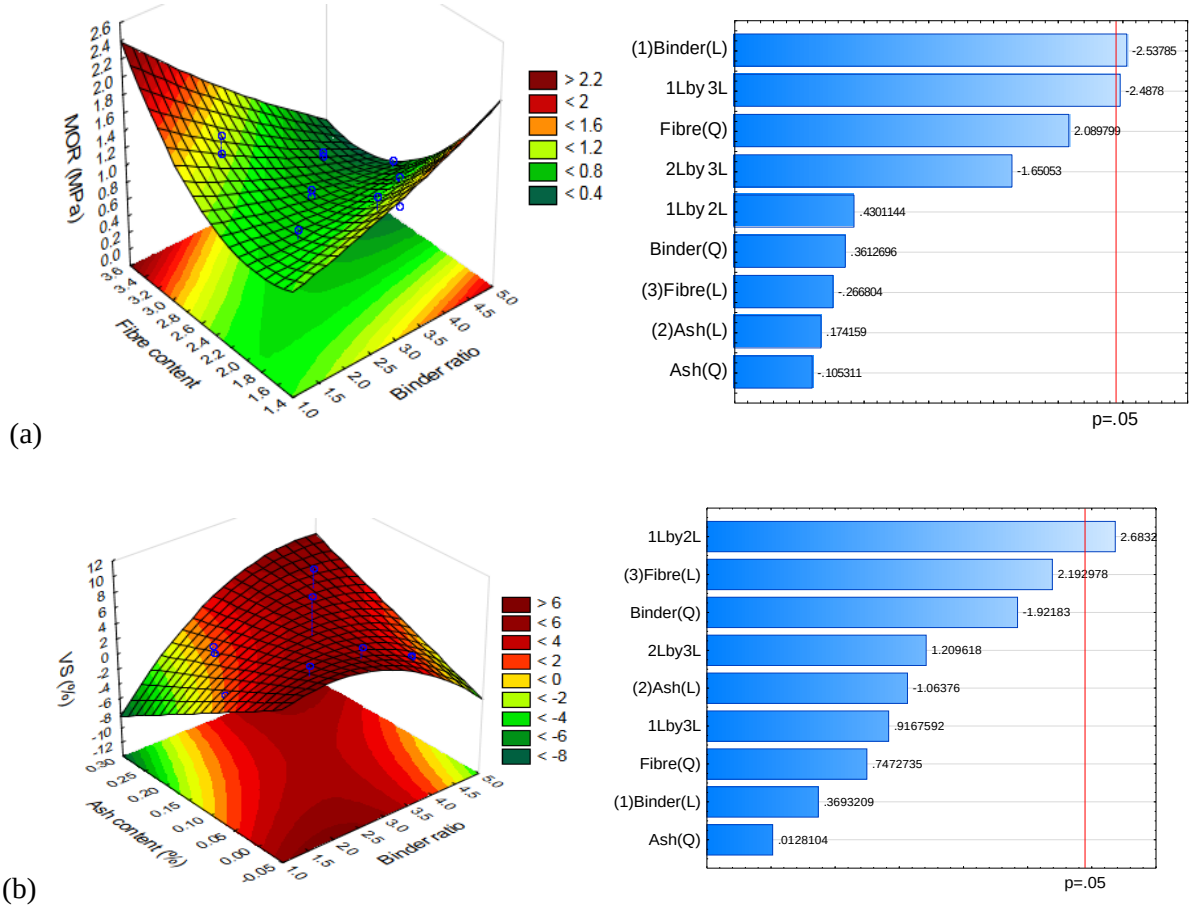


Fig. 2 Response surface plots and Pareto charts showing the effects of variables on (a) MOR and (b) volume swelling of paper sludge boards

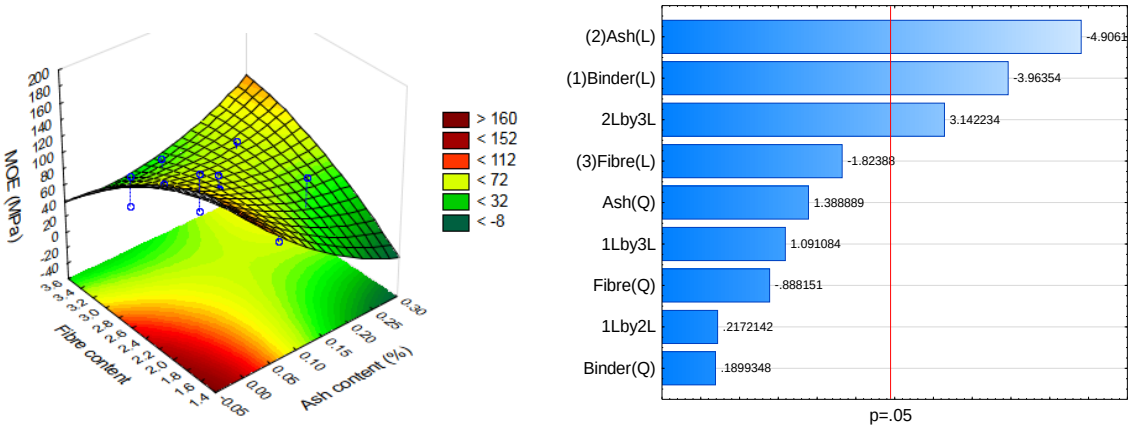


Fig. 3 Response surface plot and Pareto chart showing the effect of variables on the MOE of waste paper board

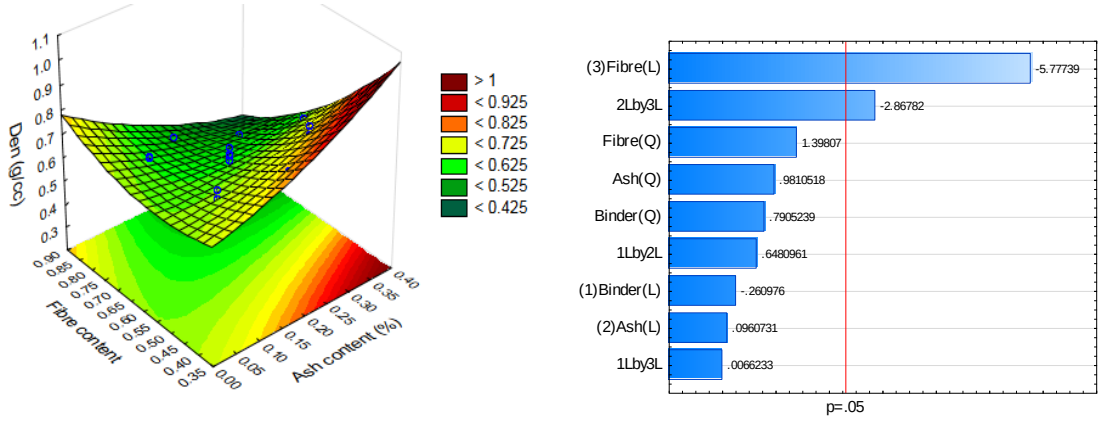
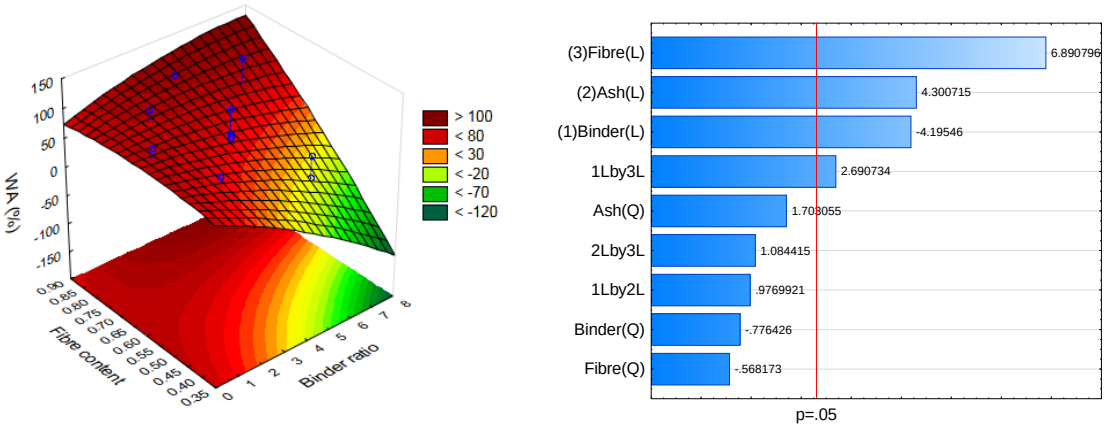
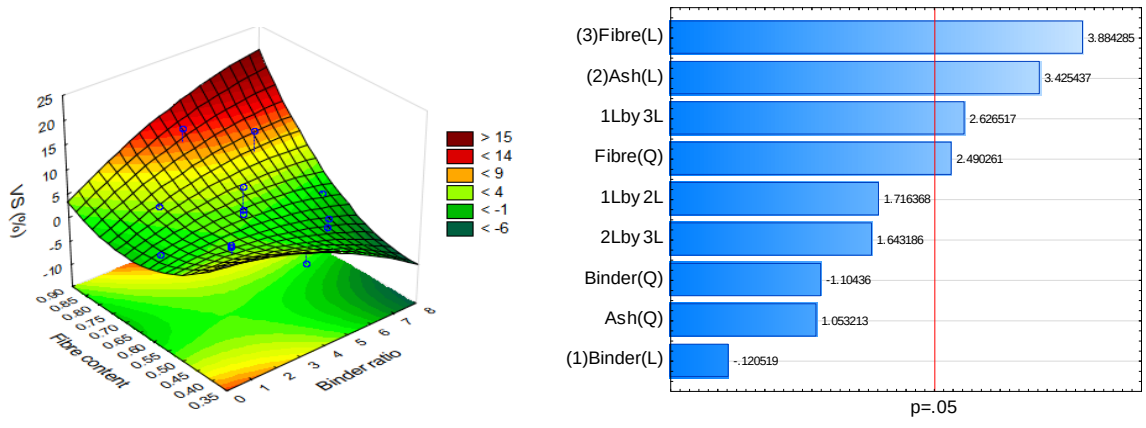


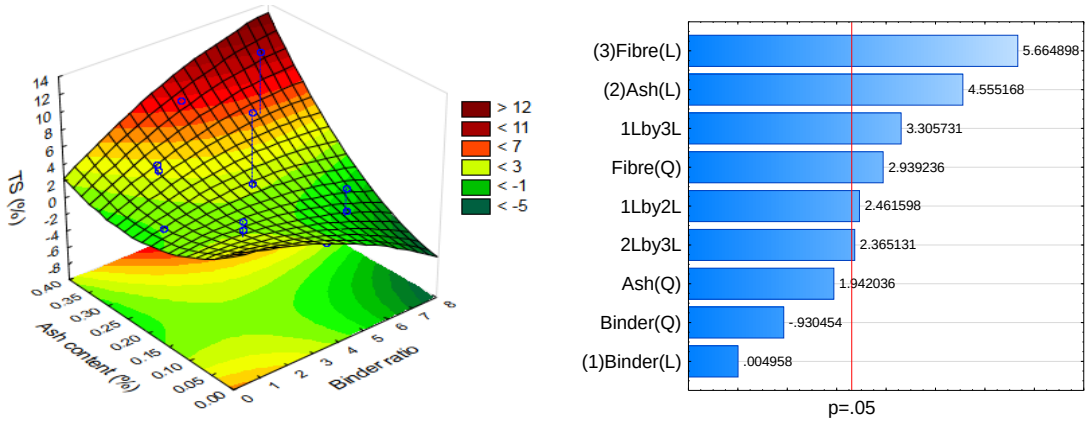
Fig. 4 Response surface plot and Pareto chart showing the effect of variables on the density of bagasse boards



(a)



(b)



(c)

Fig. 5 Response surface plots and Pareto charts showing the effects of variables on (a) water absorption (WA) (b) volume swelling (VS) and (c) thickness swelling (TS) of hemp boards

4.4 Data analysis

The effects of each variable and their interactions on the measured property were studied using analysis of variance (ANOVA) (Tables 3-5). It is clear from the analysis that the binder ratio and fly ash content have significant effects on the MOR and MOE of waste paper composite boards ($p < 0.05$). High binder content with less of the fly ash component results in better bonding between fibres (Donahue and Aro, 2010). The improved bonding results in higher strength and better compaction of the composite boards. Binder ratio also had a significant effect on MOR of paper sludge and on the TS and VS of pine composite boards. The fly ash and fibre content was significant on the moisture responses (WA, TS and VS) of hemp boards. Fibre content was found to have a significant effect on the MOE, density and moisture responses of bagasse boards. Fibres play a significant role in increasing the specific gravity of composites and impart additional energy absorbing capacity to the product (Mohr et al., 2004).

Table 3
ANOVA of the effect of binder ratio on the measured properties of the composite boards

Properties		Species	(p values)		
	Wastepaper	Paper sludge	Pine	Hemp	Bagasse
MOR	0.002*	0.044*	0.109	0.633	0.212
MOE	0.007*	0.243	0.602	0.666	0.234
Density	0.225	0.094	0.926	0.050	0.800
WA	0.316	0.243	0.417	0.003*	0.092
TS	0.242	0.407	0.017*	0.996	0.294
VS	0.267	0.724	0.017*	0.907	0.109

* denotes significant values at $p < 0.05$

Table 4

ANOVA of the effect of fly ash content on the measured properties of the composite boards

Properties		Species	(p values)		
	Wastepaper	Paper sludge	Pine	Hemp	Bagasse
MOR	0.000*	0.867	0.072	0.247	0.468
MOE	0.002*	0.752	0.151	0.465	0.525
Density	0.062	0.648	0.670	0.734	0.925
WA	0.004*	0.240	0.230	0.002*	0.094
TS	0.689	0.169	0.491	0.001*	0.470
VS	0.513	0.328	0.351	0.009*	0.577

* denotes significant values at $p < 0.05$

Table 5

ANOVA of the effect of wood/fibre content on the measured properties of the composite boards

Properties		Species	(p values)		
	Wastepaper	Paper sludge	Pine	Hemp	Bagasse
MOR	0.093	0.798	0.630	0.928	0.132
MOE	0.117	0.755	0.463	0.710	0.029*
Density	0.889	0.246	0.729	0.150	0.000*
WA	0.012*	0.177	0.336	0.000*	0.001*
TS	0.644	0.495	0.117	0.000*	0.012*
VS	0.990	0.070	0.108	0.004*	0.034*

* denotes significant values at $p < 0.05$

4.5 Optimisation of the independent variables

From the foregoing analysis, it is clear that the variables and their interactions had varying effects on the board properties. As a result, optimum conditions for the production of phosphate bonded composite boards using pine, wastepaper, paper sludge, hemp and bagasse was required. Profiles of predicted values and desirability were established to estimate the optimum conditions to predict board properties. The optimum composite manufacturing processes for making durable products within the experimental design was found to contain a ratio of KH_2PO_4/MgO = 2.6, 10% fly ash, wood/inorganic ratio of 0.96 for pine; KH_2PO_4/MgO = 2.0, 8% fly ash, fibre/inorganic ratio of 3.34 for paper sludge; KH_2PO_4/MgO = 2.3, 7% fly ash, fibre/inorganic ratio of 2.92 for waste paper; KH_2PO_4/MgO = 3.0, 20% fly ash, fibre/inorganic ratio of 0.83 for bagasse; KH_2PO_4/MgO = 4.83, 28% fly ash, fibre/inorganic ratio of 0.83 for hemp fibres. With the optimum experimental variables established, the maximum predicted

responses for each material was determined from the response desirability profiler available in STATISTICA (v5).

The empirical relationship between the response variable and the independent variables were expressed by a second order polynomial model;

$$y = x_0 + ax_1 + bx_2 + cx_3 + a^2x_1 + b^2x_2 + c^2x_3 + abx_1x_2 + acx_1x_3 + bcx_2x_3 \quad (2)$$

(Where y = predicted response, x_0 = intercept, a,b,c = linear coefficients, a^2,b^2,c^2 = quadratic coefficients, ab, ac, bc = interaction, x_1, x_2, x_3 = independent variables).

Using numerical optimization, significant models were established to estimate each board property as influenced by the independent variables. The adequacy and fitness of the model were tested by regression analysis. The analysis showed a high precision of the model. The high degree of fitting between predicted and experimental data reflects the accuracy and applicability of the quadratic model in the optimization process (Zhao et al., 2008). However, the suitability of the developed quadratic model is valid within the specified range of process parameters as explained by Maran and Manikandan, (2012).

5. Conclusions

This study has demonstrated the feasibility of incorporating agricultural and industrial residues into a magnesium phosphate binder to produce low and medium density panels at room temperature. The manufacturing of board products could be incorporated into the management practices aimed at disposal alternative and providing environmentally friendly process and products. By applying the methodology of the desired function, the optimum process conditions of binder ratio, fly ash and wood/fibre content for achieving the maximum desired board property within the experimental design was determined. The MOE of hemp boards ranged from 1.37-11.22 MPa, bagasse boards ranged from 1.75-9.43 MPa, pine boards ranged from 38.15-464.36 MPa, paper sludge boards ranged from 67.02-196-48 MPa and wastepaper boards ranged from 31.99-150.86 MPa. To our best knowledge, this is the first time that this binder system has been optimised for such particleboards. The physical properties of the boards showed that density, TS and VS met the minimum requirement for low density particle boards (EN 634-2:2007).

The binder is robust enough to accommodate the variability in these residues and is not affected by the raw material composition. However, while fly ash can be incorporated to reduce binder cost and the overall cost of the production process, at high quantities, it proved to have a negative effect on strength properties. The variables considered i.e. binder ratio, fly ash and wood content have significant effects on the physical and mechanical properties of the boards to varying degrees within the experimental

design. The proposed product can be used for interior wall finishes and partitions. The authors recommend testing of other properties that are important to the use of panels in building components. A market and product development concept will need to be considered to evaluate the potential of these products in the target market.

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Conference Paper I

Phosphate Bonded Natural Fibre Composites

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Abstract

Wood residue of Slash Pine (*Pinus elliottii* Engelm.) was collected, dried, screened and characterized. The screened sample was used in the production of phosphate bonded wood composites. The magnesium phosphate cement was formulated from a heavy magnesium oxide and monopotassium phosphate. The mixture was blended with fly ash and water and was compressed at a pressure of 110KPa. The composites set firm in about 5 minutes. The variables considered were binder ratio and fly ash content. The binder ratio was the ratio of the magnesium base to the acidic phosphate determined at 1:2, 1:1 and 2:1 respectively. The formed composites were tested and characterized. The study demonstrated that wood residues can be incorporated into a magnesium phosphate cement binder to produce environmentally friendly composites that can be engineered to meet industry performance standards and consumer acceptance taste. All properties evaluated exceeded the minimum requirement for LD-1 grade particleboard.

Keywords: Binder ratio, fly ash, magnesium phosphate cement, phosphate bonded wood composites, *Pinus elliottii*

1. Introduction

Annually, South African wood mills produce 4-6 million tons of wood waste in the form of forest residues, saw dust, shavings, off cuts, bark, etc. This waste poses disposal problems and is often landfilled, land spread or burnt to power steam boilers used to dry lumber. In some cases, the residues and off cuts are sold to local merchants as fuel wood. It is proffered that all of this waste can be used to develop value-added products such as in composite boards. In view of the emerging opportunities for phosphate adhesives in bio-based composites, this study seeks to address the potential of wood composite based on the commercially available tree species of Pines. The waste generated during the processing of these trees constitutes the biomaterial for this research.

Slash Pine (*Pinus elliottii* Engelm.) has been used in composites production with cement and polymer resin. Different wood particle sizes are used to develop cement bonded boards, resin bonded boards and wood plastic bonded boards that are applied in many applications. Cement bonded boards require a

much larger particle size than resin bonded boards (Semple and Evans, 2004) while wood plastic composites require finer wood particles (Youngquist, 1999). Durability, toughness, high strength, dimensional stability and fire resistance are features that have made cement bonded composites superior to other conventional bonded composites (Frybort et al., 2008). However Ceramicrete®, a chemically bonded phosphate ceramic has significantly better properties as compared with Portland cement and polymer resin (NRRI, 2008). In this study, Slash Pine residue from the saw mill was characterized and incorporated into formulated magnesium phosphate cement (MPC) to develop phosphate bonded wood composites.

As a type of chemically bonded phosphate ceramics (CBPC), magnesium phosphate cement has been increasingly used in architecture and other civil applications (Wagh, 2004). Since phosphate binders are not affected by the sugars and hemicelluloses in wood (Laufenberg and Aro, 2004), it allows the use of many wood species. Although several authors have investigated the potentials and durability of phosphate bonded fibre composites (Ding *et al*. 2014; Donahue and Aro 2010), the interfacial properties between wood and MPC can be affected by pH value and water content of the slurry, aggregates used and formulation design of the MPCs (Chi, 2012). This study investigates the use of fly ash and binder ratio on the physical and mechanical properties of phosphate bonded wood composites. The rationale for this study is to provide an alternative means for the utilization of this enormous waste generated by wood mills in South Africa.

2. Materials

2.1. Wood (Pinus elliottii)

This study utilized waste residues from Cape Pine saw mill, Stellenbosch, Western Cape, South Africa. The residues were dried to a moisture content of about 7%. The residues were screened for size and fractions less than 1.0mm were kept in the conditioning room at 20^0C and 65% relative humidity for 96 h. The residue was thereafter characterized and was used for board making. The properties of the wood residue are listed in Table 1.

Table 1

Characterization of *Pinus elliottii*

Chemical composition	
Parameter	Result (%)
Cellulose	46.9
Acid soluble lignin	2.9
Klason lignin	27.1
Ash in Lignin	3.8
Ash	0.2
Water soluble extractives	4.1
Ethanol soluble extractives	0.7
Moisture content	5.6

Values represent the mean of three replicates

2.2. Magnesium oxide

The magnesium oxide utilized for this study was MAGOXBPPO, a heavy magnesium oxide from Macco Organiques, Zahradnl, Czech Republic. This material had the following composition: Assay 96% min; Calcium <1.1%; Iron <0.05%; Acid insoluble substances <0.1%; Free Alkali and soluble salts <2.0%, Heavy metals <0.002%; Arsenic <0.0003%; Loss on ignition <10.0% and Bulk density (loose) 400-600 g/l.

2.3. Monopotassium phosphate

Monopotassium phosphate is commonly used as plant fertilizers and as a food ingredient (salt). For this research, we used MKP 0-52-34, a white crystalline product purchased from Shijiazhuang Lvhe Fertilizer Technologies Co. Ltd, China. This product had the following composition: KH_2PO_4 >98%; P_2O_5 >51.2%; K_2O >33.5%; Chloride <0.2%; Water insoluble <0.2%; Moisture <1.0% and PH 4.3-4.7. Wagh (2004) reports that acid phosphates with a P_2O_5 content of 50-60% may be suitable for the production of chemically bonded phosphate ceramics.

2.4. Fly ash

This product was obtained from Ulula Ash, South Africa and complies to the SANS 50450-1:2011 Class S specification. Class S Fly ash (SFA) is an ultra-fine powdery residue obtained from coal fired power plants and it is a South African Bureau of Standards (SABS) approved product. It is of structural concrete grade, finer than cement and is used as a partial replacement for cement. In addition to acting as extenders or fillers in Chemically Bonded Phosphate Ceramics, fly ash reduces the heat of the acid-

base reaction, increases the quantity of binder in the mix by generating more binders and enhances durability and strength of the final product (Wagh 2004; Wagh 2013).

3. Methods

3.1. Material characterization

The chemical properties of the wood residue were evaluated according to TAPPI standards T1-T272. The results of the analysis are presented in Table 1.

3.2. Board formation

The screened wood residue was mixed with magnesium oxide, mono potassium phosphate, fly ash and water as outlined in Table 2. Four replications of each board were produced. The materials were mixed for about 10 minutes at which time the exothermic conditions that characterize acid-base reactions was observed by a steady rise in the temperature of the mixture components. The mixture was poured on a metallic plate placed in a rectangular mould measuring 300mm X 300mm and pressed at 100 ± 10KPa for 5 minutes. The temperature of the press was set to 120^0C. After pressing, the formed boards were removed from the mould and stacked in the laboratory for 24 h. Thereafter, the boards were trimmed with an angle grinder to sizes of 300mm X 50mm and 50mm X 50mm and kept in the conditioned mechanical testing laboratory for 72 h.

Table 2
Composition of the boards

Boards	Weight (g)					Binder ratio	Flyash: binder ratio	Wood: binder ratio
	MgO	KH_2PO_4	Fly ash	Wood	Water			
A	50	100	150	200	250	0.5	1	1.33
B	66.7	133.3	100	200	250	0.5	0.5	1
C	83.3	166.7	50	200	250	0.5	0.2	0.8
D	75	75	150	200	250	1	1	1.33
E	100	100	100	200	250	1	0.5	1
F	125	125	50	200	250	1	0.2	0.8
G	100	50	150	200	250	2	1	1.33
H	133.3	66.7	100	200	250	2	0.5	1
I	166.7	83.3	50	200	250	2	0.2	0.8

3.3. Testing

The physical and mechanical properties of the selected boards were evaluated according to American Society for Testing and Materials (ASTM) D1037-99. The tests evaluated were density, water absorption, thickness/volume swelling, modulus of rupture (MOR) and modulus of elasticity (MOE).

4. Results

4.1. Density

Figure 1 shows the mean densities of the nine board types. Board A had the highest density of 1086.18 kg/m^3 while Board G had the lowest density of 875.26 kg/m^3. At a binder ratio of 1:2, the densities of the boards decreased slightly with decreasing ash content. This suggests that fly ash plays a role in the cementing mechanism of phosphate composites. As can be observed, the densities of Boards D, E and F increased steadily with decreasing ash content. This is due to the fact that the boards contain increasingly more binder, which gives better compaction of the components. This clearly indicates that the density increases with increasing binder content for a binder ratio of 1:1. However, at a binder ratio of 2:1, the density increases with increasing binder contents to a certain extent and then decreases slightly. This indicates that when the ratio of fly ash-binder content recedes 0.5, the density decreases, probably due to the low amount of fly ash in the composite mixture.

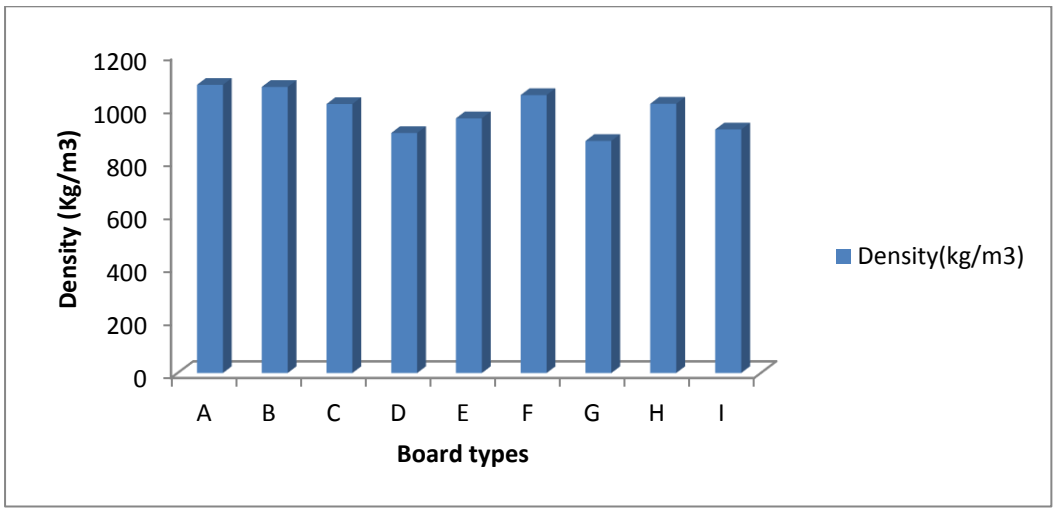

Fig.1. Board density

4.2. Water absorption

The mean water absorption of the composites is shown in Figure 2. The absorption is calculated as the percentage increase in the weight of the boards after a 24 h water immersion. Boards A-C had the lowest rates of water absorption of 37.3-41.9% while Boards G-I had the highest water absorption rates of

60.6-64.3%. This clearly indicates that the rate of absorption of water is a function of the density and binder ratio. The absorption rate was low where the base/acid ratio was low and high where the binder ratio was high. At a binder ratio of 1:2, the water absorption rate increased with decreasing ash content despite an increased amount of binder. This is likely due to the decreasing amount of fly ash, which is highly resistant to moisture. However at higher binder ratios, the relationship between water absorption rate and the ash content was non-linear, showing peaks at low binder and high ash contents, and decreases as the fly ash content decreases with a corresponding increase in the binder content.

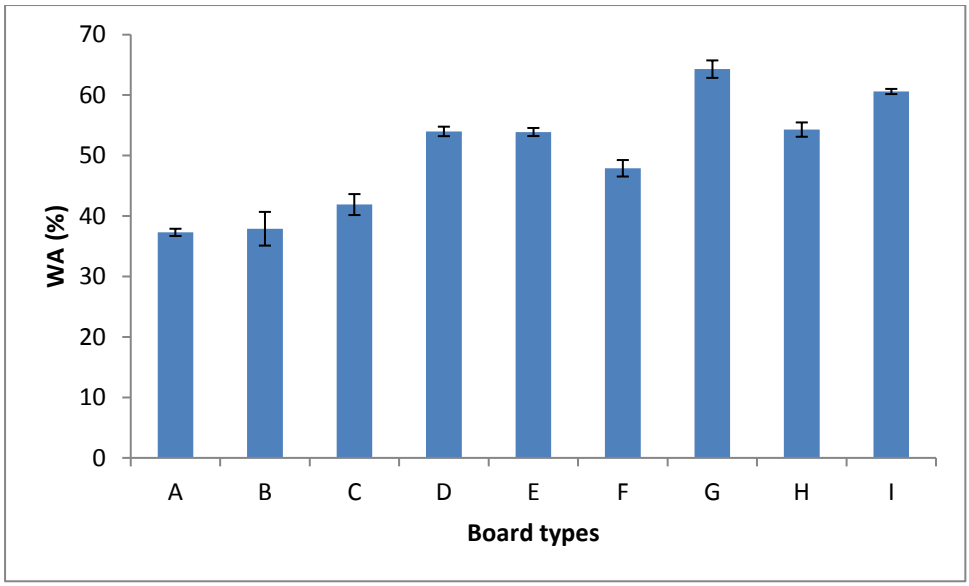

Fig.2. Water absorption

4.3. Thickness/volume swelling

Figure 3 shows the percentage thickness and volume swelling of the boards after a 24 h water immersion. Board D had the lowest rate of thickness and volume swelling of 2.8 and 3.1% respectively. At binder ratio of 1:1, and high ash content, there is better encapsulation of the cellulose fibres which makes it difficult for linear and edge-wise expansion. This results in reduced thickness and volume swelling. Board G had the highest percentage of volume swelling (12.4%) probably due to the low density of the board. Donahue and Aro (2010) also reported high volume swelling in phosphate bonded waste paper boards of low density. At binder ratios of 1:2 and 1:1, volume swelling increases as the ash content decreases, supporting the claim that fly ash increases the water resistance of the hygroscopic wood particles. However, at a binder ratio of 2:1, volume swelling reduces with the fly ash content. This could be due to higher basic components in the composite mix.

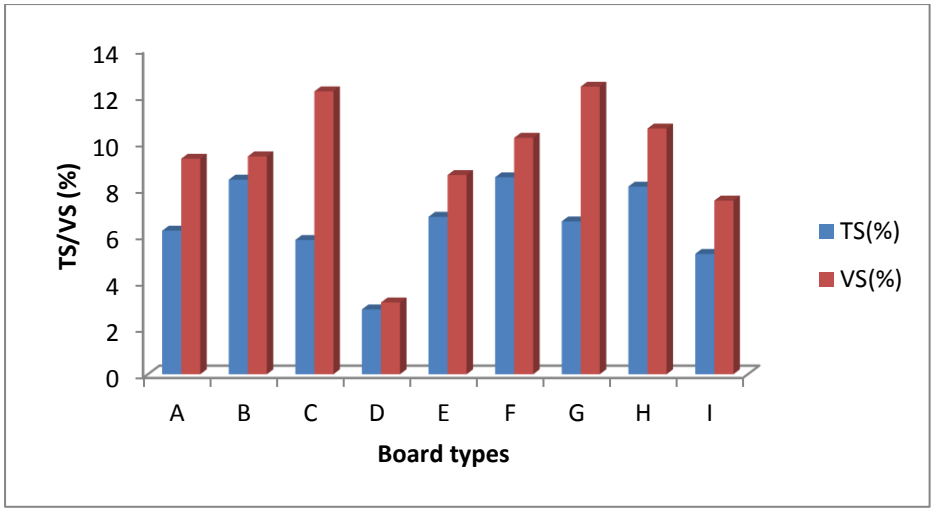

Fig.3. Thickness and volume swelling

4.4. Modulus of rupture

Figure 4 shows the modulus of rupture (MOR) of the boards. Board A had the highest MOR of 8641.6 KPa and Board D had the lowest MOR of 2424.3 KPa. The results showed that Boards made with a binder ratio of 1:2 are generally stronger than boards made with higher binder ratios. This is possibly due to better compaction in the boards as a result of the higher phosphate values necessary for the production of more $MgKPO_4.6H_2O$ mineral during hydration. This results in better bonding between the fibres and hence higher strength properties. This can also be observed from the high densities of these types of boards. Density has an important role in the mechanical response of cements and ceramics (Colorado *et al*., 2011). However, the MOR decreases as the ash content decreases suggesting that fly ash plays a role in improving the MOR of the composites. Wagh (2013) reported improved mechanical properties when fly ash was added to phosphate bonded composites. However, with a maximum fly ash-binder ratio of 1.33, this result is contrary to the report of Donahue and Aro (2010), who stated that a fly ash-binder ratio of 0.40-0.45 may be beneficial for improving the MOR of phosphate bonded paper sludge composites. At higher binder ratios, MOR increases as the fly ash content decreases, with maximum values of MOR determined at fly ash-binder ratio of 1:5. This is probably due to the increase binder in the mix.

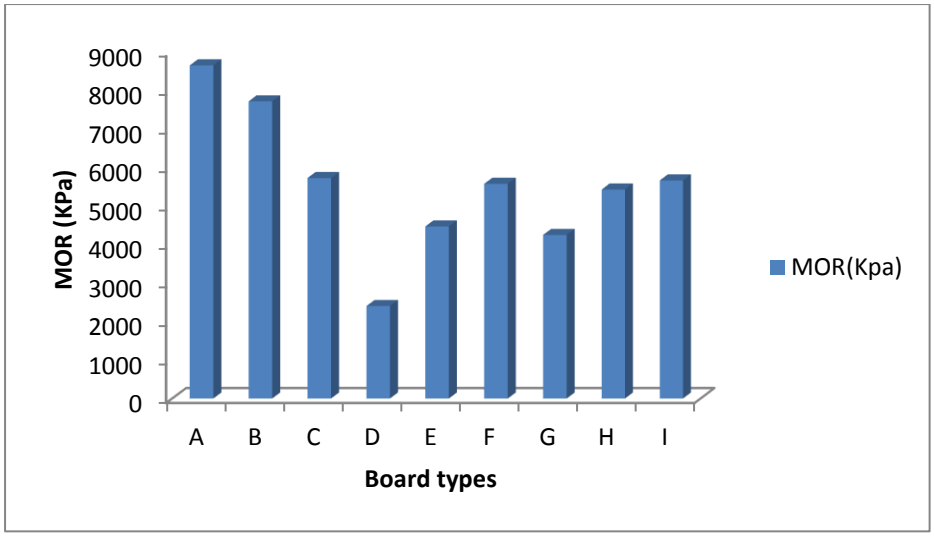

Fig.4. Modulus of rupture

4.5. Modulus of Elasticity

The modulus of elasticity (MOE) of the composites is shown in Figure 5. The ability of a material to withstand applied stress within its elastic limit is required for certain applications. Board A had the highest MOE of 1337.7 MPa while board D had the lowest value of 473.1 MPa. Boards made from a binder ratio of 1:2 had higher MOE than boards made with higher binder ratios. This also explains that low base-acid ratio is necessary for improving the MOE of the composites by the formation of more crystalline magnesium phosphate around the cellulose fibres. The variation in the MOE is similar to that in the MOR observed. However, at binder ratio of 2:1, MOE increases as the ash content reduces up to a point and then decreases sharply. This suggests that at binder ratio of 2:1, MOE decreases when the fly ash: binder ratio is below 0.5.

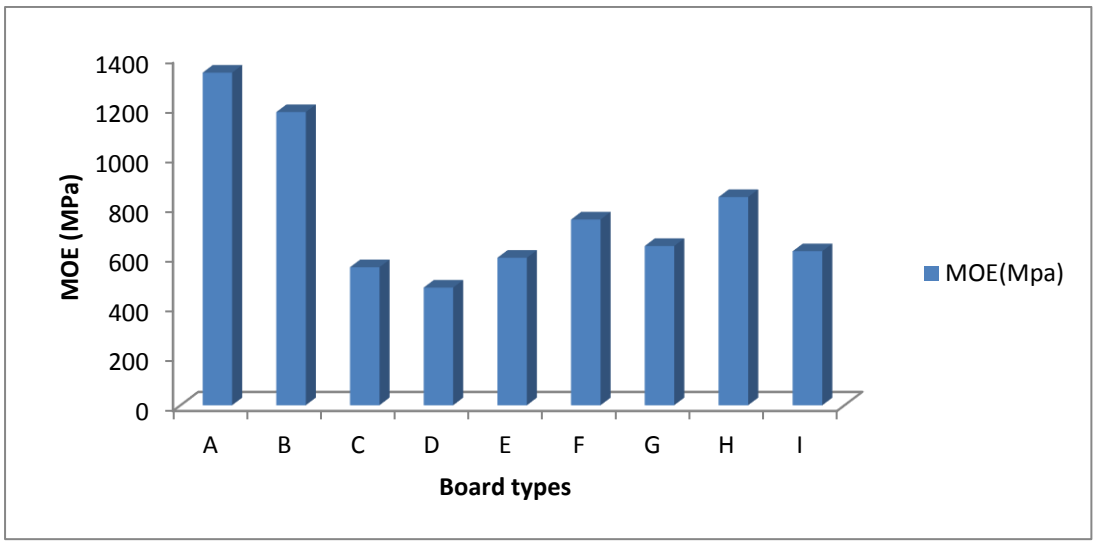

Fig.5. Modulus of elasticity

5. Conclusion

Phosphate bonded wood cement board can be made by consolidating wood residue, magnesium oxide, potassium phosphate, fly ash and water under pressure and heat for a short time. The composites set within 5 minutes. Properties such as density, water absorption, thickness/volume swelling, modulus of rupture and modulus of elasticity were determined. All properties exceeded the minimum requirement for LD-1 grade particleboard. There is potential for these products to be utilized as fire-rated non-structural applications like wall claddings, partitioning and ceilings.

From this study, it was observed that a binder ratio of 1:2 provided the best effects in all properties evaluated. Therefore, future research will investigate the properties at lower ratios of the base/acid contents. Due to the preliminary nature of this study, it is recommended that other advanced techniques such as phase bonding between wood and phosphate cements be conducted to reveal the properties and behaviour of these environmentally friendly composites.

Acknowledgements

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CHAPTER FIVE

Paper III

Phosphate bonded wood composite products from invasive Acacia trees occurring on the Cape Coastal plains of South Africa

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Abstract

The feasibility of manufacturing phosphate bonded wood composite board products from four locally occurring invasive acacia tree species (*Acacia cyclops, A. saligna, A. mearnsii* and *A. longifolia*) was studied using a formulated magnesium oxide (MgO) and monopotassium phosphate (KH_2PO_4) binder system. The optimization for the manufacturing process was studied using a central composite statistical design, whereupon the following factors were considered i.e. KH_2PO_4: MgO ratio, the fly ash content as partial replacement for the binder and the wood content as a ratio of wood to the total inorganic content. A fitted response surface plot was used to show the effect of the main factors and their interactions on the measured board properties. A response surface model was developed to predict the parameters leading to the best board properties. All physical properties evaluated met or exceeded the minimum requirements for low density particleboards. The results showed that the variables considered have significant effects on the physical properties of the boards. The optimum composite manufacturing process for making durable products within the scope of the studied species was found to be a KH_2PO_4/MgO ratio of 1.66, an ash content of 2.7% and a wood/inorganic ratio of 0.96 for the selected wood species.

Keywords: Fitted response surface, invasive species, phosphate bonded wood composites, process optimization, response surface model

1. Introduction

This study describes an assessment of potentially exploiting the woody biomass of invasive Australian wattle species occurring in areas of the Eastern and Western Cape, South Africa for particleboard manufacturing. A review of plant invasions in South Africa suggests that invaders, such as acacias act as ecosystem engineers by rapidly changing disturbance regimes (Richardson and Wilgen 2004). Such

changes can alter the flow and availability of nutrients, living space, sediment, light and water (Macdonald et al. 1986; Gorgens and Wilgen 2004). In South Africa, the environmental management of these invasive species, which focuses on harvesting based eradication, has resulted in the generation of wood waste, as the trees are typically harvested before they reach merchantable size. According to Theron et al. (2004), the total green woody biomass with a minimum diameter of 2.5 cm is about 10 million tonnes, which covers an area of more than 100 000 ha. This suggests a substantial quantity of raw materials that can be used for wood composite manufacturing.

Conventional wood-based composite products are made with a thermosetting or heat-curing adhesive. Thermoplastics and inorganic binders are used to manufacture wood plastic and inorganic bonded wood products respectively (Youngquist 1999; Irle et al. 2013). These adhesives are chosen based upon their suitability for the particular product and consumer specifications. In the context of a competitive wood composite market, the development of affordable panels with a low carbon footprint is of significant importance. The innovative phosphate binder used in concrete repairs and civil engineering has found increasing application in other fields of manufacturing, including the composite panel industry.

Phosphate binder is made from an acid-base reaction between an acidic phosphate and an alkali base. According to Wagh (2004), the reaction is highly exothermic and the binder sets within minutes into a rigid mass that can be referred to as chemically bonded phosphate ceramic (CBPC). Phosphate bonded composite products are light, durable, moisture resistant and possess good flexural and compressive strength properties (Donahue and Aro, 2010). The phosphate based binder is an environmentally friendly material as it contains major elements also used as plant fertilizers i.e. potassium (K) and phosphorus (P), thus displaced products may enrich the soil nutrients (Laufenberg and Aro, 2004).

In order for the proposed products to attain consumer acceptance, standards and command a market premium, a manufacturing process optimization is imperative. Studies have shown that wood and other materials can be bonded with the magnesium phosphate cement (MPC) binder to produce panels with a comparative advantage compared to Portland cement and polymer resin (Jeong and Wagh 2002, Donahue and Aro 2010, Colorado et al. 2011, Wagh 2013). However, very few studies have been conducted on the process optimization of the phosphate based binder in wood composite panels. Ibrahim et al. (2011) optimised the process conditions for encapsulating lead battery waste. The authors reported that a minimum porosity was achieved by using a molar ratio of Mg: K of 1:1, and that a pressing time of 10 minutes was sufficient to reach compacts of low permeability. Chi and Englund (2014) studied the alkalinity, workability and fluidity of binder ratios and MPC formulations. Using a pull-out test procedure to evaluate the interfacial properties between MPC and sugar maple, a 3:1 weight ratio of KH_2PO_4 and MgO was found to have the best performance (Chi and Englund, 2014). Formosa et al. (2015) optimized the process for manufacturing MPC using MgO-containing by-products as raw materials and boric acid as additives to obtain good mechanical properties and proper setting times.

The benefits of MPC bonded wood products as a green building material can be enhanced with the addition of fly ash from coal based energy generation. Fly ash increases durability and strength in chemically bonded phosphate ceramics, improves workability of MPC paste, lowers the heat of the acid-base reaction and increases the total binder content (Laufenberg and Aro 2004, Wagh 2013). The objective of this study was to produce green building panels utilizing wood waste and eco-friendly materials with a low carbon footprint. Board composition i.e. binder ratio, fly ash and wood content was optimized at laboratory scale to achieve the desired properties.

2. Materials

2.1 Wood species

The selected tree species used in this study were Black wattle (*Acacia mearnsii*), Long-leaved wattle (*A. longifolia*), Port Jackson (*A. saligna*) and Rooikrans (*A. cyclops*). These species were supplied by EC Biomass Fuel Pellets (Pty) Ltd, Port Elizabeth, South Africa. The trees were harvested in the Green bushes area in Port Elizabeth, and the wood was supplied as wood waste from processed logs. The Black wattle was about 6 years old while the other acacia species were about 3 years old at the time of harvest.

2.2 Magnesium oxide

The magnesium oxide was MAGOXBPPO, a heavy magnesium oxide from Macco Organiques, Zahradnl, Czech Republic with the following composition: assay 96% min; calcium <1.1%; iron <0.05%; acid insoluble substances <0.1%; free alkali and soluble salts <2.0%, heavy metals <0.002%; arsenic <0.0003%; loss on ignition <10.0% and bulk density (loose) 400-600 g/l.

2.3 Monopotassium phosphate

Monopotassium phosphate is commonly used as plant fertilizer and as a food ingredient (salt). For this project, MKP 0-52-34, a white crystalline product was purchased from Shijiazhuang Lvhe Fertilizer Technologies Co. Ltd, China. It had the following composition: KH_2PO_4 >98%; P_2O_5 >51.2%; K_2O >33.5%; chloride <0.2%; water insoluble <0.2%; moisture <1.0% and pH 4.3-4.7. Wagh (2004) reports that acid phosphates with a P_2O_5 content of 50-60% may be suitable for the production of chemically bonded phosphate ceramics.

2.4 Fly ash

Fly ash was obtained from Ulula Ash, South Africa and complies to the SANS 50450-1:2011 class S specification. Class S Fly ash (SFA) is an ultra-fine, powdery residue obtained from coal fired power plants and it is a South African Bureau of Standards (SABS) approved product. It is of structural

concrete grade, finer than cement and is used as a partial replacement for cement. It had the following composition: SiO_2 <60%; Al_2O_3 <35%; CaO <10%; MgO <5%; Fe_2O_3 <5%; TiO_2 <5%.

3. Methods

3.1 Wood preparation

The wood residue was hammer milled and sieved through a 1 mm sieving slice. The differences in the particle distribution were not considered in this study since the aim was to simulate an industrial wood milling process. The resultant wood particles were conditioned at 20 ^oC and 65% RH for 96 h. The equilibrium moisture content of the material was found to be 7%.

3.2 Board formation

The materials were mixed thoroughly by mass (Table 1). The amount of water added was based upon formulation using the formula

$$W = B + (FSP - MC) \times F$$

W = Amount of water (ml)
B = Amount of inorganic components (g)
FSP = Fibre Saturation Point (%)
MC = Moisture content of fibre (%)
F = Amount of fibre (g)

Table 1

Design and formulations

Exp. Run	KH_2PO_4/MgO	Fly Ash (g)	Wood/inorganic	Water (ml)
1	2:1 (53.3/26.7)	0	0.63:1 (50/80)	91.5
2	2:1 (53.3/26.7)	0	0.88:1 (70/80)	96.1
3	2:1 (42.7/21.3)	0.2 (16)	0.63:1 (50/80)	91.5
4	2:1 (42.7/21.3)	0.2 (16)	0.88:1 (70/80)	96.1
5	4:1 (64/16)	0	0.63:1 (50/80)	91.5
6	4:1 (64/16)	0	0.88:1 (70/80)	96.1
7	4:1 (51.2/12.8)	0.2 (16)	0.63:1 (50/80)	91.5
8	4:1 (51.2/12.8)	0.2 (16)	0.88:1 (70/80)	96.1
9	1.32:1 (41/31)	0.1 (8)	0.75:1 (60/80)	93.8
10	4.68:1 (59.3/12.7)	0.1 (8)	0.75:1 (60/80)	93.8
11	3:1 (60/20)	0	0.75:1 (60/80)	93.8
12	3:1 (43.9/14.6)	2.7 (21.5)	0.75:1 (60/80)	93.8
13	3:1 (54/18)	0.1 (8)	0.54:1 (43.2/80)	89.9
14	3:1 (54/18)	0.1 (8)	0.96:1 (76.8/80)	97.7
15	3:1 (54/18)	0.1 (8)	0.75:1 (60/80)	93.8
16	3:1 (54/18)	0.1 (8)	0.75:1 (60/80)	93.8

The pre-calculated amount of water was added to the materials and the mixture was stirred. The paste was poured into a steel mould measuring 218 x 77 x 40 mm and a steel bar 27 mm thick was placed on the slurry to fit into the mould. The set-up was transferred to the laboratory press and a pressure of 200 KPa was applied for 5 minutes at room temperature. Thereafter, the mould was removed from the press and the board was demoulded. The same procedure was repeated for all wood species. The formed boards were allowed to air-cure in the laboratory for 24 h. Thereafter, they were conditioned at 20 ^{o}C and 65% RH for 96 h before testing.

3.3 Testing

Testing of the boards was carried out according to ASTM Standards (D1037-99). The properties evaluated include density, modulus of rupture (MOR), modulus of elasticity (MOE), water absorption (WA), and thickness/volume swelling (TS/VS). The sorption tests were determined after 24 h immersion in distilled water. Samples for sorption tests were cut using an angle grinder with a concrete blade into dimensions of 75 x 50 mm. The thickness of all samples used in the test was 13 ± 1.2 mm based on the set-up configuration of the steel mould.

3.4 Statistical analysis

The experiments were designed and analysed based on a central composite design (CCD) using the STATISTICA software v5. Three factors were considered within one block, namely the binder ratio of KH_2PO_4/MgO, the fly ash content as partial replacement of the binder and the wood content as ratio of wood to the total inorganic content. ANOVA was used to determine the significant variables that affected board properties. The response surface method (RSM) was used to establish a statistical relationship between experimental variables and responses, from which the optimal experimental conditions could be predicted for achieving optimum performance (Bloor and England, 1991). Table 2 shows the factors and the corresponding levels for the response surface design.

Table 2
Factors and corresponding levels for response surface design

Factors	Level		
	Low	Medium	High
KH_2PO_4/MgO	2	3	4
Fly ash (%)	0	0.1	0.2
Wood/inorganic	0.63	0.75	0.88

4. Results and discussion

4.1 Test result

From the design, a total of 16 experimental runs were conducted at random. The test results are presented in Tables 3-6. Analysis of variance (ANOVA) of the main effects and their interaction was considered for each wood species and the results are presented in Tables 7-9. Fitted response surfaces were plotted for variables where the interactions were significant ($p < 0.05$) (Figs. 1-8). The ANOVA analysis showed that there is no significant effect of the factors on the mechanical properties of the boards indicating that none of the variables considered significantly influenced the board strength properties within the experimental design. However, the effect of the independent variables was significant on some physical properties of the boards.

Table 3

Experimental runs and test results for *A. cyclops*

Exp. run	MOR (MPa)	MOE (MPa)	Den (g/cc)	WA (%)	TS (%)	VS (%)
1	0.92	31.48	0.88	10.08	0.39	1.00
2	1.17	26.59	0.95	10.04	0.34	1.76
3	0.52	17.12	0.90	11.22	0.19	1.08
4	0.88	20.10	0.83	15.24	0.20	0.91
5	0.81	25.86	0.85	9.23	0.63	2.26
6	1.36	20.39	0.85	11.40	0.24	1.61
7	0.70	15.84	0.82	10.57	0.44	1.61
8	0.84	12.65	0.79	13.60	0.21	0.84
9	1.22	25.16	0.88	14.36	0.65	3.60
10	0.89	15.10	0.77	12.81	0.15	1.12
11	1.65	30.18	0.81	10.92	0.02	0.35
12	1.18	23.22	0.80	15.07	0.77	3.62
13	0.84	22.54	0.80	10.84	1.21	5.07
14	1.71	21.35	0.78	17.30	0.96	5.12
15	1.56	24.03	0.81	13.10	0.79	3.68
16	1.71	27.49	0.77	14.27	0.23	1.43

Table 4

Experimental runs and test results for *A. longifolia*

Exp. run	MOR (MPa)	MOE (MPa)	Den (g/cc)	WA (%)	TS (%)	VS (%)
1	1.66	29.61	0.91	9.80	0.11	0.09
2	0.85	13.71	0.81	16.15	0.51	2.51
3	0.73	15.85	0.74	14.63	0.55	2.25
4	1.32	19.81	0.79	19.00	1.36	6.38
5	0.82	19.89	0.79	11.99	0.26	0.90
6	1.52	23.02	0.78	14.37	0.48	2.02
7	1.00	13.76	0.77	12.38	0.93	3.62
8	0.96	14.84	0.74	10.32	0.74	2.83
9	1.39	23.02	0.83	15.62	0.09	0.87
10	0.99	15.55	0.84	13.84	0.64	3.20
11	1.94	27.08	0.90	9.49	0.51	2.48
12	1.26	20.01	0.81	18.02	0.71	3.85
13	1.14	19.35	0.78	11.96	0.71	2.63
14	0.78	9.57	0.63	26.66	1.88	8.68
15	1.42	17.81	0.82	13.95	0.83	3.28
16	1.77	21.83	0.82	14.22	1.81	7.47

Table 5

Experimental runs and test results for *A. mearnsii*

Exp. run	MOR (MPa)	MOE (MPa)	Den (g/cc)	WA (%)	TS (%)	VS (%)
1	2.01	27.37	0.83	10.27	0.69	3.78
2	4.51	64.51	0.77	14.15	0.06	1.24
3	1.37	26.67	0.77	15.18	0.18	0.40
4	1.95	23.48	0.84	16.47	0.54	3.66
5	1.24	20.32	0.90	8.99	0.58	3.07
6	1.99	21.26	0.77	12.11	0.91	3.78
7	0.73	12.64	0.73	13.65	0.04	0.67
8	0.85	19.75	0.72	17.39	0.86	4.21
9	1.60	23.88	0.88	13.83	0.86	4.71
10	0.78	11.67	0.71	12.05	0.21	0.85
11	1.58	21.14	0.84	10.74	0.27	0.42
12	1.26	18.64	0.77	14.36	0.60	1.60
13	0.79	14.68	0.82	9.91	0.00	0.63
14	3.41	37.08	0.84	13.93	1.23	5.52
15	2.29	32.42	0.93	9.89	0.78	3.91
16	1.64	21.07	0.87	10.03	0.10	0.44

Table 6

Experimental runs and test results for *A. saligna*

Exp. run	MOR (MPa)	MOE (MPa)	Den (g/cc)	WA (%)	TS (%)	VS (%)
1	1.61	32.23	0.83	12.91	0.93	4.46
2	3.52	41.99	0.83	14.34	0.26	0.15
3	1.00	21.11	0.82	14.31	0.20	1.83
4	1.82	28.48	0.86	16.22	0.69	4.28
5	0.81	16.37	0.84	11.02	0.06	0.75
6	1.57	21.76	0.79	14.36	0.57	2.56
7	0.64	14.05	0.76	13.74	0.45	1.53
8	1.61	26.88	0.76	17.35	0.35	2.36
9	1.28	26.14	0.95	12.33	1.29	6.49
10	1.59	25.13	0.82	13.05	0.67	3.56
11	1.47	29.07	0.89	10.93	0.65	3.33
12	0.91	21.98	0.81	15.33	0.67	3.34
13	1.27	28.83	0.83	10.49	0.11	0.28
14	1.36	25.70	0.88	14.49	1.02	5.55
15	1.25	23.98	0.84	12.72	0.24	0.29
16	1.99	35.50	0.83	13.39	0.02	0.56

4.2 Effect of the independent variables on board properties

4.2.1 Effect of binder ratio on the board properties

The interaction between fibre/inorganic ratio and fly ash content on the MOE of *A. cyclops* is presented in Fig. 1. It would be observed that at a binder ratio of 2:1, no fly ash content and a wood/inorganic ratio of 0.63:1, the highest MOE value was recorded for *A. cyclops* i.e. 31.48 MPa. At higher fly ash loadings to about 20 %, the MOE decreased. This can be explained by the fact that the binder was reduced, and the board did not achieve sufficient stiffness with increasing ash content. However, the strength properties increased with increasing fibre content. High fibre content is known to increase the MOE of fibre reinforced composites (Mohr et al, 2004) as a result of the transmission of the applied stress to the fibres (Cantwell and Morton, 1991). Figures 2-3 show the effect of the interaction between binder ratio and fly ash content on the board properties. The effect of the binder was significant on the WA of the boards for *A. mearnsii* and *A. longifolia* (Table 7). From the WA fitted surface graphs, it was observed that at low levels of ash content and a corresponding increase in binder content, WA will be lower for the studied species. High binder content increases bonding in wood composites and encapsulates the hygroscopic wood fibres, thereby reducing water absorption.

Table 7

Effect of binder ratio on the board properties

	p-values					
Wood species	MOR	MOE	Density	WA	TS	VS
A. mearnsii	0.2073	0.2778	0.2124	0.0485*	0.8539	0.7384
A. longifolia	0.5527	0.2909	0.0677	0.0244*	0.8726	0.9789
A. saligna	0.5988	0.5305	0.0620	0.5909	0.2773	0.0566
A. cyclops	0.5756	0.1726	0.1586	0.3239	0.8527	0.7214

*denotes significant values ($p < 0.05$)

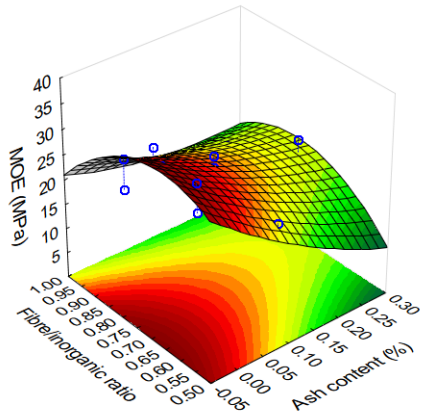


Fig. 1 Fitted surface of MOE for *A. cyclops*

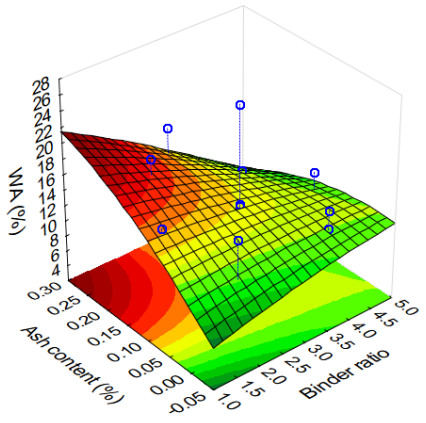


Fig. 2 Fitted surface of WA for *A. longifolia*

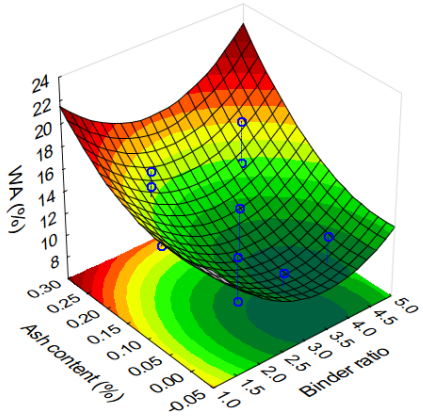


Fig. 3 Fitted surface of WA for *A. mearnsii*

4.2.2 Effect of fly ash content on the board properties

Fly ash plays a role in phosphate bonded composite products by improving its workability and generating more binder (Laufenberg and Aro 2004; Wagh 2013). However, the findings in this study revealed that the partial replacement of phosphate binder with fly ash, without increasing the wood

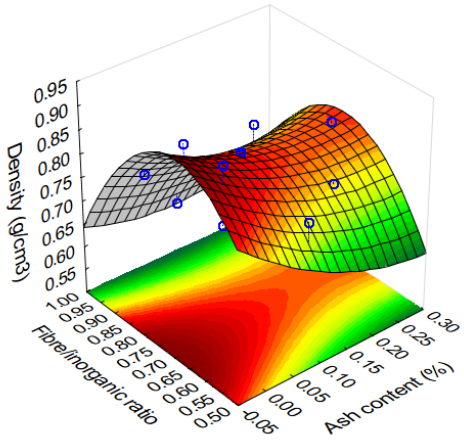
content, decreased board strength properties, and decreased WA and TS/VS. As binder ratio increases with fly ash content, strength properties increased. A high binder ratio with more fly ash produces more $MgKPO_4.6H_2O$ mineral during hydration resulting in better bonding between fibres (Donahue and Aro, 2010). The effect of the fly ash content was significant for both density and WA of *A. longifolia* and WA of *A. mearnsii* (Table 8). Figures 4-5 show the interaction between fibre/inorganic ratio and fly ash content at a binder ratio of 3:1 for *A. longifolia* and *A. saligna*. It would be observed that density increases as fibre content and fly ash increase for *A. saligna*. However, with increasing fibre content, fly ash did not contribute to the density of *A. longifolia*. At high loadings of fly ash, the density of *A. longifolia* decreased which had a negative effect on the strength properties (Table 4).

Table 8

Effect of fly ash content on the board properties

	p-values					
Wood species	MOR	MOE	Density	WA	TS	VS
A. mearnsii	0.2148	0.3625	0.2029	0.0091*	0.9997	0.8682
A. longifolia	0.2822	0.3041	0.0218*	0.0387*	0.9213	0.8229
A. saligna	0.3509	0.4320	0.1197	0.0660	0.6135	0.1023
A. cyclops	0.0862	0.1391	0.7686	0.2054	0.9599	0.9474

*denotes significant values ($p < 0.05$)



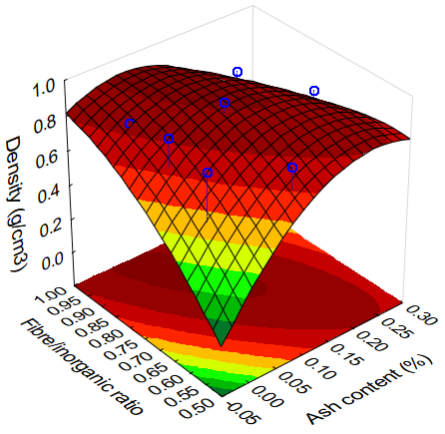


Fig. 4 Fitted surface of density for *A. longifolia.* Fig. 5 Fitted surface of density for *A. saligna*

4.2.3 Effect of wood fibre content on the board properties

Fibres play a significant role in increasing the specific gravity of composites and impart additional energy absorbing capacity to the product (Mohr et al., 2004). In this study, wood content was found to have a significant effect on the density of *A. longifolia* and on the density and VS of *A. saligna*. The wood content also had a significant effect on the WA of the boards. Generally, moisture absorption

increased with increase in wood content. This is a result of the hygroscopic nature of lignocellulosic fibres. Figures 6-8 show that the WA and VS of the boards decreased as the fibre and fly ash content decrease. By increasing binder ratio at low fibre content, the WA of the boards decreases. On the other hand, WA increases as the fibre content increases. Increased binder ratio with corresponding low ash content increases the bonding between fibres, and since the hygroscopic fibres are low in the board, WA is reduced (Amiandamhen et al., 2016).

Table 9

Effect of wood fibre content on the board properties

	p-values					
Wood species	MOR	MOE	Density	WA	TS	VS
A. mearnsii	0.1686	0.3161	0.8784	0.0141*	0.3008	0.3144
A. longifolia	0.9403	0.4262	0.0214*	0.0156*	0.4594	0.3946
A. saligna	0.3051	0.5047	0.0340*	0.0688	0.1948	0.0386*
A. cyclops	0.1087	0.5786	0.3695	0.0942	0.6581	0.8614

*denotes significant values ($p < 0.05$)

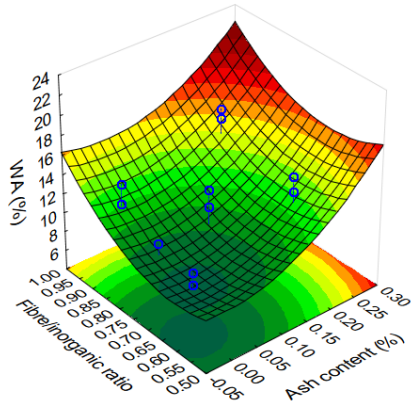


Fig. 6 Fitted surface of WA for *A. mearnsii*

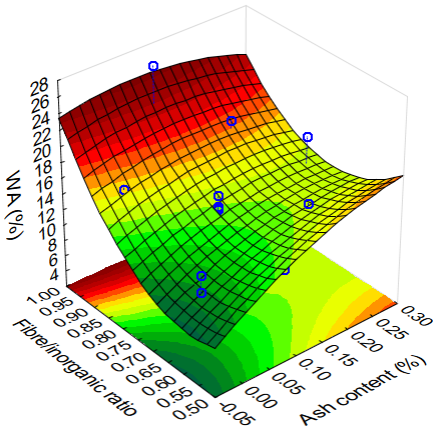


Fig. 7 Fitted surface of WA for *A. longifolia*

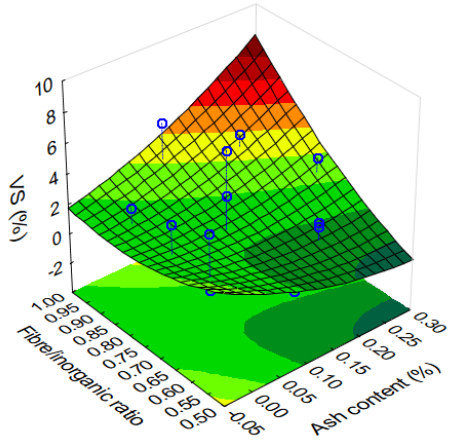


Fig. 8 Fitted surface of VS for *A. saligna*

4.3 Optimization of the independent variables for prediction of board properties

The optimum conditions for predicting the properties in the manufacturing of composite products from wood and agricultural residues were determined from the desirability profiler available in STATISTICA software (v5). As explained by Maran and Manikandan (2012), the desirability function searches for factor combination levels that jointly optimize a set of responses by satisfying each response requirements in the design. The scale of the desirability function ranges between 0 (completely non-desirable) and 1 (fully desired response) (Gonzalez et al., 2007). Using the STATISTICA, individual desirability is obtained by specifying the goals for each response. Also, a weight factor, which defines the shape of the desirability function for each response is assigned, and is usually between 0.1 and 10. A weight factor of 1 was selected for the purpose of this study.

Using numerical optimization, profiles of predicted values and desirability were generated to estimate each response as influenced by the independent variables. From the established conditions, the optimum process conditions of binder ratio, fly ash and wood content for achieving the desired board properties are presented in Tables 10-13. With the optimum values provided, it was observed that the maximum predicted values of MOR of *A. mearnsii*, *A. longifolia*, *A. saligna* and *A. cyclops* are 4.7, 1.74, 3.72 and 1.72 MPa respectively compared to the observed values of 4.51, 1.94, 3.52 and 1.71 MPa respectively. Based on the regression model, the quadratic equation for each response variable can be written as follows;

$$y = \mu + ax + bx + cx + a^2x + b^2x + c^2x + abx + acx + bcx$$

The adequacy and fitness of the models were tested by regression analysis. The analysis shows a high precision of the model. The high degree of fitting between predicted and observed results reflects the accuracy and applicability of the model in the optimization process (Zhao et al., 2008).

Table 10

Summary of optimized factors for predicting board properties of *A. mearnsii*

Factors	Opt. value to MOR	Opt. value to MOE	Opt. value to density	Opt. value to WA	Opt. value to TS	Opt. value to VS
KH_2PO_4/MgO	1.66	1.66	2.66	3.34	4.68	4.68
Fly ash	0.054	0.027	0.081	0.027	0.27	0.27
Wood/inorganic	0.96	0.96	0.75	0.71	0.67	0.71
Desirability	4.70 MPa	65.23 MPa	0.90 g/cc	8.95%	-0.25%	0.33%

Table 11

Summary of optimized factors for predicting board properties of *A. longifolia*

Factors	Opt. value to MOR	Opt. value to MOE	Opt. value to density	Opt. value to WA	Opt. value to TS	Opt. value to VS
KH_2PO_4/MgO	2.66	1.32	1.66	4.68	4.68	4.68
Fly ash	0.00	0.00	0.00	0.27	0.27	0.27
Wood/inorganic	0.71	0.62	0.75	0.88	0.96	0.96
Desirability	1.74 MPa	29.71 MPa	0.91 g/cc	8.91%	-0.26%	-1.01%

Table 12

Summary of optimized factors for predicting board properties of *A. saligna*

Factors	Opt. value to MOR	Opt. value to MOE	Opt. value to density	Opt. value to WA	Opt. value to TS	Opt. value to VS
KH_2PO_4/MgO	1.32	1.32	1.66	4.68	3.67	3.67
Fly ash	0.00	0.00	0.27	0.027	0.16	0.22
Wood/inorganic	0.54	0.88	0.96	0.58	0.54	0.62
Desirability	3.72 MPa	38.39 MPa	0.96 g/cc	10.38%	0.056%	0.14%

Table 13

Summary of optimized factors for predicting board properties of *A. cyclops*

Factors	Opt. value to MOR	Opt. value to MOE	Opt. value to density	Opt. value to WA	Opt. value to TS	Opt. value to VS
KH_2PO_4/MgO	3.00	2.66	1.32	4.68	4.68	4.68
Fly ash	0.081	0.00	0.054	0.27	0.00	0.27
Wood/inorganic	0.88	0.75	0.96	0.67	0.92	0.96
Desirability	1.72 MPa	31.49 MPa	0.96 g/cc	8.58%	0.0082%	0.32%

Conclusions

This study has demonstrated the feasibility of manufacturing board products from alien invasive tree species found locally in South Africa. The manufacturing of board products could be incorporated into the management practices aimed at controlling the spread of such species. All physical properties evaluated - including density, WA, TS and VS - met the minimum requirements for low density particleboards (EN-634: 1995). The optimum composite manufacturing process for making durable products within the scope of the studied species was found to contain a ratio of KH_2PO_4/MgO = 1.66, 2.7% fly ash content and a wood/inorganic ratio of 0.96. To our best knowledge, this is the first time that this binder system has been optimised for such particleboards.

The binder is robust enough to accommodate the variability inherent in these wood species and is not affected by the chemical composition of the species. However, while fly ash can be incorporated to reduce binder cost and the overall cost of the production process, at high quantities, it proved to have a negative effect on strength properties. Although, the variables considered i.e. binder ratio, fly ash and wood content have significant effect on the physical properties of the board, the effect on the mechanical properties was not significant within the experimental design.

Acknowledgement

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Conference Paper II

Effect of Bark on the Physical and Mechanical Properties of Phosphate Bonded Wood Composites of Black Wattle (*Acacia mearnsii* De Wild)

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Abstract

In South Africa, forestry and wood processing generates about 4-6 million tons of wood waste per year. In this study, the effect of bark on properties of phosphate bonded wood composites was investigated. Bark and sawdust of black wattle (*Acacia mearnsii* De Wild.) were collected from EC Biomass, South Africa. After drying, the bark were chipped, milled and sieved through a 1.0 mm mesh. The binding matrix was prepared using a reactive magnesia, phosphoric acid and class S fly ash. The ash was added at 10 - 50% loading. The bark was added to the wood at 10, 20, 30, 40 and 50% loading and mixed thoroughly with the inorganic matrix. A control experiment without ash and bark was also considered. The experiments were carried out in four replicates. The composites were formed in a rectangular mould and compressed at room temperature and a pressure of 200KPa. After de-moulding, the composites were cured in a conditioned room for 96 h. Thereafter, physical and mechanical tests were conducted to evaluate the properties of the composites. A central composite design (CCD) was used to determine the best conditions to optimize the properties of the composites. The study demonstrated that bark of *Acacia mearnsii* can be incorporated into wood residues in phosphate bonded composites with a significant improvement in properties. The products are environmentally friendly and can be engineered to meet industry performance standards and consumer acceptance taste. The proposed product can be used for ceiling, partitioning, wall claddings and underlayment.

Keywords: *Acacia mearnsii*, fly ash, magnesia, mechanical properties, phosphate bonded wood composites, phosphoric acid, physical properties

Introduction

The application of chemically bonded phosphate ceramics (CBPC) has been increasing over time. This 21st century material is employed in architecture and civil engineering. It can be used as adhesives, cements or as coatings for materials, therefore providing a wide range of applications (Laufenberg and Aro, 2004). Chemically bonded phosphate ceramics (CBPCs) are formed by acid-base reactions between an acid phosphate (such as that of potassium, ammonium, or aluminium) and a metal oxide

(such as that of magnesium, calcium, or zinc) (Jeong and Wagh, 2002). The reaction is exothermic and sets rapidly into a crystalline mass similar to ceramic (Wagh, 2004). They are mainly magnesium and iron-phosphate ceramics, although specialty formulations have been developed for biomaterials applications using calcium-phosphate based ceramics. The most employed of the basic elements is magnesium due to its moderate solubility between calcium and iron in the phosphoric acid medium (Wagh, 2013). CBPCs are produced at ambient conditions and can be applied in high volumes. They are applied in stabilization of hazardous and radioactive wastes, structural materials including road repair and architectural products (Jeong and Wagh, 2002).

Preliminary investigations proved that wood and other industrial waste can be recycled to produce phosphate bonded composites. Studies by Laufenberg and Aro (2004), Donahue and Aro (2010), Chi (2012) produced phosphate bonded fibre composites using magnesium phosphate cement. In one report, Pine shavings and sawdust were used as raw materials for a set of baseline experiments with one-third phosphate binder. Pressing to three densities (0.6-1.25 g/cc), the mechanical properties obtained compared with those of wood cement products (Laufenberg and Aro, 2004). In another report, waste paper sludge was bonded with phosphate binder using different ratios of waste fibre to binder (0.63-1.1) with the addition of fly ash as fillers. All properties evaluated on the composites except the modulus of rupture (MOR) compared with those of low-density particle board (Donahue and Aro, 2010). Chi (2012) investigated the interfacial properties between sugar maple and magnesium phosphate cement. The author reported that using a phosphate/magnesium ratio of 3:1, failure and initial crack stress values can be maximized.

In this study, industrial waste streams from the wood industry were incorporated into prepared magnesium phosphate matrix, and the materials were mixed and compressed to form composite boards. This study aims to provide value additions to wood waste such as sawdust and barks while investigating their effects on composite properties.

Materials

Waste Residues

The residues utilized for this research were barks and saw dust of Acacia *mearnsii*. The materials were sourced locally in South Africa.

Magnesium oxide

The magnesium oxide utilized for this study was MAGOXBPPO, a heavy magnesium oxide from Macco Organiques, Zahradnl, Czech Republic. This material had the following composition: Assay 96% min; Calcium <1.1%; Iron <0.05%; Acid insoluble substances <0.1%; Free Alkali and soluble

salts <2.0%, Heavy metals <0.002%; Arsenic <0.0003%; Loss on ignition <10.0% and Bulk density (loose) 400-600 g/l.

Monopotassium phosphate

Monopotassium phosphate is commonly used as plant fertilizers and as a food ingredient (salt). For this research, we used MKP 0-52-34, a white crystalline product purchased from Shijiazhuang Lvhe Fertilizer Technologies Co. Ltd, China. This product had the following composition: KH_2PO_4 >98%; P_2O_5 >51.2%; K_2O >33.5%; Chloride <0.2%; Water insoluble <0.2%; Moisture <1.0% and PH 4.3-4.7. Wagh (2004) reports that acid phosphates with a P_2O_5 content of 50-60% may be suitable for the production of chemically bonded phosphate ceramics.

Fly ash

This product was obtained from Ulula Ash, South Africa and complies to the SANS 50450-1:2011 Class S specification. Class S Fly ash (SFA) is an ultra-fine powdery residue obtained from coal fired power plants and it is a South African Bureau of Standards (SABS) approved product. It is of structural concrete grade, finer than cement and is used as a partial replacement for cement. In addition to acting as extenders or fillers in Chemically Bonded Phosphate Ceramics, fly ash reduces the heat of the acid-base reaction, increases the quantity of binder in the mix by generating more binders and enhances durability and strength of the final product (Wagh 2004; Wagh 2013).

Methods

Board formation

The waste material was dried and milled with a hammer mill to pass through a 1 mm sieve screen. Milled samples were conditioned for about 72 h at 20 ^{o}C and 70% relative humidity (RH). The materials for the boards were measured out from the central composite design (CCD). The mass of water used was calculated from a modified formula used in wood cement composites as;

$$W = P + (F - M)\,2B \quad \text{Equation 1}$$

W is mass of Water in the board; P is mass of phosphate binder; F is fibre saturation point; M is moisture content of the fibre; B is mass of fibre.

The materials were mixed thoroughly by mass and water was added while stirring the composites together. The slurry was poured into a steel mould measuring 218 x 77 x 40 mm and a steel bar 27 mm thick was placed on the composite to fit into the mould. The set up was arranged in the laboratory press and a pressure of 200 KPa was applied at room temperature. After 5 minutes, the mould was removed

from the press and the composite was demoulded. The same procedure was repeated for all the replications in the experiment. The formed boards were allowed to air-cure in the laboratory for 24 h. Thereafter, they were conditioned at 20 ^{o}C and 70% RH for 96 h before testing.

Testing

Testing of the boards was carried out according to ASTM Standards (D1037-99). The properties evaluated include density, modulus of rupture (MOR), modulus of elasticity (MOE), water absorption (WA), and thickness/volume swelling (TS/VS). Samples for sorption test were cut using an angle grinder with a concrete blade into dimensions of 75 x 50 mm. The thickness of all samples used in the test was 13 ± 1.2 mm based on the set-up configuration of the steel mould.

Statistical analysis

The experiment was designed on a central composite design (CCD) using STATISTICA Software v5. In this study, two (2) variables were considered. They include the bark content from 10 - 50% of the total wood content; and the fly ash content from 10 – 50% of the total inorganic content. The binder ratio of KH_2PO_4 to MgO was kept constant at 3:1 (100 g wt.) while the wood content was also kept constant at 50 g. The CCD was used to prepare the combinations of the materials in the design. This resulted in 10 experimental runs using the standard design. A control experiment without considered variable was also carried out giving a total number of 11 board types (Table 1). Four replications of all the experiments were carried out resulting in a total of 44 experiments.

Table 1 Combinations of the experiment based on CCD

Board types	Bark content (g)	Ash content (g)	Wood and bark (g)	Water (ml)
A	5	10	55	122.7
B	5	50	55	162.7
C	25	10	75	127.3
D	25	50	75	167.3
E	0.85	30	50.85	141.7
F	29.14	30	79.14	148.2
G	15	1.72	65	116.7
H	15	58.28	65	173.2
I	15	30	65	145.0
J	15	30	65	145.0
K (Control)	0	0	50	111.5

Results and discussion

Density

The mean densities of the boards ranged from 0.98 to 1.25 g/cc. Board D with a high bark and fly ash content had the highest density of the boards. Bark is a heavy and heterogeneous material and so invariably contributes to the density of the boards. Board K had the lowest density of 0.98 g/cc. This is due to the fact that the boards did not contain bark and fly ash as it is the control.

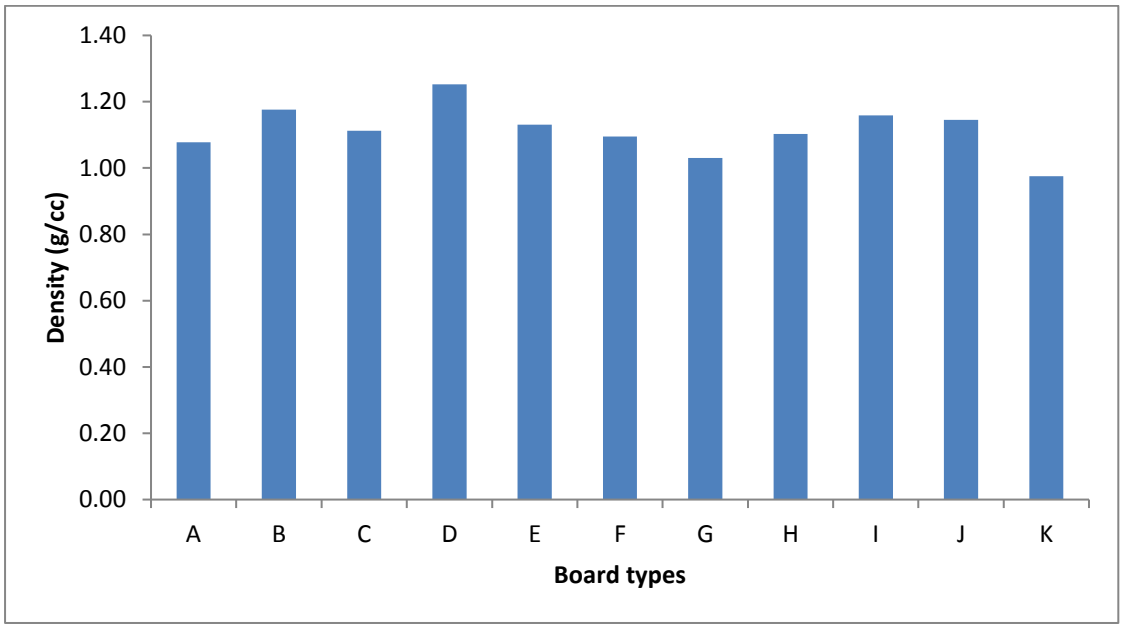

Fig. 1 Mean Density of the Boards

Modulus of Rupture (MOR)

The mean MOR of the boards is shown in the figure below. Board D had the highest MOR (7.32 MPa) possibly as a result of the high content of bark. Bark contains substances which may react with the phosphate values and lead to the formation of more bonds. This results in better bonding in the composites and hence higher density and strength properties. Since density has an important role in the mechanical response of cements and ceramics (Colorado *et al.*, 2011), it is a major determinant of the strength properties of composites. Therefore, it is expected that the denser boards have better strength properties. In a similar way, board K which has the lowest density also has the lowest MOR of 2.29 MPa.

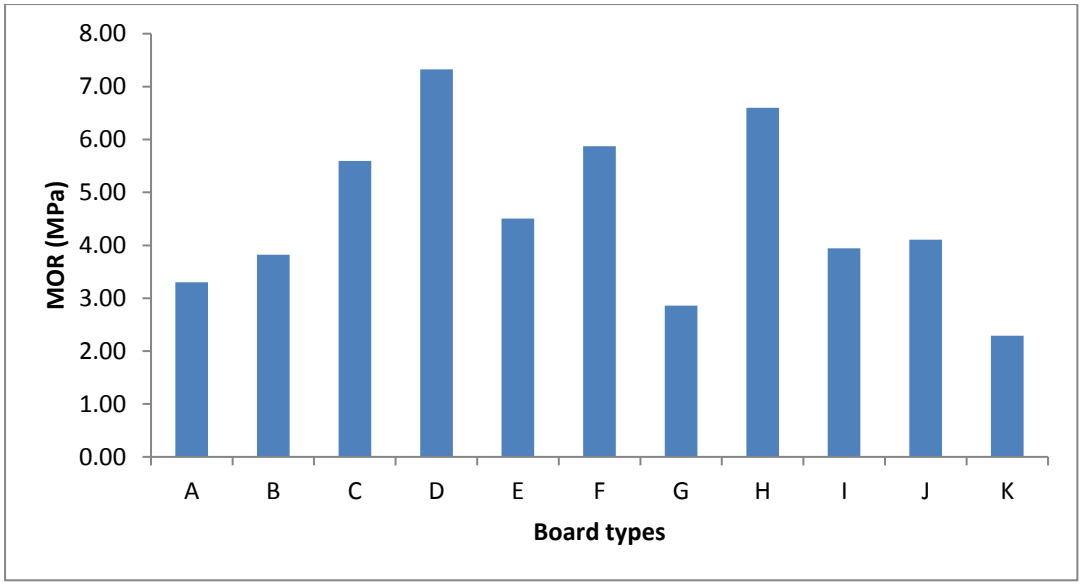

Fig. 2 Mean MOR of the Boards

Modulus of Elasticity (MOE)

The mean MOE values follow same trend with the MOR as a mechanical property. Board D had the highest mean value of 88.3 MPa while board K had the lowest mean value of 31.33 MPa. This is also due to better compaction in Board D as a result of high content of bark and fly ash. Fly ash enhances the cementing mechanism of phosphate composites (Wagh, 2013)

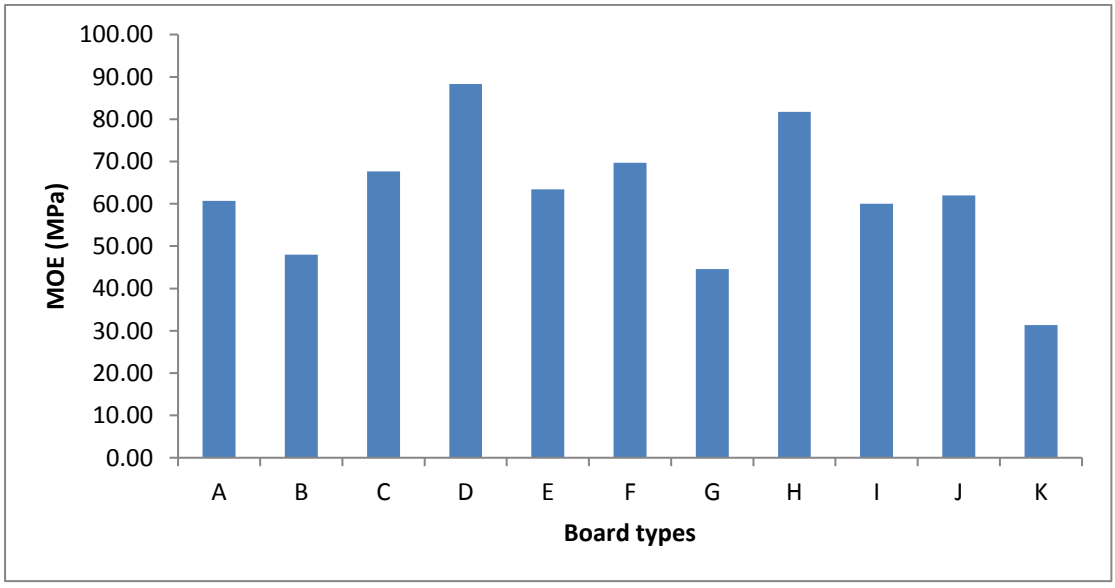

Fig. 3 Mean MOE of the Boards

Water Absorption (WA)

The mean WA of the boards varied from 14.52 – 23.48%. Board D has the lowest WA due to better compaction of the boards. Board G had the highest WA followed by the control with a mean value of 22.40%. This result suggests that bark and fly ash content play a major role in enhancing compaction and reducing moisture movement in the composites.

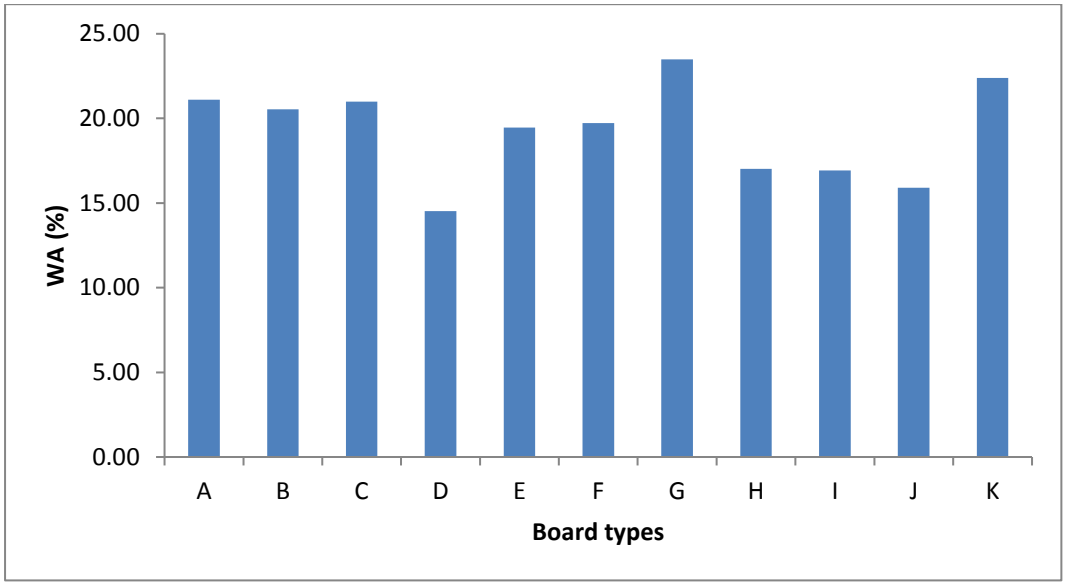

Fig. 4 Mean WA of the Boards

Thickness/Volume swelling (TS/VS)

The mean TS/VS of the boards are low ranging from 0.09 – 5.48% for TS; and 0.06 – 4.71% for VS. Board E with the lowest bark content had the highest TS and VS of all the boards followed by the control. This indicates that high bark and fly ash content enhances encapsulation of the cellulosic fibres and prevents edge and linear expansion. Board B had the lowest TS while Board J had the lowest VS of 0.09% and 0.06 respectively.

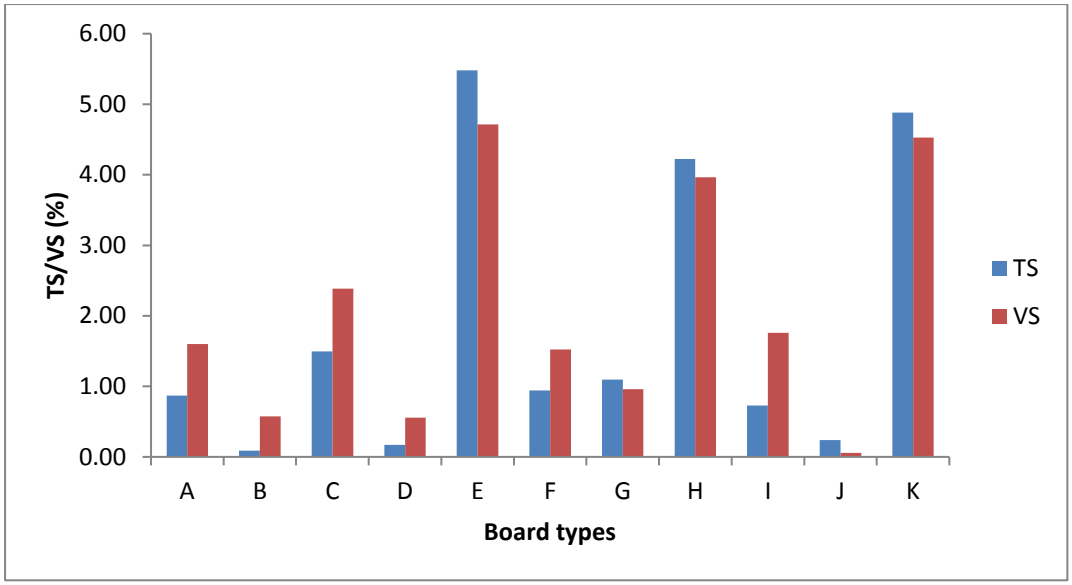

Fig. 5 Mean TS/VS of the Boards

Conclusion

From this study, it is clear that ground bark can be added to phosphate bonded wood composite to enhance its properties. A mixture of bark and fly ash in adequate amount increases all properties including density, MOR, MOE while decreasing WA, TS and VS. The best effect was obtained at 50% loading of bark and fly ash. Within the study design, addition of bark improves all the properties evaluated. The result did not show the limit to which bark can be added favorably to phosphate bonded composites. Therefore, other studies should be directed to determine the maximum limits for the addition of barks, beyond which reduction of properties if any may be encountered. The proposed product can be used for ceiling, partitioning, wall claddings and underlayment.

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CHAPTER SIX

Paper IV

Calcium phosphate bonded wood and fibre composite panels: Optimization of panel properties using response surface methodology

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Short title: Calcium phosphate bonded wood and fibre composites

Abstract

The development of phosphate bonded composite products provides a value addition approach to bio-based residues as opposed to disposal in land fill sites or incineration. These residues can be used in the manufacture of environmentally friendly light-weight and durable composite products that can compare with current Portland cement bonded products. Further, the use of the phosphate binder promises to reduce the energy requirements in the overall production process of cement based products. This study investigates the application and optimization of calcium phosphate cement; a cold-curing binder with a low carbon footprint, in the production of light-weight and durable wood and fibre composites from wood and agricultural processing residues as well as pulp mill sludge and waste paper. The specific lignocellulosic residues screened in the study include slash pine saw dust, black wattle and blue gum processing residues, sugar cane bagasse, hemp hurds, pulp mill sludge and waste paper. The manufacturing process was laid out on a central composite design using the response surface methodology to optimize the processing conditions. Physical and mechanical test were conducted on the composite products and the effect of the processing variables was evaluated using the Pareto analysis of variance. The density of the wood based panels ranged from 0.68 to 1.21 g/cm^3, the agricultural fibres ranged from 0.59 to 1.15 g/cm^3 while the paper pulp panels ranged from 0.81 to 1.21g/cm^3. The bending modulus of the panels ranged from 1.63 to 4.92 MPa for wood, 0.37 to 3.28 MPa for the agricultural fibres, and 0.65 to 3.87 MPa for paper pulp based fibres. The physical properties of the composite products met the requirements for Portland cement bonded particleboard (EN, 2007).

Keywords: Bio-based residues, central composite design, phosphate bonded composite products, response surface methodology

Introduction

In a world constantly driven by innovation, harnessing the vast quantity of waste generated globally into new-value products comes as a logical choice. According to the World Bank, the current global waste generation is about 1.3 billion ton per year, and this is expected to increase to about 2.2 billion ton per year by 2025. This represents a 40% increase in total waste generation. About 46% of this is organic waste which consists of wood and other industrial residues. It is therefore critical to develop technologies to utilize solid waste, especially those of bio-based industrial residues. Apart from the availability of valuable raw materials for bio-composite production, the industrial exploitation of these materials contributes to the protection of the environment (absorption of CO_2) and gives economic potential to developing countries (Papadopoulou et al. 2015). This study utilized lignocellulosic residues from industrial processing plants to produce calcium-phosphate bonded composite panels. The rationale for this study was the need to reduce the energy requirements of conventional cement-based manufacturing process, reduce the energy requirements in disposal of residues and provide low-cost and environmentally friendly building materials for the wood composite industry.

Since the beginning of civilization, agricultural residues such as wheat straw, leaves and stems have been used in reinforcement of clay bricks, and in recent times, both natural and synthetic fibres have been used as fillers and reinforcements in cementitious composites and polymers (Frybort et al. 2008; Kabir et al. 2012; Huang et al. 2012). In the emergence of chemically bonded phosphate ceramics (CBPCs), synthetic fibres such as carbon, glass and graphite nano-platelets reinforced calcium phosphate cement has been developed for bone tissue engineering (Canal and Ginebra, 2011) and high performance composites (Colorado et al. 2011b). Many studies on CBPCs have been focused on the use of dead burned magnesium oxide and monopotassium phosphate. Magnesium oxide has been the preferred alkali because of its moderate solubility in the acid solution when compared to calcium and iron oxides (Wagh and Jeong, 2003). Calcium oxide is highly soluble and the exothermic reaction makes large scale production of calcium phosphate ceramics virtually impossible (Wagh, 2013). However, small scale usage such as in dental cement (Chow, 2000) and in bone repair (Canal and Ginebra, 2011) may be produced. The use of setting retardants such as boric acid has been shown to improve workability to some extent at large applications in the manufacture of CBPC products (Wagh 2004; Colorado et al. 2011a; Ding et al. 2014). In order to produce calcium-based CBPCs, it is imperative to use calcium minerals that release calcium ions very slowly in the solution (Wagh, 2013). The development of phosphate bonded natural fibre composites has been limited to paper mill sludge and magnesium-based CBPC (Mg-CBPC) (NRRI 2008; Donahue and Aro 2010), probably due to the ease of handling, processing and suitability of the sludge to form hardened products with improved performance. The interfacial properties between Sugar maple (*Acer saccharum*) and magnesium phosphate cement have been studied (Chi and Englund, 2014). Laufenberg et al. (2004) demonstrated

in preliminary trials that magnesium phosphate bonded products from pine residues could be produced. Recently, Amiandamhen et al. (2016) also demonstrated that magnesium phosphate bonded products could be produced from various raw materials including slash pine, blue gum, bagasse, hemp hurds, paper mill sludge and waste paper. Despite the progress made on Mg-CBPC, the technology for calcium based phosphate bonded natural fibre composite has not yet been developed.

High temperature manufacturing, especially those of concrete and ceramic materials contributes to global warming (Colorado et al., 2011a). As a result, there has been increased drive towards low-energy manufacturing and sustainable processes for cementitious composite materials. With the emergence of CBPC materials, high value composite products have been developed that not only reduces the energy requirements of current manufacturing processes (Wagh 2004; 2016), but also possess excellent fire resistance and thermal insulation properties (Colorado et al., 2011a). Due to its low carbon footprint, the CBPC is environmentally friendly compared to cement and other inorganic bonded products. It also contains chemical elements such as potassium K and phosphorus P, therefore at its end of life; the residues from disposed products may add to soil nutrients and be beneficial to plants and aquatic life (Wagh, 2013). CBPCs have been produced from different materials involving phosphoric acid or acidic phosphate and a slightly soluble oxide or hydroxide of alkali metals (Wagh and Jeong, 2003). The acid-base reactions producing the neutral salt precipitates into a solid mass that can bond to all earth metals including concrete (Wagh, 2013). This reaction product is often referred to as a phosphate binder, and can be used as an adhesive, a surface coat or cements (Laufenberg et al., 2004). The chemical processing of the phosphate binder makes it inexpensive in high volume production and has been used to develop materials for road repairs and solar reflective roofing tiles (Wagh, 2013).

Studies on calcium phosphate cements utilizing calcium silicates are rare in literature. Wagh et al. (2003) reported that silicates and silicas, i.e. sand, are stable materials, and do not dissolve in acidic solutions, neither do they react in an aqueous environment. However, amorphous silica released from Wollastonite ($CaSiO_3$) in an aqueous solution chemically reacted with phosphate anions from Ceramicrete (magnesium-based CBPC) binder to produce a glassy phase within the structure of the ceramic (Wagh et al. 2003). Colorado et al. (2011b) fabricated a Wollastonite-based CBPC (Wo-CBPC) with Wollastonite powders and a phosphoric acid formulation. The authors reported that when the phosphoric acid formulation and the Wollastonite powder mixture was stirred, the sparsely alkaline oxide dissolved and an acid-base reaction was initiated. This hardened into a ceramic product as a result of gelation by salt formation and the dissociation of the calcium cations from the calcium silicate. The molecules form an ordered structure which grows into crystals to form CBPC (Colorado et al. 2011b). Since the reactivity of calcium oxide limits the general application of the mineral in formation of CBPCs, a probable alternative was found in this research using a very low reactive unslaked lime in the

presence of calcium silicate powder. This alternative can be used to produce calcium-based CBPCs on a large scale for composite materials. Calcium silicate dissociates in the phosphate solution as follows

$$CaSiO_3 \rightarrow Ca\ (aq)^{2+} + SiO_3^{2-} \quad [1]$$

$$KH_2PO_4 \rightarrow 2H^+ + K^+ + PO_4^{2-} \quad [2]$$

The overall equation of reaction is given as

$$CaSiO_3 + CaO + 2KH_2PO_4 + 2H_2O \rightarrow 2CaHPO_4.3H_2O + K_2SiO_3 \quad [3]$$

The formulated calcium phosphate cement, like Wo-CBPC and Magnesium-based CBPC (Mg-CBPC) can be produced at ambient conditions, but do not set rapidly unlike the latter minerals. Generally, phosphate cements, unlike Portland cement is not affected by the chemical composition of wood and other ligno-cellulosic fibres. Therefore, it is possible to incorporate natural fibres and wood processing industrial residues into the binding cement matrix to develop new products. These products show potential of competing with current wood-based composite materials in the market and promise to reduce the energy requirements in the disposal of residues, with a significant reduction in product cost and environmental footprint. Fly ash can be added to complement the properties of the basic material, as it contains SiO_2 and CaO. The addition of fly ash to CBPC has been shown to generate more binder by reacting with phosphate anions (Wagh, 2013). Fly ash also increases the strength of the composite and improves the bonding between the phosphate groups within the cement binder (Zhu and Zongjin 2005; Wagh 2016). This study describes the potential application and optimization of calcium phosphate cement produced by incorporating calcium silicate, unslaked lime and fly ash in the formulation of the CBPC. The CBPC so formulated was used to demonstrate the feasibility of producing commercially-viable composite products by employing low-cost minerals with monopotassium phosphate.

This study employed a response surface methodology (RSM) to establish optimum conditions for the manufacturing of the composite products. RSM has been used in testing multiple process factors and their interactive effects (Maran and Manikandan, 2012) and can also be used to investigate the interaction effect of process variables and build a mathematical model needed to describe the overall process (Jin et al. 2012). RSM uses experimental designs such as Box-Behnken and central composite design to fit a model by least squares technique (Ahmadi et al. 2005). The adequacy of the model is then revealed by diagnostic checking test. In this study, the effects of various processing parameters such as acid-alkali ratio, fibre and fly ash contents on the properties of composite products from natural fibres were investigated by applying RSM under a central composite design. The optimum conditions were determined to predict the maximum desirable panel properties.

Experimental

Residues

The residues utilized in this research were hemp hurds (*Cannabis sativa*) from Hemporium, a South African hemp processing company, bagasse (*Saccharum officinarum*) from TSB Sugar Ltd, slash pine (*Pinus elliottii*) from Cape Pine; a local subsidiary of the Global Environment Facility (GEF), black wattle (*Acacia mearnsii*) from EC Biomass Fuel Pellets (Pty) Ltd, blue gum (*Eucalyptus globulus*) also from EC Biomass, paper mill sludge from MPact Ltd; a Southern African paper and plastic packaging company, and office waste paper collected within the University of Stellenbosch.

Unslaked lime (Calcium oxide)

The metal oxide used was unslaked lime purchased from Bontebok Lime Works (Pty) Ltd, Bredasdorp, South Africa. It has the following composition; assay 70-88% Ca as CaO, CO_2 1.5%, phosphorus as P_2O_5 <0.01, specific gravity 3.37, pH 12.5, bulk density 1.1-1.3 g/cm^3 and vapour density 1.9. It is used as protective wall coatings.

Calcium silicate

The calcium silicate used was Microcal ET purchased from PQ Corporation, Warrington, UK. It has the following composition: assay >87% SiO_2 basis, 12-22% CaO, <7.0% loss on drying, particle size 7.0-10.0 µm, pH 9.5-11.5, and density 2.9 g/ml. It is used as an absorbent, antacid, filter for paper and paper coatings, food additive (anticaking agents) and manufacture of glass.

Monopotassium phosphate

Monopotassium phosphate is commonly used as plant fertilizer and as a food ingredient (salt). For this study, MKP 0-52-34, a white crystalline product was purchased from Shijiazhuang Lvhe Fertilizer Technologies Co. Ltd, China. It had the following composition: KH_2PO_4 >98%; P_2O_5 >51.2%; K_2O >33.5%; chloride <0.2%; water insoluble <0.2%; moisture <1.0% and pH 4.3-4.7. Wagh (2004) reports that acid phosphates with a P_2O_5 content of 50-60% may be suitable for the production of chemically bonded phosphate ceramics.

Fly ash

The fly ash was supplied by Ulula Ash, South Africa. The product complies to the SANS 50450-1:2011 class S specification and is approved by South African Bureau of Standards (SABS). Class S fly ash (SFA) is an ultra-fine, powdery residue obtained from coal fired Ulula Ash Kriel power plant. It is of structural concrete grade, finer than cement and used as a partial replacement for cement

(www.ululaflyash.com). In this study, the fly ash was used as a complement to the basic material. It had the following composition: SiO_2 <60%; Al_2O_3 <35%; CaO <10%; MgO <5%; Fe_2O_3 <5%; TiO_2 <5%.

Material preparation

The slash pine planer shavings, black wattle and blue gum residues, hemp hurds and the dried crushed sugarcane bagasse were milled using a hammer mill fitted with a 1 mm sieving slice. The resultant particles were conditioned at 20ºC and 65% relative humidity (RH) for 96 h. The equilibrium moisture content of the materials was determined as 7%. The dried paper mill sludge was soaked in water for 1 h while the waste paper was soaked for 12 h. The wet paper was shredded in a Pulper and both paper fibres were dewatered using a spin dryer. The paper fibres were oven dried at 60ºC for 24 h and subsequently conditioned for 96 h at 20ºC and 65% RH.

Panel fabrication

The prepared materials were used in the fabrication of the panels. The materials were measured according to a central composite design (CCD). A pre-determined quantity of water was added in each run and the mixture was stirred thoroughly in a planetary style. The paste was poured into a steel mould measuring 218 x 77 x 40 mm and a steel bar with a thickness of 27 mm was placed on the slurry to compress the panels to a final thickness of 13 mm. The purpose of the steel bar was to remove entrapped air and squeeze out excess free water in the composite. This process minimizes the formation of voids in the panels. The set-up was transferred to the laboratory press and a pressure of 300 KPa was applied for 10 minutes at room temperature. Thereafter, the mould was removed from the press and the panel was de-moulded. The formed panels were dried in ambient temperature for 14 days. A drying plateau of 13 days has been established from previous experiments. Thereafter, they were conditioned at 20ºC and 65% RH for 96 h before testing.

Testing

The properties of the formed panels were evaluated to investigate the effect of binder formula, fibre content and fly ash content on the density, flexural strength and dimensional stability of the composites. Flexural test specimens were tested according to ASTM D1037-06a using an Instron testing machine fitted with a 5 KN load cell, operated at a rate of 5 mm/min. The specimens were tested to failure and the modulus of rupture (MOR) and apparent modulus of elasticity (MOE) were calculated from the formula outlined in ASTM (2006).

Water absorption (WA) characteristics and thickness swelling (TS) tests were carried out by submerging conditioned specimens horizontally in fresh water for 24 h. After submersion, the specimens were suspended to drain for 10 min and excess water was removed from the surface. The specimens were weighed and the thickness was determined as an average of four measurements. The

WA of the specimen was calculated from the increase in weight and expressed as a percentage of the conditioned weight, while the TS was calculated as a percentage of the conditioned thickness.

Experimental design

The design consists of four variable factors namely binder ratio (which is the ratio of the monopotassium phosphate (KH_2PO_4) to the total basic components of calcium oxide and calcium silicate ($CaO+CaSiO_3$)), calcium oxide/calcium silicate ratio ($CaO/CaSiO_3$), binder/fibre ratio, and fly ash as a percentage of the total binder content. This design was maintained for each wood/fibre material. The variable factors were laid out on a central composite design (CCD) and were represented as x_1, x_2, x_3 and x_4. The variables were coded at three levels -1, 0 and 1 representing the low, middle and high level (Table 1). The selection of the variable levels was based on the results obtained from previous experiments.

The number of experiments (N) required for the development of the CCD is defined by the relationship outlined by Ahmadi et al (2005) as

$$N = 2^{k-p} + 2k + C_p \quad [4]$$

(Where k is the number of factors, C_p is the number of centre points, and fractionalization element p = 0 for a full design). In this study, the design included 26 experiments and 2 centre points (used to determine the experimental error). The RSM was used to establish a statistical relationship between experimental variables and responses. This was then used to predict the optimum experimental conditions for achieving optimum performance.

Statistical analysis

The statistical analysis was performed using the STATISTICA software (version 5). The data was analysed by the analysis of variance procedure (ANOVA) to determine the variable(s) that are significant on the board properties. The overall contribution of each variable on the panel property was studied using Pareto analysis. Regression analysis was used to test the adequacy and fitness of the developed polynomial models.

Results and Discussions

Panel properties

The physical and mechanical properties of the panels are presented in Table 2.

ANSI (1999) classified particleboard between 0.64 – 0.8 g/cm^3 as medium density panels and above 0.8 g/cm^3 as high density panels. In the wood panels, the density generally ranged from 0.68 – 1.21

g/cm^3. The fibre panels ranged from 0.59 – 1.15 g/cm^3 while the paper boards were high density panels. In material development, the density is important as it influences other fundamental properties including strength of the material. The ability of a material to withstand deformation stresses in bending and tension is required in certain applications. The MOR and MOE, which are the bending modulus and tensile elasticity obtained in this study, were not adequate compared to the requirements of ordinary Portland cement bonded particleboards but compared favourably with the requirements for low density grade 1 and 2 particleboards bonded with formaldehyde resin system (ANSI, 1999). The bending MOR and static MOE of Portland cement bonded particleboards with a density of 1g/cm^3 is 9 MPa and 14.5 GPa respectively (EN, 2007). As a result, the general application of the panels may be restricted to non-load bearing applications.

The WA of the panels after a 24 h submersion in water varied considerably, but was generally lower in the paperboards (19.67 – 39.84% for paper sludge boards and 15.73 – 51.83% for wastepaper boards). The wood panels have WA of 17.21 - 64.82 for black wattle and 21.92 – 52.71 for blue gum panels. These values were generally within the requirements of WA in particleboards (IS 1985-50%; EN 2007-25%). TS, which is the change in thickness of the panels after 24 h submersion in water met the minimum requirements for Portland cement bonded particleboards for use in dry, humid and external conditions (1.5% EN, 2007).

Effect of processing variables on the properties of the composite panels

The effect of the processing variables on the panel properties was analysed using the ANOVA. RSM was used to show the factor interactions in the composite panels on a 3D response plot, and model the relationship between the experimental variables and the predicted result. The RSM plot showed the experimental units of two predictor variables in two axes (x, y) and fixed units of other variables on the surface plot. The response variable is the z-axis. The Pareto analysis showed the overall contribution of each variable and interactions on the properties evaluated. It also shows the variables and intersections that were significant ($p < 0.05$). The variables were presented as KH_2PO4/ ($CaO+CaSiO_3$) (1), $CaO/CaSiO_3$ (2), binder/fibre (3) and fly ash content (4), and were expressed in both linear and quadratic terms (L, Q). The Pareto analysis is a statistical technique useful in decision making to select a limited number of variables that produce significant overall effect (Haughey, 2015).

Fig. 1a shows the density of the wood panels. It is evident from the RSM that the density increases as the ratio of the binder to the fibre content increases. The density of the panels also increases as the binder ratio of acid phosphate to the alkali oxide increases. This is similar to the observations by Donahue and Aro (2010) and Wagh (2013). The Pareto analysis shows that the binder/fibre ratio is the most significant variable that influences the density of the wood panels (Fig. 1b). However, the WA of the wood panels depends largely on the binder ratio and not the binder/fibre ratio (Fig. 2b). It was

observed that high $CaO/CaSiO_3$ increases the WA of the panels (Fig. 2a). As the binder ratio increases, the proportion of the phosphate ions increases and are able to form stronger bonds with the alkali metals (Wagh 2004; 2016). This encapsulates the wood in the composites and reduces water absorption.

In bagasse panels, high binder content positively influenced the density, which increases the strength of the panels (Figures 3a and 4a). The analysis shows that the binder/fibre interaction has the most significant contribution to the density of the panels (Fig. 3b). However, the binder ratio has the most significant effect on the MOE (Fig. 4b). This pattern of relationship was also observed for the wood and paper panels. Fig 4a shows that increasing fly ash and the alkali components have a combined negative effect on the MOE. This is probably due to the proportions of unreacted alkali from the calcium minerals and fly ash, which affects the stiffness of the panels. At increasing binder ratio and fibre content, the bending modulus and stiffness of the materials are improved. Amiandamhen et al. (2016) reported that the stiffness of paper panels is a function of the amount of binder and fibre in the panels. High binder content with low fly ash results in better compaction between fibres and improved strength (Donahue and Aro, 2010).

Fig.5a shows the response surface between fly ash content and $CaO/CaSiO_3$ ratio, at a binder ratio of 6:1 and binder/fibre ratio of 2.5:1. The MOR increases as the fly ash content increases to about 25% of the total binder content, and then decreases with further fly ash addition. However, Donahue and Aro (2010) reported that a fly ash content of 40-45% is beneficial for increasing MOR of paper sludge boards produced with a magnesium phosphate cement binder. With a calcium-based phosphate cement binder, low ratio of $CaO/CaSiO_3$ gave better bonding with the phosphate mineral, hence higher MOR. In paper sludge panels, as with the waste paper panels, the binder ratio had the most significant effect on the MOR of the panels (5b). Donahue and Aro (2010) and Amiandamhen et al. (2016) also reported positive correlation between high binder content and MOR of paper sludge panels. In a similar way, the binder ratio was the most significant determinant on the TS of the paper panels (Fig. 6b). As binder ratio increases, with increasing binder/fibre ratio, the TS of the paper panel decreases as seen in Fig. 6a.

Desirability profile and optimization

The optimum conditions for predicting the properties in the manufacturing of composite products from wood and agricultural residues were determined from the desirability profiler available in STATISTICA software (v5). As explained by Maran and Manikandan (2012), the desirability function searches for factor combination levels that jointly optimize a set of responses by satisfying each response requirements in the design. The scale of the desirability function ranges between 0 (completely non-desirable) and 1 (fully desired response) (Gonzalez et al. 2007). Individual desirability is obtained by specifying the goals for each response. A weight factor, which defines the shape of the desirability

function for each response is assigned, and is usually between 0.1 and 10. A weight factor of 1 was selected for the purpose of this study.

In order to optimize the processing conditions for manufacturing composite products, profiles of predicted values and desirability were established. Processing variables were set to maximum desirability. In numerical optimization, the desired value is preferred for each variable and response. The possible values are usually within range for the independent variables and maximum for the response variable (Maran and Manikandan, 2012). By applying the methodology of the desired function, the optimum levels of the variables were obtained and are presented in Tables 3-5 for selected materials.

Fitting of regression models

The behaviour of the response surface plot was investigated for the response function (y) using the second-order polynomial multiple regression equation

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{44} x_4^2 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{14} x_1 x_4 + \beta_{23} x_2 x_3 + \beta_{24} x_2 x_4 + \beta_{34} x_3 x_4 \quad [5]$$

Where β_0 is the intercept, (β_1, β_2, β_3, β_4) are linear coefficients, (β_{12}, β_{13}, β_{14}, β_{23}, β_{24}, β_{34}) are interactions, (β_{11}, β_{22}, β_{33}, β_{44}) are quadratic coefficients, (x_1, x_2, x_3, x_4) are coded variables.

Significant models were established to estimate each panel property as influenced by the independent variables. The final equations obtained in terms of coded factors are presented for selected properties and materials

$$\text{MOR (black wattle)} = 2.34 + 0.73x_1 - 0.03x_2 + 0.73x_3 + 0.16x_4 - 0.18x_1^2 + 0.20x_2^2 + 0.26x_3^3 + 0.01x_4^4 - 0.02x_1x_2 + 0.01x_1x_3 + 0.01x_1x_4 - 0.01x_2x_3 + 0.06x_2x_4 + 0.03x_3x_4 \quad [6]$$

$$\text{Density (bagasse)} = 0.84 + 0.02x_1 + 0.0007x_2 + 0.09x_3 - 0.01x_4 - 0.01x_1^2 - 0.003x_2^2 - 0.02x_3^3 - 0.01x_4^4 - 0.001x_1x_2 - 0.02x_1x_3 - 0.01x_1x_4 + 0.01x_2x_3 + 0.15x_2x_4 - 0.01x_3x_4 \quad [7]$$

$$\text{TS (paper sludge)} = 1.46 - 1.15x_1 - 0.04x_2 - 0.39x_3 - 0.54x_4 + 0.34x_1^2 - 0.19x_2^2 + 0.61x_1^3\, 0.69x_1^4 + 0.19x_1x_2 - 0.30x_1x_3 - 0.23x_1x_4 - 0.76x_2x_3 - 0.42x_2x_4 + 0.21x_3x_4 \quad [8]$$

The adequacy and fitness of the models were tested by regression analysis. The analysis showed a high precision of the model. For equations [6-8], the coefficient of determination (R^2) was 0.951, 0.998 and 0.994 respectively. R^2 explains the proportion of the total variation in the response predicted by the model (Ghafari et al. 2009). A high R^2 coefficient ensures a satisfactory adjustment of the quadratic model to the experimental data (Maran and Manikandan, 2012). In bagasse panels, the values of R^2 were calculated as 0.964, 0.961 and 0.948 for MOR, MOE and TS respectively. The adjusted-R^2 value

(0.795 for MOR, 0.781 for MOE and 0.705 for TS) corrects the R^2 value for the sample size and explains the correlation between the observed and predicted values. Similar results were observed for black wattle, blue gum, slash pine and paper sludge panels. The high degree of fitting between the observed and predicted data reflects the accuracy and applicability of the quadratic model in the optimization process (Zhao et al., 2008). However, the suitability of the developed quadratic model is valid within the specified range of process parameters as explained by Maran and Manikandan (2012).

The coefficients from the analysis of variance are presented in Tables 6-8. The coefficients, expressed in both linear and quadratic terms were used in the regression models. The *p*-values (in parenthesis) are also presented in the tables. *P*-value is the probability of obtaining a result equal to or more extreme than the observed data (Hubbard, 2004). A low *p*-value ($p < 0.05$) and high R^2 indicate that the model is significant and represents the actual relationship between the independent and the response variables. The main effects and interactions that are significant are identified with an asterisk (*).

Conclusions

The variables considered in this study i.e. calcium oxide/calcium silicate ratio ($CaO/CaSiO_3$), binder ratio (which is the ratio of the monopotassium phosphate (KH2PO4) to the total basic components of calcium oxide and calcium silicate ($CaO+CaSiO_3$)), binder/fibre ratio, and fly ash as a percentage of the total binder content had significant effects on the properties evaluated ($p < 0.05$). The binder ratio had the greatest influence on the panel properties. The relationship between the variables was studied and the optimum variable levels were determined to predict panel properties. The physical properties of the proposed products met the minimum requirements for dry and humid conditions according to EN [12]. The achieved strength properties of the panels are adequate for such applications as wall finishes, ceilings and partitions. A market and product development concept will need to be considered to evaluate the potential of these products in the target market. The utilization of industrial residues in composite products promises to reduce the energy requirements of disposal, reduce the dependence on virgin fibres, protection of the environment and brings economic potential to developing countries. The development of an environmentally friendly calcium phosphate binder can also help to reduce the carbon footprint of current composite product making process. To our best knowledge, calcium phosphate cement has not been experimented in large scale productions involving lignocellulosic fibres.

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Table 1

Independent variables and their levels used for the CCD

Variable	Factors		Coded levels	
		Low (-1)	Medium (0)	High (1)
KH_2PO4/ ($CaO+CaSiO_3$)	x_1	2	6	10
$CaO/CaSiO_3$	x_2	2	6	10
Binder/fibre	x_3	2	2.5	3
Fly ash (%)	x_4	10	20	30

Table 2

Panel properties

		Properties			
Panels	Density (g/cm^3)	MOR (MPa)	MOE (MPa)	WA (%)	TS (%)
Black wattle	0.7-1.15	0.73-4.15	2.65-8.71	17.21-64.82	0.54-5.88
Blue gum	0.68-1.21	0.52-4.01	4.28-10.43	21.92-52.71	0.47-6.17
Slash pine	0.75-1.19	1.63-4.92	4.72-8.92	19.26-44.39	0.9-3.94
Hemp hurds	0.59-1.15	0.79-3.28	2.81-5.63	25.9-65.81	0.94-6.45
Bagasse	0.63-0.92	0.37-3.07	2.05-5.95	27.84-69.83	2.59-7.47
Papermill sludge	0.81-1.21	0.65-2.58	2.19-4.72	19.67-39.84	0.72-5.32
Office waste	0.84-1.21	0.56-3.87	1.19-4.72	15.73-51.83	0.18-4.82

Table 3

Profiles for predicted values and desirability at optimum levels for black wattle panels

	Opt. value	Opt. value	Opt. value	Opt. value	Opt. value
Factors	Density	MOR	MOE	WA	TS
KH_2PO_4/(CaO/$CaSiO_3$)	8.73	8.73	8.73	8.73	8.73
CaO/$CaSiO_3$	11.11	11.11	11.11	11.11	11.11
Binder/fibre	3.34	3.34	3.34	3.34	3.34
Fly ash content	34.29	34.29	34.29	34.29	34.29
Predicted value	1.23 g/cm^3	5.6 MPa	10.96 GPa	10.24%	1.34%
Observed value	1.15 g/cm^3	4.15 MPa	8.71 GPa	17.21%	0.54%

Table 4

Profiles for predicted values and desirability at optimum levels for bagasse panels

	Opt. value	Opt. value	Opt. value	Opt. value	Opt. value
Factors	Density	MOR	MOE	WA	TS
KH_2PO_4/(CaO/$CaSiO_3$)	11.29	11.29	11.29	11,29	11.29
CaO/$CaSiO_3$	9.88	9.88	9.88	9.88	9.88
Binder/fibre	3.26	3.26	3.26	3.26	3.26
Fly ash content	19.29	19.29	19.29	19.29	19.29
Predicted value	0.94 g/cm^3	3.20 MPa	5.75 GPa	21.29%	2.00%
Observed value	0.92 g/cm^3	3.07 MPa	5.95 GPa	27.84%	2.59%

Table 5

Profiles for predicted values and desirability at optimum levels for paper sludge panels

Factors	Opt. value Density	Opt. value MOR	Opt. value MOE	Opt. value WA	Opt. value TS
$KH_2PO_4/(CaO/CaSiO_3)$	9.88	8.90	8.90	8.90	8.90
$CaO/CaSiO_3$	10.41	11.3	11.3	11.3	11.3
Binder/fibre	3.10	3.24	3.24	3.24	3.24
Fly ash content	16.36	33.85	33.85	33.85	33.85
Predicted value	1.22 g/cm^3	2,63 MPa	4.50 GPa	5.38%	0.45%
Observed value	1.21 g/cm^3	2.58 MPa	4.72 GPa	19.67%	0.72%

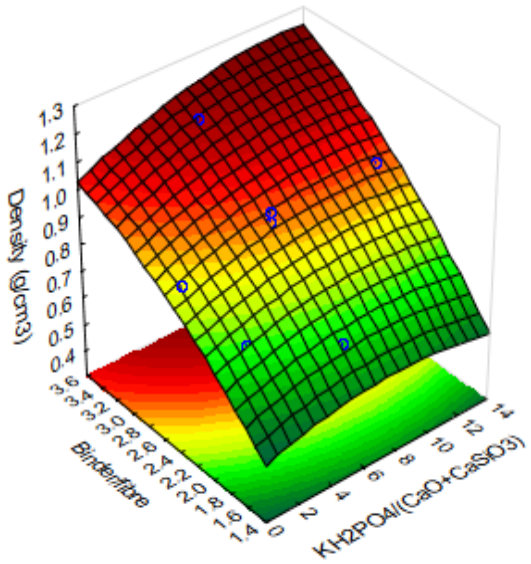

Fig. 1a Response surface plot for density

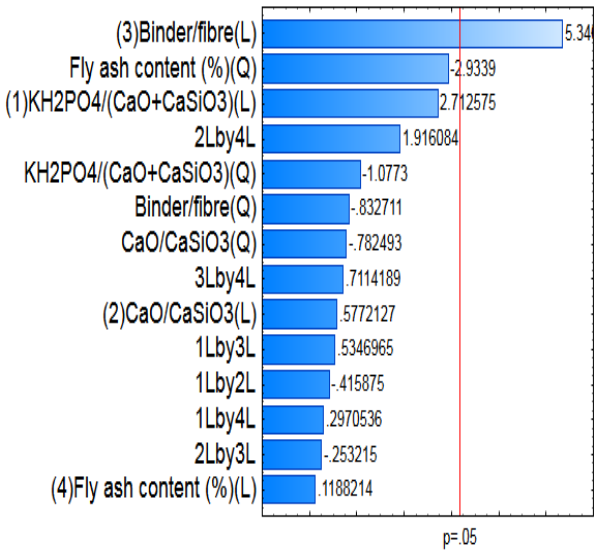

Fig. 1b Pareto chart for density

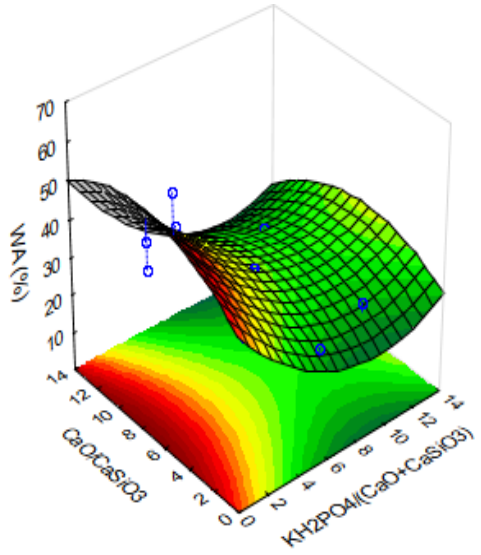

Fig. 2a Response surface plot for WA

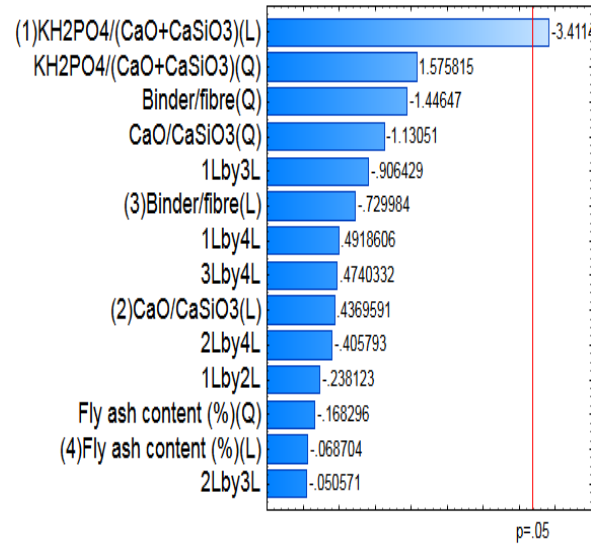

Fig. 2b Pareto chart for WA

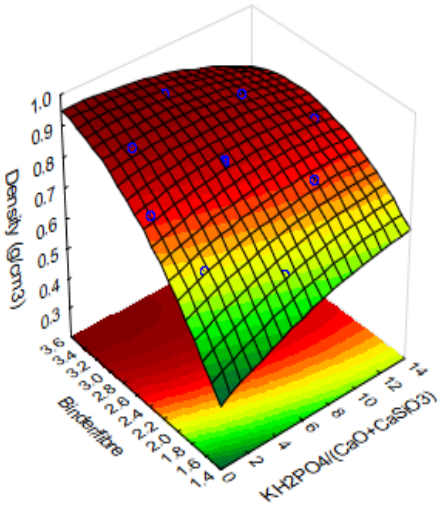

Fig. 3a Response surface plot for density

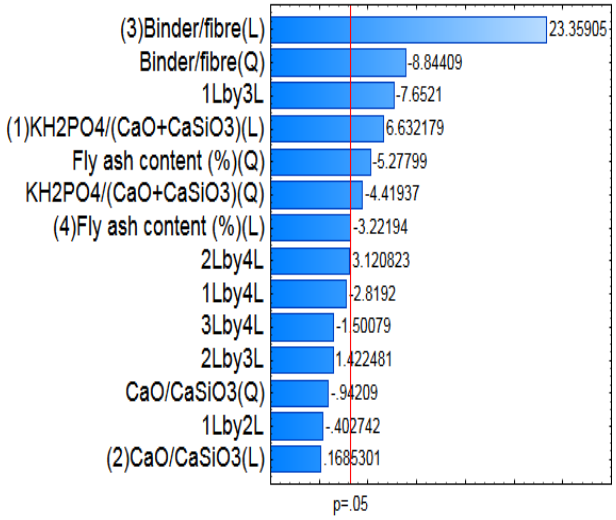

Fig. 3b Pareto chart for density

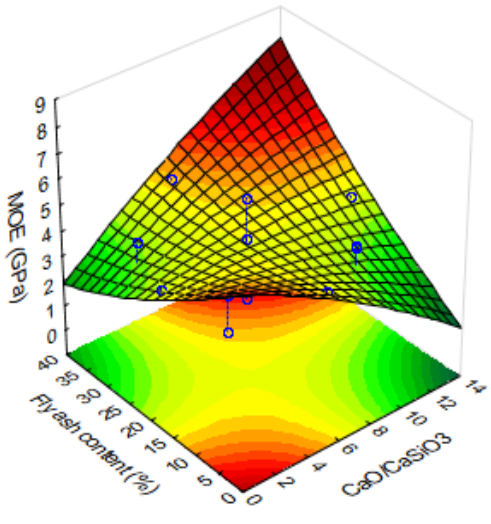

Fig. 4a Response surface plot for MOE

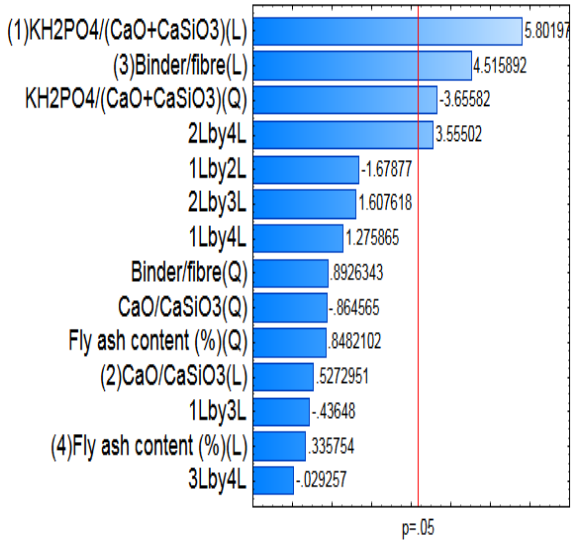

Fig. 4b Pareto chart for MOE

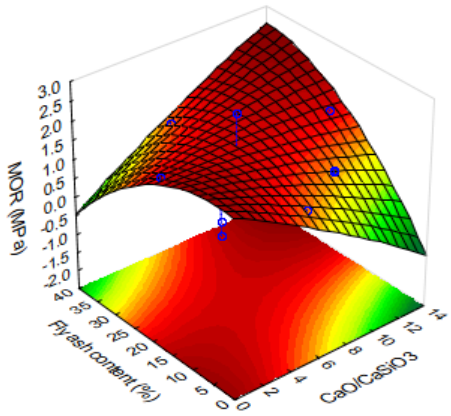

Fig. 5a Response surface plot for MOR

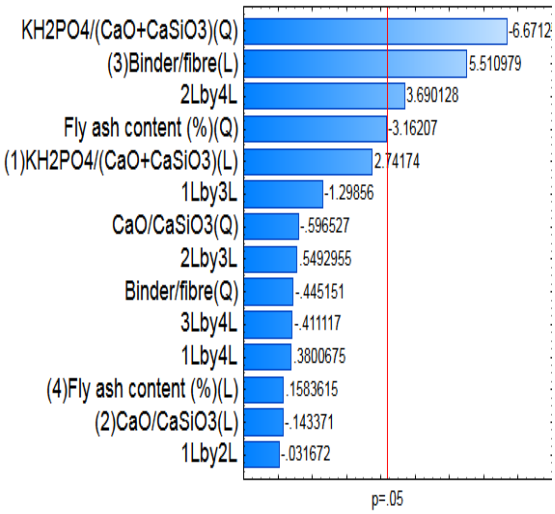

Fig. 5b Pareto chart for MOR

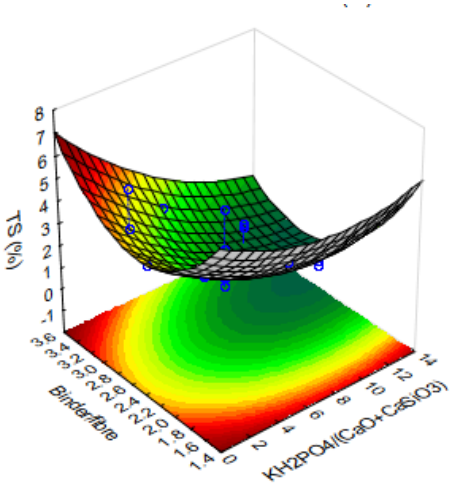

Fig. 6a Response surface plot for TS

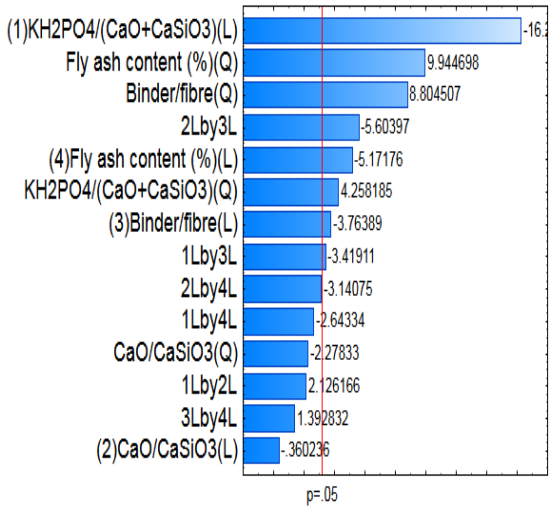

Fig. 6b Pareto chart for TS

CHAPTER SEVEN

Paper V

Surface treatments of natural fibres and their effects on the properties of phosphate bonded composite products

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Abstract

Phosphate bonded composites are an emerging class of building materials produced from natural fibres and phosphate based cement pastes. They are durable and possess mechanical strength properties similar to those offered by Portland cement. They have a low environmental impact as they are prepared at room temperature and are derived from bio-based residues. However, despite the aforementioned desirable attributes, the moisture absorption of natural fibre can lead to swelling and the formation of voids which may result in the reduction of the mechanical strength properties and negatively affect the eventual long term performance and dimensional stability of the products. This study was aimed at the modification through pre-treatment of initial properties of some bio-based residues used as raw materials in order to enhance the final properties of the phosphate bonded composite product. Three different treatments were evaluated viz. 1% caustic alkali, 1% acetic anhydride and hot water on natural fibres derived from slash pine, black wattle and bagasse. The effect of the treatment on the fibres was evaluated via HPLC, SEM and FTIR. Further, the performance of the treated fibres was evaluated in composite panels bonded with magnesium phosphate and calcium phosphate cement pastes against the controls. The manufactured panels were tested for flexural properties and dimensional stability. In untreated panels, the mean density was 0.76, 078 and 0.75 g/cm^3, while in alkalized panels, the mean density was 0.81, 0.81 and 0.81 g/cm^3 for wattle, pine and bagasse panels respectively. In the bagasse panels, the water absorption was 54.61% for untreated, 48.74% for hot water extracted, 42.21% for acetylated and 36.44% for alkalized panels. This represents a percentage improvement of 11%, 23% and 33% respectively. Alkali treated fibres had the best effect overall for all measured properties.

Keywords: Composites, dimensional stability**,** flexural strength, natural fibres, phosphate cements, treatment

Introduction

Lignocellulosic natural fibres have the potential to be used as replacements for traditional reinforcement materials in composites because of their stiffness, impact resistance and flexibility (Sgriccia et al., 2008). In addition, natural fibres are renewable and biodegradable, and possess several other desirable properties such as high tensile strength and modulus of elasticity, which are currently being exploited in many fields of composite technologies including biocomposites and nanocomposites. The wide spread availability and low cost are some of the factors responsible for the renewed interest and research on natural fibres for use in composite manufacturing. Apart from the availability of valuable raw materials for biocomposite production, the industrial exploitation of these materials contributes to the protection of the environment (absorption of CO_2) and gives economic potential to developing countries (Papadopoulou et al., 2015).

The manufacturing of chemically bonded phosphate composite products relies on the reaction between an alkali metal oxide and a weak acidic phosphate to form a sparingly soluble salt (Wagh, 2004). This reaction is highly exothermic and sets into a solid mass within minutes with a high early strength. However, the behaviour and strength development of the composites is likely to be affected with the addition of natural fibres. As with concrete and other cementitious composites, the major limitations to the use of natural fibres in chemically bonded composites include the sensitivity to moisture and variable fibre properties, coupled with the inherent incompatibility between the hydrophilic fibres and the hydrophobic matrix. The hydrophilicity of natural fibres results in high moisture absorption and weak adhesion with hydrophobic matrices. These limitations result in inadequate fibre distribution in the matrix and subsequently poor stress transfer from the matrix to the fibres (Hajiha et al., 2014). Hence, the ultimate strength of phosphate bonded natural fibre composites is a fraction of the strength of the pure matrix. The mechanical properties of biocomposites depend largely on the interfacial bonding between the fibres and the matrix.

Natural fibres can be modified to reduce the amount of hydrophilic hydroxyl groups and improve the adhesion to matrix materials (Kabir et al., 2011; Hajiha et al., 2014). There are different physical and chemical treatment methods that have been employed to modify the surfaces of natural fibres. Surface fibrillation, cold plasma treatment and electric discharge method, for example, are physical treatments that can alter the surface properties of fibres and enhance mechanical bonding between fibres and matrix (Mohanty et al., 2005; Abdelmouleh et al., 2007). Chemical treatment of fibres is widely used to reduce the hydrophilic properties of natural fibres and improve compatibility with the matrix. Several chemical treatments including alkalization, acetylation, salinization, benzoylation and peroxidation have been applied to modify the surfaces of natural fibres and improve their properties.

Amiandamhen et al. (2016) has recently for the first time optimised the manufacturing conditions for phosphate bonded composite products. While the physical properties of the boards produced met the minimum requirements for cement bonded particleboards according to EN 634-2 (2007), some properties such as the bending strength could still be improved to offer more flexibility in terms of application of the products. The current study investigated the effects of three treatments, viz. caustic alkali, acetic anhydride and hot water treatment of natural fibres on the properties of phosphate bonded composite products. In general, alkaline treatment changes the orientation of crystalline cellulose and forms amorphous regions by swelling the fibre cell wall. It also reduces the lignin and hemicelluloses content, as well as volatile products through the rupture of alkali sensitive hydrogen bonds (Li et al., 2007). This combined effect partially removes the hydrophilic hydroxyl group (Equation 1) and improves moisture resistance (Kabir et al., 2011).

$$\text{Fibre} - \text{OH} + \text{NaOH} \rightarrow \text{Fibre} - \text{O} - \text{Na} + \text{H}_2\text{O} \quad [1]$$

In addition, the stress transfer capacity between fibre cells improves due to the improved fibre-matrix interfacial adhesion.

Acetylation, which is generally known as an esterification method is used to stabilize the cell walls against moisture absorption by plasticising the cellulose fibres. Fibres may be acetylated with or without an acid catalyst to graft acetyl group onto the cellulose structure (Kabir et al., 2011). The acetyl group replaces the hydroxyl group (Equation 2) resulting in improved dimensional stability of the composites. Esterification also causes cellulosic fibres to be more compatible with hydrophobic matrices.

$$\text{Fibre} - \text{OH} + \text{CH}_3 - \text{C}\,(=\text{O}) - \text{O} - \text{C}\,(=\text{O}) - \text{CH}_3 \rightarrow \text{Fibre} - \text{O} - \text{C}\,(=\text{O}) - \text{CH}_3 + \text{CH}_3\text{C}\,(=\text{O}) - \text{OH} \quad [2]$$

Hot water hydrolysis remains the oldest and cheapest method of fibre treatment. Hot water extraction is an autocatalytic thermochemical process for the fractionation of easily accessible sugars in natural fibres (Pelaez-Samaniego et al., 2014). Hot water hydrolysis depolymerizes hemicellulose into monomers and oligomers with partial depolymerisation of cellulose and lignin (Garrote et al., 1999). Lignin may also be subjected to partial solubilisation and plasticization (Pelaez-Samaniego et al., 2013). These reactions alter the chemical composition and properties of the fibres. Thus, the treated fibres have improved properties for composite manufacturing in terms of lower water affinity and better dimensional stability (Boonstra et al., 2006).

2. Experimental

2.1 Materials

Dried industrial crushed sugarcane bagasse (*Saccharum officinarum*) supplied by TSB Sugar Ltd, South Africa, black wattle (*Acacia mearnsii*) supplied by EC Biomass Fuel Pellets (Pty) Ltd, Port Elizabeth, and slash pine (*Pinus elliottii*) supplied by Cape Pine; a local subsidiary of the Global Environment Facility (GEF), were used as the fibre raw materials in this study. Analytical grade NaOH (98% purity), acetic anhydride (98% purity), acetic acid (99% purity) and sulphuric acid (98% purity) were used in the treatment of the fibres. The composite binding matrix was prepared from monopotassium phosphate (MKP 0-52-34), a white crystalline product with > 98% assay. This product was purchased from Shijiazhuang Lvhe Fertilizer Technologies Co. Ltd, China. The study also utilized MAGOXBPPO, a heavy magnesium oxide with 96% minimum assay, purchased from Macco Organiques, Zahradnl, Czech Republic. The unslaked lime was purchased from Bontebok Lime Works (Pty) Ltd, Bredasdorp, South Africa, and it has a minimum assay of 70-88% Ca as CaO. The calcium silicate used was Microcal ET purchased from PQ Corporation, Warrington, UK. It has an assay of >87% SiO_2 basis and 12-22% CaO.

2.2 Fibre treatments

The fibres were treated with hot water and solutions of NaOH and acetic anhydride using a solid/liquid ratio of 1/10 (g/mL). All the treatments were carried out in a 5 L stainless steel laboratory size pulp digester, and the predetermined temperature settings were controlled by a proportional integral derivative (PID) system (Beckermann and Pickering, 2008). Fibres treated with hot water were heated to a temperature of 100 ^{o}C for 1 h as described by Ferraz et al. (2016). Alkalization was carried out at 60 ^{o}C for 1 h according to a method described by Oladele et al. (2015). According to this method, a 0.25 M NaOH solution (1% wt.) was prepared to treat the fibres. The treatment was meant to be less severe than actual de-lignification in alkaline pulping process. Fibres treated with acetic anhydride were heated to a maximum temperature of 90 ^{o}C for 1 h as described by Bledzki et al. (2008). Acetylation was carried out using a 1% wt. solution of acetic anhydride with 0.1% wt. sulphuric acid as buffer. The ester was prepared from a 1:1.5 ratio of acetic anhydride to acetic acid (Hajiha et al., 2014). After each treatment, the fibres were washed with distilled water until neutral pH was reached. Thereafter the treated fibres were dewatered using a spin dryer. The wet fibres were oven dried at 60 ^{o}C for 24 h and then conditioned at 20 ^{o}C and 65% relative humidity (RH) for 72 h. Subsequently, the fibres were weighed to determine the fibre yield from each treatment.

2.3 Chemical analyses of the fibres after treatment

The aim of the study was to modify the fibres to improve the eventual properties of the board products. The effect of treatment on the chemical composition and yield of the fibres was determined through chemical analysis of treated fibres in comparison to the controls. The ash content was determined according to TAPPI T211 (2004) by heating 2.0 g of oven-dried material at 525 ^{o}C for 3 h after which the residue was weighed. The acid-insoluble lignin was determined according to the National Renewable Energy Laboratory (NREL) Analytical Procedure (LAP 013) (Sluiter et al., 2012). According to this method, 3 ml of 72% sulphuric acid was added to 0.3 g of material in a test tube, stirred and placed in a water bath at 30 ^{o}C for 1 h. The material was washed with 84 ml distilled water into a flask to dilute the acid concentration to 4%. The solution was then heated in an autoclave for 90 minutes. The sample was transferred quantitatively on a crucible and was washed with 250 ml boiling water. Acid-insoluble lignin was determined as the mass of residue after drying at 105 ^{o}C and was based on the oven dry sample. The sugar composition i.e. glucose, cellobiose, xylose and arabinose were determined from the hydrolysate via high pressure liquid chromatography (HPLC). The HPLC system used for quantification comprised of a spectra system P2000 pump, an auto-sampler (AS3000), a UV1000 detector and a Shodex RI-101 refractive index detector. The sugars were measured with the RI detector and the column was operated at 65 ^{o}C with a mobile phase of 5mM H_2SO_4 and a flow rate of 0.6 mL min^{-1} (Vena et al., 2010).

2.4 Fourier Transform Infrared Spectrophotometer (FTIR)

FTIR was performed to identify chemical changes in functional groups of the untreated and treated fibres. FTIR was conducted with a Thermo-Scientific Nicolet iS10 model consisting of an attenuated total reflectance unit and a transmission-FTIR unit. A minimum of 32 scans were run in the range of 500-4000 cm^{-1} and a resolution of 4 cm^{-1}.

2.5 Scanning Electron Microscopy (SEM)

SEM analysis of the fibres was performed to study the effect of the treatments on the morphological characteristics of the fibres at a magnification of 1.0 K X. The samples were mounted on metal stubs with double-coated carbon adhesive tape. The samples were thereafter sprayed with carbon using a high vacuum S150A sputter coater prior to the imaging. The micrographs of the treated and untreated fibres were examined using a LEO 1430VP MERLIN FE-SEM equipped with an energy dispersive X-ray spectrometer (EDS) GENESIS XM2. EDS was performed using a focussed beam of x-rays at random positions into the samples at a magnification of 500x.

2.6 Composite fabrication

Two types of phosphate binders were fabricated in the study using pretreated materials against the controls. These include magnesium phosphate ($MgPO_4$) and calcium phosphate ($CaPO_4$). Magnesium phosphate bonded composite boards were prepared according to an optimised method developed by Amiandamhen et al. (2016). According to this method, the fibres were milled using a hammer-mill fitted with a 1 mm sieve. The screened fibres were conditioned at 65% RH and 20 ^oC for 48 h. Thereafter the materials were measured and mixed thoroughly with a magnesium phosphate on a binder/fibre ratio as described by Amiandamhen et al. (2016). Calcium phosphate based boards were prepared according to a method that has been recently developed by (Amiandamhen et al., unpublished). According to this method, the optimum binder ratio of monopotassium phosphate to unslaked lime and calcium silicate was 8.73:1, while the binder/fibre ratio was 3.34:1 for black wattle and pine, and 11:1 and 3.26:1 for bagasse respectively. For both board types, a pre-determined amount of water was added to the mix as pre-calculated by Amiandamhen et al. (2016). The materials were mixed until homogeneity was achieved. The mixture was poured into a metallic mould measuring 218 x 77 x 40 mm and cold-pressed at 200 KPa for 5 min. The final thickness of the formed panel was 13 mm due to a 27-mm thick steel bar placed in the mould. The panel was de-moulded and weighed to calculate its wet specific gravity. The panels were stacked in ambient temperature to dry over a period of 14 days, after which they were weighed at intervals to determine the loss in panel weight. The untreated and treated fibres were used in the fabrication of the composite panels. After drying, the panels were conditioned for 72 h before testing.

2.7 Composite testing

The properties of the formed panels were evaluated to investigate the effect of fibre treatment on the flexural strength and dimensional stability of the composites. Flexural test specimens were tested according to ASTM D1037-13 using an Instron testing machine fitted with a 5 kN load cell, operated at a rate of 5 mm/min. The specimens were tested to failure and the modulus of rupture (MOR) and apparent modulus of elasticity (MOE) were calculated from the formula outlined in ASTM (2013). Water absorption (WA) characteristics and thickness swelling (TS) tests were carried out by submerging conditioned specimens horizontally in fresh water for 24 h. After submersion, the specimens were suspended to drain for 10 min and excess water was removed from the surface. The specimens were weighed and the thickness was determined as an average of four measurements. The WA of the specimen was calculated from the increase in weight and expressed as a percentage of the conditioned weight, while the TS of the specimen was calculated as a percentage of the conditioned thickness.

2.8 Micro computed tomography (µCT)

Based on the outcome of the composite tests, µCT was used to characterize and compare the microstructure of the pre-treated fibre-based composites against the controls. For this purpose, only the board prepared from alkali treated fibres were evaluated due to their overall better performance as well as cost of the technique. A numerical technique was used to quantify the cement matrix, fibre and void phases and their distribution in the samples. The composite samples were cut with a band saw into nominal dimensions of 10 x 10 x 13 mm^3. The samples were placed on the rotation stage and probed with a polychromatic X-ray beam using a General Electric Phoenix VTomeX L240 microCT scanner equipped with the Datos reconstruction software. The Volume Graphics VGStudio Max3 was used to construct 3-D images of the composites from stacks of 2-D images. The 3-D images were used to generate the actual phase distribution for void, fibre and cement matrix within the specimens. Two-phase segmentation steps were performed i.e. between the matrix, fibre and voids, and between the voids, matrix and fibre. These two segmentations were combined to delineate the fibre phase. Data sets were visualized in 2 and 3-D using volume rendering in which a transfer function assigns each voxel a colour and transparency (Evans et al., 2010). Volume rendering was performed using the VGStudio Max3. Numerical values were derived for the volumes of fibre, matrix and void across the thickness of a representative board sample using maximal sphere modelling. This defines for every point within the board, the diameter of the largest sphere which fully lies within the void, matrix or fibre phase and covers that point (Evans et al., 2010).

2.9 Experimental design and data analysis

The experiment was laid out on a completely randomized design with four replications. Three fibre treatments, i.e. alkali, acetic anhydride and hot water, and untreated fibres (control experiment) were designated as independent variables in the design. Three bio-based residues were investigated independently in the study. They include black wattle, slash pine and bagasse. These residues were bonded with a $MgPO_4$ and $CaPO_4$ cement matrix. The data was analysed using STATISTICA (V13) to evaluate the effects of fibre treatments on the physical and mechanical properties of the panels. Duncan's multi-stage range test was used in the separation of means for comparison.

3. Results and discussion

3.1 Effect of the treatment on fibre yield and characteristics

3.1.1 Yield and chemical composition

Generally mild conditions including low chemical concentrations, low temperature and short contact duration were employed so that the fibres were not significantly degraded. The bagasse fibre yields

were 97.1%, 87.9% and 92.1% for hot water treatment, alkali treatment and acetic anhydride treatment respectively. The pine fibre yields were 93.7%, 90.3 % and 96.5% for hot water treatment, alkali treatment and acetic anhydride treatment respectively. The wattle fibre yields were 91.7%, 87.2% and 92.1% for hot water treatment, alkali treatment and acetic anhydride treatment respectively. The yield from alkalization was the lowest for all three species, probably due to partial removal of some fibre components in the black liquor (Table 1). As the treatments were not meant to be destructive on the raw material, high values were obtained compared to such processes as conventional Kraft or soda pulping which are about 45-65% (Kanungo et al., 2009; Vena et al., 2010).

In general, the presence of soluble sugars in natural fibres inhibits the hydration of Portland cement bonded composites (Karade et al., 2003). This makes pre-treatment of fibres an option which can be costly. Phosphate binders, on the other hand, are not known to be affected by the sugars and hemicelluloses in natural fibres. However, the presence of hydroxyl groups in sugars and other carbohydrates may affect the durability of the composites. This study was carried out to determine the effect of pre-treatments on the chemical properties of the fibres and the composite properties. The chemical composition of the untreated and treated fibres is presented in Table 1. All the treatments reduced the lignin content in the fibres, but the effect was less in hot water treated fibres. Hot water hydrolysis depolymerizes hemicelluloses into monomers and oligomers with partial depolymerisation of cellulose and lignin (Garrote et al., 1999). Hot water extraction also reduced the total xylose and glucose in wattle fibres. This condition was observed in the FTIR analysis of hot water treated fibres (Figures 4-6). Alkalization was observed to proportionally increase the ash content of the fibres. This may be due to the removal of organic matter, which proportionally increases the percentage of the inorganic materials. On the contrary, acetylation decreased the ash content of the fibres. Alkalization also proportionally increased the xylose and glucose contents in pine and bagasse fibres due to the removal of lignin. Alkalization had the greatest effect on the lignin content of bagasse fibres. The HPLC analysis did not detect any traces of arabinose and cellobiose in the fibres.

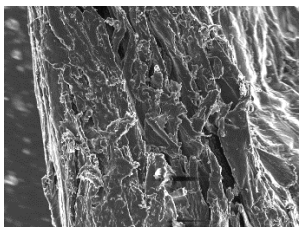
Table 1
Yield and chemical composition of untreated and treated fibres (%)

Fibres	Treatment	Lignin	Glucose	Xylose	Ash	Yield
Wattle	Untreated	18.17±1.0	42.73±5.0	10.81±1.31	0.47±0.001	
	Hot water	17.42±3.63	40.14±0.48	10.09±0.15	0.47±0.001	91.7
	Acetylation	17.71±2.50	41.84±1.17	9.96±0.53	0.10±0.000	92.1
	Alkalization	16.07±4.32	42.95±0.40	9.79±0.23	1.94±0.002	87.2
Pine	Untreated	27.32±1.40	36.29±0.92	12.07±0.29	0.40±0.001	
	Hot water	26.31±1.25	38.36±2.46	12.47±0.87	0.37±0.000	93.7
	Acetylation	25.02±0.97	41.54±0.05	13.75±0.30	0.16±0.000	96.5
	Alkalization	25.27±0.94	44.08±1.08	14.07±0.49	2.51±0.01	90.3
Bagasse	Untreated	23.33±4.17	40.20±0.79	11.40±0.29	2.55±0.003	
	Hot water	23.56±3.32	39.07±1.66	10.62±0.29	2.16±0.001	97.1
	Acetylation	21.66±0.93	37.41±2.44	10.45±0.58	2.40±0.001	92.1
	Alkalization	13.47±2.72	48.68±4.22	15.00±2.85	3.14±0.001	87.9

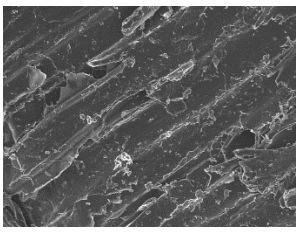
Values represent mean of three replicates and standard deviation

3.1.2 SEM

In general, the treatments resulted in defibrillation of the fibres which may increase mechanical interlocking with the cement matrix. Acetylated and alkalized fibres showed cleaner surfaces due to the removal of waxy substances and lignin from the fibre surface during treatments. It is expected that the cleaner surfaces result in better bonding with coupling agent during composite development (Li et al., 2007; Pickering et al., 2007; Hajiha et al., 2014). The SEM micrographs below show the surface morphologies of treated and untreated fibres for the three species (Figures 1-3). Differences were observed in the alkali treated fibres where surface impurities such as waxes and pectin were removed. This was also observed in other studies (Pickering et al., 2007; Le Troedec et al., 2008; Hajiha et al., 2014). Acetylation was also found to remove some impurities from the fibre surfaces as observed in the wattle and pine fibres. It is believed that waxy substances of the fibres are removed (Tserki et al., 2005) and hydroxyl groups are replaced by acetyl groups (Li et al., 2007; Hajiha et al., 2014) making the fibres more less hydrophilic. There were no differences in the SEM micrographs of untreated and hot water extracted fibres of pine and bagasse. Hot water extracted fibres show evidence of impurities on the surface of the fibres indicating that the treatment was not efficient in cleaning the fibres. It is however, believed that hot water extraction alters the chemical composition of fibres by fractionating easily accessible sugars and hemicelluloses (Pelaez-Samaniego et al., 2013, 2014).



(a)



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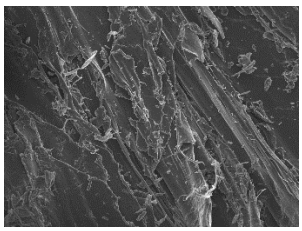

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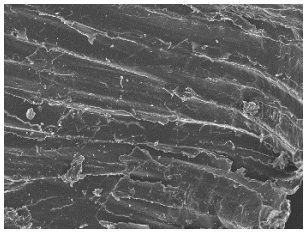
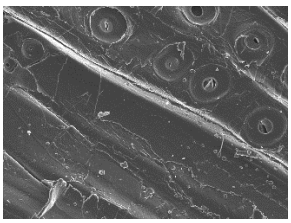
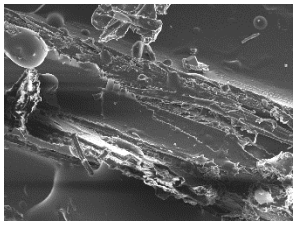


(d)

Fig. 1 SEM micrographs of untreated (a), hot water extracted (b), acetylated (c) and alkalized (d) wattle fibres (Magnification = 1 K X; scale bar = 10 µm)



(a)



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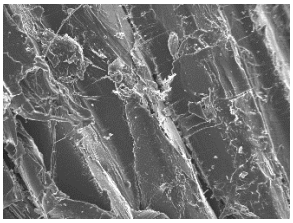

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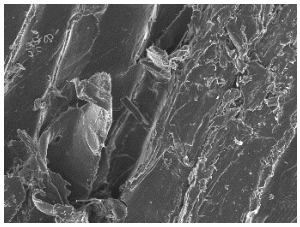
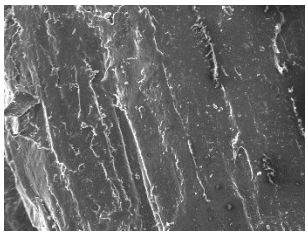
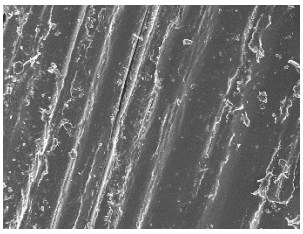


(d)

Fig. 2 SEM micrographs of untreated (a), hot water extracted (b), acetylated (c) and alkalized (d) pine fibres (Magnification = 1 K X; scale bar = 10 µm)



(a)



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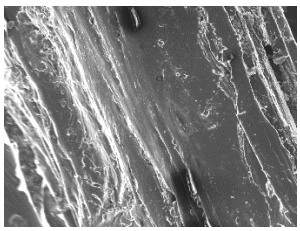

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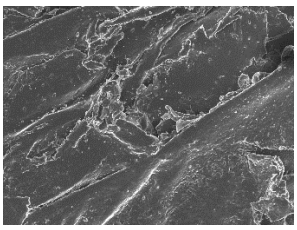


(d)

Fig. 3 SEM micrographs of untreated (a), hot water extracted (b), acetylated (c) and alkalized (d) bagasse fibres (Magnification = 1 K X; scale bar = 10 µm)

Energy dispersive spectroscopy (EDS) was used to characterize the treated and untreated fibre samples. The spectral diagrams obtained were used to generate the elemental composition of the samples and the means of two random observations are presented in Tables 2-4 for each species. It was observed that all fibres contain carbon, oxygen, sodium, potassium and calcium while magnesium, aluminium, silicon, iron and copper were only detected in some samples. The treatments were observed to be effective in removing sodium from the fibres. Untreated bagasse fibres were more hydrophobic than untreated wattle and pine fibres due to the higher C/O ratio. According to Sgriccia et al. (2008), cellulose, hemicellulose and pectin have a C/O ratio of 1.21, while lignin has a ratio of 2.86. Since the treated and untreated samples have C/O ratios greater than 1.21, this shows that some wax and lignin remained in the fibres. It is important to note that actual C/O ratios of the samples may be lower than the obtained values. This is due to the additional amount of carbon used in coating the samples prior to SEM.

Table 2
Elemental composition (%) of surface treated wattle fibres

Spectral label	Untreated	Hot water	Acetylated	Alkalized
C	55.7	58.18	60.91	59.31
O	42.2	41.76	38.73	40.46
Na	0.9	-	-	-
Si	-	0.08	-	-
Cl	-	-	0.09	-
K	0.07	0.05	0.21	-
Ca	0.18	-	0.09	0.14
Cu	-	-	-	0.22
C/O ratio	1.32	1.39	1.57	1.47

*C-content values are slightly higher than the actual values. All fibres were coated with a thin layer of carbon prior to microscopy.

Table 3
Elemental composition (%) of surface treated pine fibres

Spectral label	Untreated	Hot water	Acetylated	Alkalized
C	56.33	60.72	59.64	58.77
O	42.78	39.14	39.95	40.20
Na	0.78	-	0.12	-
Mg	-	-	-	0.22
Si	-	-	-	0.09
P	-	0.09	-	0.18
Cl	-	0.05	0.12	-
K	0.09	0.16	0.21	0.27
Ca	0.06	-	0.1	0.16
Cu	-	-	-	0.13
C/O ratio	1.32	1.55	1.49	1.46

*C-content values are slightly higher than the actual values. All fibres were coated with a thin layer of carbon prior to microscopy.

Table 4
Elemental composition (%) of surface treated bagasse fibres

Spectral label	Untreated	Hot water	Acetylated	Alkalized
C	58.91	62.19	63.37	62.11
O	38.97	37.21	32	35.23
Na	0.89	-	-	-
Mg	0.13	0.1	0.16	0.12
Al	0.13	0.1	0.09	0.18
Si	0.3	0.2	4.01	1.87
P	0.1	0.08	0.12	0.05
S	0.05	0.08	0.05	0.06
Cl	0.09	0.05	0.09	-
K	0.17	0.11	0.24	-
Ca	0.17	0.09	0.09	0.28
Fe	0.17	-	0.1	0.24
Cu	0.12	-	-	-
C/O ratio	1.51	1.67	1.98	1.76

*C-content values are slightly higher than the actual values. All fibres were coated with a thin layer of carbon prior to microscopy.

3.1.3 FTIR

The FTIR spectra of the untreated and treated fibres are shown in Figures 4-6. The C-H symmetrical stretch around 2,916 cm^{-1} is present in all fibres except alkalized pine fibres. The intensity of the peak was highest in hot water extracted bagasse. The peak at 3303 cm^{-1} is also present in all fibres examined. This peak corresponds to the axial stretching of hydroxyl group (-OH) (Sawpan et al., 2011). The CH_2 peaks at around 1415 cm^{-1} are present in all treated and untreated fibres. This peak signifies the existence of the symmetric bending of cellulose (Hajiha et al., 2014), while the peak at 1223 cm^{-1} represents the C-O-C asymmetric bridge stretching of lignin (Kaczmar et al., 2011). These peaks are however minimal in alkalized pine fibres, indicating that there was partial removal of the fibre materials (also see Table 1). The C-C stretching was also present at 1023 cm^{-1}, and this relates to the β-glucosidic linkages between the sugar units in hemicelluloses and cellulose (Sawpan et al., 2011; Hajiha et al., 2014). The peak at 1730 cm^{-1} is present in all the acetylated fibres as well as in the hot water extracted fibres of bagasse and wattle. It is also present in untreated pine fibres. This peak is usually attributed to the C=O stretching of the acetyl groups of hemicelluloses (Liu et al., 2004). The intensity of this peak decreases after hot water extraction and alkalization in pine and wattle, meaning that hemicelluloses were partially removed. This was also observed by (Pelaez-Samaniego et al. (2014). The peak was, however, not affected by acetylation. It is evident in this study that the peak may have been enhanced due to the acetylation treatment, since the peak is not stretched in the untreated fibres of the other species. The intensity of the broad band at 3217 to 3368 cm^{-1} showed partial removal of the OH group in alkali and hot water treated pine. There were no important changes after treatment in bagasse and wattle. Since these bands are assigned to the hydrogen-bonded OH groups in intramolecular cellulose (Kobayashi et al., 2009), it appeared cellulose was not degraded in both species during the treatments.

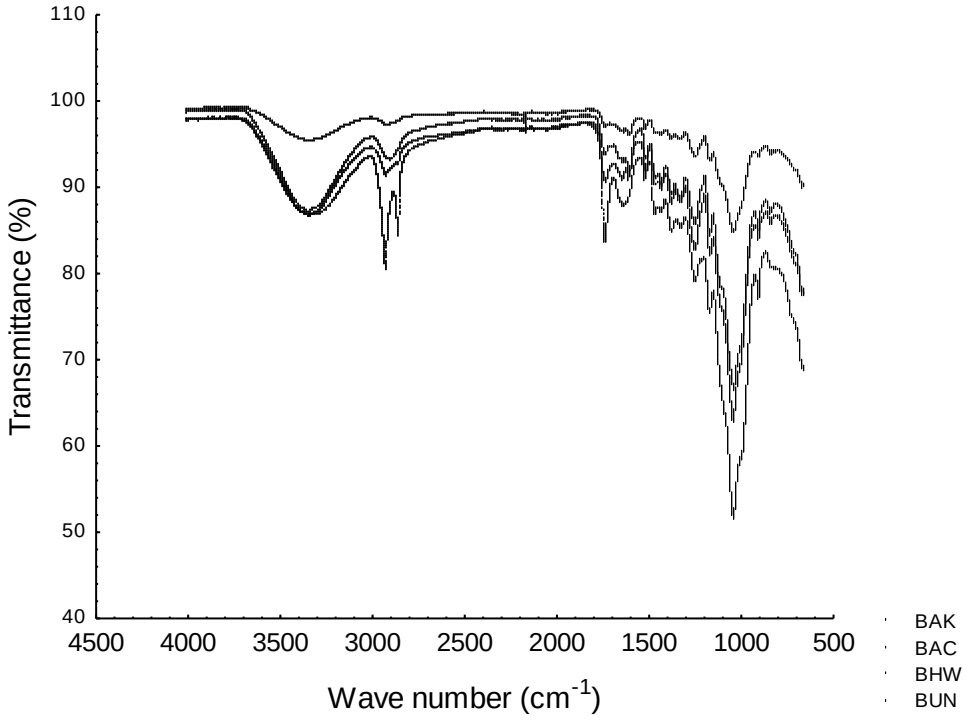


Fig 4: FTIR spectrum of treated and untreated bagasse fibres (BAK = Alkalized; BAC = Acetylated; BHW = Hot water extracted; BUN = Untreated)

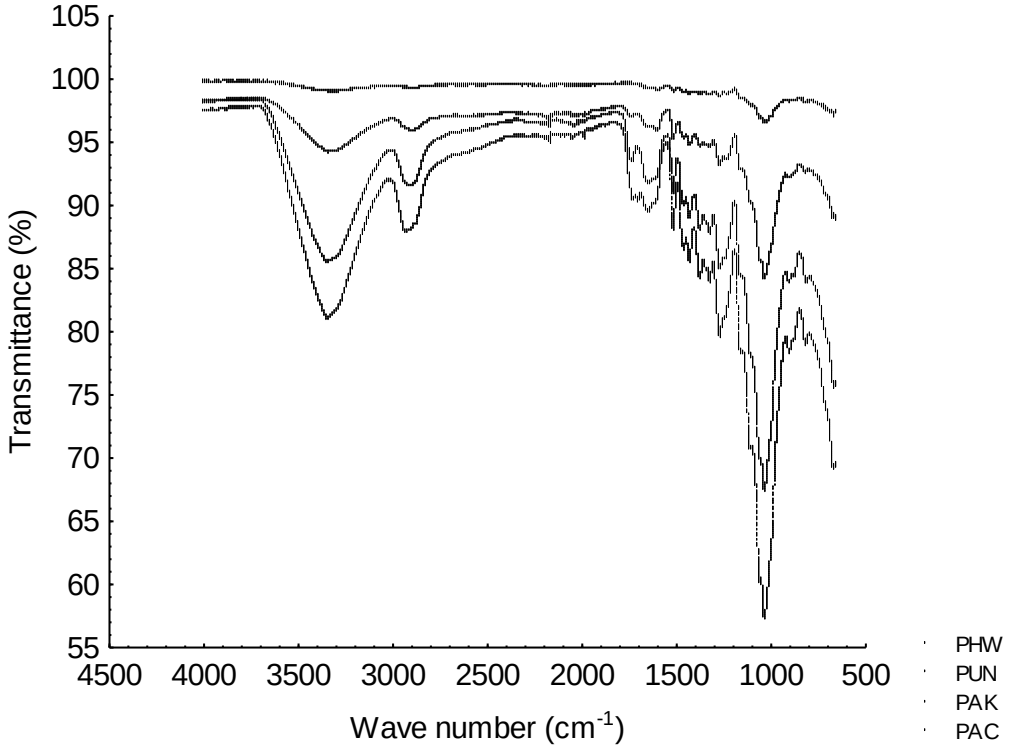


Fig 5: FTIR spectrum of treated and untreated pine fibres (PAK = Alkalized; PAC = Acetylated; PHW = Hot water extracted; PUN = Untreated)

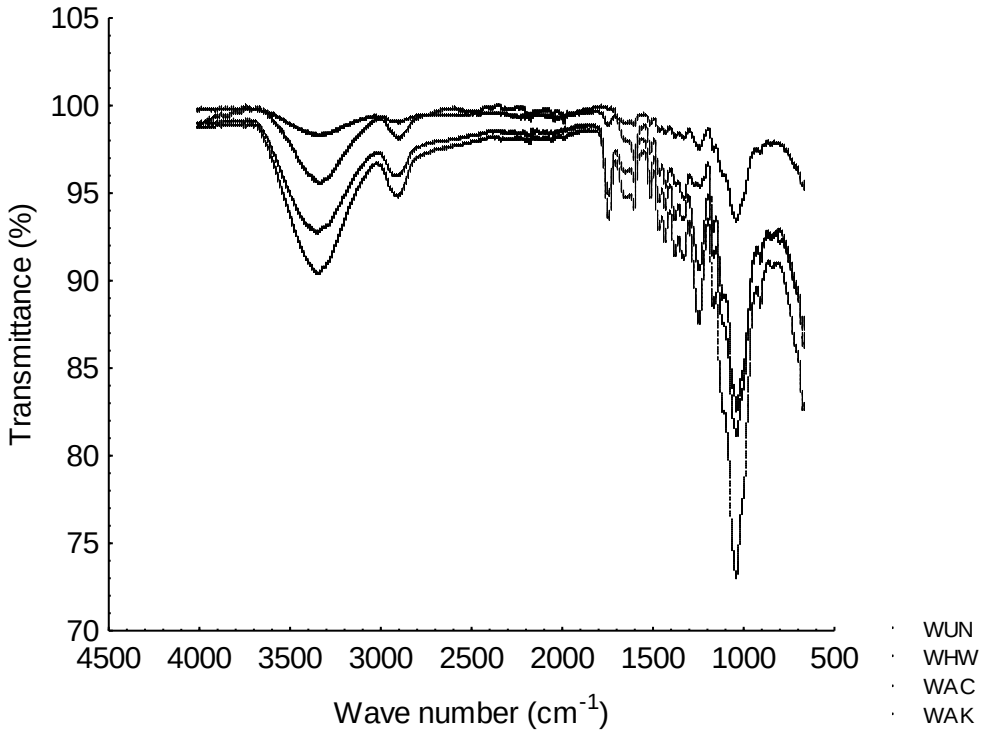


Fig 6: FTIR spectrum of treated and untreated wattle fibres (WAK = Alkalized; WAC = Acetylated; WHW = Hot water extracted; WUN = Untreated)

3.2 Effect of the treatment on panel properties

3.2.1 Data analysis

The data was analysed using the one-way ANOVA by STATISTICA (V13). The analysis revealed that treatment had a significant effect on MOR, WA and TS of all the panels ($p < 0.05$). The effect of the treatments was highly significant on the properties of the bagasse panels, except on the density (Table 5). Since density plays a major role in determining the strength properties of composite panels, the treatment also influenced the MOR but the effect on the MOE was not significant except in bagasse panels. Table 6 shows the comparison of means using Duncan's multi-stage range test. Although the effect of the treatment was not significant on the MOE of pine panels, there was a difference between the means. The same observation was made for density of bagasse panels. However, there was no difference between the means in the MOE of black wattle panels (Table 6).

Table 5
p-values showing the effect of treatment on the properties of the panels

Property	Black wattle	Slash pine	Bagasse
Density	0.000*	0.000*	0.171
MOR	0.007*	0.048*	0.000*
MOE	0.246	0.273	0.000*
WA	0.026*	0.000*	0.000*
TS	0.002*	0.000*	0.000*

*- denotes values that are significant ($p < 0.05$)

Table 6
Mean comparison using Duncan's multi-stage range test

			Property		
Panels	Density (g/cm3)	MOR (MPa)	MOE (MPa)	WA (%)	TS (%)
BUN1	0.75^{ab}	0.55^{b}	150.04^{ac}	54.61^{a}	4.91^{c}
BHW1	0.76^{ab}	0.73^{a}	156.08^{abc}	48.74^{de}	4.32^{bc}
BAC1	0.79^{ab}	0.80^{a}	165.42^{b}	42.21^{c}	3.61^{ab}
BAK1	0.81^{ab}	0.79^{a}	159.75^{ab}	36.44^{b}	3.35^{a}
BUN2	0.70^{a}	0.43^{c}	134.73^{d}	55.25^{a}	$8,15^{d}$
BHW2	0.74^{ab}	0.55^{b}	144.61^{cd}	51.82^{a}	7.91^{d}
BAC2	0.78^{ab}	0.75^{a}	157.83^{ab}	43.74^{cd}	5.97^{e}
BAK2	0.85^{b}	0.80^{a}	159.75^{ab}	33.24^{b}	4.21^{abc}
PUN1	0.78^{ab}	0.69^{a}	158.20^{a}	45.24^{b}	3.96^{ab}
PHW1	0.78^{a}	0.80^{ab}	197.44^{ab}	44.87^{b}	5.12^{b}
PAC1	0.83^{bc}	0.84^{ab}	202.87^{ab}	34.83^{a}	3.25^{a}
PAK1	0.81^{ab}	1.06^{b}	224.98^{ab}	33.98^{a}	1.73^{c}
PUN2	0.69^{d}	0.62^{a}	245.05^{ab}	44.27^{b}	5.10^{b}
PHW2	0.79^{ab}	0.69^{a}	253.64^{ab}	33.61^{a}	3.64^{a}
PAC2	0.87^{c}	0.77^{a}	270.49^{ab}	27.97^{d}	3.40^{a}
PAK2	0.92^{c}	0.77^{a}	425.44^{b}	23.86^{c}	1.71^{c}
WUN1	0.76^{d}	0.74^{a}	130.68^{a}	34.91^{a}	2.34^{ab}
WHW1	0.80^{b}	1.03^{a}	220.88^{a}	32.24^{ab}	1.29^{a}
WAC1	0.78^{c}	1.20^{ab}	294.12^{a}	30.73^{b}	1.60^{a}
WAK1	0.81^{b}	1.66^{b}	248.28^{a}	30.29^{b}	1.12^{a}
WUN2	0.60^{a}	0.88^{a}	213.11^{a}	35.91^{a}	5.28^{c}
WHW2	0.60^{a}	0.83^{a}	585.98^{a}	35.10^{a}	4.84^{c}
WAC2	0.60^{a}	0.73^{a}	514.42^{a}	33.42^{ab}	4.40^{bc}
WAK2	0.64^{a}	1.18^{ab}	208.99^{a}	32.63^{ab}	2.42^{ab}

Means in the same column with the same or similar letters are not significantly different ($p < 0.05$)
(B = bagasse; P = pine; W = wattle; UN = untreated; HW = hot water; AC = acetylated; AK = alkalized; 1 = $MgPO_4$; 2 = $CaPO_4$)

3.2.2 Density

The density of the boards is presented in Table 6. It was observed that the density increased slightly with each treatment compared to untreated panels for wattle, pine and bagasse. A similar pattern was observed for both phosphate bonded panels. However, the density did not vary in black wattle panels bonded with calcium phosphate, except for alkali treated panels. Also, treatment did not increase the

density of hot water treated pine panels bonded with magnesium phosphate. The increase in density may be due to better interlocking between the fibres and the cement matrix, thereby forming less-porous and solid materials. This behaviour was verified in the µCT numerical analysis, and the effect of this relationship can be observed in the flexural performance of the composites (Figures 7-9). Since density is a major determinant of mechanical properties, it is expected that the treatment would also influence the properties of the composite panels.

3.2.3 Flexural properties

The trend in the flexural properties of the panels is shown in Figures 7-9. In $MgPO_4$ bonded panels of black wattle and pine, the mean MOR increased gradually from untreated to alkalized panels while $CaPO_4$ bonded panels showed a linear increase in MOR. In $CaPO_4$ bonded panels, both hot water and acetylation caused a decline in the MOR of the composites, but the MOR increased in alkaline treated panels. The increase in MOR in the alkalized panels using both binders could probably be due to the surface modification of the fibres which enhanced the bonding with the matrix. A similar pattern of variation was observed in the MOE of the panels. However, treatment did not have a significant effect on the MOE of wattle and pine panels (Table 5). The MOE decreased in alkalized panels compared to acetylated panels for bagasse and wattle (Table 6). The MOE of the panels did not change much for the two binder types but the alkali treated $CaPO_4$ pine panels had the highest MOE of 425 MPa. The bagasse treated boards showed a slightly different pattern from the other two species. There was a gradual increase in the MOR and MOE of the panels compared to the untreated panels. Alkalization resulted to a slight decrease in MOR of the magnesium phosphate bonded panels. This may be due to the partial degradation of some cellulosic components (as evident in Table 1 and Figures 4-6) during the treatment and the eventual loss in strength of the fibres prior to composite manufacturing.

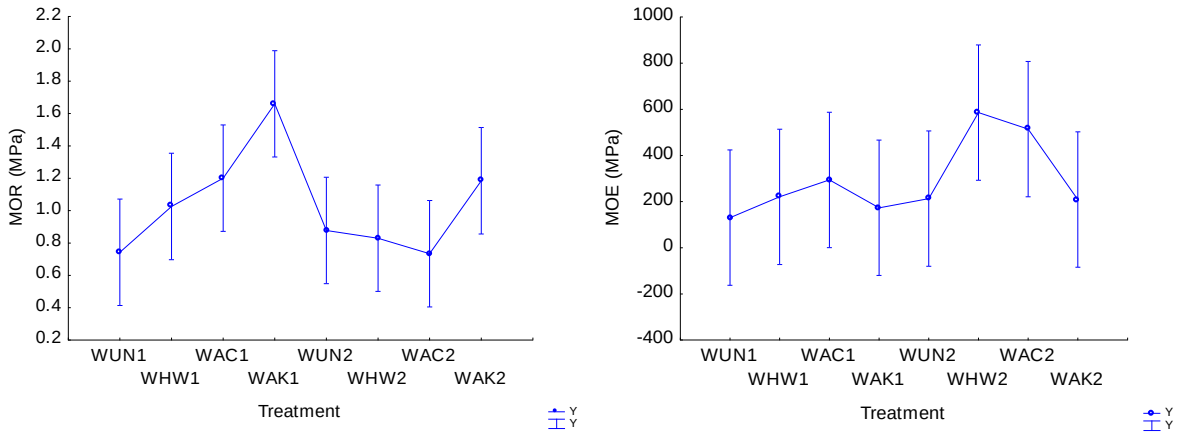


Fig. 7 Trend in MOR and MOE of phosphate bonded composite panels from black wattle (UN = untreated; HW = hot water; AC = acetylated; AK = alkalized; 1 = $MgPO_4$; 2 = $CaPO_4$)

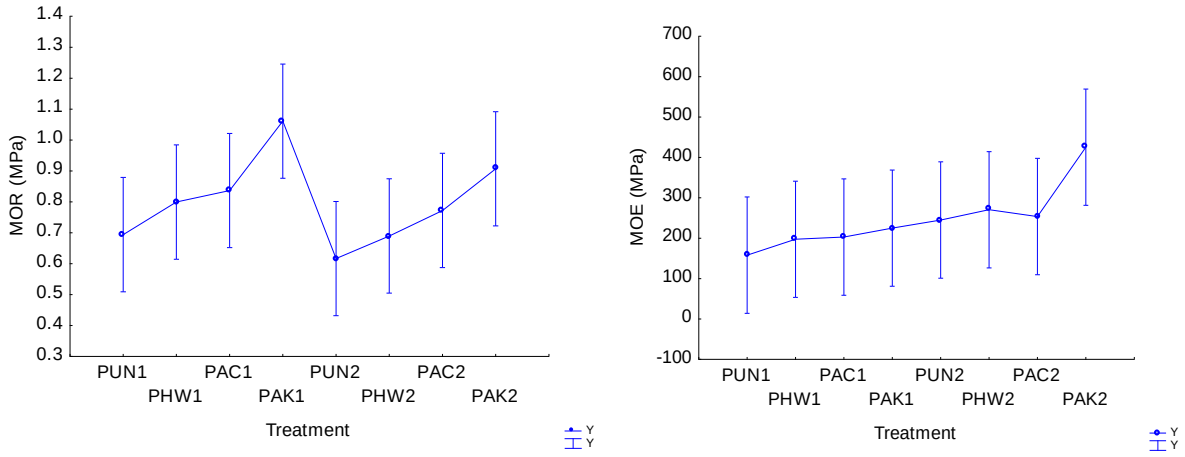


Fig. 8 Trend in MOR and MOE of phosphate bonded composite panels from slash pine (UN = untreated; HW = hot water; AC = acetylated; AK = alkalized; 1 = $MgPO_4$; 2 = $CaPO_4$)

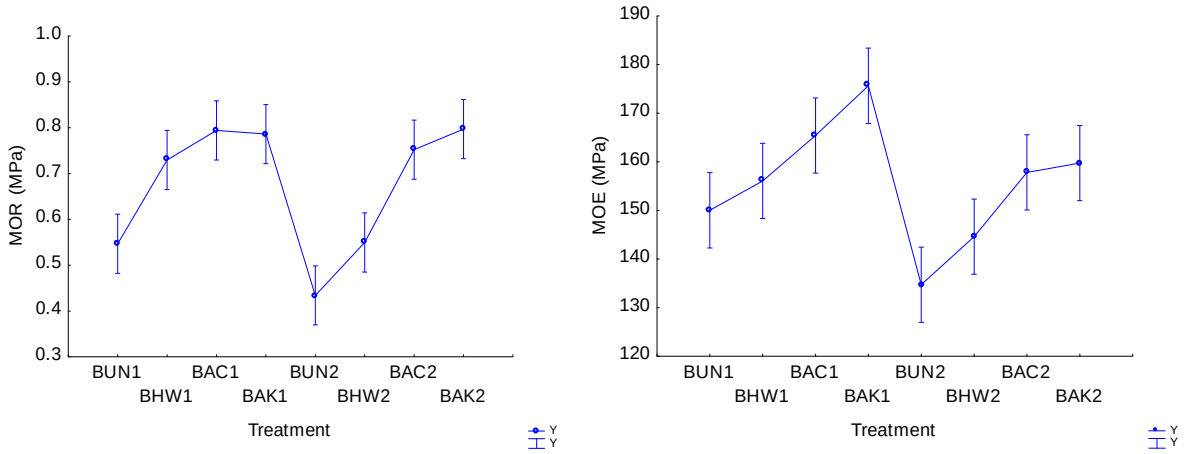


Fig. 9 Trend in MOR and MOE of phosphate bonded composite panels from bagasse (UN = untreated; HW = hot water; AC = acetylated; AK = alkalized; 1 = $MgPO_4$; 2 = $CaPO_4$)

3.2.4 Dimensional stability

The TS and WA of the composite panels are shown in Figures 10-12. A decreasing trend in TS and WA can be observed in both $MgPO_4$ and $CaPO_4$ bonded panels after treatment. In all panels, alkalized panels had the lowest TS and WA. This proved that alkali treatment is effective in reducing the hydrophilic groups on natural fibre surfaces. It was also observed that $CaPO_4$ bonded composites generally had high values of TS and WA. This indicates that stronger fibre-matrix bonding exists in $MgPO_4$ composites, which generally inhibits moisture migration to the composites. The pattern of variation is however irregular in pine boards. There was an increase in TS for boards treated with hot water compared to the untreated panels. However, alkalized panels had the lowest TS of the panels. This was not the case with $CaPO_4$ bonded panels, where untreated panels had the highest TS. In bagasse panels, the WA and TS of the panels decreased after treatments with a steep slope.

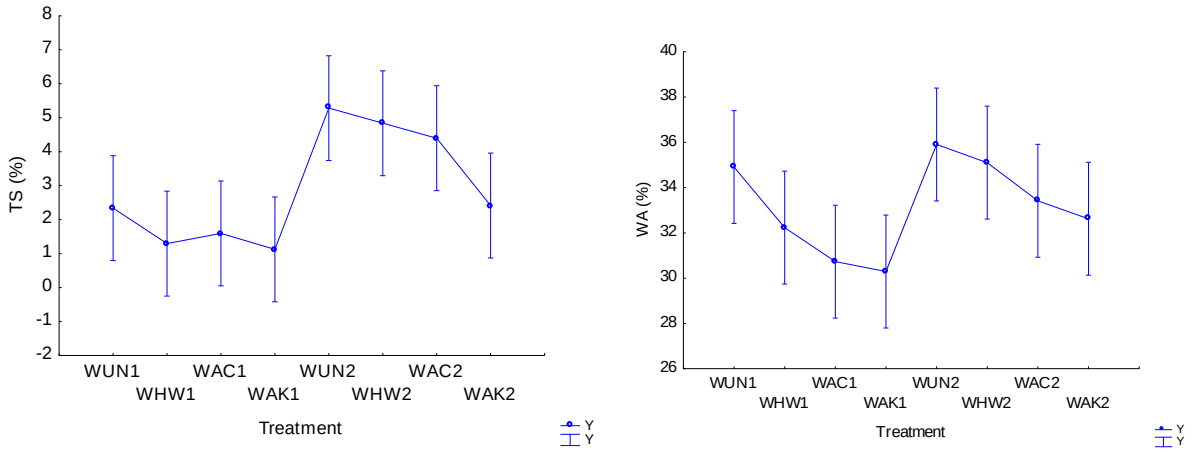


Fig. 10 Trend in TS and WA of phosphate bonded composite panels from black wattle (UN = untreated; HW = hot water; AC = acetylated; AK = alkalized; 1 = $MgPO_4$; 2 = $CaPO_4$)

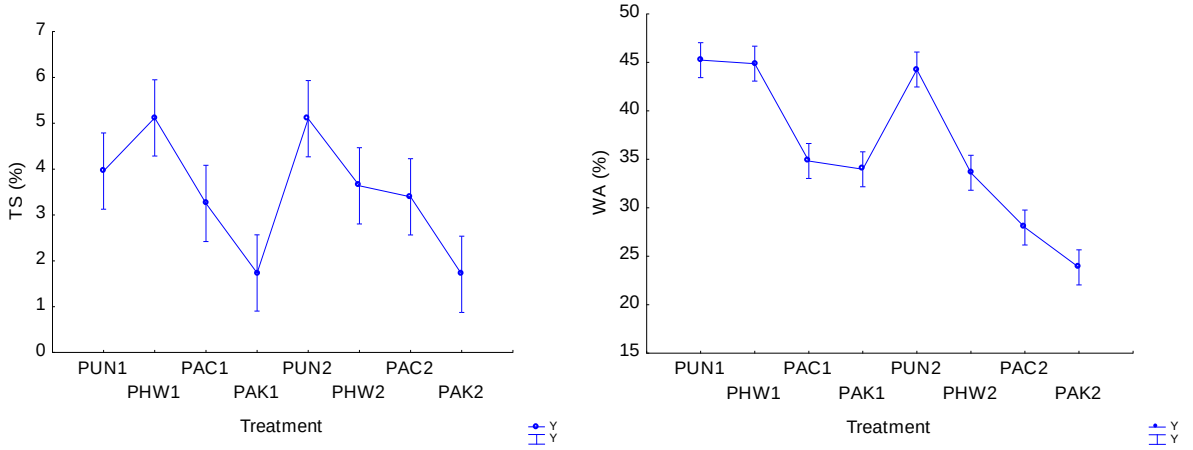


Fig. 11 Trend in TS and WA of phosphate bonded composite panels from slash pine (UN = untreated; HW = hot water; AC = acetylated; AK = alkalized; 1 = $MgPO_4$; 2 = $CaPO_4$)

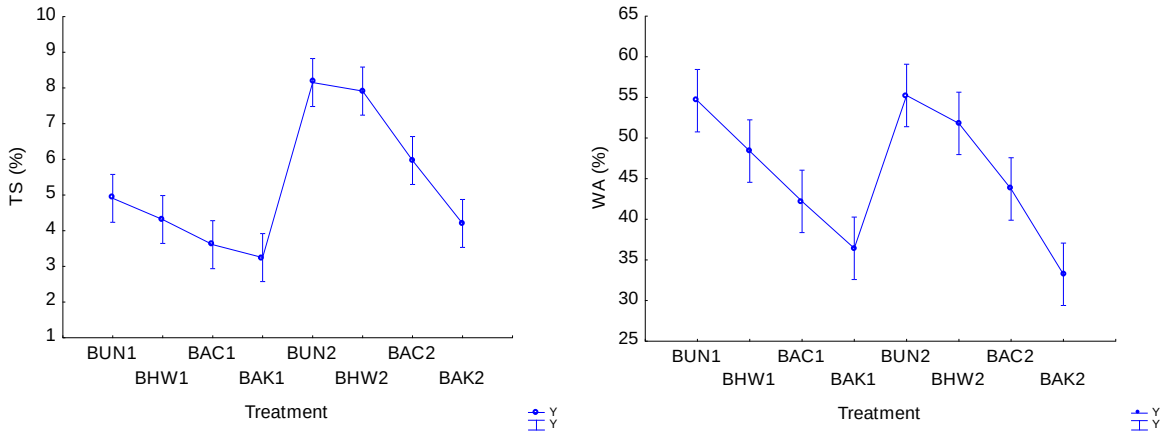


Fig. 12 Trend in TS and WA of phosphate bonded composite panels from bagasse (UN = untreated; HW = hot water; AC = acetylated; AK = alkalized; 1 = $MgPO_4$; 2 = $CaPO_4$)

3.3 Visualization of particle distribution in untreated and alkali treated composite panels

3.3.1 Distribution of phases in the panels

µCT has been used successfully to examine the structure and interfacial ability of biocomposites materials (Wang et al., 2007; Evans et al., 2010; Kamke et al., 2014; Joffre et al., 2017). In this study, µCT was used to visualize the porous microstructure and distribution of fibres and void phases in the $MgPO_4$ bonded composites produced from untreated and alkali treated fibres. The distribution of phases in the panels can be seen in coloured 2-D images selected from tomographic sequences (Figures 13-15). In these images, the matrix is red, fibres are green and voids are black. Figures 13a and b show good interparticle contact within the matrix, with few void spaces for untreated and alkali treated bagasse composites. Contrary, Figures 14a and b show in-plane views of part of the panel with larger particle sizes and voids. The pine fibres used contained a large proportion of short and thick particles, hence inter-particle contact was poorer. This pattern was also observed by Evans et al. (2010), who reported that the continuity of glue-lines in particleboard appeared to depend on the degree of contact between wood flakes. It was observed that the matrix-lines were longer and more continuous in bagasse (Figure 13) and wattle (Figure 15) than in the pine composites (Figure 14). It was also observed that the matrix distribution was interrupted by the presence of large voids (Figures 14 and 15). However, the adhesive was observed to accumulate in smaller voids creating a 'spot-welds' appearance between wood flakes, and around very small particles of 'fines' (Evans et al., 2010). The µCT images revealed that the matrix network is continuous in the phosphate bonded composites. This is similar to the report of Loxton et al. (2003). The authors used a confocal laser scanning microscopy (CLSM) to observe UF resin distribution in pressed MDF and wood fibres. They found that the size of resin spots was greater on fibres in pressed MDF and this depends on the presence of wax. Evans et al. (2010) also observed that glue-lines were more continuous in areas of the composites where the degree of consolidation of flakes were high and more discontinuous where inter-particle contact was poorer.

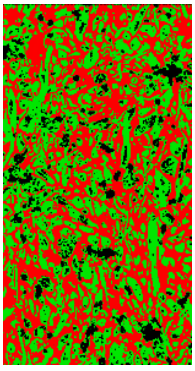
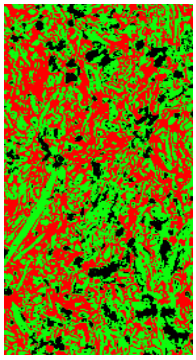
(a)  (b) 

Fig. 13 2-D segmentation of bagasse panels (a) untreated (b) alkali treated (Matrix = red, fibres = green, voids = black)

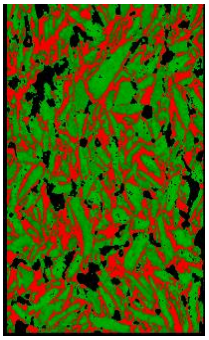
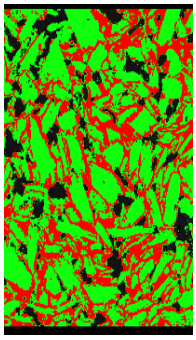
(a)  (b) 

Fig. 14 2-D segmentation of pine panels (a) untreated (b) alkali treated (Matrix = red, fibres = green, voids = black)

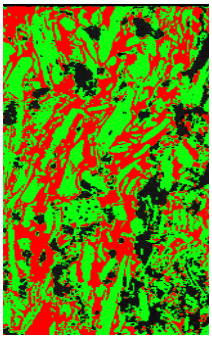
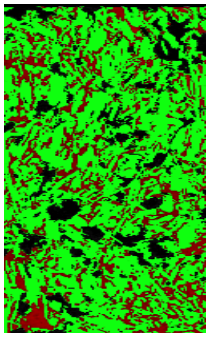
(a)  (b) 

Fig. 15 2-D segmentation of wattle panel (a) untreated (b) alkali treated (Matrix = red, fibres = green, voids = black)

3.3.2 Quantification of phases in the panels

µCT was used to generate 2-D images of the composites and its component phases. These 2-D images were then used to reconstruct 3-D images of the composites for visualization and quantification, as well as reveal spatial geometry of the matrix network and other phases. 3-D images enable computation of numerical indices for matrix distribution and its relationship to other phases in the composites (Evans et al., 2010). µCT has the potential to accurately image porous materials and quantify the void and solid phases in the materials. Quantification of the void and solid phases in fibre composites is important because of its prediction on certain properties, such as density which is a determinant of other properties of composites. To determine the relationship between the distribution of fibres, cement matrix and void space in the composite panels, numerical values were derived for the volumes of such phases across three planes of the panel using maximal sphere modelling (Thovert et al., 2001; Evans et al., 2010). The phase volume distribution in a cross-section of the panels is presented in Table 7. It was observed that the treatment increased the volumes of the different phases proportionately in bagasse and pine boards. On the contrary, alkali treatment in wattle decreased the volume of the void space and matrix while it increased the fibre volume (also see Figure 15b). This resulted in increased density (as seen in Table 6), better inter-particle contact and improved strength properties (Figure 7).

Table 7
Phase distribution in phosphate bonded composites produced from untreated and alkali treated fibres

Phase distribution	BUN	BAK	PUN	PAK	WUN	WAK
Air	142.89 (9.92)	204.19 (11.43)	148.78 (11.76)	177.79 (10.73)	204.32 (17.12)	148.22 (12.03)
Matrix	654.35 (45.43)	742.43 (41.57)	386.06 (30.51)	577.74 (34.85)	432.27 (36.22)	359.38 (29.17)
Fibres	643.09 (44.65)	839.53 (47.00)	730.68 (57.74)	902.16 (54.42)	556.75 (46.65)	724.26 (58.79)
Total	1440.33	1786.15	1265.52	1657.69	1193.34	1231.86

percentage distribution of the phases is given in parenthesis

4. Conclusions

This study revealed that pre-treatment of natural fibres improved the flexural properties and dimensional stability of phosphate bonded composites. Alkaline treatment of wattle, pine and bagasse resulted in the largest improvements in the properties evaluated. The treatment also influenced the fibre properties as measured by the chemical composition, fibre surface characteristics and functional groups in treated and untreated fibres. The study revealed that magnesium phosphate bonded composite panels had higher strength values and lower water absorption characteristics compared to calcium phosphate composite panels. 3-D imaging revealed that the phosphate cement matrix is mainly aligned in the same direction as the fibres forming a continuous network. The analysis also revealed that alkaline treatment resulted in the reduction of void spaces and a proportionate increase in solid phases in the composites. This increased the composite strength because of increased density and reduced porosity. The study concluded that a mild alkaline treatment of 0.25 M for 1 h and at 60 ^{o}C is sufficient to improve the basic properties of phosphate bonded composite boards made from black wattle, slash pine and bagasse fibres.

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CHAPTER EIGHT

8. Conclusions and suggestions for future studies

The present study opens new area of research based on phosphate bonded composite products, that is aimed at utilizing bio-based industrial residues including some selected invasive alien wood wastes, with the opportunity to produce value-added products. The technology of the phosphate binder has been gaining increasing interest in other fields but it is still at the infantile stage in wood composite development. Therefore, it is important to address this knowledge gap and provide suggestions for future studies with a view to understanding product concept development. In order to produce marketable products from laboratory results, several factors must be considered which include testing of important properties, optimization of the process parameters, scaling up of production process, design of equipment to manufacture the product and market for the proposed product (Wagh, 2013). Based on the foregoing, the following sections discuss the conclusions from this study and suggest directions for future work.

8.1 Conclusions from the study

This study investigated the potential of utilizing bio-based residues in formulated magnesium and calcium phosphate cement binders. In the first phase, we used monopotassium phosphate and magnesium oxide to produce magnesium phosphate binder. In the second phase, we used unslaked lime, calcium silicate and monopotassium phosphate to produce calcium phosphate binder as a second type of the phosphate binder. These two binders were developed to produce durable low and medium density composite panel boards. The properties of the panels were tested to products technical specifications. The production process was optimised by means of variable optimization using the response surface methodology. The use of an industrial coal-fired plant fly ash was also investigated. The rationale was to reduce the total cost of production of the binder and increase the generation of more binder, while technically complementing the properties of the basic material. To our best knowledge, this is the first time that this binder system has been optimised for such particleboards.

Based on the objectives of this study, the following conclusions can be drawn;

- We investigated the application of bio-based residues including pine sawdust, sugarcane bagasse, hemp hurds, papermill sludge and waste paper in magnesium phosphate cement binder to produce composite boards. The variables considered were the binder ratio of monopotassium phosphate (KH_2PO_4) to magnesium oxide (MgO) and the amount of lignocellulosic fibres required to achieve the maximum desirable properties. The effect of fly ash on the composite properties was also studied. The optimum composite manufacturing processes for making

durable products within the experimental design was found to contain a ratio of KH_2PO_4/MgO = 2.6, 10% fly ash, wood/inorganic ratio of 0.96 for pine; KH_2PO_4/MgO = 2.0, 8% fly ash, fibre/inorganic ratio of 3.34 for paper sludge; KH_2PO_4/MgO = 2.3, 7% fly ash, fibre/inorganic ratio of 2.92 for waste paper; KH_2PO_4/MgO = 3.0, 20% fly ash, fibre/inorganic ratio of 0.83 for bagasse; KH_2PO_4/MgO = 4.83, 28% fly ash, fibre/inorganic ratio of 0.83 for hemp fibres.

- We demonstrated that it is feasible to utilize alien wood waste including black wattle, long-leaved wattle, rooikrans and port jackson willow in the magnesium phosphate cement binder. We concluded that the presence of bark in processed wood does not negatively affect composite properties. When bark of black wattle (Acacia mearnsii) was added to the composite, maximum strength properties was obtained at a bark loading of 50% of the total wood content. Further studies on bush encroachment species using the optimized conditions established for this study resulted in maximum composite properties. In general, the physical properties of the composites met the minimum requirements for cement bonded particleboards (EN 634-2, 2007).
- The application of unslaked lime modified with calcium silicate was also investigated. To our best knowledge, calcium phosphate cement has not been used in large scale productions involving lignocellulosic fibres. Some residues were selected for this study including hardwood (black wattle), softwood (slash pine), bagasse, hemp hurds, paper mill sludge and office waste. Similar optimization procedure was conducted in this study. In addition, the ratio of the alkali minerals between calcium silicate and unslaked lime was optimised. The use of fly ash was also investigated. The physical and mechanical properties of the produced composite panels were tested to products technical specifications. The physical properties of the proposed products met the minimum requirements for use in dry and humid conditions according to EN 634-2 (2007). The achieved strength properties of the panels were adequate for such applications as wall finishes, ceilings and partitions.

The preceding studies demonstrated the feasibility of incorporating bio-based residues into magnesium phosphate and calcium phosphate cement binders to produce panel boards. It was concluded that the phosphate cement binder is robust enough to accommodate the variability in these residues and is not affected by the raw material composition. In addition, we investigated the use of fly ash and concluded that, while fly ash can be incorporated to reduce binder cost and the overall cost of the production process, at high quantities, it proved to have a negative effect on strength properties. The variables considered i.e. binder ratio, fly ash and lignocellulosic fibre contents have significant effects on the physical and mechanical properties of the boards to varying degrees within the experimental design ($p < 0.05$). As applied in cement bonded boards, the micromechanical properties of the composites could be improved by modifying the hydrophilic fibre surfaces. In the same way, we treated the lignocellulosic fibres before composite development to allow flexibility in material application and potentially improve the composite properties.

- The fourth objective describes the surface treatment of some selected lignocellulosic fibres. Based on the results of the preceding studies, we selected black wattle, slash pine and bagasse fibres for chemical treatments. These fibres were subjected differently to acetylation, alkalization and hot water extraction. The treated and untreated fibres were used in the manufacturing of composite panels using the established optimum conditions. The effect of the treatments on the fibres was studied using the FTIR, SEM and the HPLC. The physical and mechanical properties of the composites were tested to product technical specifications. Finally, μCT was used to visualize and analyse the phase volume distribution in both treated and untreated fibre composite panels. In the bagasse panels, the water absorption was 54.61% for untreated, 48.74% for hot water extracted, 42.21% for acetylated and 36.44% for alkalized panels. This represents a percentage improvement of 11, 23 and 33% respectively. The study concluded that alkali treated fibres had the best effect overall for all measured properties.

The utilization of bio-based industrial residues in composite product development promises to reduce the dependence on wood fibres, reduce the environmental impact of waste disposal and bring economic potential to developing countries. In addition, the development of environmentally friendly composite materials can help to reduce the carbon footprints of current composite product making process. With a small capital investment, satisfactory phosphate bonded composite materials can be produced on a small scale using mostly unskilled labour. However, technology can be introduced to increase the manufacturing output if the market for such composite materials increases.

8.2 Suggestions for future studies

Phosphate bonded natural fibre composites is a relatively new field of study. Some underlining properties of the phosphate binder that are likely to increase the research interest in natural fibre composites in the future are non-flammability, low porosity and extremely low water permeability (Wagh, 2013), although the presence of natural fibres may result in unpredictable properties in inorganic bonded composites due to varying physico-chemical and mechanical properties. From this study, the recommendations for future studies within the context of composites development are towards the improvement of the composites for outdoor weathering durability, and economic assessment to bring the product's concept to commercialization. An accurate evaluation of the life cycle assessment of the products from 'cradle to grave' is also recommended for future work.

8.2.1 Weathering characteristics and durability

All common materials such as concrete and wood are susceptible to environmental degradation when exposed outdoors (Evans, 2013). Studies on cement bonded composites revealed that the weathering resistance is high because the losses in strength due to weathering were offset by strength gains due to age-related hardening (carbonation) of cement (Dinwoodie and Paxton, 1989). Preliminary

investigations have shown that phosphate bonded composites are durable, dimensionally stable and offer enhanced fire, insect and mildew resistance. However, nothing exists on the durability of the composites in outdoor conditions. Future studies should seek to investigate the performance of phosphate bonded composite products and determine the suitability of the products in both dry and humid outdoor conditions.

8.2.2 Economic studies

As with other consumer goods, the wood industry is conservative in their approach to accepting new products. The key to effectively developing marketable composite products for use as building materials is to identify the development and market needs for such products. A market and product development concept will need to be considered to evaluate the potential of these products in the target market. For a new product to successfully gain market acceptance, it must be an economically viable or value-added product. The rationale for future studies would be to provide an overview of phosphate bonded composite plan and estimate the cost-benefits of incorporating wood-based industrial residues into the phosphate cement binder. Future studies should also seek to estimate the important aspects of application relating to economic investment and required infrastructural facilities.

8.2.3 Life cycle assessment

The development of new composite product comes with a broader concern about the environmental suitability of the proposed product. Future work should assess the life cycle of the new product with a view to systematically evaluate the impact of the product on the environment. As with many conventional inorganic binders including Portland cement, the quantity of greenhouse gas emission depends on the raw material, processing energy efficiency and the fuel type used in plants and machinery. Quantifying these emissions is an index of the impact of the product on the environment. In addition, product consistency leaching test should be conducted to assess the effect of the ‘end of life’ of the product on soil and water.

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Appendix

Declaration by candidate and co-authors

1. With regard to Chapter two (paper I - Inorganic bonded natural fibre composites: Opportunities and state of the art in phosphate based cement), the nature and scope of my contribution were as follows:

Nature of contribution	Extent of my contribution (%)
Conceptualised and wrote the paper	80

The following co-authors contributed to the Chapter:

Name	E-mail address	Nature of contribution	Extent of contribution (%)
Martina Meincken	mmeincken@sun.ac.za	Contributed to the writing of the paper, read and approved them	10
Luvuyo Tyhoda	ltyhoda@sun.ac.za	Contributed to the writing of the paper, read and approved them	10

2. With regard to Chapter 4 (Paper II - Magnesium based phosphate cement binder for composite panels: A response surface methodology for optimization of processing variables in boards produced from agricultural and wood processing industrial residues), the nature and scope of my contribution were as follows:

Nature of contribution	Extent of my contribution (%)
Conceptualised and wrote the paper	80

The following co-authors contributed to the Chapter:

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3. With regard to Chapter 5 (Paper III - Phosphate bonded wood composite products from invasive Acacia trees occurring on the Cape Coastal plains of South Africa), the nature and scope of my contribution were as follows:

Nature of contribution	Extent of my contribution (%)
Conceptualised and wrote the paper	65

The following co-authors contributed to the Chapter:

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4. With regard to Chapter 6 (Paper IV - Calcium phosphate bonded wood and fibre composite panels: Optimization of panel properties using response surface methodology), the nature and scope of my contribution were as follows:

Nature of contribution	Extent of my contribution (%)
Conceptualised and wrote the paper	80

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5. With regard to Chapter 7 (Paper V - Surface treatments of natural fibres and their effects on the properties of phosphate bonded composite products), the nature and scope of my contribution were as follows:

Nature of contribution	Extent of my contribution (%)
Conceptualised and wrote the paper	80

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Name	E-mail address	Nature of contribution	Extent of contribution (%)
Martina Meincken	mmeincken@sun.ac.za	Contributed to the writing of the paper, read and approved them	10
Luvuyo Tyhoda	ltyhoda@sun.ac.za	Contributed to the writing of the paper, read and approved them	10