Phosphate-bonded composite products: The influence of filler materials, biomass type, and processing method on panel properties

By

Lehlohonolo Benjamin Mngomezulu

Thesis presented for the degree of Master of Science
at
Stellenbosch University
Department of Forest and Wood Science, Faculty of AgriScience

Supervisor: Dr LuvuyoTyhoda
Co-supervisor: Prof. Martina Meincken

April 2019

Declaration

By submitting this dissertation electronically, I declare that the entirety of the work contained therein is my own, original work, that I am the sole author thereof (save to the extent explicitly otherwise stated), that reproduction and publication thereof by Stellenbosch University will not infringe any third-party rights and that I have not previously in its entirety or in part submitted it for obtaining any qualification.

Date: April 2019

Abstract

There is renewed effort in the construction sector to reduce CO_2 emissions through the use of alternative binding materials to conventional Portland cements. Among the alternatives are phosphate-based binders, which have been shown to have strength properties comparableto cement, and higher strength than lime-based products, while also having a lower carbon footprint than both materials. In an effort to reduce the cost of the phosphate binder, improving performance properties of the products, as well as further reducing the carbon footprint, filler materials based on by products from industrial processes were incorporated in the binder matrix and their performance assessed in composite board products. The selected filler materials included fly ash, silica fume and calcium carbonate. Biomass samples used included pine, bagasse and black wattle(*Acacia mearnsii*).Physical and mechanical properties, such as density, water absorption (WA), thickness swelling (TS), modulus of rupture (MOR) and modulus of elasticity (MOE) were tested according to BS EN 634-2 (2007). The products were alsoinvestigatedfor thermal behaviour through exposure to heat. Physical and mechanical properties, such as colour change, shrinkage, weight loss and flexural strength were studiedbefore and after heat exposure. Furthermore, panel products were laminated with rotary cut veneer sheets of pine (*Pinus elliottii)* with a thickness of 3 mm. The fabricated laminated panels were tested for modulus of rupture (MOR), modulus of elasticity (MOE) and density, based on ISO 16893 (2016).The effect of wood lamination on phosphate panel properties was investigated.

The density of the boards produced ranged from 0.82 to 1.16 g/cm^3, WA ranged from 15.77 to 48.42%, TS ranged from 0.35 to 4.18%, MOR ranged from 2.83 to 6.16 MPa and MOE ranged from 410.57 to 1737.87 MPa. Significant improvements of boards' properties were observed after lamination, with the MOR ranging from 14.96 to 56.94 MPa and MOE ranging from 3636.33 to 6827.65 MPa compared with boards prepared without lamination. The density of laminated panel products was found to range between 0.78 to 0.93 g/cm^3.All composite panels changed colour with increasing temperature and shrinkage also increased with increasing exposure to heat. The strength properties decreased significantly after treatment. The weight loss of pine board filled with fillers (fly ash, silica fume or calcium carbonate) occurred at 65–85ºC, 199ºC-210ºC and 298ºC–310ºC.

The general conclusion proved that calcium carbonate-filled boards had highly superior properties to boards filled with fly ash and silica fume. This was due to the reaction of calcium carbonate ($CaCO_3$) with monopotassium phosphate (KH_2PO_4) which allows $CaCO_3$ todissolve in the KH_2PO_4'ssolution and form a chemically bonded phosphate cement. Additionally, the biomass type had an effect on the board properties. Black wattle – a hardwood – performed better than the other two biomasses because of the differences in chemical composition. The temperature also had an influence on the board properties which activated the distribution of adhesives to the bonding site. On the other hand, the thermal resistance,physical and mechanical properties of the composites were influenced by water evaporation, type of fillers and the degradation of high volume of biomass utilised in the production of the composite boards. Particleboard filled with silica fume had higher strength resistance to exposure atelevated temperatures than boards filled with calcium carbonate and fly ash due to the ultra-fine, pozzolanic and reactive particles of silica fume that disperse in the paste and improve thermal resistance. The reaction of fly ash with magnesium potassium phosphate results in the release of amorphous compounds, such as CaO, SiO_2, Al_2O_3, MgO and K_2O. These amorphous masses fill the voids and bond the matrix together, thus increasing hardness of the product and reducingmass loss of boards with temperature increase.The study also showed the significant mechanical improvement after the lamination of boards with veneer. It was confirmed that lamination improves the strength properties of phosphate cement-bonded particleboards to meet the standards for its use in furniture, load bearing and heavy-duty load bearing.

Keywords: Biomass, silica fume, fly ash, calcium carbonate, phosphate cement, wood composites, lamination

Opsomming

Daar is ‘n hernude poging in die konstruksie sektor om CO_2 deur die gebruik van alternatiewe verbindings materiale met gewone Portland sement te verminder. Onder die alternatiewe is fosfaat-gebaseerde verbinders, wat sterkte eienskappe getoon het in die omgewing van sement, en hoër sterkte as kalk-gebaseerde produkte, asook ook 'n laer koolstof-voetspoor as beide materiale. In 'n poging om die koste van die fosfaat verbinders te verminder, verbetering van die prestasie eienskappe van die produkte, sowel as die koolstof-voetspoor verder te verminder, is toevoeg materiale gebaseer op byprodukte van industriële prosesse opgeneem in die verbindings matriks en hul prestasie beoordeel in saamgestelde bord produkte . Die geselekteerde toevoeg materiale het vliegas, silika rook en kalsiumkarbonaat ingesluit. Biomassa monsters wat gebruik is het denne, bagasse en swartwattel (Acacia mearnsii) ingesluit. Fiesiese en meganiese eienskappe, soos digtheid, water-absorpsie (WA), dikte swelling (TS), modulus van skeuring (MOR) en die modulus van elastisiteit (MOE) was getoets volgens BS EN 634-2 (2007). Die produkte was ondersoek vir termiese gedrag deur blootstelling aan hitte. Fisiese en meganiese eienskappe, soos kleurverandering, krimping, gewigsverlies en buig sterkte was ondersoek voor en na hitte blootstelling. Verder meer, paneel produkte is vanuit roterende gesnyde fineer velle van denne (Pinus elliottii) met 'n dikte van 3 mm gelamineer. Die gelamineerde panele is getoets vir modulus van skeuring (MOR), modulus van elastisiteit (MOE) en digtheid, gebaseer op ISO 16893 (2016). Die effek van hout laminering op fosfaat paneel eienskappe was ondersoek.

Die digtheid van die borde het gewissel van 0.82 tot 1.16 g/cm^3, WA het gewissel van 15.77 tot 48.42%, TS het gewissel van 0.35 tot 4.18%. MOR het gewissel van 2.83 tot 6.16 MPa en MOE het gewissel tussen 410.57 tot 1737.87 MPa. Beduidende verbeterings van bord eienskappe is waargeneem na laminering, met die MOR wat gewissel het van 14.96 tot 56.94 MPa en MOE wat gewissel het tussen 3636.33 tot 6827.65 MPa in vergelyking met borde wat voorberei was sonder laminering. Die digtheid van gelamineerde paneel produkte is gevind om te wissel tussen 0.78 em 0.93 g/cm^3. Al die saamgestelde panele verander kleur met toename in temperatuur en krimping het ook toegeneem met toenemende hitte blootstelling. Die sterkte eienskappe het aansienlik verminder na behandeling. Die gewig van denne borde wat gevul is met vullers (vliegas, silica rook of kalsiumkarbonaat) plaasgevind het by 65-85^{o}C, 199^{o}C-210^{o}C en 298^{o}C-310^{o}C verminder.

Die algemene gevolgtrekking bewys dat kalsium-karbonaat gevulde borde, hoogs uitstaande eienskappe toon teenoor borde gevul met vliegas en silika rook. Dit was as gevolg van die reaksie van kalsiumkarbonaat ($CaCO_3$) met monokaliumfosfaat (KH_2PO_4) wat $CaCO_3$ veroorsaak om op te los in die KH_2PO_4's oplossing en vorm 'n chemies gebinde fosfaat sement. Daarbenewens het die biomassa tipe 'n uitwerking op die bord eienskappe gehad. Swartwattel - 'n hardehout – het beter as die ander twee biomassas gevaar as gevolg van die verskille in chemiese samestelling. Die temperatuur het ook 'n invloed op die bord eienskappe tot gevolg gehad, wat die verspreiding van die gom geaktiveer het tot by die bindings areas. Aan die ander kant, die termiese weerstand, fisiese en meganiese eienskappe van die saamgestelde produkte, is beïnvloed deur water verdamping, tipe vullers en die vermindering van 'n hoë volume van biomassa gebruik in die produksie van die saamgestelde borde. Spaanderbord gevul met silika rook het hoër sterkte weerstand teen blootstelling by hoër temperature as borde vol kalsiumkarbonaat en vliegas as gevolg van die ultra-fyn, pozzolanic en reaktiewe deeltjies van silika rook wat versprei in die pasta en sodoende termiese weerstand verbeter. Die reaksie van vliegas met magnesium kaliumfosfaat veroorsaak die vrylating van amorfe verbindings, soos CaO, SiO_2, Al_2O_3, MgO en K_2O. Hierdie amorfe massas vul die leemtes en bind die matriks saam en sodoende word hardheid die produk verhoog en die massa verlaag met ‘n toename in temperatuur. Die studie het ook ‘n beduidende meganiese verbetering na die laminering van die borde met fineer getoon. Dit is bevestig dat laminering verbeter die sterkte eienskappe van fosfaat-sement gebinde spaanderborde om aan die standaarde te voldoen vir die gebruik daarvan in meubels, lasdraende en swaar-lasdraende gebruik.

Kernwoorde: Biomassa, silika rook, vliegas, kalsiumkarbonaat, fosfaat-sement, saamgestelde hout produkte, laminering

Acknowledgements

With the power of God for the successful completion of my study (thesis), I wish to express my sincere gratitude and appreciation to the following people and institutions:

- Supervisor, Dr Luvuyo Tyhoda and Co-supervisor, Prof. Martina Meincken for their excellent supervision of my thesis. I thank you so much for the support and contribution to the completion of my study.
- Thank you to the Department of Forestry and Wood Science postgraduate research group, especially to Dr Stephen Osakue Amiandamhen for the guideline in contacting the research.
- Mr Wilmour Hendrikse and Mr Solomon Henry for their help and advice in the laboratory work.
- The special thanks to my financial support, National Research Foundation (NRF) South Africa (grant number 20693) and National Manpower Development Secretariat (NMDs) Lesotho
- Finally, I would like to say thank you to the Mngomezulu family, my parents, brothers and sisters for the love, financial and prayer support through the completion of my study.

Dedication

This thesis is dedicated to my God.

Table of Contents

List of Figures

List of Tables

Chapter one: Introduction

1.1 Background and motivation

Wood waste and agricultural residues from industries such as pulp mills, sugar processing and sawmill waste have previously been utilised to manufacture phosphate-bonded wood composite materials (Sinka *et al.*, 2018; Waugh, 2004;J Xiao 2018; Amiandamhen 2017; Amiandamhen *et al*, 2018;Amiandamhen *et al*. 2016). Phosphate binders can be prepared through the reaction of calcium oxide (CaO), calcium silicate $CaSiO_3$ or magnesium oxide (MgO) with monopotassium phosphate (MKP/KH_2PO_4) (Wagh, 2004). The phosphate cementso formed has excellent adhesiveproperties, which leads to high strength, as well as fire and water absorption resistance of fabricated building materials (Gardner *et al*. 2015; Wagh, 2013). Phosphate cement has been reported to have several advantages over Portland cement, which include less emission of carbon dioxide and requiring less energy for its extraction (Lloyd *et al*., 2009). However, there are some aspects that need to be resolved and understood regarding the products, including the bonding chemistry between phosphate cement and fillers, as well as the biomass fibres, thermal degradation and strength improvement when high volumes of biomass are incorporated in the products (Hajimohammadi and van Deventer, 2017;Happle and Nandjiwala, 2010).

The use of fillers and binders between matrix and reinforcement material reduces the hydrophilic properties of biomass by limiting the amount of free hydroxyl groups and flammability and results in improved physical and mechanical properties, such as moisture resistance, fire resistance, thermal degradation resistance, modulus of elasticity (MOE) and modulus of rupture (MOR) (Tajvidi andEbrahimi 2002; Xiao et al., 2018). Fillers such as fly ash, silica fume and calcium carbonate are used in cement composites largely to reduceoverall binder cost, improvement of the properties of cement, as well as converting waste materials intocomponents of marketable building materials (Musyoka et al., 2013). Fly ash is a byproduct resulting from the combustion of biomass or coal. Its use in building materials can be viewed as an alternative route aimed at its beneficiation as opposed to disposal into the environment and limited landfills. Previous studies carried out by Rajamma *et al*. (2009) andAmiandamhen *et al*. (2016) have shown that up to 20% fly ash can be mixed with phosphate cement without changing the properties of the final product. One of the advantages of phosphate-based cements is that they set at room temperature and thereby eliminate the need for additional energy inputs. However, Xiao *et al*., (2018) argued that the preparation of composite products using the hot-press method accelerates the solidification and strength development of the magnesium cement.

While fly ash has been successfully demonstrated to improve cement properties, silica fume, calcium carbonate, kaolin, and lignin residues are possible alternative fillers that can be used to minimise the cost of phosphate cement without affecting the physical and mechanical properties of the product. Silica fume, which is the subject of investigation in this study, is an ultrafine pozzolanic material, which is produced as a by-product during the melting of silicon to produce silicon metal and ferrosilicon alloys. Jiang *et al*. (2017) reported that replacing phosphate cement with more than 5% of silica fume increases the expansion of mortar, which negatively affects the volume stability of the cement. However, there is no literature detailingthe use ofsilica fume as partial cement replacement on wood-based composite products.

Further, while fly ash is showing promise as afiller in phosphate cements (Amiandamhen *etal*. 2016,Hong and Lubell, 2015), there are concerns regarding the long-term sustainability of its supply around the world due to pressure associated with its production which is coal-based electricity production. Bentz *et al*. (2017) suggested that calcium carbonate could be an alternative due to the sustainable supply as compared to fly ash, which may be limited. Calcium carbonate is an inexpensive and abundant material found in sedimentary rock and improves the properties of cement composites (Osman *et al*. 2004). Current literature shows no record detailing its incorporation in phosphate-based cement or its performance on composite board products.

The study is therefore aimed at investigating the properties of composite boards prepared with phosphate cement using calcium carbonate, fly ash and silica fume filler materials. Further, the study investigates the influence of processing temperature on composite boards filled with the respective filler materials, thermal retardant as well as strength improvement of the products.

1.2 **Research aims**

The general aim of this study is to develop value-added composite bio-fibre products from chemically-bonded phosphate ceramics and natural fibre residues. The study aims to combine the unique properties of chemically-bonded phosphate ceramicsfillers with those of biomass fibre to manufacture sustainable products that are resistant to water absorption, heat, and havehigh strength properties.

The following objectives have been identified to address the general aims of the study:

Objective 1

The first objective is to investigate and characterise the influence of fillers and temperature on mechanical and physical properties of the composite products.

To accomplish this objective, the prepared phosphates (magnesium phosphate cement) will be used with biomass fibres, namely black wattle (*Acacia mearnsii*), sugar cane bagasse (*Saccharum officinarum*) and pine sawdust (*Pinus elliottii*) waste, together with fillers as the partial replacement of binders, which include fly ash, calcium carbonate, and silica fume in the development of the panels. The panel manufacturing process will be optimised, and the effects of temperature, biomass and filler will be evaluated and characterised in the panels and the results are presented in Chapter four of this dissertation.

Objective 2

The second objective is to investigate and characterise the thermal resistance of the phosphate-bonded particleboards after their exposure to high temperature.

The optimised results from objective one will be used to investigate the thermal properties of the particleboard after being exposed to high temperature. The following properties; shrinkage, weight loss, colour change, and flexural strength will be investigated before and after the exposure to elevated temperature. The results are presented in Chapter four of the thesis.

Objective 3

The third objective is to investigate theeffect of lamination on phosphate-bonded composite properties with a single sheet of veneer.

The materials that will be used to achieve this objective are thin layers of veneer and the manufactured panels discussed in objective one. The manufacturing and design process of laminated composites will be optimised, and panel’s properties will be evaluated and characterised. The results are presented in Chapter four of thisthesis.

Chapter two: Literature review

2.1 Natural fibre composites

The concept of green chemistry and sustainability has resulted in a shift from the use of limited and non-renewable resources to renewable resources due to increased environmental awareness,promising sustainability and low cost for the building materials (Khedari *et al.*, 2004).Composite products produced from natural fibre have high strength and stiffness equivalent to conventional composites. Furthermore, they have low density but high strength in addition to being recyclable.

Composite products are materials made of two or more constituents with significantly different physical and chemical properties.These constituents producematerials with characteristics which are different from the original constituents when combined (Youngquist, 1999).

Natural fibre composite materials have been used for commercial purposes in most parts of the world as building materials for exterior/interior wall cladding, decking, ceiling, roofing, as well as shuttering. These building materials have also been used in many African countries, North America, Central America and Europe for the full construction of schools, theatres, hospital and residential homes (Olorunnisola and Adefisan, 2002). Recently most countries in the world have adopted natural fibre composite products for engineering uses due to their superior performance such as being lightweight but comparable in strength with Portland cement, and its stability.

Biocomposites however, have the disadvantage of having a lack of good interfacial adhesion, low melting points, and quality variation. However, the major problem in natural fibre composites is hydrophilicity and flammability. The hydrophilic problem causes the composite to absorb moisture, swell and rot due to fungal attack. The hydrophilic character is caused by strong polarised hydroxyl group contained in lignocellulose (Kalia *et al.*, 2009). Therefore, the solution to overcome the challenge of hydrophilic and flammability in natural fibre is the use of adhesives as the coupling agent, which reduce the moisture absorption in lignocellulose and break the chain of spreading fire in composites (Saba *et al.*, 2014;Dhakal *et al.,* 2007; Sain *et al.*, 2004)

2.2 Adhesives

The use of adhesives presents an opportunity for creating cheap and sustainable products from wood waste and agricultural residues. Adhesives are materials which are used to jointwo or more surfaces by surface attachment. The surface adhesion between fibre and adhesive plays asignificant role towards the performance of composites (Saheb and Jog, 1999). For example, water absorption in natural fibre composites can be reduced by the coupling agents (adhesives) incorporated with natural fibre in the composites. Adhesives are divided into different types, which include; thermoplastics, thermosetting resins, inorganic cement, renewable-based adhesives and wax-based adhesives that can be utilised as binders or coupling agents to fabricatecomposite products (Dhakal *et al.,* 2007*)*.

2.2.1 Thermoplastics

Adhesives such as thermoplastics have traditionally been used in wood composites since the beginning of the twenty-firstcentury in aerospace, automotive and construction(Ashori, 2008). However, they constitute only 30% of the market of composites due to their high cost.Thermoplastics are plastics that can be repeatedly heated and melted and which harden oncooling. They find wide application in composite production due to their distinct properties such as fire resistance, transparency, flexibility, toughness and they exhibit good mechanical properties and stable dimensions (Sorrentino *et al*., 2015). The well-documented example of thermoplastics used in the manufacturing of natural fibre composites include; polyurethane, polypropylene, polystyrene, and vinyl chloride. The major reason for using these adhesives is due to their low processing temperature (below 200°C) which is tolerable and prevents thermal degradation of natural fibre (Sorrentino et al., 2015; Saheb & Jog, 1999).

2.2.2 Thermosetting resins

Thermosetting resins like thermoplastics have excellent properties concerning composite products manufactured. The thermosetting resins, also known as thermosets are described as chemical liquids, soft solid or solid in a viscous state that can be changed irreversibly into infusible and insoluble network by curing reactions. The high strength of thermoset has created a wide range of uses which may include coating, adhesives in composites and electronic packaging. But their high price, flammability and combustion are stated to be limiting factors foruse in developing countries (Ma et al., 2016; Saba and Jawaid, 2018). The particleboards manufactured with thermosetting resins are classified according to grades. High-, middle- and low-particleboard grades which range from 16.5–23.5, 11.0–16.5 and 3.0–5.0 N/mm^2 respectively for modulus of rupture. High-, middle- and low-grade standards for modulus of rupture range from 2400–2750, 1725–2750 and 550–1025 N/mm^2 respectively (ANSI A208, 1999).

2.2.3 Renewable adhesives

In addition to the number of adhesives that are used in composite products, renewable adhesives are currently in the spotlight in the composite industry due to their various advantages such as raw material availability, environmental friendliness and biodegradability. These adhesives have been used since the 1940s but their interest increased recently due to environmental challenges associated with fossil-based resources. Examples include tannin-based adhesives, lignin-based adhesives, glues based on vegetable oils, soy flour-based adhesives and furan polymer-based adhesives (Lligadas et al., 2013). However, these adhesives are found to have several challenges such low strength, high cost and limited application due to less water resistance (Norström *et al.*, 2018).

2.2.4 Inorganic cement adhesives

Inorganic cement hasbeen used in the production of building material composite products, nuclear shielding materials, corrosion and fire protection industrial coatings, dental and prosthetics (Wagh, 2013). Inorganic cement includes; Portland cement, gypsum, geopolymer and phosphate cement. Inorganic cement materials are binder substances that are utilised in construction. When mixed with water they set, harden and bind other materials together. They have great potential for use in the development of various composite wood products due to their unique ability to bind various biomass-based waste materials both at room temperature and at elevated temperatures.. The composite products fabricated from inorganic cements as adhesives are classified according to BS EN 634-2 (2007) with minimum requirements in modulus of rupture, modulus of elasticity, density, thickness swelling and internal bonding of 9 N/mm^2, 4000N/mm^2, 1000kg/m^3,1.5% and 0.5 N/mm2 respectively.

2.2.4.1 Portland cement

Since the beginning of the twenty-firstcentury, concerns have been raised regarding the use of this cementing material due to its high energy consumption during extraction. This has forced many industries to shift from it and find an alternative (Liao *et al*., 2017). Portland cement is considered to consume 10–11 Ej of energy annually, which is approximately 2–3% of global primary energy use. It results in about 0.87 tons of carbon dioxide emission for every ton produced and accounts for 7% of CO_2 emissions which results in it being classified as non-environmentally friendly(Akbari *et al*., 2015). It is thus a concern in the cement and concrete industry to find a low energy, low CO_2 and high-performance binder to substitute for Portland cement.

2.2.4.2 Geopolymer cement

Geopolymers are binding materials that cure at ambient temperature. They are developed from the reaction of two materials containing aluminosilicate and concentrated alkaline solution. These are used as alternatives to conventional Portland cement. They find usesin transportation, infrastructure and construction. They emit less carbon dioxide, and are resistant to many durability agents that can plague conventional concrete (Davidovits, 2013).

2.2.4.3 Phosphate-based adhesives

Phosphate-based adhesives are used in the production of building materials, nuclear shielding materials, corrosion and fire-protectiveindustrial coatings, as well as dental and prosthetic applications (Wagh, 2013).

Phosphate cement isviewed as a potential substitute for Portland cement due to itspromising properties, including excellent adhesion, which leads to high strength of building materials (Ding *et a*l., 2012). Phosphates are naturally occurring rocks which are mainly found in Florida in the United States, inthe Western Sahara and in Kola in Russia (Wagh, 2004). Comparing phosphate cement with Portland cement, phosphateshave less energy consumption in extraction (Wagh, 2004).

Phosphate bindersare formulated through the reaction of oxide or carbonate of divalent or transition metal with metallic phosphate. Different alkaline metals such as calcium oxides CaO, Magnesium Oxide MgO, Aluminium Oxide Al_2O_3 and Iron Oxide Fe_2O_3 have been used in the formulation of binders in reaction with acid phosphate (Wagh, 2004; Amiandamhen *et al*., 2016; Amiandamhen ,2017; Amiandamhen et al., 2018). However, this study focuses only on MgO based phosphate binder that is utilised in panel production. The reaction of MgO and KH_2PO_4 is given in equation (5). The reaction of MgO and KH_2PO_4 results in the production of magnesium potassium phosphate hexahydrate $MgKPO_4$. $6H_2O$ which is called magnesium phosphate cement (MPC) or sometimes chemically bonded phosphate ceramic (CBPC). The reaction between the alkaline oxides and acid phosphates occurs in aqueous solution. Firstly, the acid phosphate in aqueous solution releases phosphate anions (as shown in equation 1) which increases its dissolution and the solubility of the alkaline components to allow part of it to dissolve in acids solution. This leads to the reaction of alkaline cations and acid anions and results in the formation of CBPCs (Wagh, 2013).

$$KH_2PO_4 \rightarrow 2H^+ + KPO_4^{2-} \qquad (1)$$

The release of hydrogen in equation (1) facilitates the dissociation of oxide. For example, if MgO is mixed in aqueous solution with equation (1), the small part of it will dissociate as shown in equation (2)

$$MgO \rightarrow Mg^{2+}(aq) + O^{2-} \tag{2}$$

The (aq) means that magnesium ion is an aqueous ion. Therefore, the reaction of cation (Mg^{2+})and anion (KPO_4^{2-}) in the solution neutralise each other and form magnesium potassium phosphate cement ($MgKPO_4$) as shown in equation (3).

$$Mg^{2+}(aq) + KPO_4{}^{2-} \rightarrow MgKPO_4 \tag{3}$$

$$2H^+ + O^{2-} \rightarrow H_2O \tag{4}$$

The water as indicated in equation (4) released and become bound water to make the reaction to be insoluble which results in the formation of CBPCs as a final product shown in equation (5) (Wagh, 2013).

$$MgO + KH_2PO_4 + 5H_2O \rightarrow MgKPO_4.6H_2O \tag{5}$$

This binder sets at room temperature, reduces the need for Portland cement, and enables the significant reduction of carbon dioxide emission(Liao *et al*., 2017; Yu *et al*., 2010). Other advantages of CBPCs include the fact that, they are not affected by the chemical composition of lignocellulosic fibre in the production of biocomposites, thus increasing their wide range of use in natural fibre composite production and contributingto a friendly environment (Amiandamhen *etal*., 2017). However, the major challenge of phosphate cement is lack of long-term durability data and lack of a standard method which measuresthe performance of products and conservative nature of the construction industry as well as high cost. The study is aiming to minimise the high cost and improve the properties of phosphate cement as well as contributing to addition of data from phosphate cement performance.

2.2.5 Filler components

Phosphate is more expensive than Portland, therefore fillers are used as partial replacement to reduce the high cost of phosphate binder and improve properties of the products (Wagh, 2004; Amiandamhen.2017). Fillers generate more binder, which improves adhesion and strength. Fillers have low carbon footprint resulting in clean and environment friendly products (Amiandamhen *et al*. 2016).

In addition, lignocellulosic material has some disadvantages of being hydrophilic in nature which brings about incapability with hydrophobic matrices and results in low or poor composite mechanical properties (Beg and Pickering, 2008). However, fillers are introduced to improve the biomass's composite properties. The use of fillers between matrix and reinforcement material reduces the hydrophilicity of biomass by limiting the excess of hydroxyl groups and results in the improvement of physical and mechanical properties such as moisture resistance, modulus of elasticity (MOE) and modulus of rupture (MOR) (Tajvidi and Ebrahimi, 2002). Fillers have the advantage of being lightweight, having reasonable strength and stiffness. The processing is flexible, ecologically friendly and economically important (Bledzki and Gassan, 1999). Some of the fillers considered in the study include fly ash, calcium carbonate, silica fume, kaolinite and lignosulphonate.

2.2.5.1 Ash

The CBPCs have been purportedto have a lower carbon footprint butcomparative strength properties with ordinary Portland cement. However, there are many aspects of CBPCs that need to be solved and understood. These may include chemical mechanisms with waste such as ash, silica fume and calcium carbonate, which are used to minimise the high cost and improve the properties of phosphate cement. Recently, fly ash as a filler in phosphate cement has been found to be more complex than hadpreviously been assumed (Lloyd *et al*., 2009). Furthermore, the development of understanding fly ash and CBPCs' chemistry and its effects on the fabrication of building materials is important in this study.

In addition, the high cost of CBPCs has triggered researchers to use fly ash as apartial replacement in the production of cement-based products as well as balancing the environmental issues (Nedeljkovic *et al.*, 2016). The utilisation of fly ash is not only important in the reduction of the cost and alleviation of disposal problems but also to improve cement properties and convert waste materials into marketable products (Hajimohammadi and van Deventer, 2017). Fly ash is a waste material from the combustion of biomass or coal from different uses. The solid biomass and coal combustion are used in many industries globally for power and heat generation. This results in major problems related to ash production as waste (Rajamma *et al.*, 2009). Coal has been used since the 1920s to produce energy which on the other hand increased ash in the environment (Ahmaruzzaman 2010). Ash produced globally from coal per annum was estimated to be around 600 million tons where 75–80% is fly ash which was also expected to increase vertically in future (Ahmaruzzaman 2010). Furthermore, in South Africa, coal is the dominant commercial fuel to produce electricity where a large quantity of coal is heavily combusted and resulted in millions of tons of ash. This is because in South Africa 90% of electricity is derived from coal combustion (Musyoka *et al.*, 2013).

The disposal of ash has been increasing and become an environmental problem. Therefore, the technology of using ash in cement in recent years has increased (Liao *et al.*, 2017). Ahmaruzzaman (2010)confirmed that the pozzolanic properties in ash and binding capacity are significant in the production of building materials. The utilisation of ash in building materials isbelieved to decrease the high rate of ash landfilled and disposal costs (Musyoka *et al.*, 2013). The studies revealed that up to 20% of ash can be incorporated in cement-based mortar without decreasing the mechanical properties of cement-based products. This means that adding more than 20% of ash in cement increases the volume and deteriorates the strength of cement-based products (Rajamma *et al*., 2009; Jiang *et al*., 2017). The use of ash in cement reduces the production cost, water demand of the paste, improves mechanical properties and lowers the exothermic output of the acid reaction which increases the cracking of a hardened paste (Amiandamhen *et al*., 2016; Wagh, 2013; Gardner *et al*. 2015). Jiang *et al*. (2017)has attested that fly ash incorporated with CBPCs such as magnesium phosphate cement improves the workability of the mortar, durability as well as physical properties in fabricated materials. However, many publications reported that fly ash improves the properties of building materials, but there is an unclear relationship between ash and CBPCs. It is therefore important to develop in-depth the relationship of fly ash and CBPCs.

2.2.5.2 Silica fume

Silica fume is a pozzolanic material which is produced as a by-product from silicon melting process. This process of melting silicon produces silicon metal and ferrosilicon alloys as the major products. Silica fume is widely used through incorporation into ordinary Portland cement in the production of building materials. It is well documentedthat silica fume improves the physical and mechanical properties of Portland cement products. It can also be used to minimise the cost and improve properties of CBPC-based building materials due to its ability to improve the mechanical and physical properties ofcement-based materials. However, high silicon fume in cement has been reported to negatively affect the properties of CBPC mortars. For example, it was stated that more than 5% of silica fume in CBPCs increases expansion of the mortar, which affects the volume stability of the cement (Jiang *et al*. 2017). It has small particles which range from 100–500nm and it is a reactive pozzolanic material, which makes it attractive for use as additives in manufacture of superior cementitious composite (Sanchez and Ince, 2009). However, there is limited literature on using silica fume with CBPCs (Jiang et al. 2017). The addition of information from this study will contribute to the limited data onsilica fume in CBPC.

2.2.5.3 Calcium carbonate

Since the beginning of thetwenty-first century, scientists have been trying to find an alternative to substitute for Portland cement due to its disadvantage to the environment. The laboratory work and practicals outside of laboratory have proven that some waste such as fly ash and slag have the ability to reduce the large amount of Portland cement that is used globally. However, there are questions that remain unanswered pertaining to the stability and sustainability of the supply of large quantitiesof fly ash for the production of building materials around the world. According to Bentz *et al.* (2017), the use of crushed stones such as calcium carbonate seems to be an alternative due to the sustainable supply of this material as compared to fly ash and slag which may be limited in the future due to environmental concerns linked to coal burning for power generation.

Calcium carbonate is a chemical component that is commonly found in sedimentary rock. It is one of the most abundant materials found on earth and it has been used in cementitious composite production (Osman *et al*., 2004). It is an inexpensive micro fibrous material that when incorporated with cement improves the mechanical properties of cementitious composite mortar (Cai and Panteki, 2016). Its low cost is economically important in the large-scale production of cement composite for construction of materials. The extraction of calcium carbonate needs less energy and releases less greenhouse gas such as carbon dioxide as compared to Portland cement. Furthermore, calcium carbonate is an inorganic single crystal with a diameter ranging from 0.5 to 2 µm. Its properties such as elastic modulus and tensile strength make it suitable to serve as microfiber in cement-based composites(Qian *et al.*, 2009; Zhou *et al.*, 2010; Beg and Pickering, 2008).

2.2.5.4 Kaolinite

Kaolinite is the most common clay mineral, with soft consistency and earthy texture. It can be easily moulded and shaped when wet. Previous studies have shown that fillers can improve some mechanical properties of composites, but can also negatively affect some properties (Mareri *et al.*, 1998). Many plastic and rubber industries use kaolin widely as a filler due to its reinforcing effect and mechanical properties such as stiffness and strength. In addition, the particle size and distribution of kaolin in composites are very important to improve mechanical properties (Mareri *et al.*, 1998).The dispersion of kaolin particles must be good to prevent agglomeration of particles that can create stress concentration in composites.

2.2.5.5 Lignosulphonate

Lignosulphonate is a brown amorphous powder and water-soluble anionic polyelectrolyte polymer. It is the by-product of wood pulp using sulphite pulping. It has been evaluated as a significant raw material for many chemical industries due to its nontoxicity, and viability. Lignosulphonate has been used by many industries as a filler in starch, petroleum-based plastics and rubber to improve strength and water resistance (Huang *et al*., 2003). Privas and Navard, (2013)reported that lignosulphonate in the form of lignin is the most abundant organic polymer on earth. It is found positioned in middle lamella as well as other cell wall components and provides the mechanical properties of cell wall and plants. In addition, lignin gives strength and improves mechanical properties of boards due to its ability to bind in nature(Park, Doherty and Halley, 2008).

2.3 Biomass raw materials

Natural fibres have been utilised since the 1970s economically and efficiently in reinforced composites. The significant improvement of biomass properties in composites such as low density, biodegradability, high strength and renewability has encouraged many industries globally to adopt natural fibre reinforced composites. Lignocellulose-based composites are also found to reduce respiratory irritation as compared to glass fibre composites. Properties of natural fibres that can influence composites include; structure of the fibre, cellulose content, the angle of fibre and degree of polymerisation. The interface between adhesives and biomass also plays an important role in the properties of composite products. Treated biomass can also influence the properties of the composite. Studies have shown that biomass treated with alkali, and acetylation processeshave improved bonding capacity which in turn improvesthe properties of composite materials(Bledzki and Gassan, 1999 andAmiandamhen, 2017). The biomass ratio to coupling agents also plays a significant role in properties of natural fibre reinforced composites. Industrial waste (sawmill, pulp mill, sludge etc.), agricultural residue (sugar cane bagasse, maize stalk,etc.) and invasive alien species (*Acacia cyclops, A. saligna, A. mearnsii and A. longifolia*) are some examples of biomass waste that can be incorporated with inorganic cement to produce building materials.

On the other hand, their use in fabrication products forms part of their management wastes. This is not only important for the environment, but also in transforming waste material to marketable products. This creates the opportunity to recycle materials at the end of their use and developusable building materials (Beg and Pickering, 2008). The biomasses used in the study are implemented as an alternative to hybrid, glass and plastics-reinforced composites because of environmental awareness. Therefore, the study aimed at using slash pine (*Pinus elliottii*), black wattle (*Acacia mearnsii*) and bagasse (*Saccharum officinarum*) from different industries' waste processes in South Africa to substitute non-renewable fibre and remove wastes from the environment.

2.3.1 Agricultural residue

Renewable materials from plants are the most significant raw materials that benefit processing in the industries owing to the short replenishment cycle resulting in a continuous flow production(Thakur *et al*., 2017). Bagasse is one of the important lignocellulosic residues left from sugar cane processing after the extraction of sugar juice from the stalk. Bagasse is a low-cost, renewable, abundant and environmentally clean material. It contains an elemental composition of; C: 45.5%, H: 5.6%, O: 45.2%and N: 0.3%.However, these properties can be influenced by sugar cane variety, soil condition, agronomic technology, climatic condition, residual foliage and the degree of cane preparation (Bilba *et al*., 2003).Mwasiswebe, (2005) reported that South Africa produces about 3.3 million tonnes of dry bagasse per year. In 2015, the production of sugarcane in South Africa was approximately 15 million tonnes, where 30% (4.5 million) was left as bagasse after the extraction of sugar juice (Cele, 2017). The excess bagasse residue is mainly utilised for furfural, pulp, paper, and electricity generation. However, a significant amount of surplus bagasse remains unused. Therefore, the production of fibre composites is one of the large industrial applications that offers a huge opportunity to reduce excess bagasse from sugar cane processing(Thakur *et al*., 2014).

Studies have been conductedto find the potential applications of bagasse residues in composite manufacture. Bagasse is technically used as an alternative to wood fibre due to the global concern for using petroleum-based fibrous materials, shortage of forests and environment issues. Ashori and Nourbakhsh, (2010) compared the performance of bagasse with sunflower stalk and corn stalk residue in composite products. The results showed that bagasse has superior mechanical properties tothe other two agricultural residues in composite products due to its chemical composition. In addition, bagasse was also reinforced with magnesium-based phosphate cements to develop building materials and to substitute Portland cement products that are environmentally unfriendly (Amiandamhen *et al*., 2016).

2.3.2 Industrial waste

Timber shavings, sawmill, pulp mill, sludge and sawdust are the most common wood wastes that are found in high volume in the South African forestry sector. Amiandamhen *et al*. (2016) reported that about 4.6 million tonnes of residues are generated annually from wood processing industries in South Africa. These wastes are produced during cutting, shaving and sawing. Many industries use pine waste to generate electricity and manufacture particleboard (Garay *et al*., 2009).*Pinus elliottii* in South Africa is planted mainly for commercial products such as timber. However, the waste from the industries is gradually increasing due to the world's increasing interest in using natural fibre and renewable materials in building, transportation and decorations. The use of these wastes not only benefitsthe environment, but also the innovation of new technology, economy and sustainability.

2.3.3 Alien invasive material

In South Africa, *Acacia cyclops*, *Acacia saligna*, *Acacia mearnsii* and *Acacia longifolia* are classified as alien invasive biomass species.

South African scientists have investigated the threat and negative impact of these invasive alien species on the environment, particularly on water, indigenous vegetables and grass. They have a negative impact on water stream flow and water yield which results in low water availability (Oelofse *et al.*, 2016). The South African government, through the working for water (WFW) programmes is working to clearthese invasive alien species, to create farmland and grassland for livestock and wildlife (Gaertner *et al.*, 2016). The invasive alien species cover $18x10^4km^2$ in South Africa, where the cleared trees are transported to forestry industries as a source of timber, and to rural communities for firewood(Zengeya *et al.*, 2017;Gwate *et al.*, 2016). Despite these applications, there remain large quantities of cleared waste from treeswhich remains unused. Part of the aim of this study is to convert wood waste into marketable products.

According to Yazaki *et al.* (1993) black wattle (*Acacia mearnsii*) contains a high amountof tannins which areanimportant source for use in leather tannin, waterproofing and in wood adhesives. Black wattle is a useful tree in South Africa because it is extremely versatile.

Forestry industries use it as a source of high-quality raw material for pulp production, timber and vegetable tannin. It is also used as firewood and building materials for rural communities. It is believed that, due to its high quantity and tannin content, it has the ability to improve adhesion in fibre-reinforced composite (Effah *et al.*, 2016).

Chapter three: Material and methods

Effects of adhesives, temperature, and fibre on the properties of phosphate-bonded panels

3.1 Materials

3.1.1 Wood waste and agricultural residues

Slash pine (*Pinus elliottii*) was supplied by Global Environment Facility (GEF); black wattle (*Acacia mearnsii*) was supplied by EC Biomass fuel pellets (Pty) Ltd and sugar cane bagasse (*Saccharum officinarum*) was obtained from Illovo Sugar Ltd.

3.1.2 Binder

The phosphate binder was produced from two products namely, magnesium oxide and monopotassium phosphate. Magnesium oxide with the following chemical 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% was supplied by the Macco Organiques from Czech Republic. Potassium phosphate mono basic is a soluble salt that is normally utilised in additives, fungicides and plant fertilizers. It was bought from Shijiazhuang Fertilizer Technologies Co. Ltd, China. Its chemical composition is: KH_2PO_4>98%; P_2O_5>51.2%; K_2O >33.5%; chloride <0.2%; water insoluble <0.2%; moisture <1.0%.

3.1.3 Fillers

Fly ash was supplied by Ulula ash from South Africa. The fly ash was obtained from coal combustion plants and its chemical composition is: SiO_2<60%; Al_2O_3<35%; CaO<10%; MgO<5%; Fe_2O_3<5%; TiO_2. Calcium carbonate ($CaCO_3$) was supplied by Kimix chemical and lab supplies Co, Cape Town, South Africa. Its chemical composition is: assay min 99.5%, chloride 0.001, heavy metal 0.0005%, and sulphate 0.005%. Silica fume, also known as micro-silica, is an ultrafine powder that is collected as the waste from the production of silicon and ferrosilicon alloys. It was supplied by MAPEI South Africa (Pty) Ltd with silica sand < 0.1%.

3.2 Methods: The effects of adhesive, temperature, and fibre on the properties of bonded panels.

3.2.1 Biomass and binder preparation

The three biomass residues from different industries namely bagasse, slash pine and black wattle were chipped and hammer-milled through a 2mm sieve. The milled samples were conditioned at 20°Cand 65% relative humidity for 24h before board production according to BS EN 634-2 (2007). The equilibrium moisture content of natural fibres was 7%.

Dead-burned magnesium oxide (MgO) and potassium dihydrogen phosphate (KH_2PO_4) were mixed together according to the ratios given in Table 1.

3.2.2 Experimental design

The experiment was designed according to Table 1 to determine the effects of different variables on the physical and mechanical properties of the cement-bonded particleboards. The design consisted of four variables namely, filler%, temperature and binder ratio where the biomass is a fixed variable. The effects of the variables are analysed and the Pareto chart and fitted response surface are used to evaluate the importance and relationship between the variables on the particleboard properties. Pareto charts and fitted response surfaces are the statistical techniques in decision-making that are used to select the number of variables that produce a significant relationship and overall effects on the product’s properties. The experiment according to CCD was design to give 16 total number of runs, 1 block, 3 replicates for each factor.

Table 1: Independent variables and levels for the central composite design.

	Levels		
Variables	Low	Medium	High
KH_2PO_4: MgO	1	3	5
Filler (%)	10	20	30
Temperature (°C)	20	85	150

3.2.3 Board formation

The conditioned biomass samples were mixed with binder and filler as shown in Table 1. The mixing proportions were designed using a central composite design (CCD). The biomass amount was kept constant at 80 g (36.71%) in all boards.

Firstly, binder, biomass and filler were dry-mixed thoroughly, and the determined amount of water was added and mixed until a homogenous mortar was formed. The amount of water was calculated according to Sotannde *et al.*, (2012) (equation 6).

$$W = B + (FSP - MC) * F \tag{6}$$

W = amount of water (ml), B = inorganic components (g), FSP= fibre saturation point (%), MC= moisture content (%) and F= biomass fibre (g).

The well-mixed paste was poured into a steel mould measuring 218x77x40 mm^3. The paste was pressed with 200 KPa pressure for 5 minutes at the corresponding temperature based on the design from Table 1. After demoulding, the board was cured at ambient temperature for 24 hours and subsequently conditioned at 20°C and 65% RH for 96 hours before testing. The experiment was repeated 3 times to minimise the errors.

3.2.4 Testing methods for particleboard properties

The conditioned particleboards were tested for modulus of rupture (MOR), modulus of elasticity (MOE), density, water absorption (WA) and thickness swelling (TS). The aims of the tests were to investigate the effect of binder ratio, fillers and temperature on the physical and mechanical properties of the resulting inorganic-bonded boards. The density of produced cement-based board was examined on the conditioned samples by weighing and measuring the dimensions.

The flexural strength test was conducted on an Instron testing machine fitted with a 250 kN load cell. The machine was set to apply load continuously throughout the test at a rate of 5 mm/min. The maximum load of deflection at the first failure was recorded and MOR and MOE were calculated according to BS EN 634-2 (2007).

Furthermore, the dimensional stability was evaluated in terms of water absorption (WA) and thickness swelling (TS). The samples were cut with an angle grinder into 75x50 mm^2 size. WA and TS test were carried out by weighing and measuring the thickness of the dry conditioned sample and submerging in water for 24 hours (BS EN 634-2 2007). After submersion, the samples were removed and drained at ambient temperature for 10 minutes, before they were weighed, and the dimensions measured again. The absorbed water and thickness swell were calculated and expressed in percentage.

3.3 Methods: Testing method for thermal resistance of phosphate-bonded particleboards

3.3.1 Blending ratios

The blended magnesium potassium phosphate cement (MKPC) formulation and filler content were designed using the STATISTICA software. Table 2 shows the optimised variables to produce the maximum predicted response. The content of lignocellulosic material was kept constant at 36.76%and the amount of water used was based according to Sotannde *et al.*, (2012).

The biomass was hammer milled and passed through a 2mm sieve. Subsequently it was conditioned at 20°C and 65% relative humidity (RH) for 96 hours before the board fabrication(ASTM: D1037, 2012). The fibre was thoroughly mixed with MKPC, fillers (fly ash, silica fume or calcium carbonate) and water until a homogenous mortar was formed. This was poured into a steel mould measuring 218 x 77 x 40 mm^3 and pressed to a minimum thickness of 13 mm with 200KPa pressure for 5 minutes at the different press temperatures, as illustrated in Table 2. The resulting cement-bonded particleboard was allowed to cure and dry at ambient temperature for 24 hours, after which it was conditioned at 20°C and 65% RH for 96 h before thermal tests were carried out. The experiment was repeated 3 times.

Table 2: The optimised variables to produce the maximum response from the desirability profile

Pine particleboards

	Fillers %	Binder (ratio) KH_2PO_4:MgO	Temperature ºC	Fibre%
Fly ash	3.18	4.86	85	36.76
Silica fume	3.68	3.18	150	36.76
Calcium carbonate	20	3.68	20	36.76

		Bagasse particleboards		
Fly ash	3.18	1	117.5	36.76
Silica fume	3.18	3.68	85	36.76
Calcium carbonate	11.59	6.36	150	36.76
		Black wattle particleboards		
Fly ash	3.18	3.36	85	36.76
Silica fume	28.40	2.86	150	36.76
Calcium carbonate	20	3.68	85	36.76

3.3.2 Thermal analysis

Before exposure to elevated temperatures, the fabricated board's dimensions were measured with a digital calliper. They were then placed in a ventilated furnace to assess their thermal degradation at 200°C, 300°C and 400°C respectively. Furnace was set to operate at the rate of 10°C/min until the target temperature reached and the final temperature was held for one hour. The furnace was then switched off to allow the specimens to cool down naturally before taking them out. The longest dimensions (Lengths) of specimen after heat exposure were measured to determine the drying shrinkage percentage of the sample. The drying shrinkage was calculated according to equation (7) (Alomayri *et al.*, 2014).

$$D = \left(\frac{lo - l}{lo}\right) * 100 \tag{7}$$

Where *lo* isthe initial length before heating and *l* is the length after the exposure to higher temperature and *D* is Shrinkage coefficient.

The samples before and after heat treatment were then subjected to three-point bending tests in an Instron testing machine. The Instron was fitted with a 5kN load cell and set to operate at a rate of 5mm/min. The maximum load at the deflection at first failure was recorded and flexural strength was calculated according to (ASTM: D1037 2012). The aim of the test was to investigate the influence of temperatures on phosphate cement-bonded boards strength properties before and after the exposure to high temperature.

The lightness of the particleboards before and after exposure to elevated temperatures was measured with a colorimeter CIE illuminate D65 with 10º observer angle and a sensor head of 6mm in diameter. L^* represents the degree of lightness ranging from white (100) to black (0)

$$\Delta L^* = {L^*}_t - {L^*}_i \tag{8}$$

Where t and i represent the treated sample and control respectively.

The weight loss percentage was determined by thermogravimetric analysis (TGA). The measured 5mg sample was put in the aluminium crucible and heated at a rate of 10ºC/min from 25°C to 400ºC in a nitrogen atmosphere. The analysis was done only on pine board filled with fly ash, silica fume and calcium carbonate due to the high cost ofusingthe thermogravimetric analysis method.

3.4 Method: Lamination of particleboards

Pinus elliottii rotary cut veneer was obtained from York Timbers, Mpumalanga, South Africa, with thickness of 3mm, a moisture content of 9%,density of 0.377 g/cm^3, and with no visible defects. The sheet dimensions were cut to 77x218mm. The veneer sheets were conditioned at 20ºC and 65% RH for 96 h before use. The surface of the veneer and boards were well cleaned by removing the dust or materials that could interfere with bonding.

Polyurethane (PUR) glue supplied by Henkel from Sempach/Switzerland was utilised as adhesive to laminate particleboard and veneer sheets. The glue was applied on one side of the veneer at a spread rate of 180g/m^2 based on wet mass. The assembly time was 20 min to allow the penetration of the glue into the veneer surface and its strength to become effective prior to the bonding formation. According to Fallis *et al*. (2011), if the assembly time for PUR is more than 45 min, it results in loss of solvents or water from the formulation hence the strength will be reduced.

Both sides of the core were laminated with veneer and pressed for 120 min at a pressure of 200 KPa. The laminated panels and controls were conditioned at room temperature and relative humidity of 65% for 96 h before further tests were carried out.

Strength properties i.e.modulus of rupture (MOR) and modulus of elasticity (MOE) of boards with three replicates were tested in an Instron testing machine fitted with a 5 kN load cell operating at a rate of 5 mm/min. The maximum load of deflection at the first failure was recorded and MOR and MOE were calculated based on ISO 16978 (2003).

Furthermore, two blocks per sample were cut with a grinder into 75x50 mm blocks to determine the density according to ISO 9427 (2003).

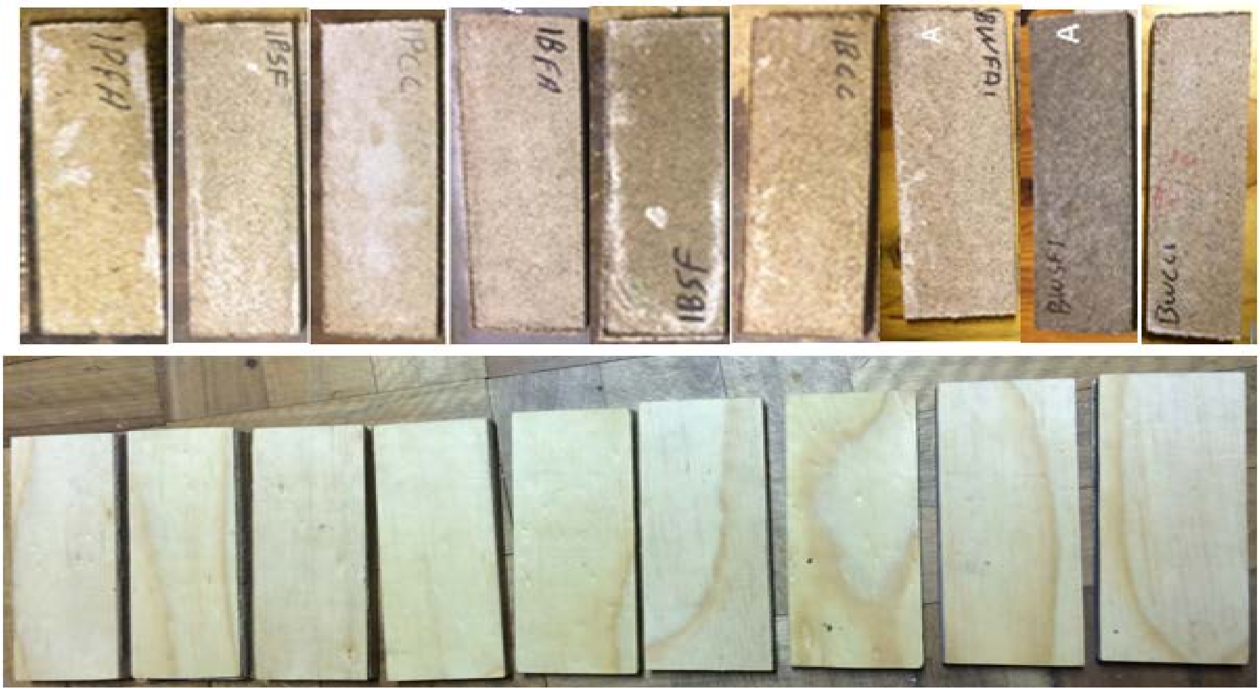


Figure 1: Laminated and non-laminated phosphate cement-bonded particleboards

Chapter four: Results and discussion

4.1 Effects of adhesives, temperature and fibre on the properties of phosphate-bonded panels

4.1.1 The optimum properties of cementitious composites from calcium carbonate, fly ash and silica fume fillers

The use of the various fillers in the study was aimed at minimising the cost of binder (KH_2PO_4: MgO) and improving composite properties. Table 3 shows the average test results obtained based on the CCD experimental design. It can be seen from the table that calcium carbonates as a filler resulted in better properties than fly ash and silica fume.

Table 3: Physical and mechanical properties of boards, using fly ash (FA), silica fume (SF) and calcium carbonate (CC) as fillers

	Pine board			**Bagasse Board**			**Black wattle board**		
Properties	**FA**	**SF**	**CC**	**FA**	**SF**	**CC**	**FA**	**SF**	**CC**
Density (g/cm^3)	0.94	0.93	0.95	0.82	0.85	0.99	1.14	1.16	1.21
WA (%)	24.14	27.32	31.01	48.42	45.23	30.63	18.45	18.32	15.77
TS (%)	2.37	1.75	1.33	4.18	3.15	3.40	0.55	0.35	0.45
MOR (MPa)	3.37	3.03	3.36	2.83	3.45	4.05	4.37	3.77	6.16
MOE (MPa)	1131.36	1194.34	959.14	410.57	542.33	697.68	1282.24	927.47	1731.87

The analysis of variance (ANOVA) procedure was used to analyse the effects of all the independent variables in the properties of particleboard produced (Tables 4–6). It was observed from analysis that the binder ratio, filler content and temperature have significant effects on the properties of the board ($p<0.05$). The response surface methodology (RSM) was used to analyse the interaction between variables and to predict desired board properties.

Table 4: ANOVA of the effect of binder ratio on the measured properties of the composite boards

Species (p values)

Properties	Fly ash			Silica Fume			Calcium carbonate		
	Pine	Bagasse	Black.w	Pine	Bagasse	Black.w	Pine	Bagasse	Black.w
Density	0.044*	0.046*	0.665	0.079	0.121	0.084	0.003*	0.077	0.026*
WA	0.256	0.008*	0.012*	0.342	0.119	0.037*	0.372	0.011*	0.021*
TS	0.720	0.351	0.127	0.108	0.154	0.104	0.075	0.475	0.371
MOR	0.007*	0.077	0.020*	0.197	0.010*	0.248	0.993	0.141	0.069
MOE	0.013*	0.040*	0.011*	0.212	0.010*	0.391	0.916	0.762	0.186

* denotes significant values at $p < 0.05$

Table 5: ANOVA of the effect of temperature on the measured properties of the composite boards

Species (p values)

Properties	Fly ash			Silica Fume			Calcium carbonate		
	Pine	Bagasse	Black.w	Pine	Bagasse	Black..w	Pine	Bagasse	Black.w
Density	0.117	0.148	0.360	0.430	0.206	0.195	0.911	0.087	0.319
WA	0.132	0.034*	0.284	0.641	0.168	0.052	0.245	0.008*	0.001*
TS	0.155	0.202	0.962	0.580	0.162	0.971	0.055	0.410	0.203
MOR	0.035*	0.982	0.335	0.981	0.014*	0.043*	0.458	0.145	0.788
MOE	0.270	0.047*	0.032*	0.204	0.006*	0.365	0.937	0.706	0.931

* denotes significant values at $p < 0.05$

Table 6: ANOVA of the effect of fillers content on the measured properties of the composite boards

Species (p values)

Properties	Fly ash			Silica Fume			Calcium carbonate		
	Pine	Bagasse	Black. w	Pine	Bagasse	Black. w	Pine	Bagasse	Black. w
Density	0.084	0.097	0.394	0.364	0.166	0.140	0.440	0.120	0.419
WA	0.077	0.007*	0.081	0.219	0.116	0.034*	0.318	0.007*	0.002*
TS	0.078	0.966	0.992	0.312	0.097	0.708	0.362	0.405	0.766
MOR	0.012*	0.071	0.079	0.092	0.008*	0.047*	0.863	0.128	0.085
MOE	0.034*	0.038*	0.080	0.054	0.003*	0.706	0.951	0.297	0.678

* denotes significant values at $p < 0.05$

4.1.2 Density

The minimum density requirement for cement bonded particleboard products is 1 g/cm^3 (BS EN 634-2). According to the results obtained, the phosphate cement-bonded particleboards manufactured from black wattle, phosphate cement using the 3 fillers met the density requirements and the board's density produced from black wattle with fly ash, silica fume and calcium carbonate as filler is 1.14, 1.16 and 1.21 g/cm^3, respectively. Based on BS EN 634-2, the boards produced from pine and bagasse residues with all fillers do not meet the cement-bonded particleboards standards.

The Pareto chart and fitted response from Figure 2a show that the fly ash and temperature significantly affected (p<0.05) the density of the pine cement-bonded boards. The significant interaction of fly ash and temperature with a binder ratio of 5:1 shows that an increase in temperature and fly ashcontent above 60 ºC and 15%, respectively, decreases the density of the pine boards. This is because an increase in fly ash above 15% increases the volume of the board without contributing to strength and density. The same results are observed by Amiandamhen *et al*, (2016). It can also be noticed from Figure 1b that there is a significant interaction between temperature and binder on the density of pine boards. An increase in binder at a fly ash content of 10% increased the density of the pine boards. The increase in binder ratio increases the formation of basic building block of the ceramic, which increases the density of the particleboards (Ding *et al.*, 2012). In addition, there is a significant effect of fly ash and temperature with a binder ratio of 5:1 on the density of bagasse boards. The response surface chart shows that fly ash and temperature have the same effect on bagasse boards ason pine board shown in Figure 2.

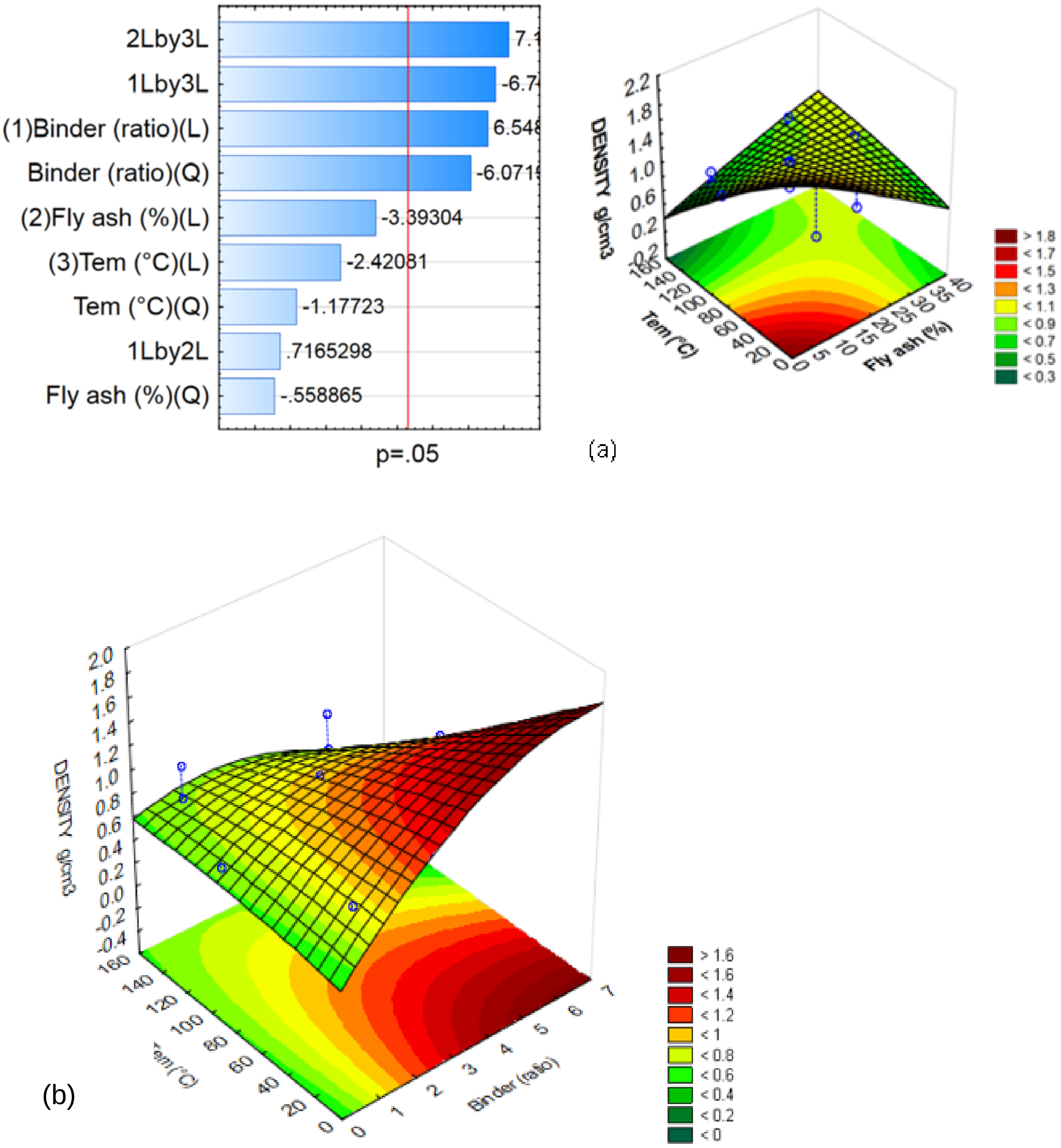


Figure 2: Pareto charts and response surfaces showing the influence of independent variables on density of pine boards and bagasse boards

4.1.3 Water absorption (WA)

The results show that some composite boards meet the WA requirements of cement-bonded particleboards, while others have a higher WA than the allowed maximum value of 25% (BS EN 634).The particleboards produced from bagasse, phosphate cement and 3 different fillers respectively, have aWA exceeding the minimum requirement. Panels produced from pine, phosphate cement and fly ash meet the requirements, while other fillers, such as silica fume and calcium carbonate have WA higher than the minimum requirements. The particleboards made from black wattle, phosphate cement and all 3 different fillers, respectively are found to perform best with regards to WA (Table 3).

The interaction between binder ratio and temperature has a significant influence on WA of the black wattle cement-bonded board. Figure 3 shows how binder ratio and temperature with 20% of silica fume filler affect black wattle board properties. Increasing the temperature to 160 °C has a little influence on WA, however increasing the binder ratio to 3:1 reduces the WA of the produced particleboards, but adding more binder increases WA again. The optimum binder ratio for WA resistance in black wattle boards was 3:1.

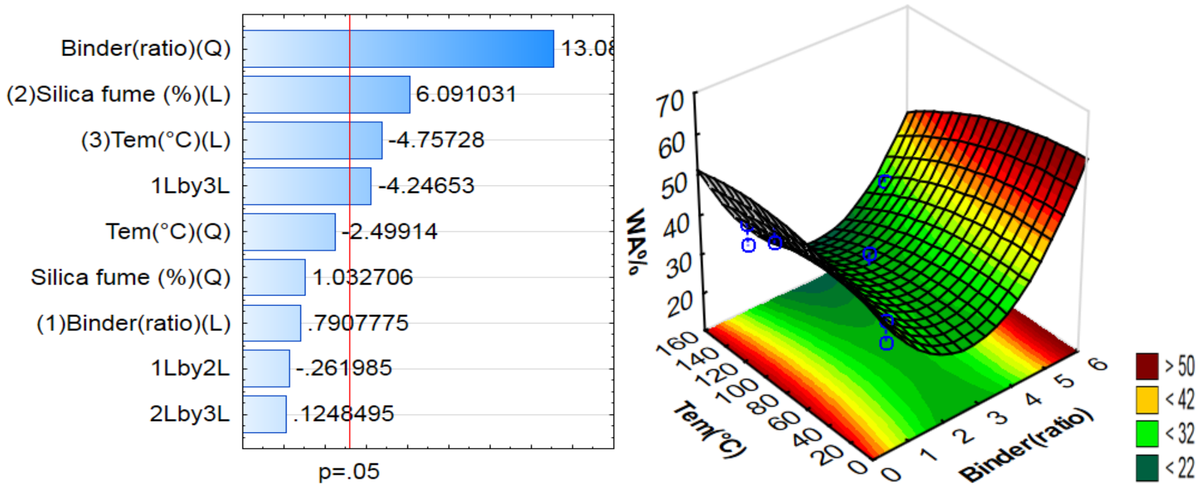
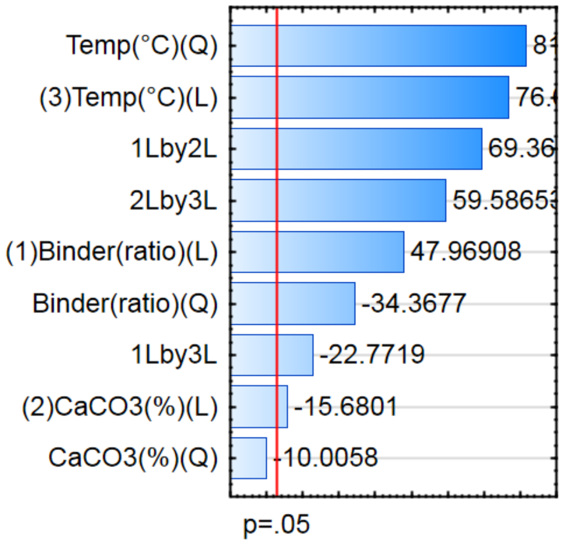
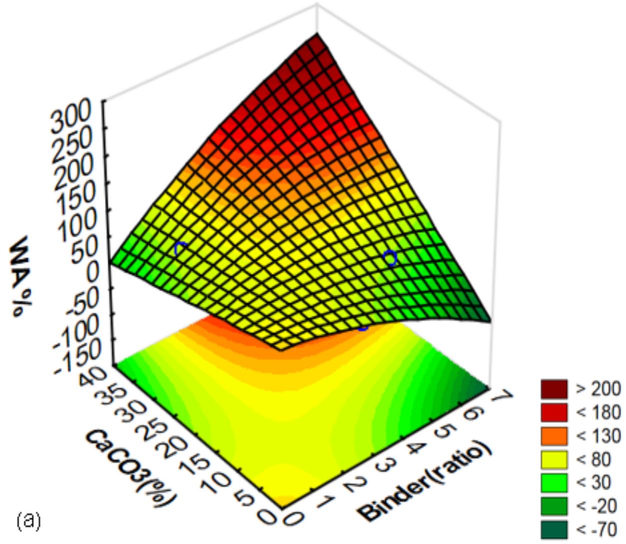


Figure 3: Pareto chart and response surface showing the influence of independent variables on WA of black wattle boards

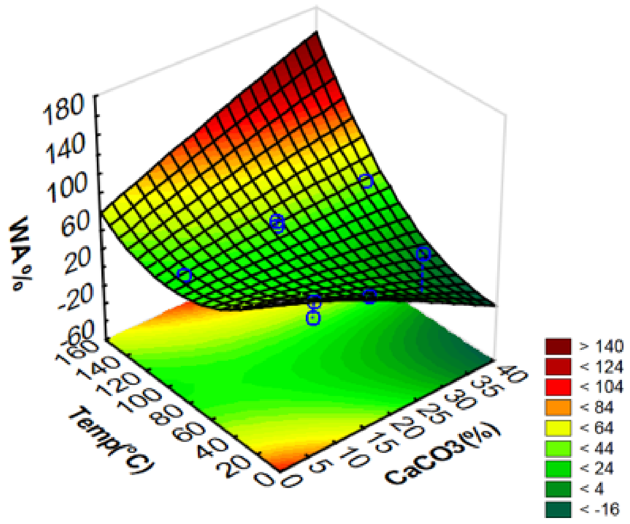
Furthermore, the interaction of $CaCO_3$ and binder ratio, temperature and $CaCO_3$ influences the WA of pine board. Figure 4 illustrates the interaction of different variables on pine boards. The results from Figure 4a show that a decrease in WA appears with increasing $CaCO_3$ and binder ratio at 150 °C. This may be due to the reaction of phosphate cements with $CaCO_3$ that forms a hard core bonded hydrated product which is water resistant (Wagh, 2013). In addition, the temperature and $CaCO_3$ at a binder ratio of 3:1 have a significant effect on pine boards (Figure 4b). The results show that an increase in $CaCO_3$ above 15% decreases WA in a temperature range between 40 and 140 °C. The decreased WA due to a high $CaCO_3$ content is related to the reaction between acid phosphate and alkaline carbonate. The acid phosphate (KH_2PO_4) in aqueous solution releases phosphate anions, which increases the solubility of the alkaline component ($CaCO_3$). This allows more $CaCO_3$ to dissolve in the KH_2PO_4 solution and results in the formation of chemically bonded phosphate cement, which is resistant to water penetration, as observed by (Wagh, 2013).

Bagasse cement-bonded particleboards show the same results as pine boards, with a significant interaction between binder ratio and $CaCO_3$ at 150 °C.


Temp(°C)(Q)
8
(3)Temp(°C)(L)
76.
1Lby2L
69.36
2Lby3L
59.5865
(1)Binder(ratio)(L)
47.96908
Binder(ratio)(Q)
-34.3677
1Lby3L
-22.7719
(2)CaCO3(%)(L)
-15.6801
CaCO3(%)(Q)
10.0058
p=.05


WA%
300
250
200
150
100
50
0
-50
-100
-150
CaCO3(%)
40 35 30 25 20 15 10 5 0
Binder(ratio)
0 1 2 3 4 5 6 7
> 200
< 180
< 130
< 80
< 30
< -20
< -70

(a)


WA%
180
140
100
60
20
-20
-60
Temp(°C)
160 140 120 100 80 60 40 20 0
CaCO3(%)
0 5 10 15 20 25 30 35 40
> 140
< 124
< 104
< 84
< 64
< 44
< 24
< 4
< -16

(b)

Figure 4: Pareto chart and response surfaces showing the influence of independent variables on WA of pine boards (a) and bagasse boards (b)

4.1.4 Thickness swelling (TS)

TS is the change in thickness of the particleboard after submersion in water for 24 h. The maximum allowed for TS is 1.5% (BS EN 634) for the board to be used in external and humid conditions. TS of panels produced with black wattle for all 3 different fillers and phosphate cement meet the requirements. According to Yazaki *et al.* (1993) black wattle has a high tannin content, which is an important source of adhesive and can act as a waterproof material.

Pine boards produced with $CaCO_3$ also meet the cement-bonded particleboard standards for thickness swelling, but there is no significant interaction between the variables.

4.1.5 Modulus of rupture (MOR) and modulus of elasticity (MOE)

The minimum requirement for the MOR of cement-bonded particleboard is 9 MPa and 4000 MPa for the MOE (EN 634-2). MOR is the measure of the maximum bending load that a particleboard can withstand, while MOE is the measure of the stiffness of the board that gives the deflection from the applied load. Based on the results from table 3 the particleboards fabricated from bagasse, fly ash and phosphate cement have the lowest MOR of 2.83 MPa and MOE of 410.57 MPa, while the highest bending strength is recorded from the boards made of black wattle, calcium carbonate and phosphate cements with MOR of 6.16 MPa as well as the highest MOE of 1731.87 MPa. These can be attributed to the absence of void space in the particleboard, which enhances strength. The high mechanical strength of the board may be due to the calcium carbonate in magnesium potassium phosphate cement, which improves the early hydration degree and crystallisation in the board (Makaratat, *et al.*, 2010).

Figure 5a and 5b show the significant ($p<0.05$) interaction between binder ratio and temperature on the MOR and MOE of pine boards, respectively. An increase in binder increases MOR and MOE with a fly ash content of 10% and a change in temperature does not significantly influence MOR and MOE. This is due to the exothermic reaction of acid phosphate with alkaline oxides, which does not depend on temperature to set (Wagh and Jeong, 2003).

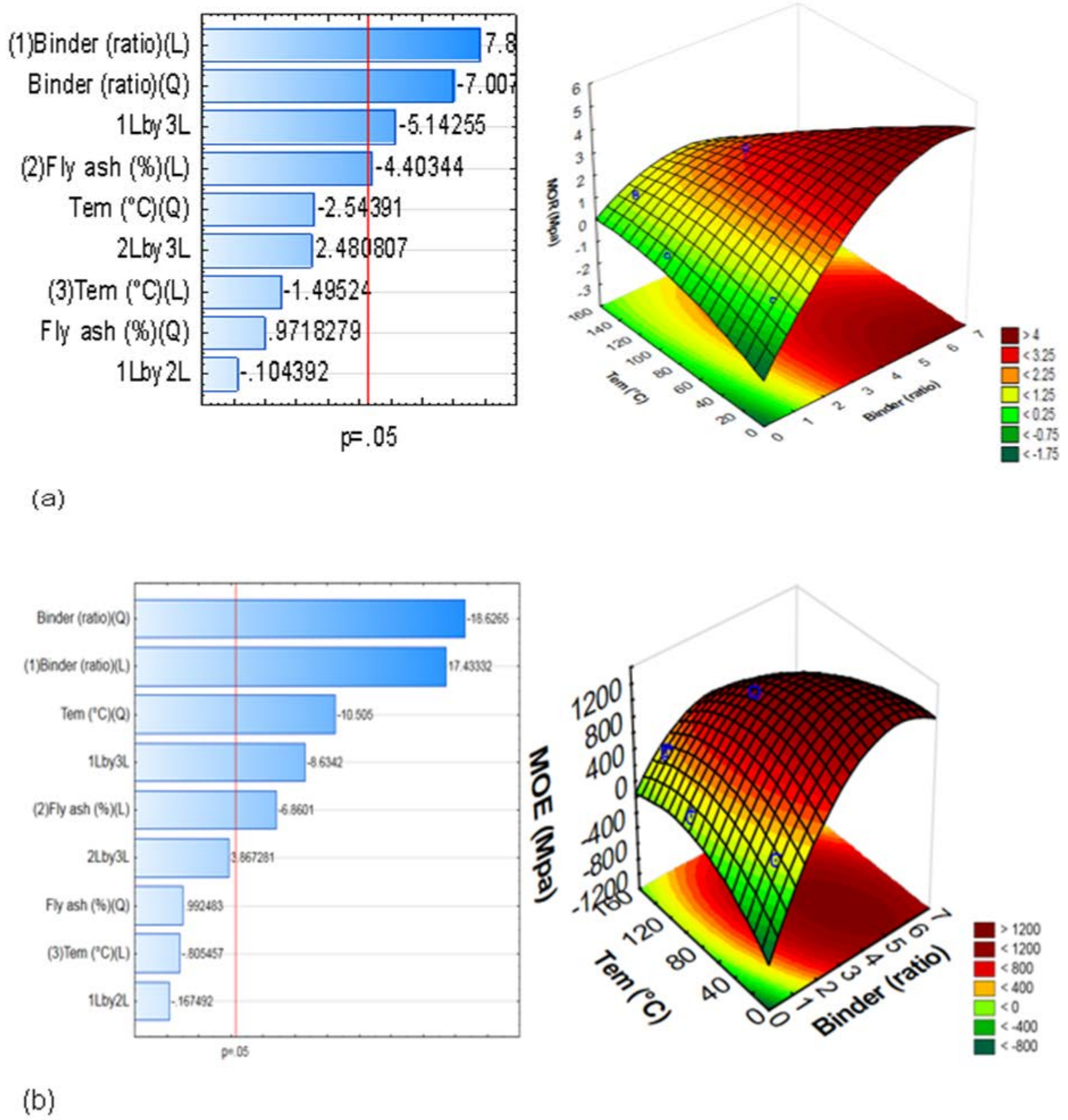


Figure 5: Pareto charts and response surfaces showing the influence of independent variables on (a) MOR, and (b) MOE of pine boards

Figure 6showsthat there is significant interaction between binder and fly ash content on the MOE of bagasse board at room temperature (20 °C). The fitted response surface plot shows that an increase in fly ash beyond 25% decreases the MOE of the bagasse boards. Although the chemistry between fly ash and magnesium potassium phosphate cement is not well understood, Xu *et al*. (2017)revealed that usinga high fly ash content in phosphate cement reactions results in poor composite strength.

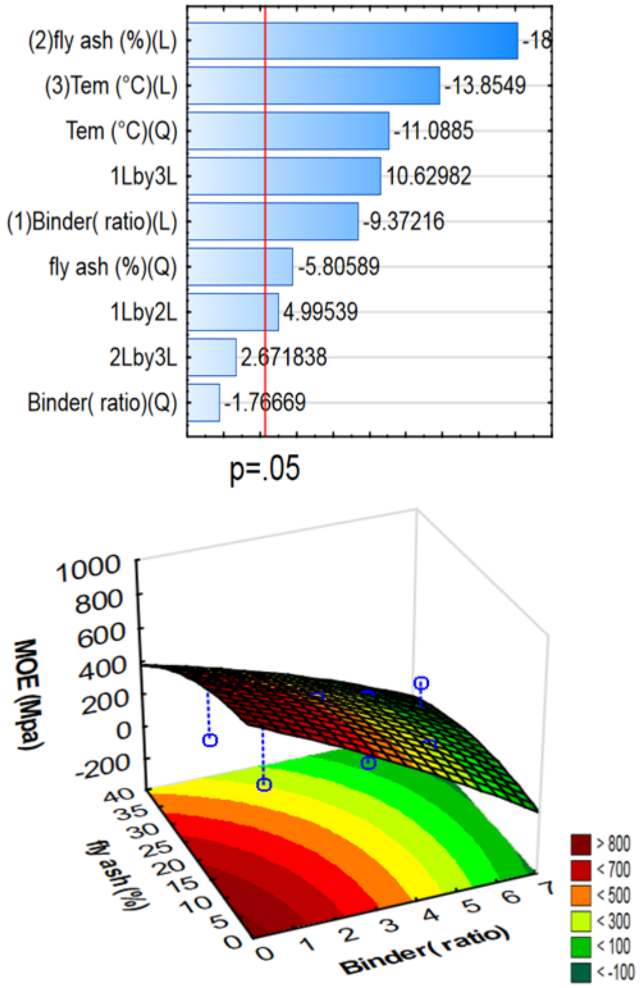
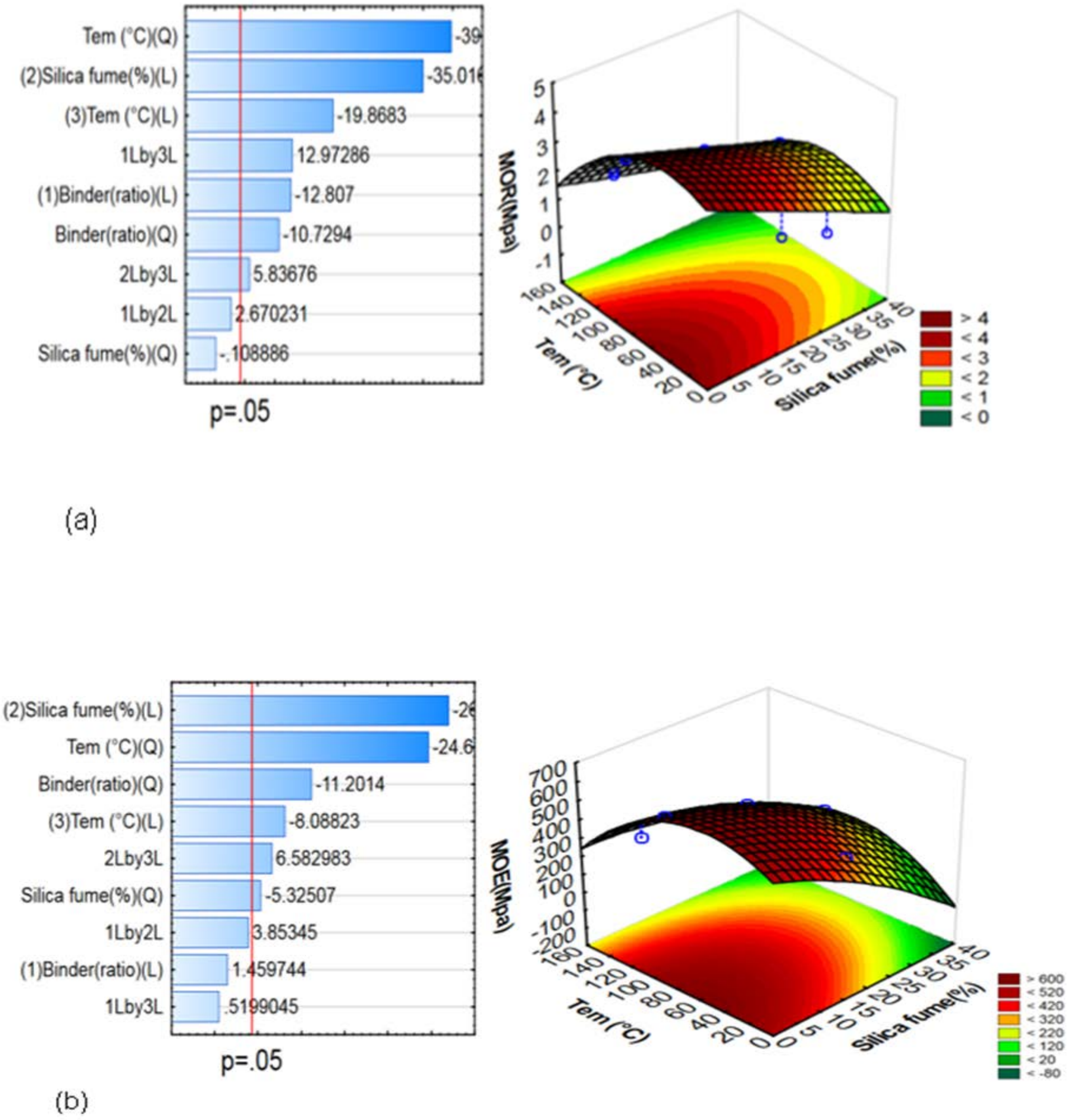


Figure 6: Pareto chart and response surface showing the influence of independent variables on MOE of bagasse boards.

The MOR of the bagasse board shown in Figure 7a is influenced by the interaction between silica fume and temperature. Taking into account the relationship between silica fume and temperature on MOR of bagasse particleboard, the figure shows that the increase in temperature beyond 120 °C and silica fume over 15% at a binder ratio of 3:1 decreases MOR. The same applies to the MOE of bagasse cement-bonded boards represented in Figure 7b. Silica fume is a very reactive pozzolanic material, like volcanic ash, and has the ability to improve the mechanical properties of cement mortar. However, the addition of silica fume above 15% decreases mechanical properties. This is because of the part densification of the interfacial zone between cement and silica fume as observed by Chung (2002).



(a)

(b)

Figure 7: Pareto charts and response surfaces showing the influence of independent variables on (a) MOR, and (b) MOE of bagasse boards.

The replacement of magnesium potassium phosphate cement with 10, 20 and 30% of silica fume in pine boards has a significant effect on MOE, as shown on the Pareto chart in Figure 8. Based on the fitted response surface, an increase in temperature and silica fume content to 15% at fixed binder ratio of 3:1 increases the MOE of pine board (Figure 8a). The higher temperature increases the distribution of adhesives between pine particles to the interfacial zone, hence the bonding reaction is improved, which results in increased MOE. Figure 8b shows the effect of binder and silica fume interaction on the MOE of pine cement-bonded board. An increase in binder ratio up to 5:1 and silica fume to 15% increases the MOE of the pine board. The improvement of MOE when silica fume is added below 15% may be due to fine particles which fill between cement particles. In addition, the chemical reaction of silica fume in hydrated cements improves mechanical properties due to its larger surface area and amount of amorphous silica. However, addition of silica fume above 15% decreases mechanical properties because of the high degree of crystallisation, which leads to high porosity that reduces the strength of the cement-bonded particleboard (Saad *et al.*, 1996).

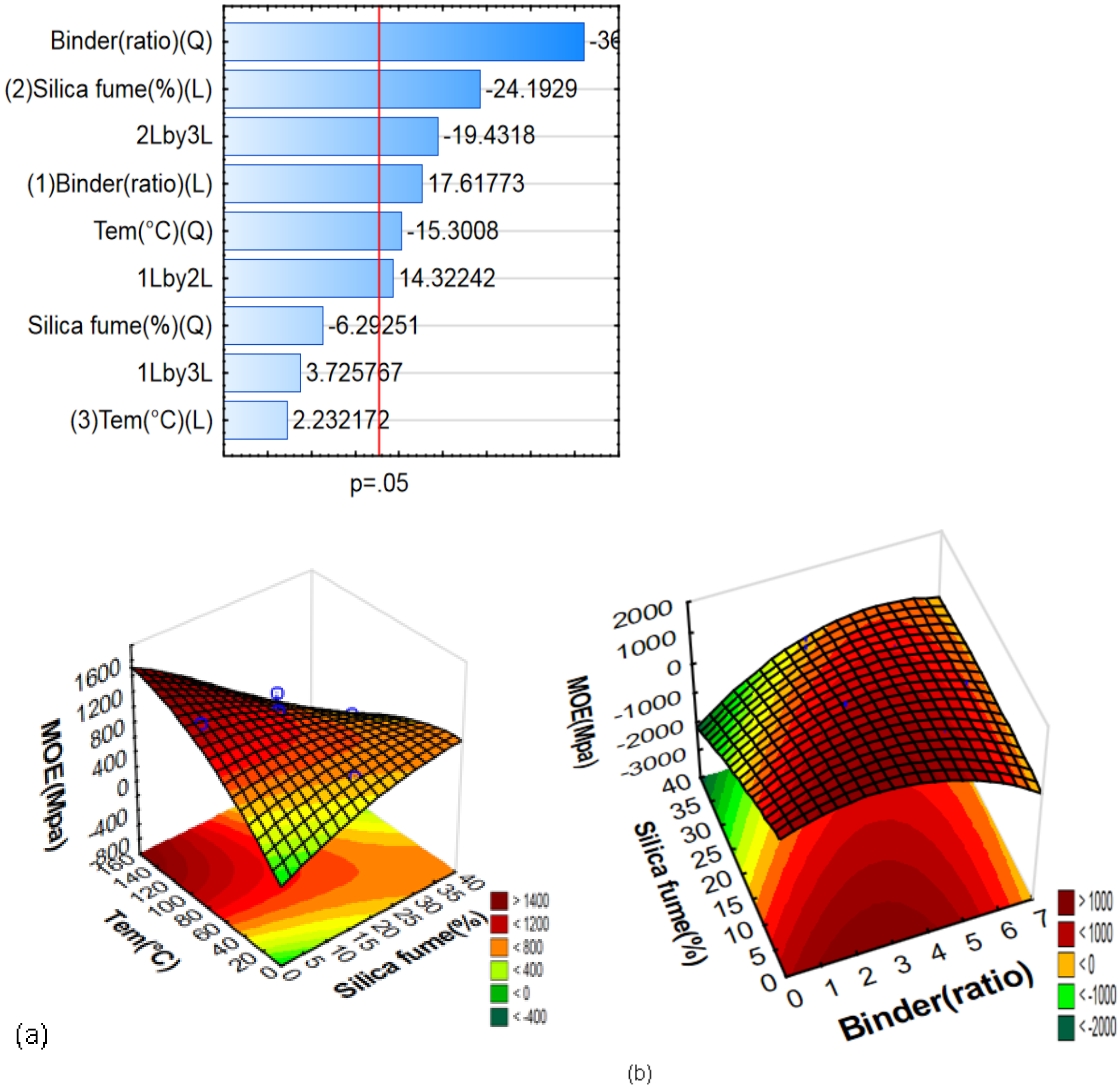


Figure 8: Pareto chart and response surfaces showing the influence of independent variables on MOE of pine boards

4.1.6 Influence of biomass on board properties

The biomass content in this research was kept constant (36.76%) to evaluate the influence of independent variables on board properties. The properties of boards produced from black wattle were superior to properties of pine and bagasse boards when using fly ash as filler (Table 3). This allows the assumption that the properties of black wattle play an important role in improving board properties due to its chemical composition i.e. high tannin content and high bulk density compared to pine and bagasse. Amiandamhen (2017) showed that increasing the black wattle content in phosphate cement boards without increasing binder content results in poorer board properties, such as highwater absorption. However, these observations were made from boards prepared at room temperature (without use of temperature).

Black wattle boards prepared with phosphate cements, where $CaCO_3$ is used as filler show better properties than the other biomass for all fillers. Based on the analysis of variance, black wattle boards with $CaCO_3$ as filler show no significant interaction between any of the variables and board properties. This can also be due to the chemical composition of black wattle, such as high tannin content, which influenced the properties of the board. Tannin is anatural polyphenol that is sticky when condensed and it is resistant to water penetration. It is extracted from different plants and used as environmentally friendly adhesives. Kim (2009) used natural tannin as an alternative adhesive to formaldehyde-based resin to minimise the emission of volatile organic compounds in the production of composite materials.

4.1.7 The optimisation of independent variable for MOR

Modulus of rupture is the most important variable for mechanical properties in determining load bearing of natural fibre reinforced composites applications (Bal, 2014).This study showed that the variables and their interaction have a significant influence on the particleboard properties. Therefore, the determination of the optimum conditions for the development of phosphate-bonded composite is required. The desirability profile in STATISTICA was used to establish the optimum variable levels that can used to predict MOR. The predicted MOR from different biomass, fillers, phosphate cement and temperature was derived from the analysis (Table 7). The optimum levels were then used to develop the observed response of the MOR.

Table 7: The optimum variables on predicted and observed MOR of the particleboards

MOR of pine board

	Fillers %	Binder (ratio) KH_2PO_4:MgO	Temperature ºC	Predicted MOR(MPa)	Observed MOR (MPa)
Fly ash	3.18	4.86	85	3.37	4.89
Silica fume	3.68	3.18	150	3.03	4.18
Calcium carb	20	3.68	20	3.36	4.75

MOR Bagasse Board

	Fillers %	Binder (ratio) KH_2PO_4:MgO	Temperature ºC	Predicted MOR(MPa)	Observed MOR (MPa)
Fly ash	3.18	1	117.5	3.12	4.29
Silica fume	3.18	3.68	85	3.45	5.15
Calcium carbonate	11.59	6.36	150	4.05	5.49

MOR of black wattle board

	Fillers %	Binder (ratio) KH_2PO_4: MgO	Temperature ºC	Predicted MOR (MPa)	Observed MOR (MPa)
Fly ash	3.18	3.36	85	4.37	5.51
Silica fume	28.4	2.86	150	3.77	5.27
Calcium carb	20	3.68	85	6.16	7.24

A polynomial model as shown in equation 9 presents the relationship between the response variable and independent variables.

$$y = x0 + ax1 + bx2 + cx3 + a2x1 + b2x2 + c2x3 + abx1x2 + acx1x3 + bcx2x3 \quad (9)$$

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.

Regression analysis was used to test the fitness of the developed model. An adjusted R-square value of 0.976 indicates a reasonable precision of the model. The degree of the model fitting between predicted and observed demonstrates an accurate in the optimisation of the variables.

4.2 Thermal resistance of phosphate-bonded particleboards

4.2.1 Thermogravimetric analysis (TGA)

The results of thermal analysis are illustrated through TGA by their derivative DTA curves in Figure 9. The analysis was done to measure the weight loss of pine particleboards (P) filled with fly ash (FA), silica fume (SF) and calcium carbonate (CC) fillers as a function of temperature. Table 8 represent four peak positions of pine boards observed from TGA

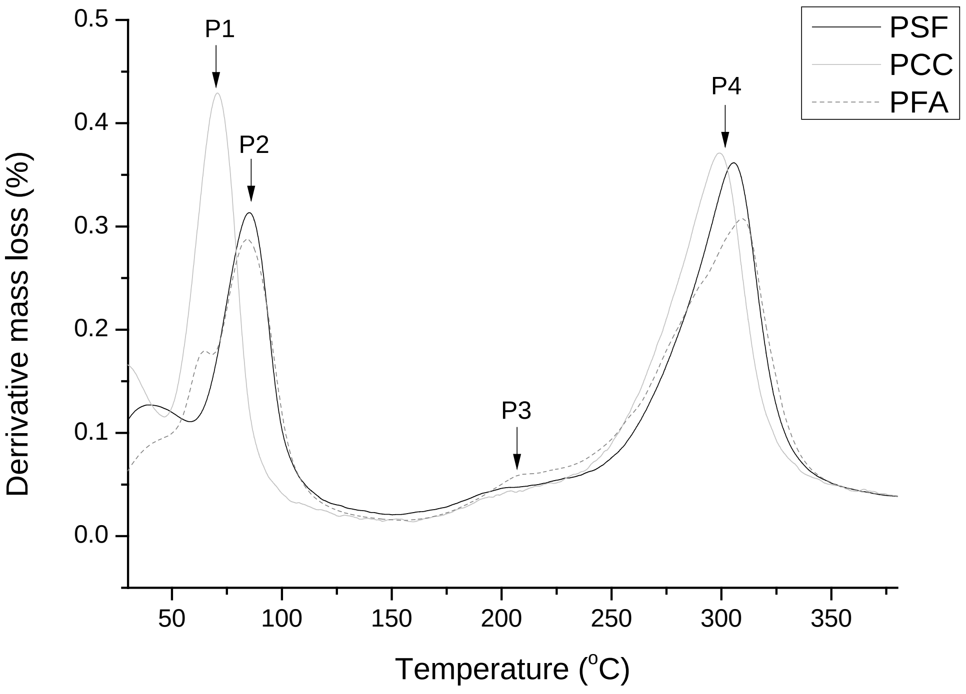


Figure 9: DTA curve of phosphate cement reinforced Pine boards where fly ash, silica fume and calcium carbonate are fillers

Table 8: DTA peak position of pine boards filled with fly ash, silica fume and calcium carbonate

Samples	Peak1 (ºC)	Peak 2 (ºC)	Peak 3 (ºC)	Peak 2 (ºC)
Pine / fly ash	65	85	210	310
Pine / silica fume	_	85	199	306
Pine / calcium carbonate	70	_	202	298

The mass loss after the exposure to high temperatures was influenced by water loss, filler types and degradation of biomass components. The DTA curves show four peaks for the pine boards made with different fillers. The first peak was observed at 65 ºC for fly ash and at 70 ºC for calcium carbonate and the second peak at 85 ºC for fly ash and silica fume. These peaks can be attributed to water loss. The loss of water at fairly low temperatures could be related to magnesium potassium phosphate, which is reported by Ma *et al*. (2014) to lose adsorbed water and decompose from around 60ºC onwards.

The third peak, which only appears as a small shoulder, was observed at temperatures between 199ºC and 210ºC and can be associated with the initial degradation stage for hemicelluloses and lignin (Brebu and Vasile, 2010). The fourth peak is observed in the range of 298ºC to 310ºC and is caused by the degradation of the cellulose inpine particles (Yang *et al.*, 2007).

According to Figure 9, boards made with fly ash as filler proved to be more resistant to weight loss caused by thermal degradation than the boards produced with silica fume and calcium carbonate. The reaction of fly ash with magnesium potassium phosphate results in the release amorphous compounds, such as CaO, SiO_2, Al_2O_3, MgO and K_2O. This amorphous mass fills the voids and bonds the matrix together, thus increasing hardness of the product and reducingdegradation as temperature increases (Li and Chen, 2013).

4.2.2 The effect of temperature on particleboard shrinkage

The shrinkage of the natural fibre reinforced phosphate cement increased with temperature as demonstrated in Figures 10-12. This tendency was observed in all samples at different temperatures. The shrinkage of the composites can be influenced by many factors including the type of biomass, adhesives and their content.

According to Figure 10, pine board made with calcium carbonate (CC) as a filler shows less shrinkage at elevated temperatures than the boards filled with silica fume (SF) and fly ash (FA). This could be due to the rigidity of calcium carbonate, which reduces thermal contraction (Lu and Dou, 2017).

However, Figure 11 indicates that there was less shrinkage on the bagasse board where fly ash was used as a filler, while the black wattle board shows less shrinkage for silica fume (SF) as a filler (Figure 12). According to Bakharev, (2006)fly ash and silica fume increase their volume with increasing temperature by forming a foam, and hence show little or no shrinkage.

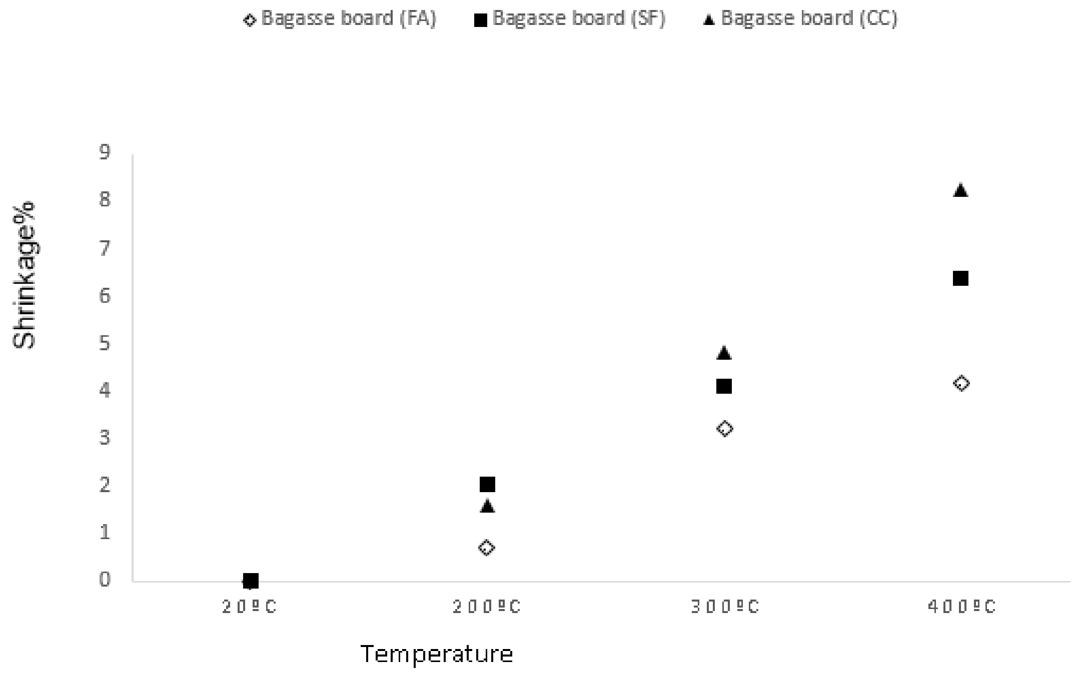


Figure 10: Shrinkage of pine particleboard at various temperatures

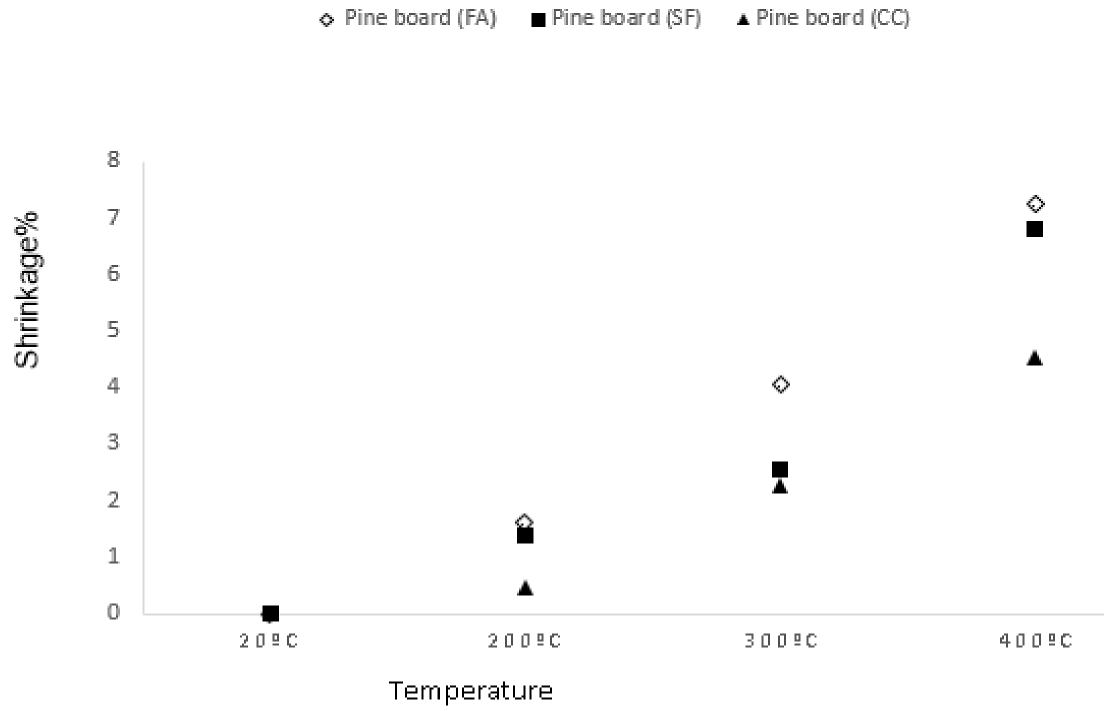


Figure 11: Shrinkage of bagasse particleboard at various temperatures

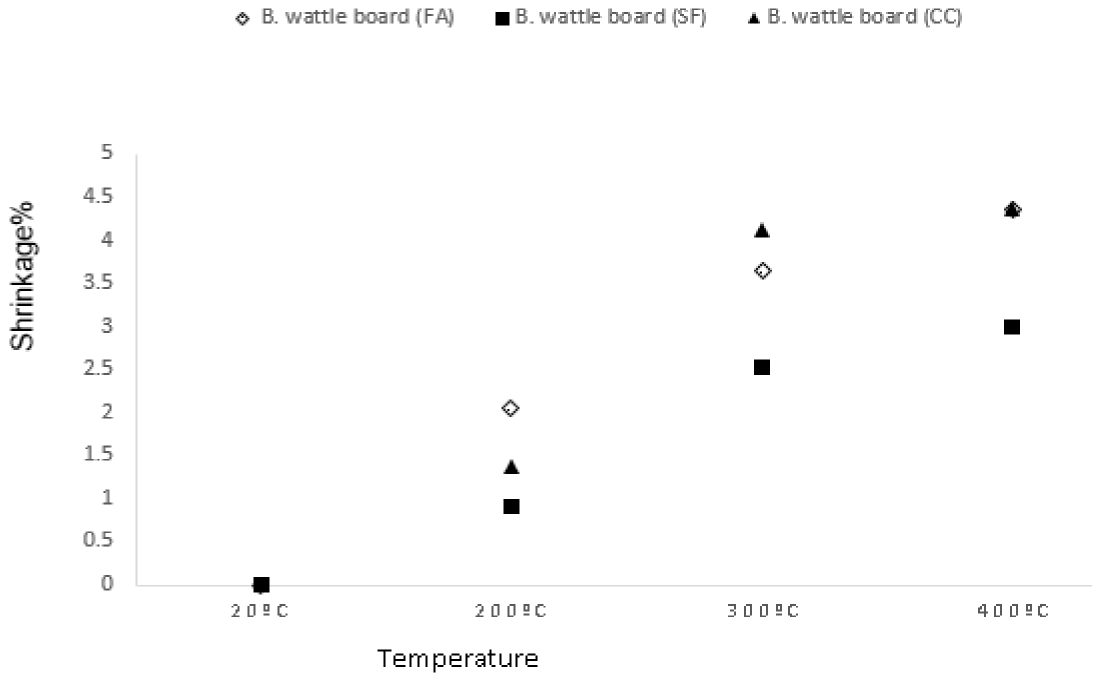


Figure 12: Shrinkage of black wattle particleboard at various temperatures

4.2.3 Change in lightness with an increase in temperature

The colour change of the particleboard is the first thing to be seen after intense heat. The colour change is a useful tool for estimatingthe amount of heat that can destroy a particleboard. It is also significant in the estimation of the mechanical properties ofbuilding materials after their exposure to intense heat. However,obsevation of colour by the naked eye is not consistent and can be affected by factors such as environment and colour variation. Therefore, the use of electronic colour measurement is important and consistent in theevaluation of the change in colour of the samples with increasing temperature (Aydin and Colakoglu, 2005).

Based on the colour parameters, specifically L^* (degree of lightness), results show that the particleboards become darker with an increase in temperature with the exception of pine board filled with calcium carbonate and black wattle board filled with silica fume.Figures 13, 14 and 15 show the changes in lightness of the fabricated boards from different biomass and fillers with respect to heat treatment.

The lightness of pine boards filled with fly ash and silica fume decreases significantly with an increase in temperature, while the lightness of the pine board filled with calcium carbonate decreased after exposure to 200ºC and increased after exposure to 300ºC (Figure 13). This might be caused by the colour change of calcium carbonate after exposure to high temperatures.

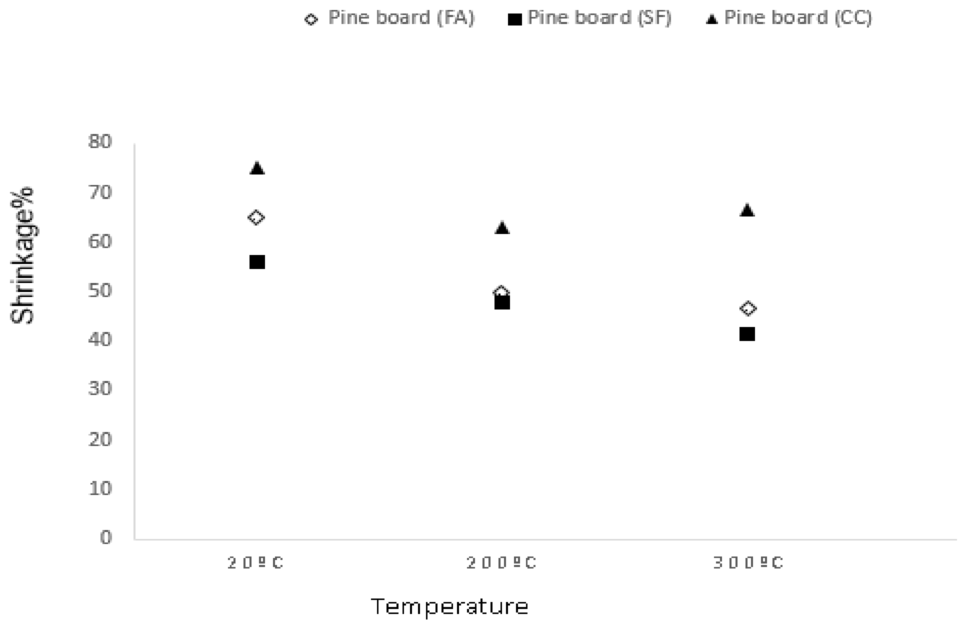


Figure 13: The effect of high temperature on the shrinkage of pine boards filled with fly ash (FA), silica fume (SF) and calcium carbonate (CC).

Bagasse boards filled with fly ash, silica fume and calcium carbonate show a steady decrease in lightness after exposure to high temperatures (Figure 14). The highest reduction in lightness was observed in the bagasse board filled with calcium carbonate.

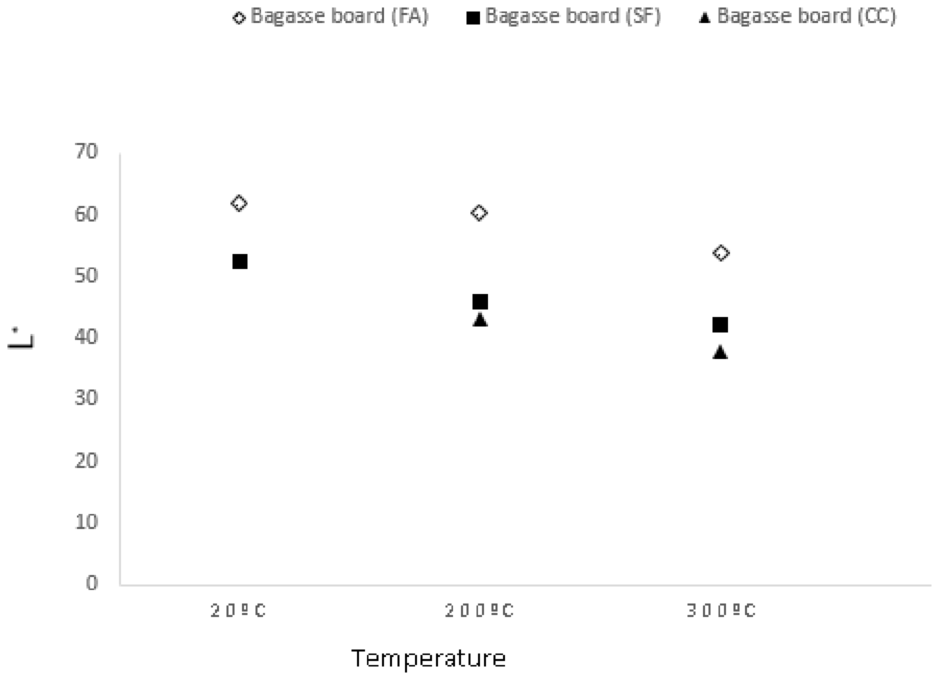


Figure 14: The effect of high temperature on the colour change of bagasse boards filled with fly ash (FA), silica fume (SF) and calcium carbonate (CC)

Figure 15 shows the change in lightness as a function of exposure temperature for black wattle particleboards with different fillers. The lightness decreased in boards with fly ash and calcium carbonate fillers with increase in temperature. However, the lightness of the board filled with silica fume decreased after exposure to 200ºC and then increased after exposure to 300ºC. This could be influenced by colour change of silica fume from grey to light grey as temperature increases.

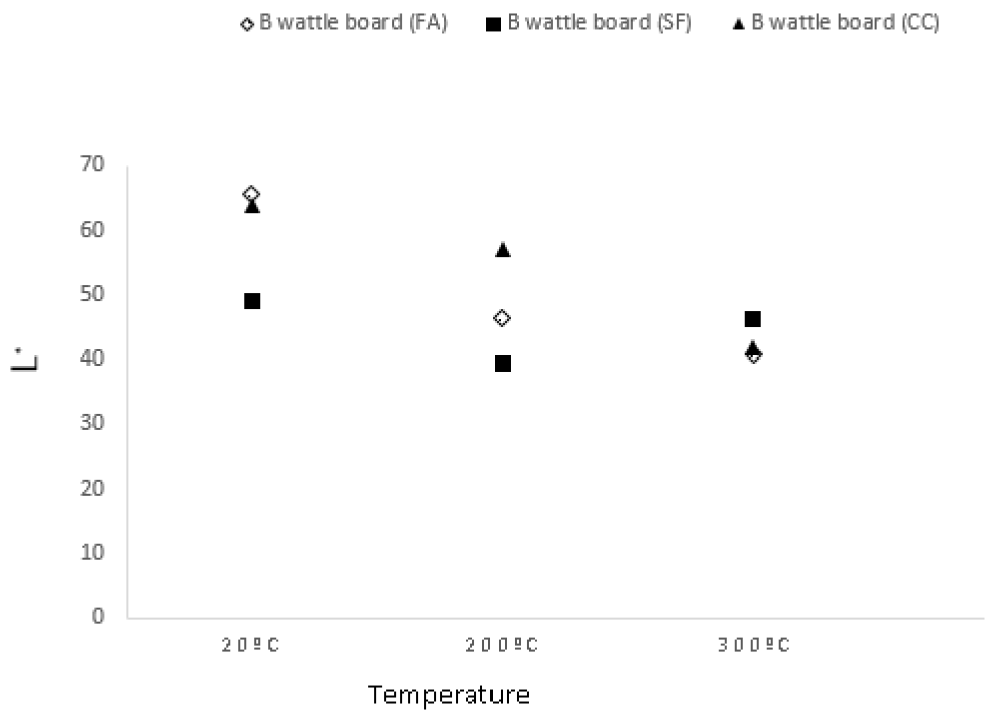


Figure 15: The effect of high temperature on the colour change of black wattle boards filled with fly ash (FA), silica fume (SF) and calcium carbonate (CC)

4.2.4 Flexural strength

The influence ofhigh temperatures on the flexural strength of natural fibre reinforced cement composite is demonstrated in Table 6. The strength of all composite boards from all three fillers and biomass degrades with the increase in temperature. In general, the increase in temperature increases the porosity and degradation of natural fibre composites which results in decreased strength (Alomayri *et al.*, 2014). The flexural strength at 400ºC is lower than at 300ºC and 200ºC respectively. The degradation of biomass at a higher temperature could be the main source of strength loss in natural fibre composites.

Pine board strength decreased with the increasein temperature. At 200ºC, the flexural strength of pine board where fly ash, calcium carbonate, and silica fume are fillers was reduced by 58.18, 50.90, and 14.83% respectively. At 300ºC the strength of pine board was reduced by 69.99% and 84.28% where silica fume and calcium carbonate were used as fillers. At 300ºC and higher, the biomass content degradedin all particleboards filled with fly ash. The incorporation of silica fume in pine board production shows higher thermal resistance as compared with other fillers.

The same results were observed with bagasse boards where silica fume was used. The boards showed less reduction in strength after the exposure to a temperature of 200ºC. The percentage reduction in the strength of bagasse boards where calcium carbonate, fly ash and, silica fume were used was; 49.55%, 38.13% and, 33.47% respectively. The exposure of bagasse boards to 300ºC where all three fillers were used in the production of boardsreduced flexural strength by 81%.

Black wattle boards filled with silica fume were more resistant to thermal degradation than black wattle boards filled with fly ash or calcium carbonate after being exposed to 200ºC for an hour. The percentage reduction in the black wattle particleboard where fillers are calcium carbonate, fly ash and, silica fume are; 54.24%, 24.01% and 19.11% respectively after being heated to 200ºC. At 300ºC, strength of black wattle board filled with fly ash was reduced by 82.75% as demonstrated in Table 9.

The higher thermal resistance of silica fume in all fabricated boards can be due to the ultra-fine, pozzolanic and reactive particles of silica fume that disperse in the paste and generate a large number of nucleation sites(Morsy *et al.*, 2014). As a result there is an increasein the homogenisation and density of fine particle distribution, which activates a reaction and bonding between natural fibre and adhesive particles. This results in fewer pores and high strength. However, after exposure to 300ºC heat, pine board shows 10% more resistancethan the other biomass fillers.

Table 9: Initial and residual flexural strength of particleboards before and after exposure to elevated temperature

	T (ºC)	Fly ash	Silica fume	Calcium carbonate
Pine boards (MPa)	Room T	5.89	4.17	5.75
	200	2.42	3.56	2.82
	300	_	1.25	0.90
	400	_	_	_

Bagasse boards (MPa)	Room T	5.29	6.15	5.49
	200	3.28	4.09	2.77
	300	300	1.17	1.06
	400	_	_	_
Black wattle board (MPa)	Room T	7.51	7.51	8.24
	200	5.71	5088	3.77
	300	1.30	_	_
	400	_	_	_

4.3 Lamination of particleboards results

The average density, MOR and MOE of the laminated and unlamented particleboards made from different fillers and biomass are shown in Tables 10–12. The results show that all the laminated boards have significantlyimproved properties, as compared with un-laminated boards. This improvement is due to glue and veneer which play an important role in the improvement of the mechanical properties of the natural fibre boards (Rowell, 2012). According to ISO 16893, (2006) standards 10, 11, 15 and 18 MPa are the minimum requirements for the bending strength of particleboard for general purpose, furniture, load-bearing and heavy-duty load-bearing particleboard for use in dry conditions respectively. The results show that all un-laminated boards prepared in such a way that a high content of biomass is incorporated in the products do not satisfy the requirements for particleboards' bending strength if the board is going to be used in weight-bearing applications.However, the laminated boards meet the bending strength for heavy-duty load bearing with the exception of boards made from bagasse filled with calcium carbonate. The bagasse board filled with calcium carbonate has an MOR of 14.96 MPa which meets the bending strength of general purpose and furniture grade boards for use in dry conditions (Table 12).

The modulus of elasticity of particleboards to be used for furniture, load bearing and heavy-duty bearing purposes in dry conditions should meet the ISO standards requirements of 1600, 2100 and 2900 MPa respectively. The MOE of un-laminated boards ranges from 1101.71 to 2996, 96 MPa (Tables9, 10 and 11),while all the laminated boards meet the minimum requirements for heavy-duty load-bearing particleboards where their average MOE ranges from 3636.33 to 6827.65 MPa (IOS 16893: 2016).

It can be seen that the laminated boards with veneer have a significant improvement in mechanical properties. However, the average density of the laminated boards is lower than that of the un-laminated boards. The average value of the un-laminated board’s density is found to be in the range of 1.03–1.19g/cm^3. The highest density of the un-laminated boards was observed in black wattle particleboard filled with 28% of silica fume and black wattle boards filled with 3.36% of fly ash. The lowest density of 1.03 g/cm^3 of un-laminated board is found on pine boards filled with 3.18% of silica fume.According to Tables10, 11 and 12, the average density of the laminated boards ranges from 0.78 to 0.93g/cm^3. This variation of the densities between laminated and un-laminated boards is influenced by the thickness of the veneer incorporated in laminated particleboards. The veneer sheet thickness and low mass contribute to the volume increase of laminated boards without significantly increasing mass, hence the density decreases.

Table 10: Properties of laminated (LB) and controls (ULB) fly ash-filled boards.

Types of boards	Filler % (fly ash)	KH_2PO_4: MgO (ratio)	T^{O}C	ULB MOR (MPa)	LB MOR (MPa)	ULB MOE (MPa)	LB MOE (MPa)	ULB density g/cm^3	LB density g/cm^3
Pine board	3.18	4.86	85	4.89	28.05	1382.22	5425.41	1.04	0.84
Bagasse board	3.18	1	118	4.18	20.32	1220.04	3636.33	1.34	0.83

Black wattle boards	3.18	3.36	85	4.75	56.94	1266.31	6390.40	1.19	0.92

Table 11: The variables of laminated (LB) and unlaminated (ULB) silica fume-filled boards

Types of boards	Filler % (silica fume)	KH_2PO_4: MgO (ratio)	T^{O}C	ULB MOR (MPa)	LB MOR (MPa)	ULB MOE (MPa)	LB MOE (MPa)	ULB density g/cm^3	LB density g/cm^3
Pine board	3.68	3.18	150	4.29	21.64	1400.11	4480.56	1.03	0.81
Bagasse board	3.18	3.68	85	5.15	23.35	1101.71	3966.45	1.15	0.79
Black wattle boards	28	2.86	150	5.49	18.67	2219.06	3798.39	1.19	0.82

Table 12: The variables of laminated (LB) and unlaminated (ULB) calcium carbonate-filled boards

Types of boards	Filler % (Ca CO_3)	KH_2PO_4: MgO (ratio)	T ^{O}C	ULB MOR (MPa)	LB MOR (MPa)	ULB MOE (MPa)	LB MOE (MPa)	ULB density g/cm^3	LB density g/cm^3
Pine board	20	3.68	20	5.51	24.20	1929.79	4500.50	1.11	0.82

Bagasse board	11.59	6.36	150	5.27	14.96	2771.00	4546.39	1.10	0.78
Black wattle boards	20	3.68	85	7.24	50.50	2996.90	6827.65	1.18	0.93

Chapter five: Conclusion

In conclusion, the research evaluated the effect of fillers (fly ash, silica fume and calcium carbonate), temperatures and biomass (*Saccharum officinarum*, *Pinus elliottii* and *Acacia mearnsii*) on phosphate-bonded particleboards. All the variables had a significant influence on the particleboard properties. However, calcium carbonate and black wattle as compared with other fillers and biomass respectively, had better properties than other variables. Calcium carbonate ($CaCO_3$) reacts with monopotassium phosphate (KH_2PO_4) in the solution to form a chemically bonded phosphate cement with high strength and resistance to water absorption. The use of temperature in the production of black wattle boards activated tannin content and accelerated magnesium reaction solidification, which binds the wood particles together and improves physical and mechanical properties. The temperature was not only important in energising the chemical components of board but also in the distribution of adhesives through natural fibre particles.

Furthermore, characterisation of the phosphate-bonded particleboards under elevated temperature changed with increases in temperature. However, better performance with regards to residual strengthafter exposure to high temperature was observed on boards prepared with silica fumecompared with other fillers. This was attributed to ultra-fine, pozzolanic and its reactive particles. Silica fume disperses in the paste due to fine particles and improves thermal resistance.Mass loss of the particleboard for pine board filled with fly ash was lower than all pine board filled with calcium carbonate and silica fume. In addition, pine board filled with calcium carbonate lost more water at low temperature than other boards hence its mass was easily influenced. The major contribution of mass loss was due to water evaporation from specimens and degradation of natural fibre at a high temperature. All the specimens change in colour after treatment with an elevated temperature and shrinkage percentage increases gradually with an increase in temperature.

The investigation of laminated cement-bonded particleboard witha thin sheet of veneer showed significant improvement in the strength properties compared to unlaminated boards. All the laminated particleboards had higher MOR and MOE which meet the standard for furniture, load bearing as well as heavy-duty load bearing for use in dry conditions. However, the MOR of all unlaminated boards did not meet the standards due to high biomass wastes used in the design of particleboard production. Unlaminated particleboards produced from pine, bagasse and black wattle board filled with calcium carbonate met the minimum MOE requirements standards for use in furniture, load bearing and heavy-duty load-bearing applications respectively. This was due to calcium carbonate ($CaCO_3$) that dissolves in the

KH_2PO_4 solution to form chemically bonded phosphate cement with high strength properties.The density of the boards was reduced after the laminations due to the increase in volume caused by veneer without significantly increasing the mass of the boards. The study revealed that the lamination of phosphate-bonded particleboards with a thin sheet layer of veneer meets the standards for use in furniture, load bearing and heavy-duty load bearing.

The use of phosphate cement in binding veneer and particleboard together remains unanswered. Therefore, it is recommended that further study is needed to evaluate and characterise the particleboards laminated with phosphate cements to bind thin sheets of veneer to the core. In addition, based on the analysis of variance, black wattle boards with $CaCO_3$ as filler showed no significant interaction between any of the variables and board properties, but indicated better properties than the other biomass and fillers. Therefore, further research is required to evaluate the tannin content from black wattle species' interaction with phosphate cement and fillers on the properties of produced board.

References

Ahmaruzzaman, M. (2010) ‘A review on the utilization of fly ash’, *Progress in Energy and Combustion Science*. Elsevier Ltd, 36(3), pp. 327–363.

Akbari, H., Mensah-biney, R. and Simms, J. (2015) ‘Production of Geopolymer Binder from Coal Fly Ash to Make Cement-less Concrete’, pp. 1–8.

Alomayri, T. *et al.* (2014) ‘Mechanical properties of cotton fabric reinforced geopolymer composites at 200–1000 °C’, *Journal of Advanced Ceramics*, 3(3), pp. 184–193.

Amiandamhen, S. O. (2017) ‘Phosphate Bonded Wood and Fibre Composites’, (March).

Amiandamhen, S. O., Meincken, M. and Tyhoda, L. (2016) ‘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’, *Industrial Crops and Products*. Elsevier B.V., 94, pp. 746–754.

Amiandamhen, S. O., Meincken, M. and Tyhoda, L. (2018) ‘The effect of chemical treatments of natural fibres on the properties of phosphate-bonded composite products’, *Wood Science and Technology*. Springer Berlin Heidelberg, 52(3), pp. 653–675.

ANSI A208 (1999) ‘Particleboard, American National Standard, Composite Panel’, *Association, Gaithersburg (1999)*.

Ashori, A. (2014) ‘Wood – plastic composites as promising green- composites for automotive industries ! (Review Paper)’, (August 2008). doi: 10.1016/j.biortech.2007.09.043.

Ashori, A. and Nourbakhsh, A. (2010) ‘Bio-based composites from waste agricultural residues’, *Waste Management*. Elsevier Ltd, 30(4), pp. 680–684.

ASTM:D1037 (2012) ‘Standard Test Methods for Evaluating Properties of Wood-Base Fiber and Particle Panel Materials’, *Current*, (June), pp. 1–8.

Aydin, I. and Colakoglu, G. (2005) ‘Effects of surface inactivation, high temperature drying and preservative treatment on surface roughness and colour of alder and beech wood’, *Applied Surface Science*, 252(2), pp. 430–440.

Bakharev, T. (2006) ‘Thermal behaviour of geopolymers prepared using class F fly ash and elevated temperature curing’, *Cement and Concrete Research*, 36(6), pp. 1134–1147.

Bal, B. C. (2014) ‘some mechanical properties of plywood produced’, 16(1), pp. 99–108.

Beg, M. D. H. and Pickering, K. L. (2008) ‘Reprocessing of wood fibre reinforced polypropylene composites. Part I: Effects on physical and mechanical properties’, *Composites Part A: Applied Science and Manufacturing*, 39(7), pp. 1091–1100.

Bentz, D. P. *et al.* (2017) ‘Limestone and silica powder replacements for cement: Early-age performance’, *Cement and Concrete Composites*. Elsevier Ltd, 78, pp. 43–56.

Bilba, K., Arsene, M. A. and Ouensanga, A. (2003) ‘Sugar cane bagasse fibre reinforced cement composites. Part I. Influence of the botanical components of bagasse on the setting of bagasse/cement composite’, *Cement and Concrete Composites*, 25(1), pp. 91–96.

Bledzki, A. K. and Gassan, J. (1999) ‘Composites reinforced with cellulose based fibres’, 24, pp. 221–274.

Brebu, M. and Vasile, C. (2010) ‘Thermal degredation of Lignin-A Review’, *Cellulose Chemistry and Technology*, 44(9), pp. 353–363.

BS EN 634-2 (2007) ‘Cement-bonded particleboards −Specifications- Part 2: Requirements for OPC bonded particleboards for use in dry, humid and external conditions’, *British Standard (2007)*.

Cai, J. ming and Panteki, J. (2016) ‘Using Calcium Carbonate Whisker in Engineered Cementitious Composites’, *Proceedings of the 9th International Conference on Fracture Mechanics of Concrete and Concrete Structures*, pp. 1–11.

Cele, N. P. (2017) ‘Beneficiation of sugarcane bagasse for materials development and energy generation in South Africa’, *NMISA celebrates 70 years of accurate scientific measurement (metrology) and 10 years of Institution existence!*, pp. 1–12. Available at: http://www.nla.org.za/conferences/proceedings_archive/2017/Presentations/Monday 31 July/M106 - Beneficiation of sugarcane bagasse for materials development and energy generation in South Africa.pdf.

Chung, D. D. L. (2002) ‘Review: Improving cement-based materials by using silica fume’, *Journal of Materials Science*, 37(4), pp. 673–682.

Dhakal, H. N., Zhang, Z. Y. and Richardson, M. O. W. (2007) ‘Effect of water absorption on the mechanical properties of hemp fibre reinforced unsaturated polyester composites’, *Composites Science and Technology*, 67(7–8), pp. 1674–1683.

Ding, Z. *et al.* (2012) 'Cementing mechanism of potassium phosphate based magnesium phosphate cement', *Ceramics International*. Elsevier, 38(8), pp. 6281–6288. doi: 10.1016/j.ceramint.2012.04.083.

Effah, B. *et al.* (2016) 'CHEMICAL FORCE MICROSCOPY ANALYSIS OF WOOD-PLASTIC COMPOSITES PRODUCED FROM DIFFERENT WOOD SPECIES AND COMPATIBILIZERS', 49(2), pp. 1–12.

Fallis, A. ., Gagnon, S. and Pirvu, C. (2011) *CLT Handbook: Cross-Laminated Timber*, *Journal of Chemical Information and Modeling*. doi: 10.1017/CBO9781107415324.004.

Gaertner, M. *et al.* (2016) 'Managing invasive species in cities: A framework from Cape Town, South Africa?', *Landscape and Urban Planning*. Elsevier B.V., 151, pp. 1–9.

Gardner, L. J. *et al.* (2015) 'Cement and Concrete Research Characterisation of magnesium potassium phosphate cements blended with fl y ash and ground granulated blast furnace slag', *Cement and Concrete Research*. Elsevier B.V., 74, pp. 78–87.

Gwate, O. *et al.* (2016) 'Exploring the invasion of rangelands by Acacia mearnsii (black wattle): biophysical characteristics and management implications', *African Journal of Range and Forage Science*, 33(4), pp. 265–273.

Hajimohammadi, A. and van Deventer, J. S. J. (2017) 'Characterisation of One-Part Geopolymer Binders Made from Fly Ash', *Waste and Biomass Valorization*. Springer Netherlands, 8(1), pp. 225–233.

Hong, L. T. and Lubell, A. S. (2015) 'Phosphate cement-based concretes containing silica fume', *ACI Materials Journal*, 112(4), pp. 587–596.

Huang, J., Zhang, L. and Chen, F. (2003) 'Effects of lignin as a filler on properties of soy protein plastics. I. Lignosulfonate', *Journal of Applied Polymer Science*, 88(14), pp. 3284–3290.

ISO16893 (2006) 'Wood-based panels -- Particleboard', *International Organization for Standardization*, p. 18.

ISO16978 (2003) 'specifies a method for determining the apparent modulus of elasticity and bending strength of wood-based panels in flatwise bending.', *International Organization for Standardization*, p. 5.

ISO9427 (2003) ‘specifies a method for determining the density of wood-based panels’, *International Organization for Standardization*, p. 3.

Jiang, Z., Qian, C. and Chen, Q. (2017) ‘Experimental investigation on the volume stability of magnesium phosphate cement with different types of mineral admixtures’, *Construction and Building Materials*. Elsevier Ltd, 157, pp. 10–17. doi: 10.1016/j.conbuildmat.2017.09.037.

Khedari, J. *et al.* (2004) ‘New low-cost insulation particleboards from mixture of durian peel and coconut coir’, 39, pp. 59–65.

Kim, S. (2009) ‘Environment-friendly adhesives for surface bonding of wood-based flooring using natural tannin to reduce formaldehyde and TVOC emission’, *Bioresource Technology*. Elsevier Ltd, 100(2), pp. 744–748.

Li, Y. and Chen, B. (2013) ‘Factors that affect the properties of magnesium phosphate cement’, *Construction and Building Materials*. Elsevier Ltd, 47, pp. 977–983.

Liao, W. *et al.* (2017) ‘Potential large-volume beneficial use of low-grade fly ash in magnesia-phosphate cement based materials’, *Fuel*. Elsevier, 209(May), pp. 490–497.

Lligadas, G. *et al.* (2013) ‘Renewable polymeric materials from vegetable oils: A perspective’, *Materials Today*, 16(9), pp. 337–343.

Lloyd, R. R., Provis, J. L. and Van Deventer, J. S. J. (2009) ‘Microscopy and microanalysis of inorganic polymer cements. 1: Remnant fly ash particles’, *Journal of Materials Science*, 44(2), pp. 608–619.

Lu, Q. C. and Dou, Q. (2017) ‘Investigation of the microstructures, properties, and toughening mechanism of polypropylene/calcium carbonate toughening masterbatch composites’, *Journal of Applied Polymer Science*, 134(46), pp. 1–16.

Ma, H., Xu, B. and Li, Z. (2014) ‘Magnesium potassium phosphate cement paste: Degree of reaction, porosity and pore structure’, *Cement and Concrete Research*. Elsevier Ltd, 65, pp. 96–104.

Ma, S. *et al.* (2016) ‘Research progress on bio-based thermosetting resins’, *Polymer International*, 65(2), pp. 164–173.

Makaratat, N., Jaturapitakkul, C. and Laosamathikul, T. (2010) ‘Effects of Calcium Carbide Residue-Fly Ash Binder on Mechanical Properties of Concrete’, *Journal of Materials in Civil*

Engineering, 22(11), pp. 1164–1170.

Mareri, P. *et al.* (1998) 'Mechanical behaviour of polypropylene composites containing fine mineral filler: Effect of filler surface treatment', *Composites Science and Technology*, 58(5), pp. 747–752.

Montecuccoli, S. O. A. Z. and Barbu, M. M. M. C. (2017) 'Phosphate bonded wood composite products from invasive Acacia trees occurring on the Cape Coastal plains of South Africa', *European Journal of Wood and Wood Products*. Springer Berlin Heidelberg, 0(0), p. 0.

Morsy, M. *et al.* (2014) 'Effect of Fire on Microstructure and Mechanical Properties of Blended Cement Pastes Containing Metakaolin and Silica Fume', (October).

Musyoka, N. M. *et al.* (2013) 'Synthesis of zeolites from coal fly ash using mine waters', *Minerals Engineering*. Elsevier Ltd, 53, pp. 9–15.

Mwasiswebe, D. (2005) 'Production of Activated Carbon from South African Sugarcane Bagasse', *Congress of the South African Sugar Technologist Association*, pp. 477–489.

Nedeljkovic, M. *et al.* (2016) 'Physical Properties and Pore Solution Analysis of Alkali Activated Fly Ash-', (August).

Norström, E. *et al.* (2018) 'Green Binders for Wood Adhesives', *Applied Adhesive Bonding in Science and Technology*, pp. 49–71.

Oelofse, M. *et al.* (2016) 'The impact of black wattle encroachment of indigenous grasslands on soil carbon, Eastern Cape, South Africa', *Biological Invasions*. Springer International Publishing, 18(2), pp. 445–456.

Olorunnisola, A. O. and Adefisan, O. O. (2002) 'Trial production and testing of cement-bonded particleboard from rattan furniture waste', *Wood and Fiber Science*, 34(1), pp. 116–124.

Osakue, A. S., Martina, M. and Luvuyo, T. (2017) 'Calcium phosphate bonded wood and fiber composite panels: Production and optimization of panel properties', *Holzforschung*, 71(9), pp. 725–732.

Osman, M. A., Atallah, A. and Suter, U. W. (2004) 'Influence of excessive filler coating on the tensile properties of LDPE-calcium carbonate composites', *Polymer*, 45(4), pp. 1177–1183.

Park, Y., Doherty, W. O. S. and Halley, P. J. (2008) 'Developing lignin-based resin coatings and composites’, *Industrial Crops and Products*, pp. 163–167.

Piñeiro, G. *et al.* (2008) ‘How to evaluate models: Observed vs. predicted or predicted vs. observed?’, *Ecological Modelling*, 216(3–4), pp. 316–322.

Privas, E. and Navard, P. (2013) ‘Preparation, processing and properties of lignosulfonate-flax composite boards’, *Carbohydrate Polymers*. Elsevier Ltd., 93(1), pp. 300–306.

Qian, S. *et al.* (2009) ‘Self-healing behavior of strain hardening cementitious composites incorporating local waste materials’, *Cement and Concrete Composites*. Elsevier Ltd, 31(9), pp. 613–621.

Rajamma, R. *et al.* (2009) ‘Characterisation and use of biomass fly ash in cement-based materials’, 172, pp. 1049–1060.

Rowell, R. M. (2012) *Handbook of Wood Chemistry and Wood Composites*. Second Edi. Madison: CRC Press.

Saad, M. *et al.* (1996) ‘Effect of temperature on physical and mechanical properties of concrete containing silica fume’, *Cement and Concrete Research*, 26(5), pp. 669–675.

Saba, N. and Jawaid, M. (2018) ‘A review on thermomechanical properties of polymers and fibers reinforced polymer composites’, *Journal of Industrial and Engineering Chemistry*. The Korean Society of Industrial and Engineering Chemistry.

Saba, N., Tahir, P. M. and Jawaid, M. (2014) ‘A review on potentiality of nano filler/natural fiber filled polymer hybrid composites’, *Polymers*, 6(8), pp. 2247–2273.

Saheb, D. N. and Jog, J. P. (1999) ‘Natural Fiber Polymer Composites : A Review’, 18(4), pp. 351–363.

Sain, M. *et al.* (2004) ‘Flame retardant and mechanical properties of natural fibre – PP composites containing magnesium hydroxide’, 83, pp. 363–367.

Sanchez, F. and Ince, C. (2009) ‘Microstructure and macroscopic properties of hybrid carbon nanofiber/silica fume cement composites’, *Composites Science and Technology*. Elsevier Ltd, 69(7–8), pp. 1310–1318.

Sinka, M. *et al.* (2018) ‘Comparative life cycle assessment of magnesium binders as an alternative for hemp concrete’, *Resources, Conservation and Recycling*. Elsevier, 133(November 2017), pp. 288–299.

Sorrentino, L. *et al.* (2015) ‘Thermoplastic Composites Based on Poly(ethylene 2,6-naphthalate) and Basalt Woven Fabrics: Static and Dynamic Mechanical Properties’, *Polymers and Polymer Composites*, 16(2), pp. 101–113.

Sotannde, O. A. *et al.* (2012) ‘Evaluation of cement-bonded particle board produced from Afzelia africana wood residues’, *Journal of Engineering Science and Technology*, 7(6), pp. 732–743.

Susheel Kalia, B.S. Kaith, I. K. (2009) ‘Pretreatments of Natural Fibers and their Application as Reinforcing Material in Polymer Composites—’, *Engineering*, 47, pp. 21–25.

Tajvidi, M. and Ebrahimi, G. (2002) ‘Water Uptake and Mechanical Characteristics of Natural Filler – Polypropylene Composites’, (February).

Thakur, V. K., Thakur, M. K. and Gupta, R. K. (2014) ‘Review: Raw Natural Fiber–Based Polymer Composites’, *International Journal of Polymer Analysis and Characterization*, 19(3), pp. 256–271..

Vijay Kumar Thakur, Manju Kumari Thakur, M. R. K. (2017) *Handbook of Composites from Renewable Materials, Structure and Chemistry*. first. River street, Hoboken USA: john wiley & sons Inc.

Wagh, A. S. and Jeong, S.-Y. (2003) ‘Chemically Bonded Phosphate Ceramics’, *Journal of the American Ceramic Society*, 86(11), pp. 1838–1844.

Wagh.A.S (2004) *Chemically Bonded Phosphate Ceramics.* first edit. United Kingdom: Elsevier.

Wagh, A. S. (2013) ‘Recent Progress in Chemically Bonded Phosphate Ceramics’, 2013.

Xiao, J. *et al.* (2018) ‘Preparation and characterization of straw / magnesium cement composites with high-strength and fire-retardant’, *Journal of Adhesion Science and Technology*. Taylor & Francis, 4243, pp. 1–15.

Xu, B. *et al.* (2017) ‘Influence of fly ash on compressive strength and micro-characteristics of magnesium potassium phosphate cement mortars’, *Cement and Concrete Research*. Elsevier, 99(April), pp. 86–94.

Yang, H. *et al.* (2007) ‘Characteristics of hemicellulose, cellulose and lignin pyrolysis’, *Fuel*, 86(12–13), pp. 1781–1788.

Yazaki, Y. *et al.* (1993) ‘Analyses of Black Wattle *(Acacia mearnsii)* Tannins — Relationships Among the Hide-Powder, the Stiasny and the Ultra-Violet (UV) Methods’, *Holzforschung*. Walter de Gruyter, Berlin / New York, 47(1), pp. 57–61.

Youngquist, J. A. (1999) ‘Wood-based Composites and Panel Products’, *Wood Handbook - Wood as an engineering material*, pp. 1–31.

Yu, Y. *et al.* (2010) ‘Colloids and Surfaces B : Biointerfaces Evaluation of inherent toxicology and biocompatibility of magnesium phosphate bone cement’, 76, pp. 496–504.

Zengeya, T. *et al.* (2017) ‘Managing conflict-generating invasive species in South Africa: Challenges and trade-offs’, *Bothalia*, 47(2), pp. 1–11.

Zhou, J. *et al.* (2010) ‘Development of engineered cementitious composites with limestone powder and blast furnace slag’, *Materials and Structures/Materiaux et Constructions*, 43(6), pp. 803–814.