PERFORMANCE CHARACTERISTICS OF COCONUT (*Cocos nucifera* L) HUSK FIBRE-REINFORCED COMPOSITE ROOFING TILES BONDED WITH SELECTED CEMENT ADMIXTURES AND CURED IN CARBON(IV)OXIDE

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DEDICATION

This research work is dedicated to Jason, Charis and Kayte dynasty.

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ABSTRACT

The ban on asbestos-cement roofing sheets in many countries due to the associated health hazards of asbestos fibre resulted in the search for alternative fibres. Environmental concerns about CO_2 emissions in cement manufacturing have also necessitated research on cement admixtures and CO_2 utilisation. However, limited information exists on the properties and curing of natural fibre-reinforced cement composite tiles cured in CO_2 in Nigeria. This study was conducted to investigate the behaviour of coconut husk fibre-reinforced composite tiles produced with selected cement admixtures cured in two CO_2 media.

Coconut husk was shredded,chopped and screened into random fibre lengths of 0.5–1.9mm. Chicken Egg Shell Ash (CESA) and Rice Husk Ash (RHA), produced by incineration in accordance with standardprocedures, and Calcium Carbide Waste (CCW) were used as partial replacements for cement. Thermal-Degradation-Temperatures (TDT) of coconut husk fibre, CESA, RHA and CCW were determined using standard procedure. For flat ($30x20x0.6cm^3$) and corrugated ($40x30x0.6cm^3$) tile production, cement was partially replaced with 10%RHA, 10%CESA, 5%CCW, 15%RHA+15%CESA, 15%CCW+15%CESA and7.5%RHA+7.5%CCW+15%CESA,respectively based on preliminary tests. Coconut fibre content (4% w/w), water/cement ratio (0.4) and cement/sand ratio (1:2) were constant.Five replicate samples were used. Curing was done inwet and dry CO_2 chambers. Density, Moisture Content (MC), Water Absorption (WA), Moduli of Elasticity and Rupture (MOE, MOR) and Thermal Conductivity (TC) of the samples were determined using standard methods. Composite microstructure was examined under Scanning Election Microscope (SEM). Flat and corrugated tiles installed on roof frames for natural weathering test in Ibadan were continuously monitored for 720 days spanning dry and wet seasons. Post-installation densities were determined. Data were analysed using descriptive and inferential statistics, and ANOVA at $\alpha_{0.05}$.

The TDTs of coconut husk fibre, CESA and CCW were150, 400 and 450^oC, respectively, while RHA exhibited no thermal degradation. Tile density ranged between $1.8g/cm^3$ (10% RHA) and $2.0g/cm^3$(15%RHA+15%CESA). Moisture content (6.8–11.0%) correlated positively with the density (R^2=0.95-0.99).The WA values (7.5-8.8%) were relatively low. The MOE (1.5-2.8 GPa) and MOR (1.42-5.01MPa) of samples cured in wet CO_2 were significantly lower compared to samples cured in dry CO_2 (MOE: 12.9-29.5 GPa; MOR: 7.6-12.9 MPa). The 15%CCW+15%CESA composites cured in dry CO_2 had the highest MOE and MOR. Density correlated positively with MOE (R^2=0.85-0.98). Cement admixture and curing methods had significant effects on WA, MOE and MOR. Thermal conductivity ranged from 1.1 to 1.5 W/mK. The images revealed denser pores in fibre-matrix composites cured in wet CO_2 than those cured in dry CO_2, an indication of a stronger fibre-matrix interaction largely responsible for the superior performance of the 15%CCW+15%CESA cured in dry CO_2. Weathering resulted in reduction in density largely attributable to leaching which was more pronounced in corrugatedthan flattiles.

A mixture of cement, egg shell ash and calcium carbide waste reinforced with coconut husk-fibre, cured in dry CO_2exhibited a strong fibre-matrix interaction and performed best as a roofing tile. Flat tiles exhibited better weathering resistance than corrugated tiles.

Keywords: Chicken egg shell ash; Rice husk ash; Carbide waste; Coconut husk fibre; Roofing tiles.

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NOTATIONS

The following symbols are used in this thesis

Symbol	Description	Unit
WA	Water absorption	%
TS	Thickness swelling	%
MC	Moisture content	%
MOE	Modulus of elasticity	GPa
MOR	Modulus of rupture	MPa
FT	Fracture Toughness	jm^{-2}
RHA	Rice husk ash	
CCW	Calcium carbide waste	
ESA	Egg shell ash	
ASTM	America Society of Testing Material	

CHAPTER ONE
INTRODUCTION

1.1 Background of the Study

Composites produced from incorporation of wood fibre, strands or any other lignocellulosic materials in cement is referred to as cement-bonded composite. This composite can be produced in different forms and shapes like bricks, tiles and other construction materials (Ajayi, 2008). The incorporation of fibres into the composites improve the mechanical properties (for example brittle fracture strength) of the matrix material and retaining the fire resistance properties associated with the matrix (Pereira, 2013).Fibre can be obtained from waste wood, agricultural products and paper. Panels manufactured from natural fibre and bonded with cement have qualities of organic and inorganic materials (Olorunnisola, 2007). Cement is a product of limestone (calcium), silicon, aluminium and iron ore and it has fineness powdery property. Cement, an adhesive substance has the potential characteristics of bonding masses of solid matter to a unit when mixed with water (Schneider, 2011). Cement is very important in cement-bonded composites because it is an ingredient for setting of matrix materials.

Environmental factors, health and the economic implication of inappropriate disposal from agricultural and wood conversion factories, have facilitated the need to manufacture wood cement products (Fuwape, 2001). Versatile nature of fibre-cement products is a good advantagein manufacturing of products suchas flat boards, corrugated and flat tiles for construction purposes, industrial and agricultural construction (Ikai *et al*., 2010). Associated disadvantage in asbestos usage ledtoalternative investigation in another improved reinforcing fibres, such as vegetable fibre and also synthetic fibres. Low density, biodegradability, availability and low cost of vegetable fibres make it a widely sought-after raw material in developing countries (Ikai *et al.,* 2010). Although, this material (vegetable fibre) when incorporated in composite have some disadvantage such as problem caused by mineralization of fibre.

Mineralization of vegetable/cellulose fibres in alkali cement is a major limit in its usage for composite production. Mineralization of cellulose fibre is a product of the reaction of free ions in the dissolution of cement phases that penetrated into the fibre cavity (lumen), resulting into re-precipitation of ettringite/monosulphate and calcium hydroxide into the fibre and resulted into the thickening of the cellulose fibres. However, to solve the problem ettringite (re-precipitation) of fibres, degradationof mechanical pulp into cement matrix has been suggested (Mohr *et al*., 2005, 2006). Loss of adhesion between matrix and fibre due to mineralization account for low durability which reduces the mechanical performance of the fibre-cement composites (Tonoli *et al*., 2010; Mohr *et al*., 2005). The best solution is to protect cellulose fibres from mineralization with less belligerent matrix by bridging composite ductility, maintaining quality and fibre strength.The choice of particle or fibre material had a direct relation with availability, processing cost and compatibility with cement (due to inhibitory effect of the starch content of organic materials on cement setting). Despite these disadvantages, composites incorporated with vegetable fibres have solve some of the challenges associated with housing in developing countries.

The problem of affordable housing remains a major problem in Nigeria and many developing countries. This is on the account of insufficient supply and higherprice of the preferred cement based conventional building materials. Thus, several researchers have continued to do series of research on how cement-bonded composites could be produced from agricultural and wood residues and used for low-cost housing projects. Savastano (2000) reported observations on the production of building materials such as wall panels, tanks for water storage and roofing tiles using cement-based composite matrix reinforced with natural fibre. The ability of cement composite to be produced into different kinds of shape and form for special end use,its excellent performance tofreeze-thaw, fire, water, rot, termites, insects, and fungi attacks, machinability,simplicity in the production process and the possibility of total utilization of different lignocellulosics fibres andagricultural residues (Olorunnisola, 2007; Ajayi,2008) make these composites highly sought-afteras construction materials. Also, cement composite could be sawn, bored, nailed, plastered and/or painted and can be produced in different desired practicable sizes. The general increase in awareness on the environment and energy, necessitated a need for prompt

attention on the use natural fibres with an objectiveof protecting environment andconserving energy. Fibrous materials suitable for cement-bonded composites include Jute, Sisal, Flax, Kenaf, rattan cane, and coconut husk fibre among others have been adopted as reinforcement for composite in cement fibre production. Coconut husk fibre had proved to be a good reinforcement incement-bonded composites because its incorporation led to increase in the impact resistance (Olorunnisola and Adeniji, 2019) and toughness (Savastano and Agopyan, 1999) of composite tiles.

Coconut (*Cocos nucifera*Lee*)* is a versatile useful palms in Africa and tropical Asia. All the components of palms are mostly of good use, some made timber out of it and it is a good food source. The husk of coconut is of less use at moment for commercial purposes, though studies have been carried out on two species of coconut (*Orbingnya species* and *Cocos nucifera*) for cement board particle. Oyegade (2000) studied the dimensional stability of cement board particle produced from *Cocos nucifera* husk while Olorunnisola (2006) worked on the effect of Calcium Chloride ($CaCl_2$) on the compressive strength, water absorption and hardening time properties of the composite boards. It was concluded that the material can be used for partitioning and low-stress application in building construction.Coconut fibre consists of the thick mesocarp or coconut huskandit can be extracted manually by beating and also with mechanical extractor for fibre separation. It is an excellentraw material for production of Cement Composite Board (CCB)because of its good advantage of availability in abundance, renewable, cheap and it exhibit good mechanical properties (Paramasivam *et al.,*1984). Composites made from short coconut fibre and cement matrix showed good significance increase in its toughness (Savastano and Agopyan, 1999). Addition of natural fibre reduces the thermal conductivity and yielded a light weight material (Khedari *et al.,* 2000). Low thermal conductivity is one of the properties of composite made from coconut fibre and durian fibre and it also solve environmental and energy problem (Khedari *et al.,* 2003 and 2004). Agricultural (chicken egg shell, rice husk) and industrial (welder used calcium carbide) waste is used as partial replacement of cement in CCB reinforced with coconut husk fibre.

Carbide waste is derived from the waste products obtained when a welder combine carbide with water to get oxy-acetylene flame used in welding and cutting steel or iron scraps. When cold water is poured onto calcium carbide (CaC_2) in a cylinder, much heat is

generated to produce ethyne (acetylene) which burns in air when ignited by a flame to give oxyacetylene flame used by welders. The $Ca(OH)_2$ (slaked lime) deposits disposed in a welder's workshop can be used as a binder/filler in CCB production.Lime is been used in building and various chemical industries also use it in their production processes. Lime-based cementitous materials can be used partly incement application such as masonry, plastering, slab floor concrete and foundations etc.and this account to agood quantity of cement replacement (Singh, 2006).

One of agricultural waste is poultry eggshells and which is generated from farms, homes, restaurants, hatcheries and bakeries. This constitutes environmental menace if not properly disposed in the environment. However,ash produced from eggshell has been reported in literatureas a good accelerator for cement-based material due to its potential extra calcium oxide content(Okonkwo *et al*. 2012). Okonkwo *et al*. (2012),reported that the eggshell ash content often resulted into strength properties increase of the cement matrix up to about 35% by weight of eggshell ash is replaced in cement. Therefore, eggshells ash incorporation for cement partial replacement might increase the tiles strength. Also, Mtalib and Rabiu (2009) reported that replacement of cement partially with egg shell ash lowered the setting time of cement.It was found that higher content of eggshell ash in composite cement production accelerated the setting time of composite tiles produced.

Rice husk is generated during rice milling and it is a product of agricultural waste. In the course of milling process about 78% weight is received as rice, bran and broken rice while the remaining percentage (22%) is received as husk. The husk contains about 70% organic matter and the remaining 25% of the weight is converted into ash, called rice husk ash, during the incineration process. Rice husk ash contains about 85 – 90% silica which is mostly in the amorphous state, but the silica contents depend on the incineration temperature and the time (Thomas 2018).

Accelerated carbonation of the cement composite matrix is a good method that can be adopted to enhance the durability of composites produced from cellulose fibre-cement. This is on the account thatcarbonation decreases alkalinity of composite cement matrix, makes it lesser aggressive, lowers pH of the cellulose fibres (Toledo Filho *et al*., 2003). Also, the implication of carbonation on cement is that it enhances the stability of the

chemical hydration of the products and its mechanical properties (Soroushian *et al*., 2012). Carbonation led to densification ofthe cementitious matrix and it reduces the permeability (capillary) and porosity, which constitutes a positive effect with respect to the sealing property of the cement (Lesti *et al*., 2013). This becomes more important because carbonation involves the reaction of the cement hydration products with carbon dioxide (CO_2), which could represent a positive impact on the sustainable growth of the construction industry in the future (Silva*et al*., 2009).In fibre-cement composites, the carbonation of the cement matrix is enhanced because of its high porosity with respect tofibres effect, which enhance theCO_2penetration within the composite.

1.2 Statement of Problems

(i) Roofing is a major part of building construction. A roof serves the purpose of protecting building against the weathering effects of rain and sunlight. However, the relatively high cost of conventional roofing materials in Nigeria is major challenge that sometimes results in delays in completion of building projects at the individual building construction level. Developing alternative affordable roofing materials is a potential panacea for the challenge.

(ii) Coconut husk, calcium carbide waste, rice husk and chicken egg shell are not presently utilised on large scale across Nigeria. They contribute to environmental pollution when not disposed properly. Recycling these materials into composite roofing tiles is a way of addressing the challenges of finding alternative to conventional roofing and the negative environmental materials effects of their improper disposal.

(iii) Conventional curing of concrete products either by soaking in water, covering with wet materials or sprinkling of water is time consuming. The use of CO_2 for curing of cement-based composite helps in increasing cement hydration rate and enhances bonding interaction between natural fibre and matrix materials.

1.2 Objectives

The objectives of this study are to:

(i) Determine the physico-chemical and thermal-degradation-temperature of coconut husk fibre, rice husk ash, calcium carbide waste and chicken egg shell ash.

(ii) Investigate the effects of partial replacement of cement with calcium carbide waste, chicken egg shell ash and rice husk ash on the physico-mechanical and micro-structural properties of cement-bonded roofing tiles produced with coconut (*Cocos nucifera*Lee) husk fibres.

(iii) Investigate the effects ofcarbonation curing on the afore-mentioned properties of roofing tiles.

(iv) Investigate the effects of natural weathering on the physical properties of the flatand corrugated roofing tiles after prolonged exposure.

1.3 Justifications

Provision of affordable housing remains a major challenge in Nigeria and many developing countries. Roofing is a major cost item in building construction and most of the conventional roofing materials are relatively expensive. The use of industrial and agro-industrial waste materials in sustainable building construction will help in addressing the challenges of cost and the carbon foot print of conventional roofing materials.

Natural fibres when used in building construction have numerous advantages including sustainability, lower pollutant emission, enhanced energy recovery, reliability and biodegradability (Hassan and Salih 2016).

Natural fibre addition helps to increase the fracture toughness of the cement-bonded composite tiles with respect to impact stress on coconut fibre-reinforced cement bonded composite tiles.

The use of cement admixtures incorporating ashes is often recommended as a means of reducing the quantum of cement consumed in the building industry and mitigating the degradative effects of cement on natural fibres in cement-bonded composites.

1.4 Scope

This studyis limited to the use of rice husk and chicken egg shell ash, coconut fibre, cement, calcium carbide waste in the formulation, production and evaluation of flat and corrugated cement-bonded roofing tiles subjected to wet and dry carbonation curing and exposed to weathering effects. It involved partial replacement of cement with the

ashes and calcium carbide wastes, the physico-mechanical and microstructural evaluation of the roofing tiles.

CHAPTER TWO
LITERATURE REVIEW

2.1 The Coconut Tree

One major tree is coconut palm (*Cocos nucifera* Lee) and it has a lot of innumerable benefits. It is commonly referred to as the 'tree of life' due to its great worth. Coconut palm root, trunk, sap, flowers, leaves and fruits forms major parts of the tree. Its fruits and leaves constitute a major use as sources of food, construction materials, shelter, cosmetics products, animal feeds and as raw materials for several industries such as oleochemical industry, paint and varnish industry. The coconut tree is highly prolific and it has two types: Talls and Dwarfs. The tall variety can grow up to 20 metres or more while the dwarf can attain a height of 3 metres at maturity. Coconut palms are planted exclusively from mature seeds collected from a healthy parent coconut tree. The seeds are planted in a seed bed where it germinates under a good condition of rich soil with sufficient moisture and good drainage conditions. Seedlings from the seed nut are transferred to polythene bags. To ensure survival of the seedlings, it must be preserved from shocks and other damages that affects seedlings growth and thereby moved to field (Agustin, 2004) (Plate 2.1).

2.1.1Coconut Seed

The seed of coconut is ovoid in shape while the average mature coconut weighs 1 kg. Its takes about 12 months to reach its maturity from flowering. Green colouration is characteristics of immature coconut but it turns brownish at maturity, although some are yellowish in colour. Coconut consists of endocarp and mesocarp. The mesocarp (coconut husk) is the outer covering and it covers the hard part referred to as endocarp. Kernel meat (endocarp)is within the shell and its about 1-2 centimetres thick. Separating the kernel from the inner layer is a thin brown layer called the 'testa'. The average volume of kernel within the cavity is 300ml and it contains coconut water called endosperm liquid (Plate2.1) (Agustin, 2004).

Plate 2.1: The coconut seed and coconut tree

Coconut kernel is the most essential part. It is a good raw material for production of coconut products such as coconut milk, copra, cream, flour, powder, copra meat and oil. Coconut water is capable of dissolving renal stones, having antioxidant properties and being a good source of hydration because of its sterile properties (Sudhira and Jacob, 2000). The process of kernel production during desiccation of coconut produced testa which contains a good percentage of unsaturated fatty acid (C18:1 and C18:2). Shells are converted into charcoal and this is further activated to carbon. This can be further transformed into other valued products which can serve as food and fuel sources. Coconut husk fibre is processed for different use in textiles as geotextiles, in agriculture as soil extender and also for rope (Sudhira and Jacob, 2000).

2.2 Coconut Husk Fibre

Coconut husk fibre (coir) is located between outer cover, internal membrane and hard part of coconut. Coconut fibre is a low-quality and low-value natural fibre. It is chiefly used in making yarn, cordage, different kinds of matting, carpets, rugs, brushes, mattresses, brooms and peat substitute (Wang, 2009). The coconut husks are often available in good quantities as waste around coconut oil processing factory. Synthetic fibre has polarize the market and its being used for different end products but natural fibre still has numerous advantages over synthetic fibre because it possesses natural qualities that cannot be matched by synthetic fibre. The present situation due to environmental hazard has encourages more use of ecosystem friendly bio-products which makes coconut fibre a good potential raw material. Coir has a greater potential to upgrade rural economy in production cities. It is an eco-friendly natural raw material, sustainable, renewable and biodegradable raw material (Wang, 2009).

Coconut fibre is visco-elastic, combustible, permeable and hygroscopic natural raw products. When placed side by side with other natural fibre bundles, coir is seen to possess moderate strength and properties which made them appealing for specialized applications. The demand for coconut is directly related to coir production which thereforeindicates that coir producers meet up with the changing requirements in the market. Coir is available at a relative high cost in commercial quantities when prepared for mats, seats and other special purposes in construction. However, the cost can be reduced when coir is processed mechanically in bulky production. The relative uniform size below 100mm has not been produced in commercial quantities. Coconut harvested globally accounted for

about 55 billion but an average of 15% is recovered as coconut fibre. (Wang and Huang 2009).

2.2.1 Extraction of Coconut HuskFibres

The coconut husk fibres are extracted from matured coconut seed. Coconut husk is made up of good quantity of fibres, tough skin and its embedded in a soft tissue. Coconut fibre can be extracted from its tissue by soaking in water and this led to decomposition of soft materials around the fibres. Retting is the process of extracting the fibres and its widely used in developing countries. Also, another method for the extraction of fibre is by mechanical process and this is used in advanced countries. Fibre of best quality is extracted from husk of ripe coconut fruit and it is harvested before drying stage of the coconut (Majid Ali 2010). The general method of carrying out extraction in commercial quantities is as follow: The extractions of coconut fibre from husk of mature coconut seed often produced the best quality of coir fibre. Other means of coir fibre extraction both in small and large scale are highlighted thus:

1. The extraction method that involves separation of coconut fibre from its connecting bundle of tissues in between the fibre bundles. This is achieved by manual beating of retting husk. The long fibre also called bristle fibre have small quantity of residual pith. It is therefore of necessity to comb bristle fibre with steel spikes to remove the residues. To improve the appearance quality of coir fibre it is advisable to wash in water.
2. Fibre bundles produced from machine and mattress coir both (medium and short fibre bundles) are extracted by revolving the bundles through a drum pairs of conical-shape in a revolving screen sifter, using gravitational forces and fibre bundles are removed from the pith tissues. The fibre bundles are fed into turbo cleaner made up of radially fixed rods rotating at higher speed for advance cleaning. Other debris in the fibre bundles are removed by centrifugal process to improve the quality of coir (Jorg, 2010).

There are four types of coir fibre produced commercially, they are: bristle fibre, mattress, omat and mixed fibre bundles (Jorg, 2010).

1. **Bristle Coconut Fibre:** Fibre bundles are produced from traditional needle drum also called deferring machine. It is parallel, long, clean and is produced from retted coir husk. It has a unique characteristic which makes it highly competitive with other coconut fibre produced in many countries. When produced as twine it shows higher-strength. It is mostly produced for use in brushes, nettings and rubberized coir fibre.
2. **Omat Coconut Fibre:** Average length ranged between 70 and 135cm. It is produced from traditional needle drum (deferring machine).
3. **Mattress:** The length ranged between 30 and 69cm. A short fibre bundles and it is often referred to as waste but of great value when used as plant fertilizer. It is collected on the traditional needle drum (deferring machine).
4. **Mixed Coconut Fibre:** The length ranged between 36 and 119mm. It is green husk or brown husks and fibre bundle is extracted from mature green husk.

   Asasutjarita *et al*, (2009) noted that pre-treatments of coir fibre through boiling and washing remove dirt on the coir fibre surfaces and thereby creates voids and fibre fibrillation resulting into a good matrix/fibre adhesion and improved the fibre reinforced cement composite mechanical properties.

2.2.2 Physical and Chemical Properties of Coconut Fibre

Coconut fibre constitutes about 32-43% of cellulose and nanofibre by dry weight (Ayrilmis, 2011). Coconut husk is another substantial good source of cellulose. Coconut fibre contains lignin, cellulose and hemicellulose as primary contents. It is yellowish to dark brown in colour, and this is dependent on the species of the coconut, fruits maturity, time space between husking and retting, duration of time and water quality for retting process. Coconut fibre has a coarse nature when compared to other natural fibres. It is rich in lignin content, hence to a great extent resilient to microbe and sea water attack. Coconut fibres bundle differs in length for different samples. Coconut samples size varies depending on the species, soil type where it grows and environmental state. It is pertinent to express coir fibre bundles within a range and for other natural fibre. The length distribution of fibre varies depending on the type of extraction methods and grade adopted for coir fibre separation. The diameter of coir fibre ranged between 50 and 200mm. Also,

average weight diameter at mid-point varies depending on the coconut type (Ayrilmis, 2011).

A notable quality of all natural fibres is the ability to absorb moisture from the environs. The moisture absorptive properties of coir fibres have effects on rigidity, resistance electricity, elastic recovery and tensile strength properties. The fibres and fibre bundles tend to swell because of its absorptive properties resulting into increase in sizes, hence, the shape, stiffness and permeability of yarns or ropes can equally vary. Exposure of fibre and fibre bundles to atmosphere resulted into fibre absorbing moisture from surroundings until equilibrium is attained. Also, when fibre and fibre bundles are exposed in dry climate, it loose moisture to the surroundings until equilibrium attained. Water quantity in coir fibre is expressed in relation to moisture or humidity attained. Nawarathe *et al*, (2002) reported that for a fresh water retted fibre, moisture contents is about 10-20% while for sea water retted fibre it is about 11.31%. It can therefore be concluded that method of retting process has some effects on the absorptive moisture properties of coir fibre and fibre bundles.

Other plant fibres contain about 70% cellulose but coconut fibre bundles have some key chemical components that consist of cellulose, hemicellulose, lignin and pectins. The cellulose contents of coir fibres are lower but very high lignin contents (Dam, 2002). Cellulose is referred to as metabolic inactive structural carbohydrates with linear chain polysaccharide. Hemicellulose is a random amorphous polysaccharide with varying sugar monomers associated with cellulose. Holo-cellulose is the combination of both hemicellulose and cellulose. Lignin is a polymer of phenyl propanoid chains which led to formation of three other phenyl propane, alcohols (monolingual monomers) called coumarin alcohol, coniferyl alcohol and simple alcohol. These compounds can determine the quality of coconut fruit and varieties. Coconut husk fibre rigidity and colour on the cell wall has direct relation with the lignin which helps to maintain resistance towards compression and bending while safeguarding it from attack by micro-organisms (Majid Ali 2010).

Agopyan (2005) reported that 33 to 43% of cellulose contents was observed in coconut fibre, hemicellulose ranged between 0.15 and 0.25%, lignin 41 to 46% and pectin ranged from 2 to 4%. Coir fibre has resistance property to degradation due to its 30% or

more lignin contents compare with other plant fibres such as jute and cotton. Coconut fibre possesses natural resistance to dampness, gives cool comfort in hot climate, retains warmth in cold weather and possesses good elastic and shrinking properties. These qualities make it a good raw material for floor covering worldwide. Coconut fibre can be easily dyed and printed on to achieve desired colour and it gives a lasting colouration over a long time. It has a good property for sound wave absorptiveness due to its acoustic qualities and is often used in wall padding and floor cover in halls and auditorium for concert (Rowell 2002). Thermal and structural properties of coir fibre are enhanced by its lignin-cellulose contents, the higher the lignin, the better the thermal properties. As rightly stated by Abraham (2013), extracted lignin from coconut husk fibre can also serve as a good source of renewable energy creation with about 46% lignin (weight basis), it has higher lignin content compare with other natural fibre (Khedari 2004). Alkaline aqueous solution or organic solvent can be used to extract lignin selectively in a coir fibre (Le Digable 2006).

2.2.3 Mechanical Properties of Coconut Fibre

Ramakrishna and Sandarajan (2005b) reported the chemical composition and tensile strength of four natural fibres (coir, jute, sisal and cannabinus fibres) when exposed to dry and wet and by immersion in three mediums (water, saturated lime and NaOH) for a period of 60 days. Immersion affects the chemical composition of all the fibres. By continually exposing the fibres to a prolong immersion has side effect which might resulted into lose of tensile strength. It was recorded that coir fibre retains its best tensile strength better than other natural fibres tested during immersion condition. (Munawar *et al.*, 2007) noted inverse relationship between fibre diameter of some non-wood plant fibre bundles such as pineapple, sunsevieria, kenaf, sisal and coconut fibre. It was observed that fibre bundles diameter size has direct relation with the density (larger diameter lesser density), tensile and Young's modulus.

2.2.4 Thermal Properties of Coconut Fibre

Coconut fibre possesses natural resistance to dampness. In hot climates, it gives cool comfort and in cold weather it retains warmth. It also has good stretching and

shrinking ability. Because of these favourable properties, it is widely used for floor covering all over the world. Coir fibre can be dyed and printed easily to get the desired colours and designs with lasting finish. It can also absorb sound waves, and because of its superior acoustic qualities it frequently used for wall paneling and floor covering in auditoria and concert (Rowell 2002). The presence of lignin–cellulose compound in the raw coir fibre plays a significant role in its structural and thermal properties of the fibre. The higher the lignin the better the thermal properties of coconut fibre. Abraham (2013)had also reported that extracted lignin from coconut husk fibre is also a suitable source for renewable energy production.

2.2.5 Application of Coconut Fibre

Roofing sheets of low cost has been produced from randomly distributed coconut fibre reinforced composites (Cook *et al.,* 1978). The parameters used in the study are fibre lengths, volumes of fibre and fabrication pressure. Optimum cement composites can be produced from fibre volume of about 7.5%, fibre length of 3.75cm and fabrication pressure of 1.67MPa. In reference to cost value, composites produced were relatively cheaper than available local roofing materials (Cook *et al.,*1978). Ramaswamy *et al.,* (1983) reported that some natural fibre such as bamboo and jute coir have a good advantage in concrete mixture with effects property similar to some fibres. About 25% improvement in impact strength, ductility when subjected to static loading and low shrinkage properties of about 50% to 70% were obtained when compared to plain concrete. Johanson (2014) reported about a simple method for the production of roofing materials using cement as a binder. Ramakrishna *et al.,* (2005) reported on the effect of corroded fibres and ductility of natural fibre on the strength property of the concrete. It was concluded that coir fibre retains its initial strength than other fibres after exposure to different media.

Cold water treated coir fibres used for Coir Fibre Cement Boards (CFB) in ratio 70:30 for cement and have been used for different structural purposes such as wall panel, flooring and paneling (Penamora *et al.*, 2005; Mohd Hisbany Bin Mohd Hashim 2005). Post cracking flexural stress, ductility and toughness of mortar can be improved by the addition of coconut mesh (Li *et al.,* 2006). Treatments of coconut fibres by removal of extractives strengthen and enhance the property of panel which resulted into interfacial

adhesion between matrix and coir fibre (Asasujarit *et al.,* 2007). Composite produced from coir fibre are antifungal and termite resistant (Indian Coconut Fibre, 2007).

It was reported that the mechanical and microstructural properties of concrete composite is greatly increased when produced with addition of natural fibre and these contribute to flexural and strength performance of concrete. Reports on curing age and some mechanical property has also been studied. It was observed that compressive strength, split tensile and flexural toughness at different curing ages for both natural fibre and sugarcane enhance better performance of those parameters. The percentage increase was less than the usual concrete specimen at later curing even though natural fibres improve its strength properties during early curing ages (Sivaraja *et al.,* 2009).

Coconut fibres are versatile, ductile and energy absorbent materials and can be used for different functions in composite production such as non-structural part. It has been discovered that the fabricated composites are to a large extent cheaper when compared to available local roofing sheet materials (Ali, 2010). As reported by Abdullah *et al.,* (2011), the fracture behaviour of composite is greatly strengthened when composites were produced from the addition of coconut fibre. It has also been reported that 9% addition of coconut fibre produces higher concentration of compressive strength and modulus of rupture.

2.3 Rice Husk and Rice Husk Ash

Rice husks are hard protective coverings of rice grains which are separated from the grains during milling. Rice husk can be recycled because of its high silica content and can be used for industrial purposes. The Rice Husk Ash (RHA) contains about 85 to 90% amorphous silica (Narayan, 2002). The physical and chemical characteristics like low bulk density (0.12g/cc), harshness, slow rate of biodegradation and high silica content were properties that made RHA a good material for composite production. It has somewhat traditionally value in the country side as cattle fodder, fuel or source of manure. Though, till the present moment, as a waste material, it has created problems of disposal wherever it is produced. Recently the possibilities of its utilization in various ways have generated much interest especially in the developing countries of South-East where rice production transcends half of the production worldwide and also in Africa countries like Nigeria (Narayan, 2002) (Plate 2.2).

2.3.1 Characteristics of Rice Husk Ash

The curing process is a detailed process in concrete production and when not done properly concrete quality and strength can lessened and voids can be observed in concrete. Cement particle size is about 100 microns. RHA is a product of Silica Master Batch MM2 and its characterized with finer particle than cement because of its particle size of about 25 microns. When mixed together with cement it helps to fill the interspaces between cement in the matrix mixture. This property led to increase in the strength and low density and resulted into less quantity of cement in concrete mixture. RHA has higher silica content above 85% and can be used for specialized concrete production because of its pozzolanic property. The demand for amorphous silica in the production of specialized cement and concrete for better performance, higher strength and low permeability for use in nuclear power plants, marine and bridges is of higher demand (Habeeb and Mahmud, 2010).

2.3.2 Method of Rice Husk Ash Production

Rice husk can be converted into ash by firing process. There are several methods of producing ash such as the direct burning of rice husk paddy in an incinerator or burner (Plate 2.3). Rice husk ash burning is carried out in a controlled system below 700^0C and the ash content produced is amorphous in nature. Further burning at temperature above 850^0C transform the ash from amorphous to crystalline state (Narayan, 2002). Another method of burning rice husk for pozzolan production is by burning rice husk balls or can be caked bonded with clay (Plate 2.4) and this method resulted in almost carbon-free ash of fairly consistent quality which is ground along with a fixed quantity of lime (hydrated) to produce cementitious material. When prepared in balls, it burns faster than heaps of rice husk which resulted into some considerable quantity of urburnt carbon.

The Central Building Research Institute (CBRI) Roorkee India developed another phase which is a progressive extension of clay-bonded-rice husk balls. Lime sludge ($CaCO_3$), paper can also serve as substitute for clay (Plate 2.5). Madrid *et al.,* (2012) reported that in the process of burning, fuel value of rice husk is used in the conversion of

Plate 2.2: Rice Husk

Plate 2.3: Direct Burning of rice husk into ash

Plate 2.4: Rice husk made into cake balls before incineration

Plate 2.5: Rice husk mixed with lime before incineration

calcium carbonate to lime and the resultant ash is a mixture of rice husk silica and lime because of its hydraulic properties.

2.3.3 Forms of Silica in RHA

The ash content contains about 87-97 percent of silica with small quantity of alkalis and trace elements. Table 2.1 showed the chemical composition of rice husk ash. Temperature and duration of burning of rice husk resulted into production of amorphous and crystalline (Basha *et al.,* 2005). The properties of crystalline and amorphous are greatly different, it is of necessity to produce ash of intended requirement. The silica tetrahedral arrangement in a three-dimensional network without regular lattices structure is characterized in amorphous ash. The presence of holes and disordered arrangement where electrical neutrality is not satisfied, large surface area resulted into an open structure. This facilitates reactivity as large area is open for reaction to occur.

2.3.4 Applications of Rice Husk Ash

RHA produced by controlled incineration and RHA from rice paddy from milling industry were used for concrete development to compare and test their compressive strength up to 91 days of production. Different ratio of partial replacement of cement with RHA, at 10% and 20%, and three different water/cement ratio (0.5, 0.4, and 0.32) were adopted for the experiment. The results obtained showed positive splitting tensile strength and air permeability and this compare favourably with plain concrete without RHA. It can be deduced from the results that residual RHA showed a positive effect on compressive strength at the early stage but long-term effects of showed higher significant value of compressive strength on RHA produced from controlled temperature. The compressive strength was increased as a result water/cement ratio from 13% to 47% for 20% addition of RHA produced in a controlled incineration process (Gemma de Sensale *et al.,* 2005). Cement fibre composites were developed from partial replacement of cement with light weight RHA and this resulted into low density composite and less permeable concrete. About 5% RHA was used to replace cement to achieve a flexural strength of about 50MPa. FESEM machine was used to analysed the microstructure properties of the twomixes. The presence of high silica in concrete containing RHA resulted into formation of Calcium Silicate Hydrate (CSH) that contributes a positive effect on the strength of the

Table 2.1: Chemical Properties of Rice Husk Ash

Composition	(%)
SiO_2	88.32
Al_2O_3	0.46
Fe_2O_3	0.67
CaO	0.67
MgO	0.44
Na_2O_3	0.12
K_2O	2.91
Loss of Ignition	5.81
Specific Gravity	2.11

Source: Habeeb and Mahmud (2010)

concrete during curing. Alower water absorption was observed in concrete with the addition of RHA. The 5% RHA replacement showed a lower compressive strength than the concrete without RHA. However, the results showed that the targeted compressive strength was met (Maisarah Ali *et al.,* 2015).

The mixture of Fly Ash (FA) and RHA in a combine proportion of 30% FA and 0% RHA in a concrete with simultaneous increase in RHA by 2.5% and decrease in FA by 2.5%. The effects of partial replacement at different proportions were observed on the composite concrete. The following mechanical tests were carried out on the samples such as flexural, compressive and split tensile strength. The addition of both 22.5% FA and 7.5% RHA together resulted into increase in maximum compressive strength of about 30.15% when compared with targeted strength. Also, about 4.57% increase was observed in flexural strength at 28 days curing while a decrease of 9.58% in tensile strength was observed at 28 days when compared with control. The experimental conclusion was that both addition of FA and RHA for partial replacement of cement reduces environmental problems, produces eco-friendly and more economical concrete (Sathawane *et al.,*2013).

Divya Chopra *et al.,* (2014) reported the possibility of substituting cement with RHA as Supplementary Cementitious Materials (SCM's). At 7, 28 and 56-day tests were investigated on the compressive and tensile strength, durability properties and fresh flow (slump, U-Box and L-Flow). The partial replacement of cement with RHA for production of concrete were at 10%, 15% and 20%. It was reported that the strength increases to about 25%, 33% and 36% at 7 days, 28 days and 56 days for samples in which cement was partially replaced with 15% RHA. All mixes were less porous when compared with control of all ages and all samples showed lower range penetration of chloride. Furthermore, Hamzeh *et al.,* (2013) reported that water/cement ratio, cement fineness, temperature of curing, chemical admixtures and addition of minerals has effects on hydration process. Addition of minerals with high pozzolanic activity when added into cement matrix, it reacts chemically with calcium hydroxide which resulted into cement hydration to form additional quantity of hydration product in the matrix cement. The result indicated that addition of RHA as a pozzolanic material improved concrete resistance to water absorption. The quantity of hydration products resulted into reduction in

matrixporosity and fibre-matrix porosity transition zone and also permeability of binding material contributes to durability increase in concrete.

2.4 Calcium Carbide Residue

The waste product generated when carbide is used in the presence of water to get oxy-acetylene is called calcium carbide residue (CCR). The chemistry of the reaction is

$$CaC_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + C_2H_2(g) \text{ ---------- (1)}$$

Oxy-acetylene flame is very hot and can give a temperature of about 2200^0C. The $Ca(OH)_2$(s)slaked lime deposits are dumped as wastes in welder's workshop which is the material for many research work (Singh and Garg, 2006). The ripening of fruits in agriculture and welding of metals in industry is achieved with Acetylene (C_2H_2). CCR is used as landfills because it is considered as waste and it is detrimental to the environment. China alone generated about 2500 tons of CCR annually (Lieut *et al.,* 2011). CCR is made up of calcium hydroxide with a fraction of about 92% and its alkaline (pH > 12). The mixture of CCR with certain pozzolans, such as RHA with high silicon dioxide (SiO_2) or aluminium oxide (Al_2O_3) content, it yields pozzolanic reactions and end results is similar to products from cement hydration process (Wand *et al.,* 2013).

Efforts have been put up to minimize environmental pollution by making use of CCR for building material application since CCR has $Ca(OH)_2$ as its main constituent, thereby being a preferred raw materials in cement industry and can be used as alternative material. Similarly, Wang *et al.,* (2013) identified some researchers who have used CCR as alternative for limestone in the production of clinker. Also, mixture of CCR and fly ash or ashes can be used as cementitious material (Jaturapitakkul and Roongreing 2003; Krammart and Tangtermsirikul 2004). Calcium carbide chemical composition is presented in Table 2.2.

2.4.1 Application of Calcium Carbide Waste

Calcium carbide residues can be reacted with pozzolans to form high quality cementitious products (Krammart *et al*., 1996). This is because of high contents of $Ca(OH)_2$ and SiO_2 in the pozzolanic material (Krammart *et al*., 1996). Jaturapitakkul and Roongreung (2003) reported on experimental research that when 30% CCR and 70% fly ash and incorporation of 50:50 ground CR and RHA resulted in compressive strength of 20.9 MPa and 15.6 MPa

Table 2.2: The Chemical Composition of Calcium Carbide Waste

Ingredient	Content (%)
$Ca(OH)_2$	92.0
$CaC0_3$	2.90
SiO_2	1.32
Fe_2O_3	0.94
Al_2O_3	0.06
LOI (Loss of Ignition)	1.02

Source: Jaturapitakkul and Roongreing (2003)

respectively in the composite cement fabricated. The CCR utilization and pozzolans is advantageous in cement production (Sonma *et al.,* 2010). Sonma *et al.,* (2010), noted the incorporation of CCR and pozzolans in composite production reduced CO_2 emission. This finding can help curb release of 2.07 billion of CO_2 being dissipated in the atmosphere during cement production (Garner, 2004 and Damtoft *et al*., 2008). Hence, natural pozzolans are being used by cement producers in the production of cement binders.

2.5 Lime – Pozollan Mixture

The mixture of appropriate pozzolan such as fuel ash, powdered fired clay brick to chalk and lime at 2-3 parts by weight to form lime-pozzolan can be used in mansory works for cement base mortars. Gypsum (203%) can be admixed during grinding to improve early strength of mortar. The requirement for composition satisfies IS 4098-2000 for lime-pozzolan mixtures. Admixture of burnt clay pozzolan, cement or fly ash with sand addition can be used in composite production (fineness modulus 1.25 – 2.0) (Dass and Malhora, 1990). In these mortars, cement has been found to contribute to the early setting, strength and rigidity, whereas lime reduced shrinkage and improves mortar finishes. The mixing of mortar mechanically gives better strength to mortar than manual method, as a result of better compaction, cohesiveness and consistency reduction (Dass and Malhora, 1990).

2.6 The Egg Shell

The chemical analysis for egg shell powder as follows; CaO-50.7, SiO_2-0.09, Al_20_3-0.03, MgO-0.01, Fe_2O_3-0.02, Na_2O_3-0.19, P_2O_5-0.24, SiO-0.13, NiO-0.001, SO_3-0.57 (Jayasankar 2010). About 2.2 grams of calcium as a product of calcium carbonate are derived from commercial egg layers. The weight of dry eggshells is about 5.5grams with 95% calcium carbonate. The chicken eggshells contain an average weight 0.3% magnesium, phosphorus and trace element of zinc, sodium, potassium, copper, iron and manganese. Some factors contribute to the quality of eggshells production such as nutrients, breeding methods, flock health condition and prevailing environmental condition. The organic and inorganic shape structure of component of egg shell with respect to egg weight contributes the quality of eggshell, thin eggshells are known to be stronger when compared with thick type (Gary *et al.,* 2004). The calcium carbonate is a

product of outer part of eggshells and it has over 17,000 tiny pores. This shell is a semipermeable which allows air and moisture into the pores. It also consists of thin coating called bloom which helps in bacteria and dust in the pores. There are two membranes in egg: the outer and inner membranes which houses the shell surrounding the white (albumen). The membrane gives efficient protection against bacteria invasion and partly made of keratin. The eggshells stick to outer membrane while albumen is attached to inner membrane.

The mineral admixtures consumption by cement/concrete industry was on the increase in late 20th century and this expected to rise more. Partial replacement of cement with other material can be employed to meet the growing demand for cement and concrete (Jayasankar, 2010). The use of industry by-products as partial replacement for energy in cement can result into energy and cost savings. The cubes strength for conventional concrete is almost equal with concrete produced from incorporation of RHA, ESP and fly ash when considered under certain categories (Jayasankar, 2010). The best natural calcium is from eggshell and it is 90% absorbable (Bee, 2011).

Food joints, industries, hatcheries are places where eggshells are generated and this post a danger to the environment when disposed (Phil and Zhihong, 2009; Amu *et al*.,2005). Chicken eggshells are waste materials and it is useful as soil stabilizer for alternative use like lime because both possess similar chemical composition (Amu *et al*.,2005), yet eggshell powder has not been utilized as stabilizing agents in many parts of the world and it can serve as other type of soil stabilizer (Olarewaju *et al.,* 2011). In general, most industrial activities resulted into natural resources depletion, accumulation of excess by-products and waste which in-turn constitutes disposing problems in the environment. Amu *et al.,* (2005) concluded that eggshells can be used as soil stabilizing agent because it can be an alternative lime while Amu and Salami (2010) reported that the plastic index of laterite soil can be improved by using pulverized eggshells. Eggshells powder mixed with lateritic soil has disadvantage of low binding properties but can be used to enhance the strength of subgrade where higher performance is necessary (Olarewaju *et al.,* 2011). Eggshell powder cannot be used as stabilizing agent because it has not met minimum requirement for use as base and sub-base material for construction of road (Olarewaju *et al.,* 2011). The pulverized eggshells have potential to be used as

stabilizing agent for soil and the stabilized soil can be used as subgrade materials in road construction works. Also, pulverized eggshell can be used in making hollow blocks as alternative products to sand because of its calcium carbonate that improve the hardness and strength (Cecilia *et al.,* 2008). By using pulverized eggshell and sand to produce hollow blocks, it was observed that when the two samples at height of 600mm were dropped, it was reported that a crack was observed on samples with eggshells while sand blocks had multiple cracks and shattered (Cecilia *et al.,* 2008). This proves that incorporation of eggshell in cubes production showed a better performance and it is more effective than sand. Recycling of eggshells can help solve environmental menace and reduce cost expenses on building.

2.6.1 Reaction Mechanisms of EggShellAsh

The dominating compound in the egg shell is the calcium tcarbonate, ($CaCO_3$), and this can further degrade to CaO (calcium oxide) and CO_2 (ccarbon (iv) oxide) when subjected to incineration for ash production (equation 2).

$$CaCO_3 \rightarrow CaO + CO_2 \text{----------(2)}$$

The reaction of CaO in ash content will react with water which in-turn penetrate into the concrete and form calcium hydroxide solution while the CO_2 will escape as a gas (equation 3)

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad \text{---------- (3)}$$

Thermal stability of about 600^0C with a mass loss (Δm =1.8%) of volatile material was reported for thermogravimetric curve TG/DTG of industrial calcium carbonate. It is a single step decomposition between range of temperature 601 - 770^0C, carbon (iv) oxide of mass loss 41.7% is been released. This produces calcium oxide (equation 4):

$$CaCO_3(s) \leftarrow \text{heat} \rightarrow CO_2(g) + CaO(s) \quad \text{---------- (4)}$$

The thermal stability of about 630^0C with a mass loss of 2.6% volatile material was reported for TG/DTG curve for eggshell calcium carbonate. The decomposition thermally occurred at temperature which range between 636 and 795^0C with 42.5% mass loss of carbon (iv) oxide been released. It has been observed that industrial calcium carbonate decomposes at less temperature of about 30^0C than calcium carbonate from eggshell and this is evident from thermogravimetric analyses with a DTG_{peak} of 749.9^0C and 771.5^0C obtained for industrial and eggshell (Murakami *et al*, 2007).

The selective hydration of cement compounds affects the cement setting time. During the selective hydration of the cement compounds, the C_2S and C_3S dominate the process of hydration at the early stage. In cement hydration C_3S is dominant at early stage. Since CaO is the main chemical composition of the ash, it was assumed that the setting time in cement is accelerated. The mineral characteristics of cement influence hydration time when eggshell ash is added. The addition of water to mixture of ESA and cement resulted into reaction of the matrix with compounds of cement resulting into acceleration of hydration of cement.

2.6.2 Application of Egg Shell Ash

Egg Shell Powder (ESP) is a good substitute in cement which can be used in concrete and wall tile production and soil stabilization. The optimum strength in concrete production is due to the incorporation of 5%ESP (Amarnath, 2014; Gowsika *et al.,* 2014). A decrease was observed in compressive strength, tensile and flexural strength when ESP content was increased beyond 5%. This might be as result of expansive characteristics of ESP in concrete mixture. The eggshell fits as substitute material for re-use and recycling practices due to the presence of the $CaCO_3$ in it (Freire *et al.,* 2006). In this regard, suitable wall tiles were successfully produced by the deployment of ESP in cement mixes (Freire and Holalanda, 2006). Jayasankar *et al*., (2010) worked on fly ash and egg shell powder partial replacement in cement. The variables were varied at different percentage of M20 FA, M25 for ESP and M30 for concrete. The results showed that cubes made from FA and ESP have the same strength with conventional concrete cubes. Mtallib and Rabiu *et al.*, (2009) worked on properties of egg shell powder as admixture in concrete. It was observed from consistency test that the higher the contents of ESP in cement the faster the rate of setting in cement. This property exhibited by ESP showed that it is a compound accelerator in cement setting. A research was carried out on the ESP potential as addictive in concrete. Doh Shu Ing and Chin Siew Choo (2014) reported on the results by varying different percentage of egg shell powder in cement and were added to concrete mix of grade M25 and it was established workability was achieved in water/cement ratio of 0.4. The compressive strength and maximum strength of concrete was achieved when 10% of ESP was used as filler in concrete mixture. Also, the presence of ESP in concrete improves the flexural strength of the concrete better than the control. The resistance to

failure was improved by the addition of ESP under bending and water absorption at initial stage was also reduced.

2.7 Cement

Cement is an adhesive substance that is capable of uniting fragments or masses of solid matter to a compact whole (Ghosh, 1983). Cement functions by forming a plastic paste when mixed with water. This develops rigidity (sets) and steadily increases in compressive strength (hardness) by chemical reaction with the water (hydration). Hence, cement is hydraulic (i.e cement increase in strength even when stored under water after setting (Lea, 1970). Organic polymer based cements are also hydraulic and are used as adhesive, binders for aggregates, as hardening patching materials for damaged roads and bridge decks. However, the use of organic-based cement is limited due to its expensiveness when compared with those inorganic cements e.g. Portland cement. The properties of the final products of Portland cements are dependent on the chemical and morphological composition of clinker, gypsum and other additives introduced during the process of grinding. Changes in cement properties could occur during subsequent storage. Since the cement quality is dependent on the quality of clinker, it therefore means that any consideration of its characteristics requires a basic understanding of the factors that control the clinker quality and clinkerization process (Bye, 1983).

2.7.1 World Cement Production and Consumption

The modern housing has generally increased the demand for cement. Consequently, cement production has grown exponentially over the years. In 2002, the world production of hydraulic Portland cement was 1,800 million metric tons. The three top producers were China with 704 million tons, India, with 100, and United States of America, with 91 million metric tons. These three countries are responsible for about 1/2 the world's total production (Li Yong, 2004). In 2005, China led with 43.46 percent followed by India producing6.38 percent, then United States of America with 4.38 percent. For the past 18 years, China has consistently produced more cement than any other country in the world (Li Yong, 2004). This explains why China has the highest carbon dioxide emission in the world. In 2006 China alone manufactured 1.24 billion tons of cement constituting 44 percent of the world total cement production (NEAA 2007).

Demand for cement in China is expected to advance by 5.4 percent annually and this exceeded 1 billion tons in 2008. Cement consumption in China is expected to hit 44 percent of global demand and China will remain the world's largest national consumer of cement by a large margin (Lizabeth, 2007).

As the demand for cement increased over the years, different types of Portland cement have evolved in order to meet the demand. Type 1 or Ordinary Portland Cement (OPC) is still the best. It has the highest strength, but it is expensive. Therefore, cheaper cements of less strength or quality are now being produced. These cements (limestone and gypsum) differ in their properties due to the various supplementary materials added to the raw materials. Examples of these supplementary materials include fly ash, pozzolans, slag, condensed silica fume, volcanic ash, rice husk ash, and limestone.Based on research results, Argentina have set standards for inclusion of supplementary materials like limestone and other pozzolanic admixtures to OPC Standards (BS 882) allows up to 15 % inclusion of limestone to OPC 1.3.

2.7.2 Cement Production in Nigeria

The Federal Ministry of Commerce and Industry in Nigeria estimate that the effective demand for cement to beabout 20 million tons. According to Ian and Abidoye (2009), acute infrastructure deficit and significant demand for housing has driven domestic production volumes up to 25 % over the last four years to improve the availability of the commodity. In 2010, the government banned the importation of cement into the country in order to encourage local production and existing companies are increasing their capacities. Dangote Cement Company formerly Benue Cement Company in Benue State for instance, increased its capacity from 0.45 million to 2 million per annum in 2008 and now from 2.9 to 3 million. In 2010 UNICEM added 2.5 million tons of its capacity to local capacity while Lafarge WAPCO added 2.2 million tons in 2011. With these improved capacities the quantity of cement in the market has improved (Ian and Abidoye, 2009).

2.7.3 Limestone Composite Cement

Limestone composite cement is widely used in Europe, in fact according to Cement Bureau reported that the production of limestone composite cement in Europe increased by 7% between 2000 and 2010 (Hooton and Michael, 2002). This is partly due to its high durability, economic and environmental advantages. In some European countries like Britain and Germany, up to 35 % limestone addition to Ordinary Portland Cement has been reported by Zhor *et al.*, (2008). It was also reported that the inclusion of up to 5 % limestone does not affect properties of Portland cement markedly (Hawkins *et al.*, 2003). Limestone blended cements present different properties compared to ordinary Portland cement and it is necessary to investigate their physical and mechanical properties with varying limestone contents. The inclusion of limestone as an additive to boost quantity in Nigeria started around 2005. Benue Cement Company started adding it in 2006 (Ian and Abidoye 2009). The chemical composition of limestone Portland cement was shown in Table 2.3.

2.8 Cement Hydration and Pozzolans

Hydration is the result of chemical reaction that occurs between water and the chemical compounds present in Portland cement. Portland cement is predominately composed of two calcium silicates which account for 70 percent to 80 percent of the cement. These two compounds are calciumsilicates are dicalcium silicate (C_2S) and tricalcium silicate (C_3S). The other compounds present in are tricalcium aluminate (C_3A), tetra calcium aluminoferrite (C_4AF) and gypsum (Narayan, 2002).

The reactions of dicalcium silicate (CH) as illustrated in the following chemical reactions.

$2C_2S + 9H\ (water) \rightarrow C_3S_2H_8 + CH$ ---------- (5)

$2C_3S + 11H\ (water) \rightarrow C_3S_2G_8 + 3CH$ ---------- (6)

Calcium Silicate Hydrate (C-S-H) accounts for more than half the volume of the hydrated cement paste while CH accounts for about 25% of the paste volume. The remainder of hydrated Portland cement is predominantly composed of calcium sulfo aluminates (ettringite) and capillary pores (Narayan, 2002). C-S-H is a poorly crystalline material with a variable composition that forms extremely small particles less than 1.0 μm in size.

Table 2.3: Chemical Composition of Cement

Oxidation	Proportion (weight %)
SiO2	22.40
Al_2O_3	2.85
CaO	66.70
MgO	0.83
K_2O	0.19
Na_2O	0.17
SO_3	2.20
CO_2	1.30
CaO free	0.55
Insoluble	0.30
Alkaline	0.32

Source: Neville(2011)

C-S-H is a superior reaction product because it creates a denser microstructure that increases strength, reduces the permeability of the concrete and improves its resistance to chemical attack (Narayan, 2002). It is the main cementitious compound or glue that gives concrete its inherent strength. The structure of C-S-H becomes much more stable and resistant to subsequent environmental changes upon prolonged moist curing or curing at elevated temperature. CH contributes somewhat to concrete's inherent strength because it will form large crystals inside voids, thereby reducing porosity.

2.9 Cement Composites

Cement composites are widely utilised in many countries for both interior and exteriorapplications such as siding, roofing,cladding, fencing and sub-flooring. They are also used as sound barriers because of their acoustic properties(Moslemi 1999). The main challenge with fibre-reinforced cement composites is the incompatibility between cement and fibre because some soluble chemicals of fibre are found to hinder or obstruct the hydration of cement. This lowers the mechanical strength of fibre-cement composites (Zhengtian and Moslemi 1986; Thomas and Birchall 1983). The typical cement-hardening inhibitory components known uptill now are divided into two groups. One is comprised of structural component of high molecular weight (cellulose, hemicelluloses and lignin) while the other is non-structural components of lower molecular weight (extractives and inorganic component)(Yasuda *et al*., 2002).

2.9.1 Historyof Fibre Concrete Roofing Sheet (FCR)

According to Schilderman (1990), Fibre Concrete Roofing (FCR) is the terminology for a roofing materials produced from Portland cement, sand and water matrix with the addition of relatively small quantity of natural fibre such as coconut coir and sisal. For over a decade, the Intermediate Technology Development Group (ITDG) in Kenya was saddled with the reserach development and dissemination of information on fibre concrete roofing (FCR) in the form of sheets and tiles (Afelogun, 2002). In 1978 the group developed some sheets and these were designed to encourage asbestos-cement roofing sheets manufacturing and to cover 1m square of roof. These products were rather

heavy and required strong support and had a tendency of cracking when movement in the support structure occurs. Also, JPA (UK based private company) in 1983 developed fibre concrete roofing (FCR) and the tiles covers about $0.08m^2$ of the roof area. These tiles had the advantages of easier quality control, great flexibility on the roof, and easier handling. The production method developed by JPA was later introduced to ITDG. The process is a matrix of a ratio of 3 sand, 1 cement composition incorporating 1-2% fibres, mostly sisal (Afelogun 2002).

2.9.2 Classification of Composite Materials

Fibrous composite can be classified as short-fibre composite which consist of a matrix reinforced by a dispersed phase in form of discontinuous fibre length < 100* diameter. This could be of random orientation fibres or preffered orientations of fibres. Also, long-fibre reinforced composites consist of matrix reinforced by a dispersed phase in form of continuous fibres either by unidirectional and bidirectional orientation of fibres (Figure 2.1).

2.10 Functionsof Fibres in Cement Matrix

Fibre whether short, discrete or long plays a major role in cement matrices. It delays or controls the tensile cracking of the matrix, controls cracking, reduces deformations at all stress levels, and impact a well defined post cracking and post yielding behaviour. The fracture toughness, ductility and energy absorption capacity of the fibre reinforced composite are then substantially improved. When the the fibres are of low density, they act as fillers and reduce the weight of cement matrix. Other incidental advantages are the thermal insulation and sound absorption characteristics of the composites (Afelogun, 2002). Fibres can be added in the composite matrices to produce flat and corrugated tiles.

2.11 Advantages and Disadvantages of Flat Sheet Tiles Over Corrugated Tiles

2.11.1 Advantages of Flat Tiles

. Flat sheet does not need support strips on the decking to stay in place.

. Screws for fastening can be done at any point on the flat sheet materials.

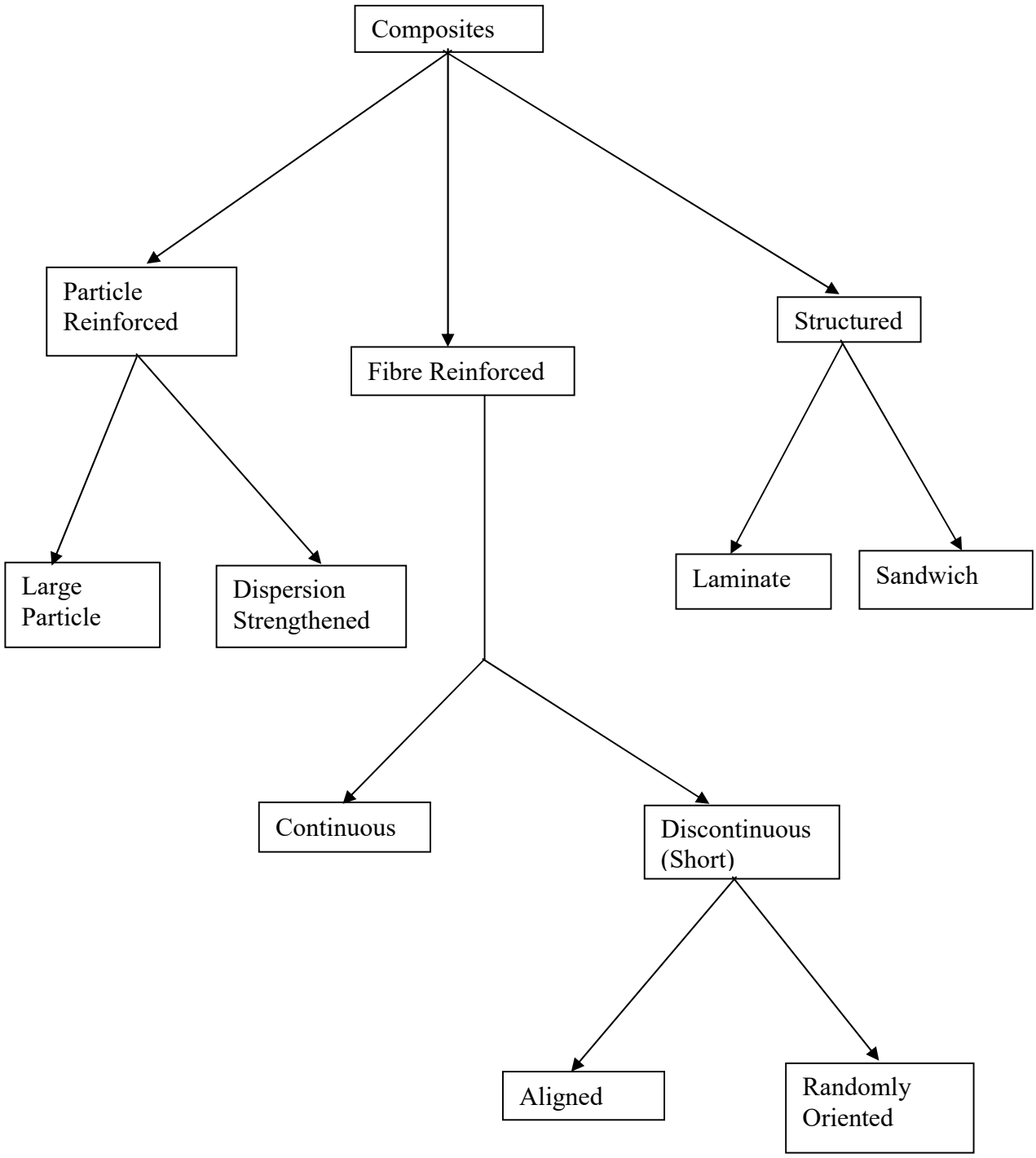


Figure 2.1: Composite Materials Classification

. Flat sheet will not flatten under the torgue of screw.
. Flat sheet keeps interior warmer by absorbing sunlight at a higher rate.
. Flat sheet is ideal for solar panel than corrugated sheet.
. Flat sheet is quicker to install than the corrugated.

2.11.2 Disadvantages of Flat Tiles

. Repeated cycles of heating and cooling can cause flat roof materials to expand and contract, this can lead to cracking of the roof sheet over time.
. There may be problem of leakage in stormy rain.
. Gradient of flat roof must be adequate enough to allow good run-off. The implication is that more roof member is required for roof construction.

2.11.3 Advantages of Corrugated Tiles

. It has good aesthetic finish.
. Overlapping ridge prevent water leakages.
. Minimum slope is required for adequate water run-off on the roof surface.

2.11.4 Disadvantages of Corrugated Tiles

. Problem of cracking may occur along the ridge over repeated cooling and heating of sheet.
. Corrugated ridges may flatten under the torgue of screws.
. Corrugated will peen off (curl up due to being dented) during a hail storm.

(Source: www.thecivilbuilder.com).

Fibre cement composites for both flat and corrugated tiles can be cured either by conventional curing or by accelerated carbonation.

2.12 Conventional Pressing Method

Conventional pressing techniques in the manufacturing process of cement-bonded particleboard require usually an 8-h to 24-h clamp time. This is to enable complete hydration and enhance sufficient boardstrength and cohesiveness. This is followed by a 28-day curing period to allow full crystallization and full-strength development. The 28 days curing period has a big disadvantage on production in comparison to short pressing cycles of hot presses (typically 6–9 s per mm inthickness) in resin bonded particleboard

production. However, there are several techniques that can be used to reduce the clamping time of cement composites (Simatupang and Geimer 1990). An example is CO_2 application

2.13 CO_2 Application

The setting (hydration) of cement involves a succession of overlapping crystallization stages, unlike the curing of thermosetting resins, which is dependent on heat activated molecular polymerization and cross-linking (Geimer, 1992). In the manufacture of a cement-bonded wood composite, the hydration process normally requires between 8 and 24 hours to develop sufficient board strength and cohesiveness to permit the release of consolidation pressure. Early work by Berger *et al.,* (1972) showed that exposure of Portland cement to carbon dioxide gas (CO_2) reduces the duration of the initial hardening stage. The phenomenon results from the chemical reaction of CO_2 with calcium hydroxide $Ca(OH)_2$ to form calcium carbonate $CaCO_3$ and water (H_2O).

$$CO_2 + Ca(OH)_2 \text{ ------} \rightarrow CaCO_3 + H_20 \text{ ---------- (7)}$$

The formation of $CaCO_3$ provides a bond in the initial stages of hydration and precedes other crystallization phases that occur during the next 14 to 28 days. Replacement of up to 5 percent of the cement with $Ca(OH)_2$ promotes the reaction, permitting removal of mat consolidation pressure in less than 5 minutes (Geimer *et al.,* 1992). Another major advantage of this gas system is the decrease in wood-cement incompatibility. The CO_2-injected boards were up to 1.9 times greater in MOE and up to 2.5 greater in MOR than similar boards pressed in the conventional manner. However, obtaining uniform gas distribution throughoutthe board can be a technical problem. The addition of carbonates, like those of ammonium, sodium or potassium, can be an alternative method to introduce carbon dioxide in the pressed mattress. The carbonates decompose during pressing and carbon dioxide is released to react with calcium hydroxide. Pressing times of 15 min were attained with pressing temperatures of the order of 85^0C (Simatupang *et al*., 1995). However, as recognised by the authors, the open time of a cement paste provided with either a solution of ammonium or sodium carbonate is too short to allow an application in the industrial production of wood-cement particleboard.

Accelerated carbonation can be an alternative route to partially solve long term durability issues of cellulosic fibre–cement and also in order to make fibre–cement

composites more stable under different humidity conditions (Pizzol *et al.,* 2014). The interaction between carbon dioxide and hydrated Portland cement at atmospheric pressure and ambient temperature conditions is a relatively well-known phenomenon. The carbonation effect in the cement pastes chemical composition, porosity and permeability has been widely reported in the literature (Almeida *et al.,* 2013) which suggested that carbonation helps to improve the properties of fibre cement composites. Accelerated carbonation curing has been identified as a technological approach which may have potential as a mitigation strategy to reduce deterioration of cellulosic fibres and to improve mechanical behaviour and volumetric stabilization of these composites (Toledo *et al.,* 2003). The initial reaction on exposure to CO_2 appears to be an accelerated hydration of the silicates to form a C– S–H like gel and calcite. The gel has a stoichiometry similar to that found in conventional hydration in air curing (Young *et al.,* 1974). The possibility of using carbon dioxide for accelerating the hardening and stabilization of composites made from Portland cement is attractive.

The application of CO_2 in the form of a supercritical fluid enabled the manufacture of cement-bonded particleboard with improved physical and dimensional stability properties in comparison to conventional curing (Hermawan *et al*., 2000). This is due to the production of high calcium carbonate content during the hydration of cement as calcium hydroxide reacts with carbon dioxide. Although the optimum properties of the boards manufactured by supercritical CO_2 curing can be similar to those of gaseous CO_2 curing, the optimum properties of the former could be achieved earlier than in the case of gaseous CO_2cured one (Hermawan *et al*., 2001a). As revealed by X-ray diffractometry (XRD), thermal gravimetry (TG-DTG) and scanning electron microscopy(SEM), the high production of calcium silicate hydrate and calcium carbonate during the hydration of cement, the interlocking between these hydration products with wood surfaces, were the main reasons for the preferred superior strength properties obtained in CO_2-cured boards.

The use of supercritical $CO_2$is an interesting and complex approach for the application of accelerated carbonation curing of fibre–cement composites. The effect of supercritical CO_2 on the structure of cements was initially investigated by the oil industry but its use as a treatment to improve the properties of cementitious composites was initiated by Jones in the late 1990s (Jones 2001). In the case of carbon dioxide, the fluid

reaches the critical point at a pressure of 7.38 MPa and a temperature of 31.1^{0}C. Above those temperature and pressure, the fluid enters the supercritical state. The supercritical CO_2 behaves like a dense gas, acting as a solvent for water, but exhibits no surface tension, allowing penetration into very fine pores, by which the complete wetting of the complex pores typical for fibre–cement matrices is possible. Thus, the carbonation reactions in cementitious materials in the curing stage can be strongly accelerated by using supercritical CO_2 (Farahi *et al.,* 2013).

On the other hand, steam injection pressing when applied to wood cement mixes with 5% sodium hydrogen carbonate ($NaHCO_3$) can result in initial hardening of the composites within 2s of the injection time and 3 min of total pressing time. Although, composites could be handled immediately after pressing, without the necessity of clamping, it was observed that the mechanical properties were significantly small and dimensional stabilities were relatively poor (Eusebio *et al*., 1995). Incorporation, of too high $NaHCO_3$ contents (15–20%) would hinder the cement hydration, since too much $CaCO_3$ will be produced which will cover the cement clinker, leading to lower strengths in the final condition (Nagadomi *et al*., 1996).

It has been suggested that there is the possibility of using an energy efficient carbon dioxide curing to replace autoclaving in cellulose fibre reinforced cement composites production (Shao *et al.,* 2011). According to these researchers, carbonation curing can save considerable amount of energy. The development of a comprehensive model that describes the variation of composition of phases with accelerated carbonation during hydration is considered a challenge for researchers, since it must consider the kinetic and thermodynamic parameters that influence the equilibrium of each phase and the interaction thereof. Therefore, the dissolution and precipitation of chemical compounds or ionic equilibrium with carbonation process vary with the temperature, ionic strength and pH solution (Tonoli *et al.,* 2010).

2.14 Curing Accelerators

Among several cement curing accelerators ($MgCl_2$, $CaCl_2$, $AlCl_2$ and NH_4Cl), $MgCl_2$ was the most effective accelerator for cement hydration which imparted a favourable effect on the mechanical properties and thickness swelling of the boards,

although it seemed to affect adversely the linear expansion and the linear shrinkage (Nagadomi *et al*., 1996b). Latter it was found that the addition of Na_2SiO_3 was more effective than $NaHCO_3$ as a fortifier, with or without the addition of $MgCl_2$, having a favourable effect on the linear dimensional stability (Nagadomi *et al*. 1996c). The mechanisms proposed for this rapid curing of cement-bonded particleboard during steam injection pressing were the production of calcium carbonate ($CaCO_3$) when $NaHCO_3$ was added and the production of amorphous silicate hydrate and cementation of SiO_2 gel when Na_2SiO_3 was used as a fortifier (Nagadomi *et al*., 1996d).

2.15 Super Plasticizer

Super plasticizer is an admixture for concrete which are added to reduce the water in a mixture or to slow the setting rate of the concrete while retaining the flow properties of a concrete mixture.Water-reducing additives restrain concrete to bepermeated with fluids and solutions. It has been established that providing highplasticity and initial and final strengths are advantages of plasticizers involved in prefabricated concretes. In this respect plasticizers mainly function as: water reducing from 18 to 20%, even potential reduction up to 40%, creation high slump, flowing andinstant self-levelling. RHA addition cause less contents of cement and exothermic rate leads to less strength at early ages. "It is well known that pozzolanic reaction occurs after the hydraulic reaction of cement because the silicate content of pozzolanic materials onlyreact with hydroxide produced during the hydration of cement. However, the rate of pozzolanic reaction is influenced by chemicalcontent as well as particle specific area. This is because the mechanism of pozzolanic hydration/reaction is dissolution and diffusioncontrolled process(Muller and Haist, 2012).

CHAPTER THREE
MATERIALS AND METHODS

3.1 Collection of Materials

Coconut husks were purchased from Badagryarea of Lagos state while Carbide waste was collected from the Mechanic Village, Bodija Oju-irin Ibadan. Rice husks were sourced from Bodija central market, Ibadan, while chicken egg shells were collected from an egg seller in Ibadan. River sand was collected from a stream on the campus of the University of Ibadan. Portland cement was procured from West African Portland Cement Company (WAPCO). CO_2gas procured from industrywas used as an accelerator and distilled water was used for mixing at room temperature (25 ± 2^0C).

3.2 Preparation of Materials

3.2.1 Coconut Fibre

The husks of coconut were shredded from the endocarp by pounding in a mortar with pestle to enhance the separation of fibres from the dust. Fibres were separated manually into strands, sun-dried and sieved to prevent effects of particle dust on cement curing. A cutter was used to cut the fibres into 10 – 19mm lengths. The fibres were used for composite production without any pre-treatment in accordance with the procedure of Technical Association of the Pulp and Paper Industry (TAPPI) standard (Plate 3.1).

3.2.2 Carbide Waste

The carbide was sun-dried for 2 days, pulverized by pounding, oven-dried for 24 hours at 60^0C and screened with a 75µm mesh size sieve.

3.2.3 Rice Husk Ash

Rice husk was sun-dried for a day, oven-dried at 60^0C for 24 hours. Thereafter, the dried husks were incinerated at a temperature of 800^0C for 3 hours for amorphous ash production in accordance with the procedure adopted by Rawaid *et al.,* (2012). The percentage of amorphous ash produced was 12% by mass of the rice husk.

Plate 3.1: Coconut Fibres

The Rice husk ash (Plate 3.2) was allowed to cool for 24 hours and was then sieved with a 75μm sieve.

3.2.4 Chicken Egg Shell Ash

Chicken egg shells were sun-dried for one day and oven-dried at 60^0C for 24 hours. Thereafter, egg shells were incinerated at a temperature of 500^0C for 2-hour while another portion was incinerated at a temperature to 900^0C for 3 hours to remove the CO_2 for calcium oxide production. The ashes obtained were allowed to cool for 24 hours, ground to fine particle and screened with 75μm mesh sieve (Plate 3.3a and 3.3b).

3.2.5 Hydrolysis of Calcium Oxide (CaO)

The calcium oxide produced from incineration of chicken egg shell incinerated at a temperature of 900^0C was hydrolysed with water at a ratio of 1 part of water to 3 parts of calcium oxide based on the molar mass. The hydrolysis led to formation of calcium hydroxide which was allowed to cool for 30 minutes (Plate 3.4).

3.2.6 River Sand Washing and Drying

River sand was washed with tap water to remove dirt and extraneous materials. This was sun-dried for two days and later oven dried at 60^0C for 24 hours. The sand was then sieved with a 0.42mm (35) mesh size sieve.

3.3 Preliminary Tests of Raw Materials

3.3.1 Bulk Density of Coconut Fibre, Rice Husk Ash, Calcium Carbide Waste and Chicken Egg Shell Ash

The bulk density of coconut fibre, rice husk ash, calcium carbide waste and chicken egg shell ash was determined in accordance with ASTM 948 – 81. The weight of the materials placed in a 350g container was measured to an accuracy of ± 0.1kg with electronic digital balance and using three replicates. Each measurement and the average of all the measurements were recorded. The length, breadth and the height of the container were measured to determine the volume of the raw materials. The bulk density was calculated as the bulk weight divided by the volume of test samples.

Plate 3.2: Rice husk ash incinerated at 800^0C

Plate 3.3a: Egg shell ash incinerated at 500^0C

Plate 3.3b: Egg shell ash incinerated at 900^0C

Plate 3.4: Hydrolysed egg shell ash i.e CaOH

3.3.2 Crude Fibre Determination

Crude fibre content of the coconut fibre was determined using ASTM C 618-05 and the Association of Official Analytical Chemist (AOAC). Five gram (5g) of coconut fibre (well grounded) was weighed (S_w) into 500ml conical flask. 100ml digestion reagent (mixture of 500ml concentrated tri-oxo nitrate (V) acid and 450ml water) was then added, washing down the sides of the flask. This was then boiled and reflux for 40 minutes. Water jacketed condenser was used to prevent loss of liquid.The reflux was removed from the boiler and allowed to cool under cold tap. The residue filtered through a 15cm of No 4 Whatman paper. The residue was later washed six times with hot water once with ethanol. The paper was opened out, the residue removed with a spatula and transferred to a silica dish. It was dried at 105^0C for six hours, then transferred to a desiccator to cool and thereafter weighed (w_1). It was later incinerated at 600^0C in muffle furnace. The temperature was reduced to 200^0C and then cooled to room temperature in a desiccator and weighed (w_2).

The fibre content was the calculated as:

$$\% \text{ Fibre} = \frac{w_2 - w_1}{s_w} \times 100\%$$

where:

w_1 is the weight before incineration

w_2 is the weight after incineration

s_w is the sample weight.

Moisture content and dry matter (percent) were determined using Moisture Extraction Oven Method as specified by AOAC (1990). Moisture content was obtained from the loss in weight of the oven dried weight.

3.3.3 Ash Content Determination

Ash content of the rattan fibre was determined using ASTM D 2017 (1998) method. The weight of porcelain crucible (w_0) was recorded. 2.5 grams of rattan sample placed in porcelain crucible (w_1) was burnt in a muffle furnace at 600^0c for 2 hours until it completely ashed(plate). It was then transferred to a desiccator and cooled at room temperature. The weight of the samples after incineration (w_2) was recorded.

$$\text{Ash content (\%)} = \frac{\text{Ash weight (g)}}{\text{Weight of sample}} \times 100$$

Or

$$\text{Ash content (\%)} = \frac{w_2 - w_1}{w_1 - w_0} \times 100$$

where:

w_0 is the weight of the porcelain crucible

w_1 is the weight of the porcelain crucible plus residue before incineration

w_2 is the weight of the porcelain crucible plus residue after incineration

3.3.4 Carbohydrate Content Determination

Carbohydrate content of a sample was evaluated by subtracting the percentage of water, ash, protein and fat from 100. The calorific value was estimated by multiplying the percentage of carbohydrate and crude protein by 4 and that of fat by 9 kilo calories per gram. Carbohydrate content of rattan sample was determined by using Ballistic Bomb Calorimeter method. A 1000ml standard flask containing about 600ml of distilled water was placed in 8.9ml of 35% HCl acid and made up to the mark. This gave approximately 0.1N HCl standardised by titration and then diluted 10 times.Protein content was determined by multiplying the total nitrogen content obtained from Kjeidal Experiment by Kjeidal factor of 6.25, since on the average 16% of most protein are Nitrogen (Association of Official Analytical Chemistry, 1990).

$$\text{\% Nitrogen} = \frac{v_s v_b \times N_{acid} \times 0.01401 \times 100x}{W \cdot Y}$$

Where:

X is the total volume of digested sample

v_s is the volume (ml) of acid required to titrate sample

v_b is the volume (mol) of acid required to titrate the blank

N_{acid} is the normality of acid 0.01N

W is the weight of sample (g)

Y is the volume pipetted during distillation

3.4 Roofing Tile Mould Design and Fabrication

The existing roofing tile mould used by previous researchers in the Department of Wood Products Engineering, University of Ibadan had dimensions of 600 x 300 x 6 mm^3. This was re-adjusted to 400 x 300 x 6 mm^3 having a roof gutter of 85mm, a ridge of 35mm and slope deviation of $18^0$to allow for proper overlapping of the roof tiles using an Aluminium sheet was (Plate 3.5). The dimensions of the mould compared favourably with the long span aluminium sheet used in roofing systems in Nigeria today. The wideness of the roof gutter was to allow for free run off of water whenever there was heavy rainfall.

3.5 Production of Fibre-Reinforced Composites

Two sets of coconut fibre-reinforced composites were produced. These are composites subjected to wet and dry carbonation curing respectively.

3.5.1 Fibre-Reinforced Composites Subjected to Wet Carbonation Curing

Composites were manufactured by manual mixing of coconut fibre, Portland-Limestone cement, sand and water (Plate 3.6aand 3.6b). For the control sample and other formulations, the fibre content was fixed at 4% by mass of cement. The cement-water ratio was set at 0.4 (mass of cement) while the cement-sand ratio was set at 1:2. For experimental samples in which cement was partially replaced, the fibre content, cement – sand ratio and cement-water ratio were the same as control. However, cement was partially replaced with Rice Husk Ash (**RHA**) at 10%, Egg Shell Ash(**ESA**) at 10% while Calcium Carbide Waste(**CCW**) at 5% by mass of cement (Table 3.1).

Fabricated composites were transferred to corrugated and flat mould, wrapped with sealed polythene sheet and damp cured. Both corrugated and flat composite tiles was demoulded after 24 hours of production and immersed in CO_2-injected water inside a controlled chamber for 4 minutes at 5.5 MPa as reported by Geimer *et al.,* (1992) (Plate 3.7). The samples wereremoved after 24 hours and damp-cured under wet towels for 27 days.

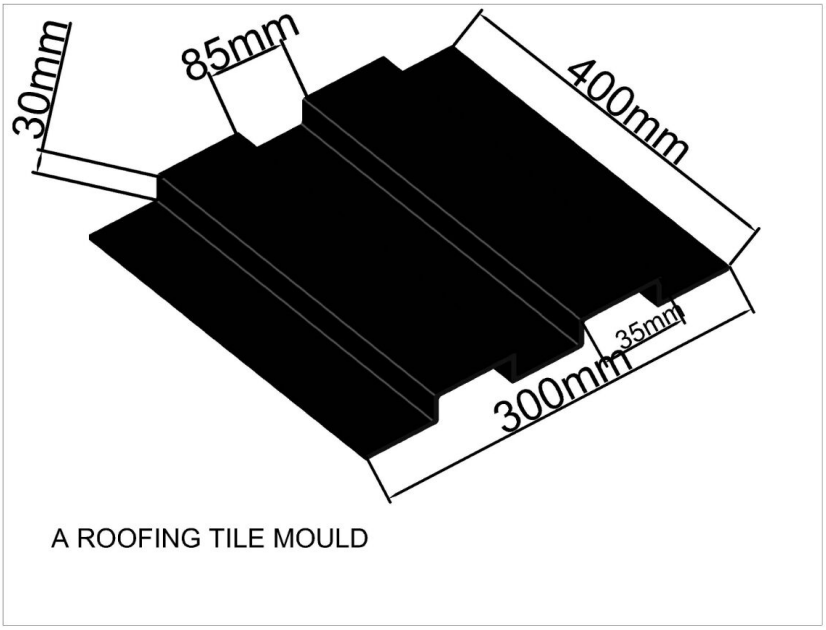


Plate 3.5: Model roofing tiles mould

Plate 3.6a: Composite mixing of coconut fibres

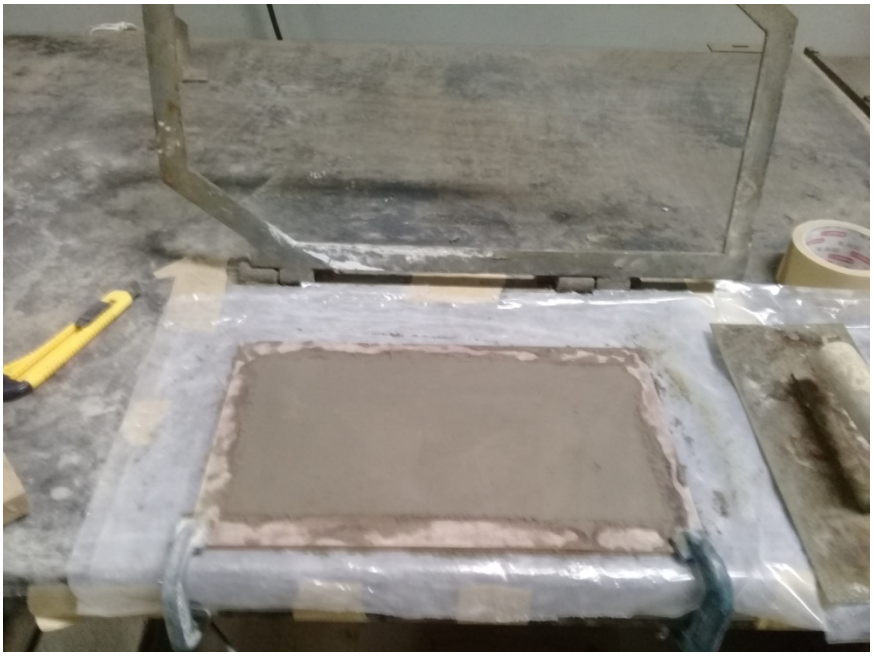


Plate 3.6b: Coconut fibre cement composites

Table 3.1 Formulations used for Production of Coconut Fibre-Reinforced Composites

Formulations	LPC (g)	RHA (g)	CCW (g)	CESA (g)	Coconut Fibre (g)	Sand (g)	Water (g)
Wet Carbonation Curing							
LPC	260.01	*	*	*	4.70	520.32	104.06
10% RHA	241.57	18.44	*	*	4.70	520.32	104.06
10% CESA	238.95	*	*	21.06	4.70	520.32	104.06
5% CCW	250.34	*	9.67	*	4.70	520.32	104.06
Dry Carbonation Curing							
LPC	260.16	*	*	*	4.70	520.32	104.06
15% RHA + 15% CESA	200.73	27.75	*	31.68	4.70	520.32	104.06
15% CCW + 15% CESA	199.47	*	29.01	31.68	4.70	520.32	104.06
7.5% RHA + 7.5% CCW + 15% CESA	200.07	13.89	14.52	31.68	4.70	520.32	104.06

LPC: Limestone Portland Cement
RHA: Rice Husk Ash
CCW: Calcium Carbide Waste
CESA: Chicken Egg shell Ash

Plate 3.7: Wet carbonation of composite samples

3.5.2 Fibre-Reinforced Composite Subjected to Dry Accelerated Carbonation Curing

Composites were manufactured by manual mixing of coconut fibre, Portland-Limestone cement, sand and water. Water/cement ratio 0.4(mass of cement), 4% coconut fibre by volume of cement and cement-sand ratio was 1:2.Meflux, a super plasticizer (an admixture for concrete which is usually used to reduce the water in a cement mixture or to slow the setting rate of the concrete while maintaining the flowing properties of a concrete mixture) was added at 0.3% volume of cement. The percentages of partial replacement of cement by volume of the composite material for samples containing egg shell ash incinerated at 500^0C were 15% rice husk ash + 15% egg shell ash, 15% calcium carbide waste + 15% egg shell ash, and 7.5% rice husk ash + 7.5% calcium carbide waste + 15% egg shell ash (Table 3.1). The second formulation was improved by increasing coconut fibre content to 6% by volume of cement and using egg shell incinerated at 900^0C and hydrolysed into calcium hydroxide as previously discussed.

Other variables and percentage of partial replacement were kept constant. The slurries were thoroughly mixed until the fibres were well coated with cement–sand paste. Each mixture was poured into the mould and spread uniformly to a thickness of 6mm, and vibrated for 60 seconds to reduce the porosity in the composite and smoothened with a hand trowel. After about 5 minutes mould was removed and composites covered with sealed plastic bag for 48 hours (Plate 3.8).

Specimens for accelerated curing were initially cured under a water vapour saturated at 25 ± 2^0C (in a sealed plastic bag) for 2 days. The pre-conditioned (water-saturated air) samples were subjected to 12 hours of accelerated carbonation in the climatic chamber at temperature of 60^0C and relative humidity of 60%. The CO_2 content in the climatic chamber was regulated and to about 15% volume at 0.34MPa. Phenolphythalene solution was prepared at 2%, diluted in anhydrous ethanol as reported by Agopyan *et al.,* (2005). The level of penetration of CO_2 was determined by observing a broken sample piece sprayed with phenophythalene (Plate 3.9 and 3.10). The carbonated samples were soaked in water for 10 minutes, placed in a sealed plastic bag and later transferred to thermal chamber at 60^0C for curing for the next 3 days (Plate 3.11).

Plate 3.8: Composites in sealed plastic bags

Plate 3.9: Dry accelerated carbonation of composites

Plate 3.10: Carbonated samples sprayed with phenolphythalene

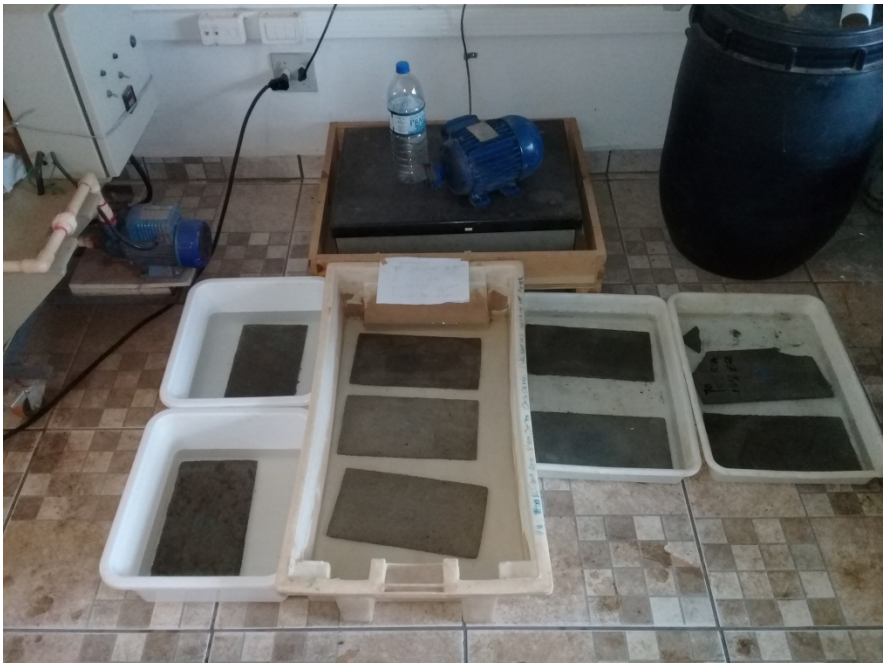


Plate 3.11: Soaking of accelerated carbonated samples in water for thermal curing

Plate 3.12: Thermal curing of composite tiles

3.6Weathering Test

Coconut fibre-reinforced corrugated and flat tiles composites were produced under wet carbonation curing method and subjected to weathering test. Corrugated composite measuring 40 x 30 x 0.6cm^3 were produced (Plate 3.13). Each vibrated composite was moved to the mould and left for 24 hours. Similarly, flat tiles of 16 x 30 x 0.6 cm^{3}were also produced using the same methodology. Both types were subjected to natural ageing tests to determine the weather effects on density, water absorption and thickness swelling.

A pitched roof truss prototype was designed in accordance with a typical roof design in Ibadan North area of Oyo state, Nigeria. The elevation angle was 18^0 while depression angle was 71.9^0 to enhance water run off on the roof surface. The slope was to expose roof tiles to direct sunlight and other prevailing weather conditions in order to ascertain weathering effects on tiles. The height (H_1) of the structure was 600.00mm while length and widthare 1200mm and 1200mm respectively (Plate 3.14). Justification for this design was to reduce degree of condensation that will form under the roof. Slope and roof height determines the number of roof members to be used. Based on this design slope, the number of roof members were reduced. Composite tiles were installed on the roof and subjected to weathering test for a period of 24 months (Plate 3.15).

Forty-two samples were exposed under natural weathering condition in a small prototype roof structure in the Department of Wood Products Engineering, University of Ibadan for a period of24 months. During this period, the maximum and minimumtemperature, average wind speed, rainfall, maximum and minimum relative humidity, and average daily solar radiation were noted respectively. At 90 days interval, samples of the composite tiles were tested for the density, water absorption and thickness swelling. The control was fabricated with asbestos roofing sheet.

Plate 3.13: Corrugated sample for natural ageing test

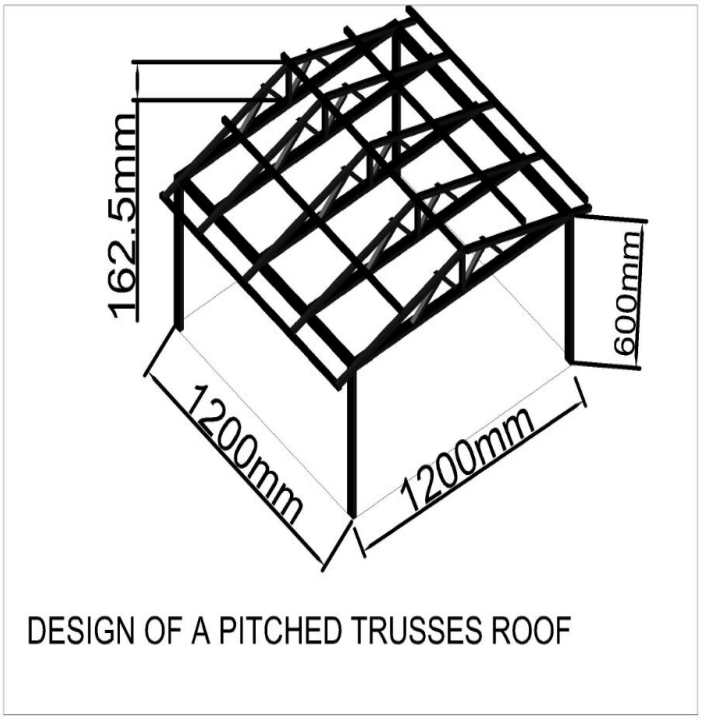


Plate 3.14: Prototype roof natural ageing

Plate 3.15: Corrugated and flat sheet composite tiles for natural ageing tests

3.7 Property Tests Conducted on Coconut Fibre-Reinforced Cement Composites

The composites produced using the two curing methods were tested for average moisture contents, density and bulk density.

3.7.1 Moisture Content Determination

Specimens of dimensions 160mm x 40mm x 6mm were weighed to an accuracy ± 0.3 percent and oven-dried at temperature 105^0C for 24 hours in accordance with ASTM D (1991) in six replicates. The weight loss was evaluated using equation (8).

$$MC_D = \frac{G_w - G_D}{G_D} \times 100\% \quad \text{---------- (8)}$$

Where:

G_w is the weight of wet materials,

G_D is the weight of dry materials (determined by the oven method specified in ASTM D 1037 (1991),

MC_D is the moisture content by oven dry basis.

3.7.2 Density and Bulk Density Determination

The densities of the composites were evaluated using equation (9) and the mass of specimen were measured to nearest 0.1g. A digital calliper was used to measure the length, width and thickness of the samples. Dry density was calculated using the relationship below:

$$\text{Density } (gcm^{-3}) = \frac{\text{Mass of test specimen (g)}}{\text{Volume of test specimen } (cm^3)} \quad \text{…… (9)}$$

The bulk density was determined from the relationship

$$B_D = \frac{W_1}{W_3 - W_2} \quad \text{---------- (10)}$$

Where:

B_D is the bulk density (g/cm^3),

W_1 is the weight of specimen of dry composite specimen (N),

W_2 is the weight of specimen suspended in cold water (N),

W_3 is the weight of soaked specimen suspended in air (N).

3.7.3 Mechanical Property Tests

The three-point bending test configuration was employed in the determination of modulus of rupture (MOR) and modulus of elasticity (MOE) of the samples subjected to wet carbonation curing. A span of 350mm, corresponding to a span to depth ratio of approximately 40, and a deflection rate of 0.5mm/min was used for all tests on an Emic model DL30000 universal testing machine equipped with load cell of 5kN. Fracture energy was obtained by integration of load-deflection curve to the point corresponding to a reduction in load carrying capacity to 50% of the maximum observed.

The four-point bending tests were performed based on the standard ASTM D3043 -00 (2011) to determine the MOR, MOE, and flexural toughness of samples subjected to dry accelerated carbonation curing (Figure 3.16). A span of 160mm corresponding to a span to depth ratio of approximately 40, and a deflection rate of 0.5mm/min was used for all the tests. Six replicate samples were tested (Plate 3.19). Data collected were subjected to ANOVA of 95% confidence level (=0.05).

3.7.4 Water Absorption and Thickness Swelling Test

The water Absorption (WA) tests were carried out in accordance with ASTM D 1037/89 (1991). Test samples of dimensions, 160mm x 40mm x 6mm were exposed to an atmosphere maintained at relative humidity of 65 ± 5percent and at room temperature until their weight (W_1) were substantially constant. After conditioning, the samples were weighed to an accuracy of 0.2 percent. The volume of each sample was computed from the dimensions. The samples were then immersed vertically in distilled water at a temperature of 26 ± 2 ^{0}C for 1 hour and 24 hours, drained to remove excess surface water and re-weighed (W_2). The water absorption was calculated as percentage weight change (w %) as shown in equation (11).

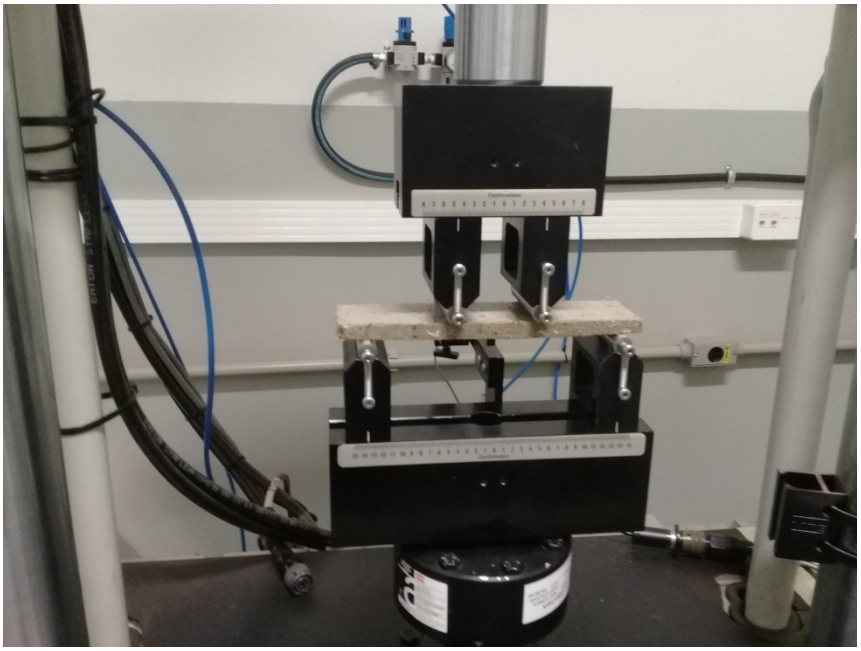


Plate 3.16: Four Point Flexural Test

$$WA\ (\%) = \frac{W_2 - W_1}{W_1} \times 100\% \quad \ldots\ldots\ldots\ldots\ldots\ldots (11)$$

Where:

W_1 is the weight of dry samples before soaking in cold water

W_2 is the weight of wet samples after 24 hours in cold water

WA is the water absorption in percent

3.7.5 Permeable Void Volume

An absorption study was carried out to understand the relative porosity permeable void volume in the composites, in accordance to ASTM C 642-82. Saturated dry surface specimen were kept in hot air oven at 105^0C until a constant weight was attained. The ratio of the difference between the mass of saturated surface and the mass of the oven dried specimen at 105^0C to the volume of the specimen gives the permeable voids in percentage as:

$$\text{Permeable voids} = \frac{A - B}{V} \times 100 \qquad \text{---------- (12)}$$

where:

A is the weight of dried saturated surface of sample after 28 days of immersion period

B is the weight of oven dried sample in air

V is the volume of sample

3.7.6 Thermal Conductivity Tests on the Roofing Tiles

The thermal conductivity of the composite roofing tiles samples subjected to wet carbonation was conducted in accordance with procedure of Behzad and Sam (2007). The thermal conductivity apparatus consisted of the heating chamber with an embedded heating coil with an electrical power supply system. A constant current and voltage of 240V was maintained over the period of supply of heat. The chamber was generally lagged withthermal insulators for the purpose of controlling and conservingmuch of the heat generated by the heater. The specimen chamber was designed to hold cylindrical specimen. A data logger was used to read the corresponding change in temperature. Triplicate samples of diameter 125mm were made for each formulation for testing.

Theory

The description of the design implies that the expression for thermal conductivity is given by K as derived by Meadan.

$$K = \frac{QL}{A(T2 - T1)} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (13)$$

And $Q = VI$ $\ldots\ldots\ldots\ldots\ldots\ldots$ (14)

Q = Quantity of electrical energy delivered per second

V = Voltage per second

I = Current delivered

L = Distance between T1 and T2.

T2 = Temperature of hot point

T1 = Temperature of cold point

A = Cross sectional area of specimen.

3.7.7 Thermal-Degredation-Temperature

Therma-Degredation-Temperature (TDT) was conducted using Mettler Toledo equipment; Model TGA-50 attached to a Mettler TC 11 4000 thermal's analyzer was used for samples subjected to dry accelerated carbonation. The samples (10–20 mg) were placed in platinum pans and heated from 20^0C to 1000^0C at the heating rate of 20^0C /min. The thermal analyzes were done in a nitrogen atmosphere at a flow rate of 20ml/min. The synthetic air atmosphere was used to simulate the usual conditions of the end-use of this material and it yielded the onset temperature of decomposition, mass loss, and maximum decomposition peak

3.7.7 Microstructural Investigations

A Scanning Electron Microscope (SEM) and image analyser was used for the characteriazation of fibre-matrix interface and the transition zone for samples subjected to wet and dry accelerated carbonation. A black scattered electron (BSE) detector was used to observe the morphological features of cut and finished surfaces. The BSE imaging permits the easy identification of cementitious phases since electron scattering goes with the atomic number. Dark and light areas are related to lighter and heavier elements, respectively. Observable characteristics through the electron microscope were recorded.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 Proximate Analyses of Coconut Fibre

The proximate analyses of coconut fibre are presented in Table 4.1. The crude fibre content (7.40%) was lower than 46.1% reported by Hussain *et al*., (2010) for *Cucurbita moschata*, a vegetable species. The crude fibre analyses showed that coconut fibre consisted mainly of hemicellulose (15 - 28), cellulose (35 - 60%) and lignin (25 – 48%). The high percentage in cellulose content for coconut fibre may have positive influence in the bending strength when used in composite production. The relatively percentage of carbohydrate (32.8%) suggests that coconut fibre would be inhibitory to cement and susceptible to fungi attacks. This is line with the reports of Badejo and Simatupang (1985) that *Terminalia superba* with a lower sugar content of 1.24% was inhibited cement curing.

The moisture content (7.51%) was less than 12.0% the upper limit recommended for storage of such materials (Wei *et al.*, 2000). This implies that coconut fibre can be stored for long periods of time before use. The ash content (1.02%) is higher than the value (0.3%) reported for some indigenous wood species such as *Tectonia grandis*, *Antiaris africana* and *Terminalia superba* (Badejo and Simatupang, 1985; Omoniyi, 2009).

4.2 Chemical Composition of Rice Husk Ash, Calcium Carbide Waste, Chicken Egg Shell Ash and Portland Limestone Cement

The chemical analyses of calcium carbide waste, rice husk ash, chicken egg shell ash and Portland cement are presented in Table 4.2. Rice husk ash had high content of silica oxide (94.04%), alumina 0.25% and iron oxide 0.14% in amorphous and chemical reactive forms and this confirms the suitability of the material as cement replacement for the production of composites. This result is in tandem with those reported for rice husk ash by Pereira *et al.,* (2013). Calcium oxide contents in egg shell ash

Table 4.1: Proximate Analysis of Coconut Fibre

Parameter	Composition (%)
Carbohydrate	36.7
Lipid	47.5
Crude Protein	10.6
Ash	1.1
Crude Fibre	7.7
Moisture	7.5
Hemicellulose	15 - 28
Cellulose	35 - 60
Lignin	25 - 48

Table 4.2: Chemical Composition of Calcium Carbide Waste, Rice Husk Ash, Chicken EggShell Ash and Portland Limestone Cement (PLC)

Component	Calcium Carbide Waste (%)	Egg Shell Ash (%)	Rice Husk Ash (%)	PLC(%)
CaO	67.08	52.15	0.62	63.5
MgO	1.26	0.60	0.44	3.13
SiO_2	1.54	1.22	94.04	19.4
Al_2O_3	0.50	0.28	0.25	4.11
Fe_2O_3	0.03	0.16	0.14	2.30
Chloride	-	0.01	-	-
TiO_2	0.32	-	-	-
MnO	0.05	-	-	-
Na_2O	0.02	-	0.02	0.24
K_2O	0.05	-	2.49	1.09
SO_3	-	-	-	2.97
LOI	26.85	-	3.52	3.26

(52.15%) and calcium carbide waste (67.08%) are acceptable for chemical reaction, i.e the calcium oxide is sufficient to react with silicious and aluminious materials to form calcium silicate hydrate similar to those obtained from hydration process of cement. It was noted however, that overall proportion of silica oxide, aluminium oxide and iron oxide in egg shell ash and carbide waste was less than the lower limit of 70% in accordance to ASTM 618 (2005) specified for pozollanic materials and on that basis cannot be categorized as pozzolan but the calcium oxide it contain is a good reactive element in cement setting..

4.3 Specific Gravity and Thermal Properties of Coconut Fibre, Calcium Carbide Waste, Rice Husk Ash and Portland Cement

The specific gravityof coconut fibre, calcium carbide waste, rice husk ash and limestone cement are presented in Table 4.3. The specific gravity, which is an index of mineral content was low for coconut fibre (1.38). The specific gravity of calcium carbide waste (2.29) is almost the same with 2.3 reported by Makaratat *et al*., (2011) but lower than 3.2 reported by Ogundipe (2016). The specific gravity of Portland cement (3.08) was less than 3.2 reported by Charonenvai *et al*., (2005). The lower specific gravity (2.2) of rice husk ash compared with calcium carbide waste and Limestone-Portland cement suggest that composites in which cement is partially replaced with rice husk ash would be lighter in weight than those incorporating calcium carbide waste.

Figure 4.1a – 4.1d showed the Thermal-Degradation-Temperature (TDT) curves for coconut fibre, rice husk ash, calcium carbide and egg shell ash. Thermal-degradation-temperature for coconut fibre showed moisture loss of about 0.7% between temperature 20^0C and 80^0C. The second weight loss was observed between temperature 110^0C and 500^0C while maximum weight loss of about 41.0% was observed between 760^0C to 900^0C. These results are comparable with TDT of wood pulp fibre as reported by Stevulova *et al*., (2016). Jonoobi *et al*., (2009) had reported that the initial decomposition of the cellulose components takes place mostly in the amorphous region which is similar to the result of coconut fibre. This result implied that cellulosic materials have higher thermal stability probably due to a much higher amount of hydrogen bonds between cellulosic chain. For rice husk ash, moisture loss was observed between 25^0C and 65^0C followed by maximum weight loss of about 19.0% at temperature between 100^0C and 880^0C. Although, this result cannot be compared with the report of Noorhaza *et al*., (2014)

Table 4.3: Specific Gravity of Test Materials

Materials	Specific gravity
Coconut Fibre	1.38
Rice Husk Ash	2.19
Egg Shell Ash	2.49
Calcium Carbide Waste	2.29
Portland Limestone Cement	3.08

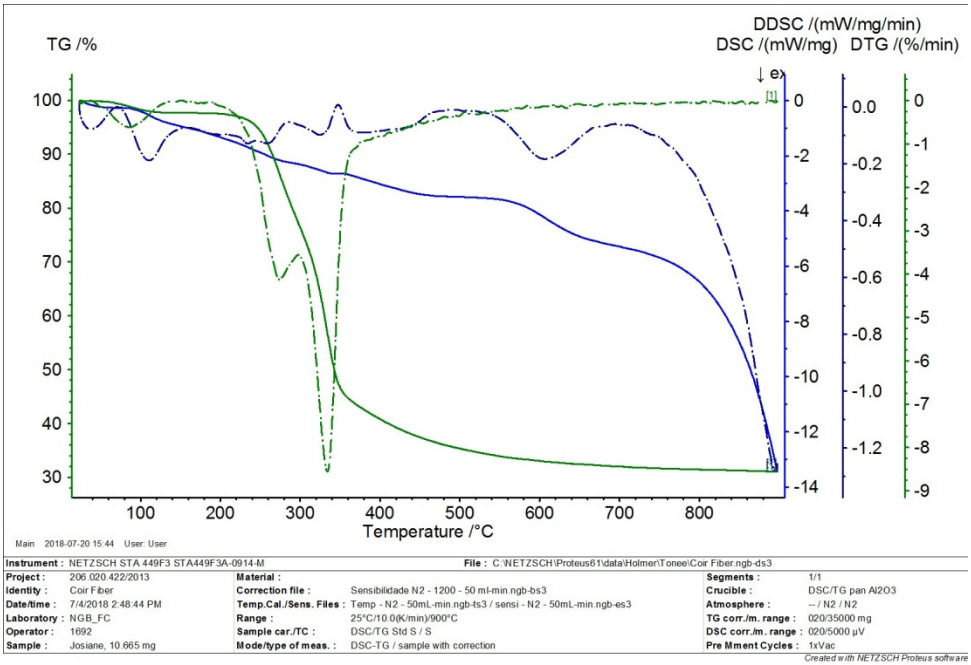


Figure 4.1a: Thermal-Degradation-Temperature of coconut fibre

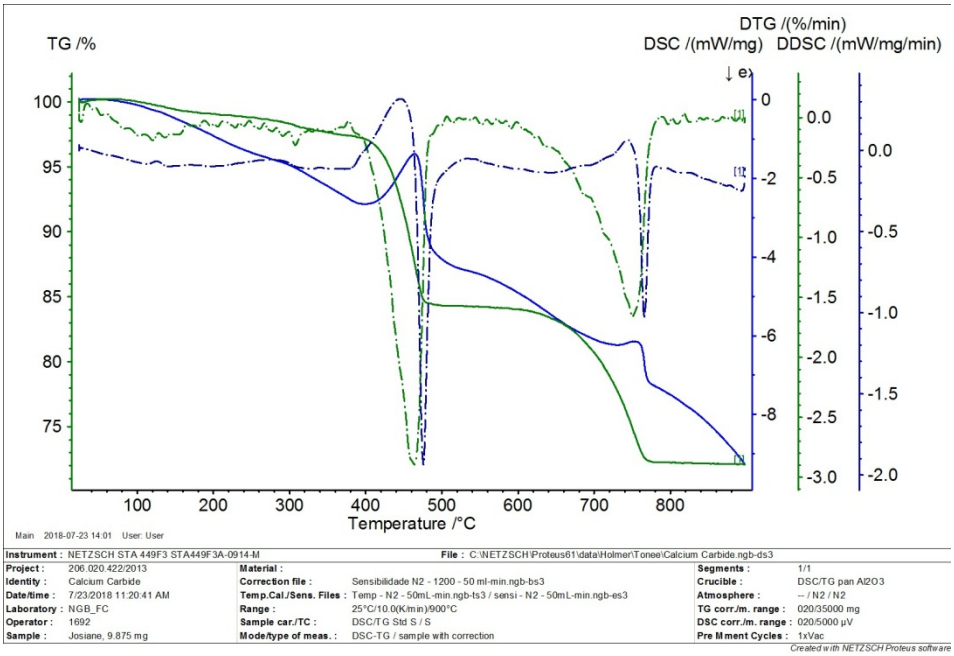


Figure 4.1b: Thermal-Degradation-Temperature of calcium carbide waste

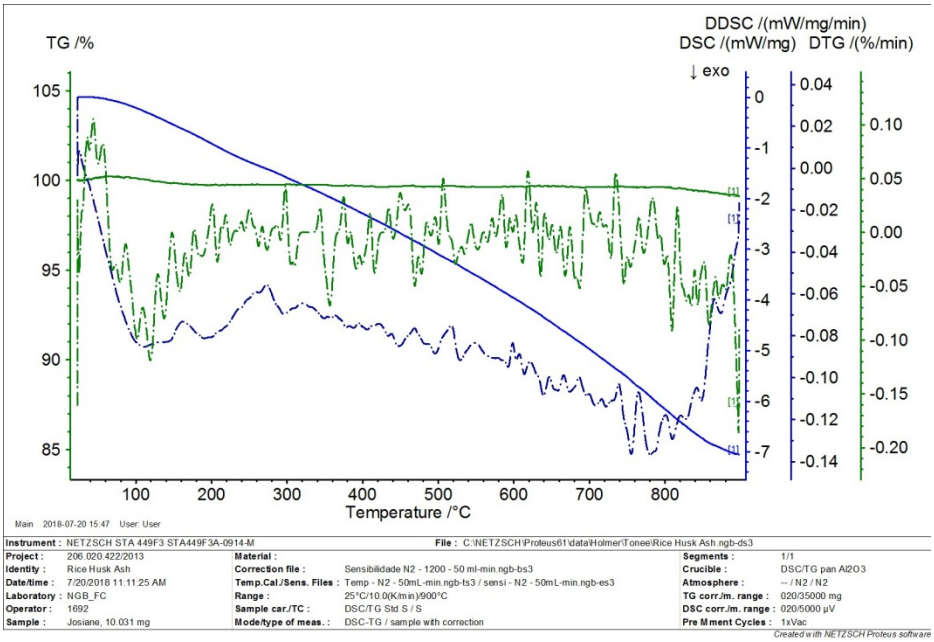


Figure 4.1c: Thermal-Degradation-Temperature of rice husk ash

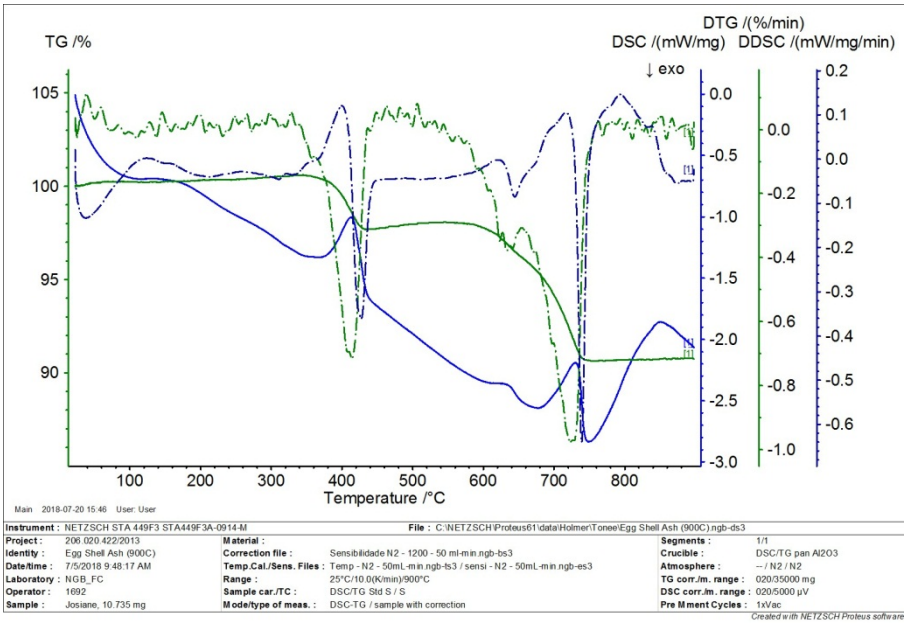


Figure 4.1d: Thermal-Degradation-Temperature of chicken egg shell ash

for TDT of rice husk ash. The degradation of rice husk ash might be as a result of larger particle sizes which yields more residue because of poor heat transfer (Stenseng *et al*., 2001 and Stresov *et al*., 2003). Calcium carbide degradation curve showed moisture loss of 2.0% between 20^0C and 120^0C and followed by weight loss between 150^0C and 400^0C. Additional weight loss was observed between 490^0C to 740^0C of about 6.0%. The egg shell ash showed moisture loss at the initial stage of 5.2% between 20^0C and 100^0C followed by weight loss of 5% between 200^0C and 400^0C. Further degradation was observed between 440^0C and 650^0C resulting in weight loss of 5.0%. This trend of results is similar to thermal degradation of Quail eggshell powder as reported by Leandro *et al*., (2017). The results showed that materials are suitable for fibre-reinforced composite production in tropical environment where degree of temperature is relatively high.

4.4 Physical and Mechanical Properties of Test Samples Subjected to Wet Carbonation

Table 4.4 showed the physical and mechanical properties tests of composite samples subjected to wet carbonation. The bulk density, water absorption and thickness swelling of composite samples subjected to wet carbonation were discussed below. Also, the MOE and MOR of the samples under the same curing regime are discussed below.

4.4.1 Bulk Density of Test Samples

The range of bulk densities (BD) for composite samples was between 1.8 - 2.0gcm^{-3} (Table 4.4). Samples containing rice husk ash had the lowest density (1.8gcm^{-3}). The observed variation in the bulk densities of the composite samples might be as a result of varied density of raw materials. The observed difference in bulk densities of composites was not significant ($P \geq 0.05$). Composite samples containing egg shell ash had the highest BD (2.0gcm^{-3}), and this may be on the account of density (2.5gcm^{-3}) of egg shell ash. The bulk densities were higher than composites tiles produced from treated coconut fibre (Olorunnisola, 2006) but have similar density to composite produced from sisal for roofing tiles (Tonoli *et al.,* 2010). The weight gain in all the composite samples might be attributable to the effects of CO_2 curing which led into precipitation of $CaCO_3$ in the mixtures and resulted into higher molecular weight. This increase in molecular weight in

Table 4.4: Physical and Mechanical Properties of Tests Samples Subjected to Wet Carbonation

Sample Formulation	Bulk Density (gcm^{-3})	WA (%)	TS (%)	MOE (GPa)	MOR (MPa)
Control	1.90 ^{A}	7.50^{A}	11.1 ^{A}	2.40 ^{A}	3.03 ^{A}
10% Rice husk ash	1.80 ^{A}	8.70^{B}	10.5^{B}	2.60 ^{B}	5.01 ^{B}
10% Egg shell ash	2.00 ^{A}	8.10^{C}	9.80 ^{C}	1.50 ^{C}	1.44 ^{C}
5% Calcium carbide Waste	1.90^{A}	7.70^{D}	7.80 ^{D}	2.80 ^{D}	4.05 ^{D}

Means with the same letters are not statistically different

composite tiles is similar to report of Moslemi *et al*., (1994) for cement-bonded particle board subjected to CO_2 curing. Samples containing calcium carbide had similar density with control because of its fineness which could have resulted into more void spaces thereby maximizing air voids (Chanroenvai *et al*., 2005). Also, the observed increase in densities of composite tiles in all formulations might be attributable to increase in moisture contents of samples when soaked in water for CO_2 curing because coconut fibre in the matrix tend to absorb moisture and resulted into density increase.

4.4.2 Water Absorption of Test Samples

The range of water absorption (WA) was between 7.5 - 8.7% as presented in Table 4.4. The observed difference was significant ($P \leq 0.05$) (see appendix AA1). These values were higher than 1.0 – 3.9% reported by Olorunnisola and Adeniji (2019) for coconut husk fibre-reinforced roofing tiles but lower than 23.9% for composite produced from *Eucalyptus grandis* (Savastano *et al.,* 2003). Samples containing rice husk ash had the highest water absorption (8.7%). Possibly due to the high inherent silica oxide content which might have formed hydrated products similar to cement. The partial replacement of cement with rice husk ash, calcium carbide waste and egg shell led to increased water absorption by the composites. The samples containing calcium carbide had the lowest WA (7.7%) and this might be as a result of higher percentage of $Ca(OH)_2$ of about 92% which reacted with siliceous materials through chemical reactions, and resulted in final products similar to cement hydration (Narayan, 2002). The WA (8.7%) observed in the sample containing rice husk ash might be attributable to water affinity of rice husk ash which tends to absorb more water because of high silica oxide to from hydrated products similar to cement. The range of values reported for all the composites were lower than what was reported in literature for composite produced from bagasse (4.8 -16.4%), aspen (24.0 – 58.0%) and larch (36.0 – 56.0%) (Moslemi *et al*., 1994; Oyegade, 2000; Ghavami, 2001; Ajayi, 2002, 2003; Okine *et al.*, 2004 and Aggrwal *et al*., 2008) It can be concluded from the results that water absorption (WA < 25%) was lower for all the samples formulation. This may be an indication that the tiles are relatively stable in moist condition and would be suitable for use in out-door applications where they would be in constant exposure to humidity and moisture conditions.

4.4.3 Thickness Swelling of Test Samples

Thickness swelling is a measure of dimensional stability of cement-composites. Table 4.4 showed partial replacement of cement resulted in a lowering of thickness swelling from 11.1% (for the control sample) to 7.8% for samples containing rice husk ash, calcium carbide waste and egg shell ash respectively. The observed difference was significant ($P \leq 0.05$). These values were higher than range of 0.5 – 3.1% reported by Olorunnisola (2009) for coconut husk-cement composite and 0.6 - 4.0% for cement–bonded rattan fibre composites (Olorunnisola and Agrawal, 2015). Samples containing rice husk ash had the highest thickness swelling (10.5%). This might be as a result of hygroscopic properties of rice husk ash. Also, coconut fibre present in the composites is subjected to swelling which might have accounted for the relatively higher thickness swelling values observed. The observed lower thickness swelling in the composites in which cement were partially replaced might be attributable to the low degree of compression involved in their production and partly due to restraining effects of fibre around cement paste. The main contributory factor to thickness swelling cement-bonded composites has been identified as the compressive strain and stress developed during production (Badejo, 1986; Xu Winistorfer, 1995). The thickness swelling results showed that composites were generally stable and will be suitable for outdoor use in construction purposes.

4.4.4 Modulus of Elasticity of Test Samples

The average modulus of elasticity of samples produced under wet carbonation curing methods arepresented in Table 4.4. The range of MOE of composites were between 1.5 – 2.8GPa. The observed difference in MOEs are significant ($P \leq 0.05$) (see appendix BB2). The average MOE obtained for sample containing rice husk ash and calcium carbide were comparable to 3.0GPa prescribed by the International Standard Organization (1989). The relatively high MOEs of the samples containing rice husk ash might be as a result of pozzolanic behaviour of rice husk ash because of its high silica oxide which helps in cement hydration.The range of MOEs was higher than composite developed from coconut husk (Olorunnisola, 2006) but lower than MOEs of Eucalyptus grandsis (Savastano *et al*., 2003). Composites containing rice husk ash (2.6 GPa) and calcium carbide (2.8 GPa) waste perform better than the control. Moslemi *et al.*, (1992) had

reported that CO_2 curing generally increase the MOEs of cement composite tiles. This is because CO_2increases the interfacial bond between Portland limestone cement and coconut fibre.

The physical properties of the samples subjected to wet carbonation tests were within acceptable limits, but the modulus of elasticity can be improved. Hence, the formulation and the curing method were both modified.

4.4.5 Modulus of Rupture of Test Samples

The average Modulus of Rupture (MOR) of samples production under wet carbonation curing method is presented in Table 4.4. The range of MORs for composites ranged between 1.5 MPa and 5.0 MPa. The observed difference was significant ($P<0.05$) (appendix BB2). However, these values were comparable to those obtained from composites reinforced with Calamus and Laccosperma (1.6 – 6.3 MPa) as reported by Adefisan and Olorunnisola (2012). Also, range of MORs is within the values (3.8 – 6.2 MPa) reported in literature for composite reinforced with sisal fibre (Apogyan 1988), but lower than the MORs (15.6 – 22.2 MPa) for composite produced from *Eucalyptus grandis* by Savastano *et al.* (2000). The failure pattern observed showed that composites were brittle. Samples containing rice husk ash showed the highest MOR (5.0 MPa) and a better performance than the control. This might be as a result of higher percentage of silica oxide being a pozzolanic material that led to increase in reactivity between matrix and formed good bonding.

4.5 Physical Properties of the Composites Subjected to Dry Accelerated Carbonation

The effects of partial cement replacement and curing methods on the bulk density and moisture contents are thus discussed.

4.5.1 Bulk Density

The bulk densities of the composites from different formulations subjected to different curing regimes are presented in Table 4.5. For the thermally cured samples partial replacement of cement resulted in a lowering of bulk density ranged from 1.77 gcm^{-3} to 1.94 gcm^{-3} while control had 2.00 gcm^{-3}. The composites containing rice husk ash

Table 4.5: Bulk Densities of Composite Tiles Produced under different Curing Methods

Formulation	Bulk Density (gcm^{-3})
Samples containing egg shell ash obtained at 500^0C and thermally cured at 60^0C	
Control	2.03 ± 0.17^{B}
Rice husk ash + egg shell ash + cement	1.77 ± 0.03^{A}
Calcium carbide waste + egg shell ash + cement	1.94 ± 0.01^{B}
Rice husk ash + calcium carbide waste + egg shell ash + cement	1.87 ± 0.02^{B}
Samples containing egg shell ash obtained at 500^0C and subjected to accelerated carbonation	
Control	$2.14 \pm 0.02^{A, B}$
Rice husk ash + egg shell ash + cement	1.93 ± 0.01^{A}
Calcium carbide waste + egg shell ash + cement	2.06 ± 0.01^{B}
Rice husk ash + calcium carbide waste + egg shell ash + cement	1.97 ± 0.05^{B}
Samples containing egg shell ash obtained at 900^0C and subjected to accelerated carbonation	
Control	$2.13 \pm 0.01^{A, B}$
Rice husk ash + egg shell ash + cement	2.02 ± 0.01^{A}
Calcium carbide waste + egg shell ash + cement	$2.07 \pm 0.01^{A, B}$
Rice husk ash + calcium carbide waste + egg shell ash + cement	2.04 ± 0.01^{A}

Means with the same letters are not statistically different

had the lowest bulk density. This might be as a result of low relatively bulk density (2.18gcm^{-3}) of rice husk ash. The control samples had highest bulk density because of the relatively high bulk density of the cement (3.08gcm^{-3}). The range of bulk density values compared favourably with the values reported by Pereira *et al*. (2013) for rice husk ash composites reinforced with green coconut fibre (1.7 – 1.9gcm^{-3}) and 1.8gcm^{-3} for composites reinforced with *Eucalyptus grandis,* but higher than the bulk density of composites reinforced with Sisal (*Agave sisalana*) (1.38gcm^{-3}) (Roma *et al.,* 2008). The observed lower bulk density for composite containing calcium carbide waste is in agreement with report of Olorunnisola and Ogundipe (2012) that addition of calcium carbide waste in composite production also resulted into a lower bulk density.

Although, the accelerated carbonation generally increased the bulk densities of the composites, including the control whose value increased from 2.03gcm^{-3} to 2.14gcm^{-3}. Again, samples containing rice husk ash still had the lowest bulk density. This observation may be attributed to the low bulk density of rice husk ash. However, sample containing rice husk ask and egg shell ash exhibited an increase in bulk density from 1.77gcm^{-3} to 1.93gcm^{-3} while the combination of rice husk ash, calcium carbide waste and egg shell ash exhibited increase in bulk density from 1.87gcm^{-3}to 1.97gcm^{-3}. The observed increases in bulk density of composite samples is in agreement with report by Almeida *et al.,* (2013) that carbonation reactions promote the filling of the pores in the matrix with carbonated products, which increases the bulk density, since calcium carbonate ($CaCO_3$), produced from carbonation is denser than calcium hydroxide ($Ca(OH)_2$) that is released in the hydration of cement. However, the range of bulk densities recorded for the composites were generally higher than 1.6gcm^{-3} obtained by Savastano *et al,* (2009) for composite reinforced with *Eucalyptus grandis*.

An increase in the incineration temperature of the egg shell from 500^{0}C to 900^{0}C coupled with accelerated carbonation did not result in much difference in the bulk density of all the composites tiles produced. The bulk densities of the cement replacement samples for egg shell incinerated at 900^{0}C ranged between 2.02gcm^{-3} and 2.07gcm^{-3} while that of the control was 2.13gcm^{-3}. The bulk density values compare favourably with the range of values 1.5 – 2.1 gcm^{-3} reported for asbestos roofing materials by Olorunnisola, (2012).

The densities results obtained for composite tiles is indication that it can be used for roofing materials.

4.5.2 Moisture Contents

The moisture contents of the composites of different formulations subjected to different curing regimes are presented in Table 4.6. For the thermally cured samples, the moisture contents range was between 9.5% and 16.1%. Composite samples containing calcium carbide waste and egg shell ash had the lowest moisture contents among the composites with partial cement replacement. There was an observed significant difference ($p<0.05$) (appendix A2) between composites partially replaced with cement. Samples containing rice husk ash had the highest moisture contents. This might be attributable to the hydrophilic nature of rice husk (Aznizam *et al.,* 2005).

Accelerated carbonation generally reduced the moisture contents of all the composites including the control. The moisture content was reduced from 9.5% to 6.8%. There was a substantial reduction in moisture contents of composites made from rice husk ash and chicken egg shell ash subjected to accelerated carbonation, (16.1% to 10.9%). This observation may be due to the fact that carbonation required water for dissolution of CO_2 into the pores by diffusion of CO_2 into the empty pores. This dissolves in the pore solution and then reacts with the OH^- and resulting in the formation of CO_3^{2-} (Frias and Goni, 2013). The range of moisture contents compared favourably with those of composite produced from washed and boiled coconut fibre (8.0% and 10.8%) as observed in literature by Asasutjarit *et al*., (2007). There was a significant difference ($P<0.05$) (appendix A2) between composite containing rice husk ash and calcium carbide waste. Composite made from eggshell incinerated at 900^0C which were subjected to accelerated carbonation had moisture contents which ranged between 7.3% and 8.7%. The moisture contents of all the composite samples were low (<8.7%) which conforms with ISO 8335 (1987) standard that MC must be lower than 12% for fibre-cement composites. There was no significant difference between ($P>0.05$) between composite containing rice husk addition but observed difference with composites containing calcium carbide waste. The results of moisture contents of composite tiles subjected to accelerated carbonation had

Table 4.6: Moisture Contents of Composite Tiles Production under different Curing Methods

Formulation	Moisture Contents (%)
Samples containing egg shell ash obtained at 500^0C and thermally cured at 60^0C	
Control	9.5 ± 0.17^A
Rice husk ash + egg shell ash + cement	16.1 ± 1.08^B
Calcium carbide waste + egg shell ash + cement	11.3 ± 0.33C
Rice husk ash + calcium carbide waste + egg shell ash + cement	12.8 ± 0.98^D
Samples containing egg shell ash obtained at 500^0C and subjected to accelerated carbonation	
Control	6.8 ± 0.10^A
Rice husk ash + egg shell ash + cement	10.9 ± 0.31^B
Calcium carbide waste + egg shell ash + cement	7.4 ± 0.11^A
Rice husk ash + calcium carbide waste + egg shell ash + cement	9.7 ± 1.05^C
Samples containing egg shell ash obtained at 900^0C and subjected to accelerated carbonation	
Control	7.3 ± 0.13^A
Rice husk ash + egg shell ash + cement	8.7 ± 0.34^B
Calcium carbide waste + egg shell ash + cement	8.1 ± 0.33^A
Rice husk ash + calcium carbide waste + egg shell ash + cement	8.4 ± 0.38^B

Means with the same letters are not statistically different

lower moisture value which is indication that composite tiles were suitable for outdoor use.

As shown in Figure 4.2a to 4.2c, There was a positive correlation between bulk density and moisture contents of composites under different curing regimes and those that cement were partially replaced. It was observed that the higher the bulk density, the lower the moisture contents of composite samples.

4.6 Effects of Partial Replacement and Curing Methods on the Mechanical Properties of the Composites Subjected to Dry Accelerated Carbonation

The effects of partial cement replacement and curing methods on the modulus of rupture, modulus of elasticity, flexural toughness of coconut fibre-reinforced cement composite are discussed below.

4.6.1 Modulus of Rupture

The moduli of rupture of the composites are presented in Table 4.7. For the thermally cured samples, partial replacement of cement resulted in a lowering of the MOR from 7.4MPa (control) to 1.7MPa for composites containing rice husk ash and egg shell ash. The MOR values were significantly different ($P<0.05$) (appendix B1). However, MOR (5.1 MPa) composites in which cement was partially replaced with a combination of calcium carbide waste and eggshell ash performed better than other composite formulations. This might be attributable to the increased hydration of silica and alumina resulting from calcium carbide addition to form calcium silicate and calcium aluminate and might led to early setting of the paste. The incorporation of rice husk ash lowered the MOR in composite production. This observation might be as a result of poor wettability of the matrix mixtures.

The range of values of MOR for thermally cured samples was lower than 11.0MPa, reported by Pereira *et al*., (2013) for composite produced from rice husk ash, reinforced with green coconut fibre and cellulosic pulp. Also, the MOR of the composites are lower than 7.7MPa reported for asbestos-cement ceiling board (Olorunnisola, 2012). However, the MOR values were comparable with those obtained from composite

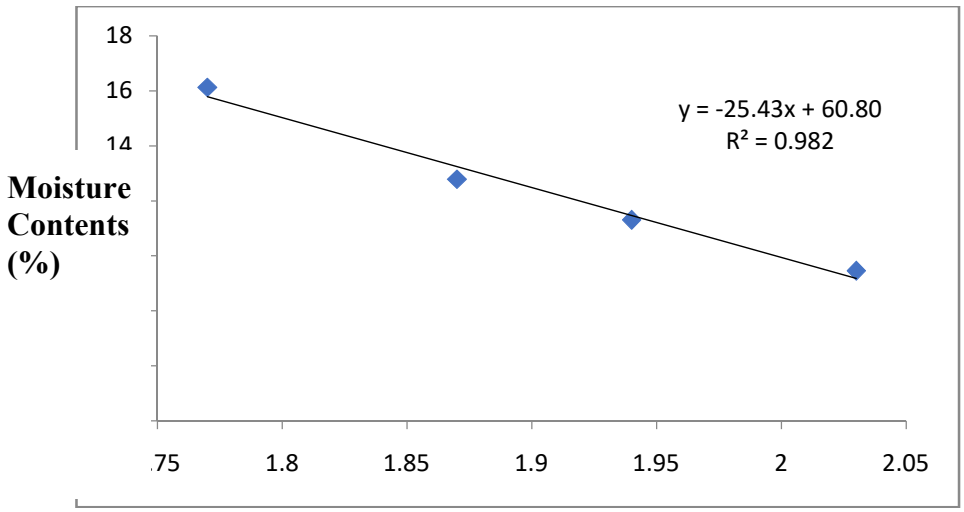


Figure 4.2a: Correlation between density and moisture contents for composite samples subjected to thermal curing

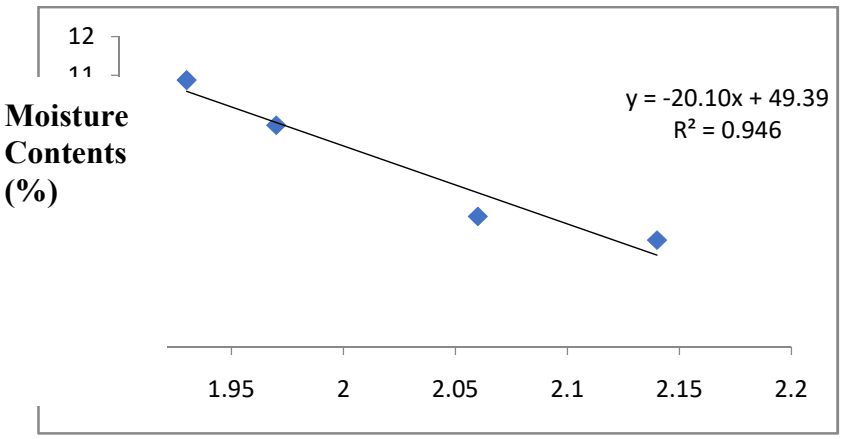


Figure 4.2b: Correlation between density and moisture contents for composite samples subjected to accelerated carbonation

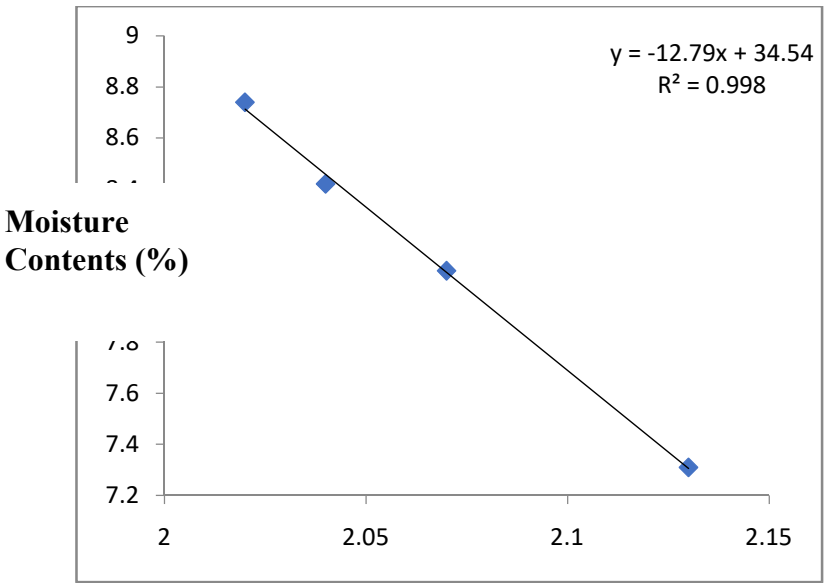


Figure 4.2c: Correlation between density and moisture contents for composite samples subjected to accelerated carbonation for calcination of egg shell at 900^0C

Table 4.7: Modulus ofRupture of Composites Produced with different Curing Methods

Formulation	Modulus of Rupture (MPa)
Samples containing egg shell ash obtained at 500^{0}C and thermally cured at 60^{0}C	
Control	7.4 ± 0.48^A
Rice husk ash + egg shell ash + cement	1.7 ± 0.44^C
Calcium carbide waste + egg shell ash + cement	5.1 ± 0.37^B
Rice husk ash + calcium carbide waste + egg shell ash + cement	2.1 ± 0.37^B
Samples containing egg shell ash obtained at 500^{0}C and subjected to accelerated carbonation	
Control	10.4 ± 2.20^A
Rice husk ash + egg shell ash + cement	8.3 ± 1.82^{AB}
Calcium carbide waste + egg shell ash + cement	9.4 ± 2.1^{AB}
Rice husk ash + calcium carbide waste + egg shell ash + cement	7.6 ± 1.75^B
Samples containing egg shell ash obtained at 900^{0}C and subjected to accelerated carbonation	
Control	9.2 ± 1.7^A
Rice husk ash + egg shell ash + cement	11.2 ± 1.10^B
Calcium carbide waste + egg shell ash + cement	12.9 ± 1.34^C
Rice husk ash + calcium carbide waste + egg shell ash + cement	10.0 ± 1.72^B

Means with the same letters are not statistically different

reinforced with rattan, *Lacoperma secundiflorum* particles (0.8 – 7.4MPa) as reported Olorunnisola, (2005). The relatively lower MOR values observed in the composites containing rice husk ash might be due to the fact that rice husk ash required more water for a given consistency due to character of its absorptive properties of the particle and the porous structure of the constituent particles (Bhanumathidas and Mehta 2004). Also, the relatively low binding property of the egg shell ash might have led to loose bonding between the composite materials (Olarewaju *et al.,* 2011). The load-deflection curve shown in Figure 4.9 showed that there was a loose bond between the samples produced from combination of rice husk ash and egg shell ash. The load deflection curves (Figure 4.3a to 4.3d) showed that all the composites failed in a brittle manner indicating that the coconut husk fibre did not contribute much to improve the ductility of the composites.

Accelerated carbonation generally improved the moduli of rupture of all the composites, including the control. The MORs increased from 7.4 to 10.4MPa. There was a considerable increase in the MOR of the composite formulation containing rice husk ash and egg shell ash with accelerated carbonation, (1.7 to 8.3MPa). The maximum value of MOR obtained was however lower than 11.8MPa reported for carbonated samples produced with partial replacement of cement with metakaolin reinforced with *Eucalyptus* pulp (Correia *et al.,* 2015). Also, the highest MOR (10.4MPa) for accelerated carbonated samples was lower than 13.1MPa reported for composites produced from *Eucalyptus grandis* pulp (Savastano *et al.,* 2003). The reported increment in MOR values of composites may be attributable to the dense and compact nature of carbonated composites. This is because carbonation improves the contact between fibres, and cement matrix and favour the better adhesion (Pizzol *et al.*, 2014). Also, Gram (1988) reported that carbonation helps in the preservation of fibre strength by lowering the alkalinity of the matrix, thus improving mechanical performance and fibre-matrix bonding of the composites and enhancing dimension stability of the fibre, after high matrix densification. Toledo *et al.* (2003 and 2013) had also reported that accelerated carbonation reduces deterioration of cellulosic fibres and to improve mechanical behavior and volumetric stabilization of composites.

An increase in the incineration temperature of the egg shell from 500^0C to 900^0C coupled with accelerated carbonation enhanced the MOR of all the composites containing

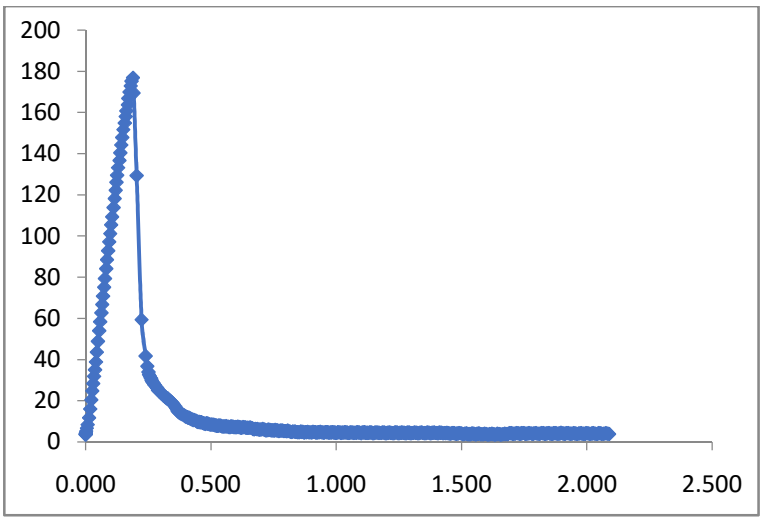


Figure 4.3a: Load-deflection curve of control samples subjected to thermal curing

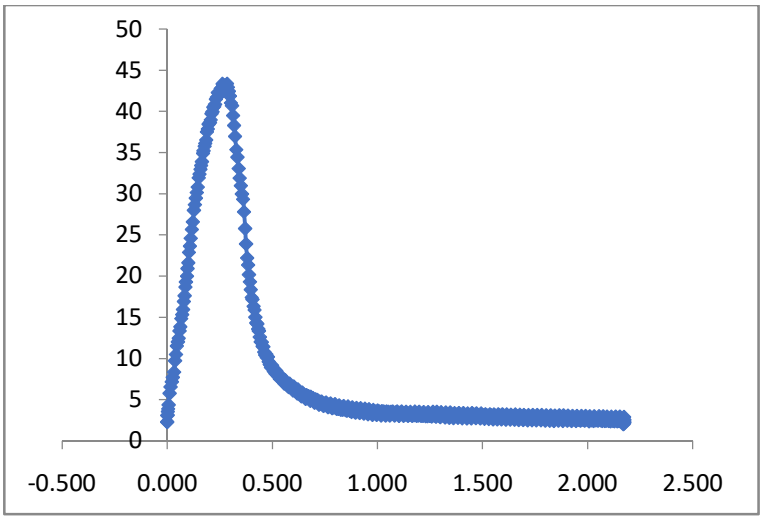


Figure 4.3b: Load-deflection curve of composite incorporated with rice husk ash and egg shell ash subjected to thermal curing

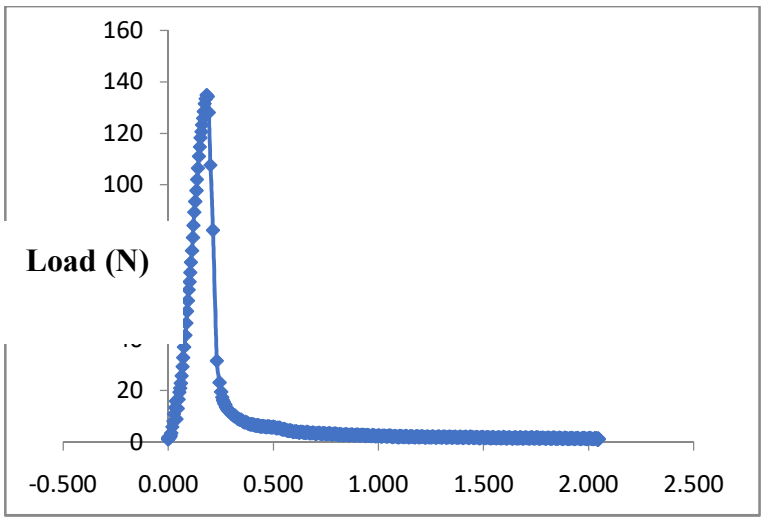


Figure 4.3c: Load-deflection curve of composite containing calcium carbide waste and egg shell ash subjected to thermal curing

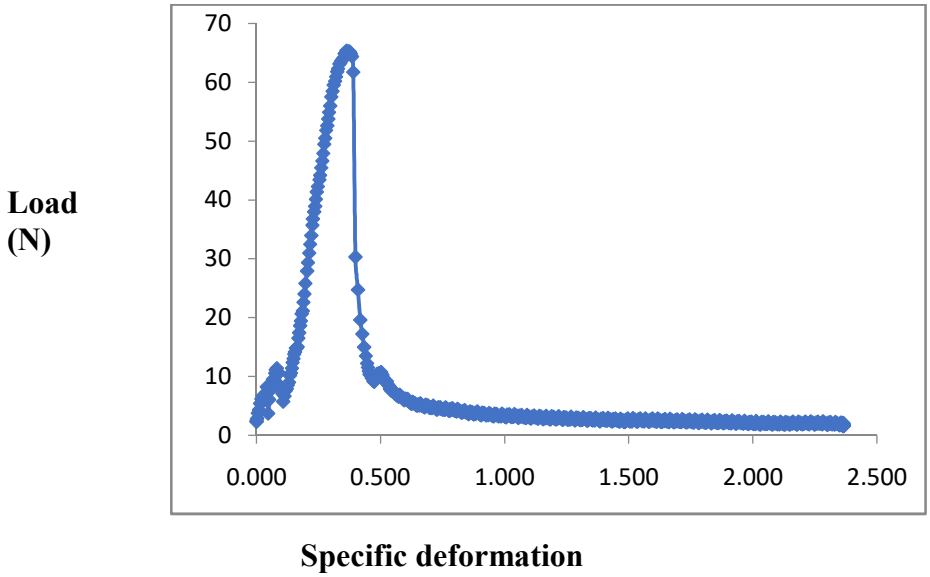


Figure 4.3d: Load-deflection curve of composite containing rice husk ash, calcium carbide waste and egg shell ash only subjected to thermal curing

Chicken egg shell ash. Okonkwo *et al.,* (2012) had reported that egg shell is composed mainly of organic matter and calcium carbonate. These organic constituents often times inhibit the formation of strong crystalline bonds. Increasing the incineration temperature of eggshells to about 900^0C to burn-off the constituents results in the production of calcium oxide. The MOR values of composites samples containing calcium carbide waste and egg shell ash compare favourably with composites made from Sisal kraft (13.1MPa) (Savastano *et al.,* 2003) but were lower than that those produced from *Eucalyptus grandis* pulp (15.6MPa) (Savastano *et al.,* 2000).

Microstructural investigation (Plate 4.1- 4.3) showed the relation between matrix materials and coconut fibre. It was observed that the egg shell ash had a strong bond with the fibre. This suggests that to improve the flexural strength of composites under accelerated carbonation, the hydrolysis of the egg shell ash will be necessary. The load-deflection curves (Figure 4.4a – 4.4.4d) also show that accelerated carbonation of egg shell incinerated at 900^0C increased the load carrying capacity of the composite but reduced the ductility. The moduli of ruptures for all the composites subjected to accelerated carbonation indicated good load carrying capacity and this suggest that it can be used as roofing tiles. It is advisable to subject composite tiles to CO_2 curing for better load bearing capacity.

Figures 4.5a to 4.5c showed the correlation between bulk density and MOR of the composites. Composites subjected to thermal and accelerated carbonation for egg shell incinerated at 500^0C showed high positive correlation while those made with egg shell incinerated at 900^0C and subjected to accelerated carbonation showed negative correlation. Negative correlation between density and MORs suggested that hydrolysed egg shell ash does not exhibited a good relationship between density and MORs. The trend of positive correlation is similar to composite produced from boiling of coconut fibre in fibre-reinforced composite as reported by Asasutjarit *et al.,* (2007).

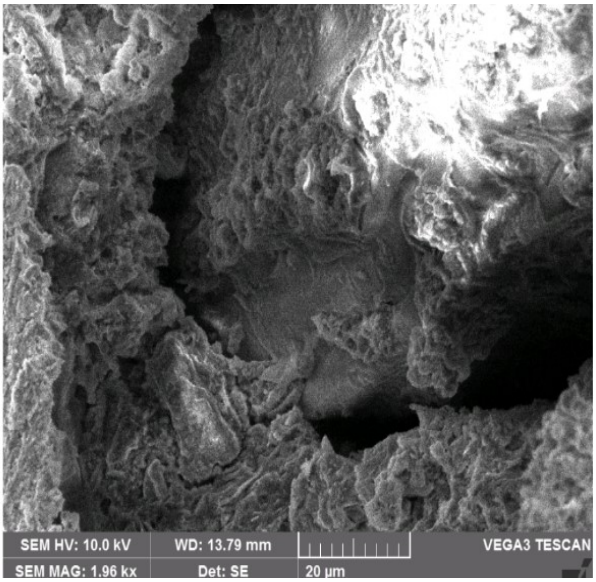


Plate 4.1: Microstructure of composites containing rice husk ash and egg shell ash

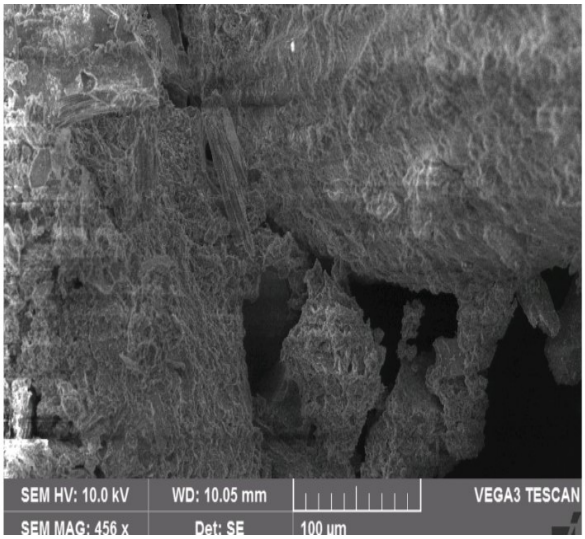


Plate 4.2: Microstructure of composites containing calcium carbide waste and egg shell ash

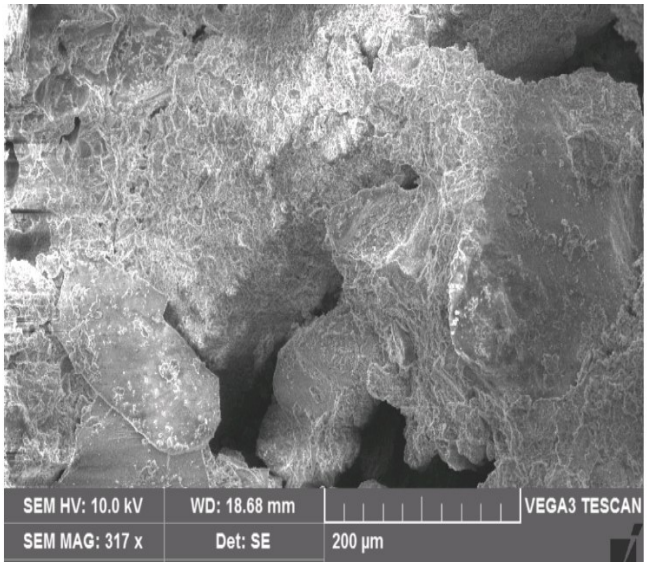
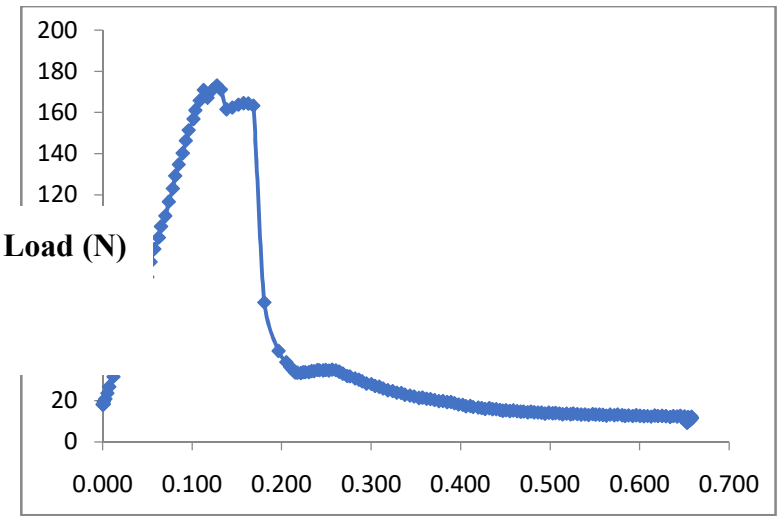
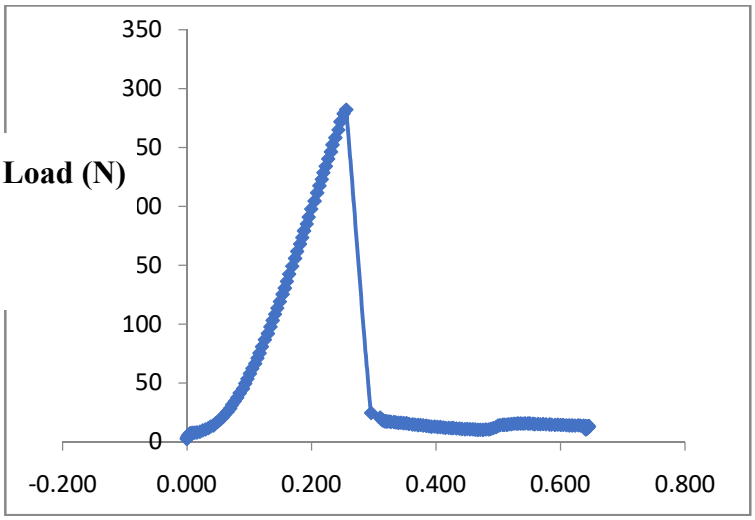


Plate 4.3: Microstructure of composites containing rice husk ash, calcium carbide waste and egg shell ash



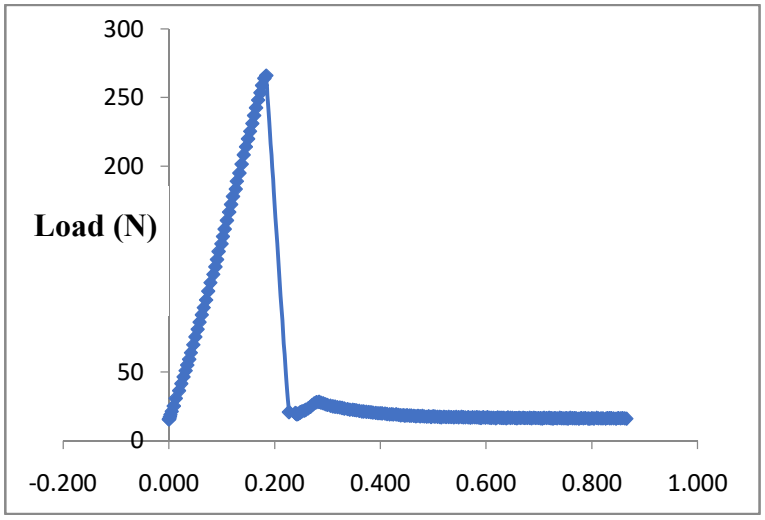
Specific deformation

Figure 4.4a: Load-deflection curve for carbonated control samples



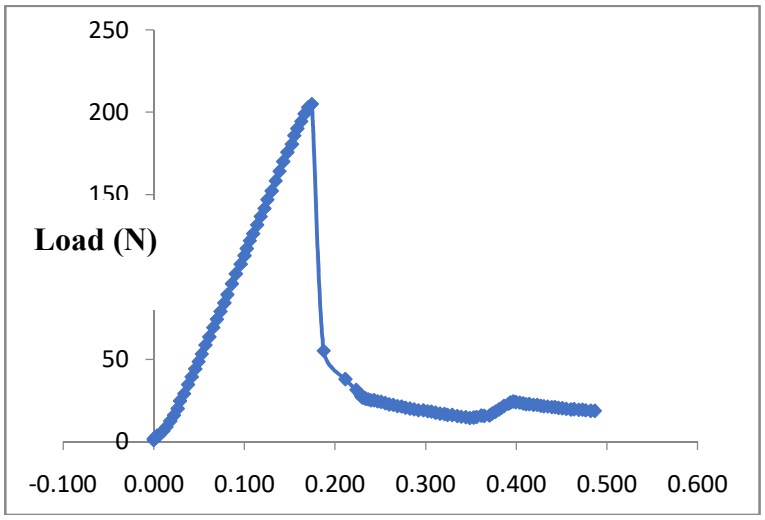
Specific deformation

Figure 4.4b: Load-deflection curve for carbonated samples containing rice husk ash and egg shell ash incinerated at 900^0C



Specific deformation

Figure 4.4c: Load deflection curve for carbonated samples containing calcium carbide waste and egg shell incinerated at 900^0



Specific deformation

Figure 4.4d: Load deflection curve for carbonated samples containing rice husk ash, calcium carbide waste and egg shell ash incinerated at 900

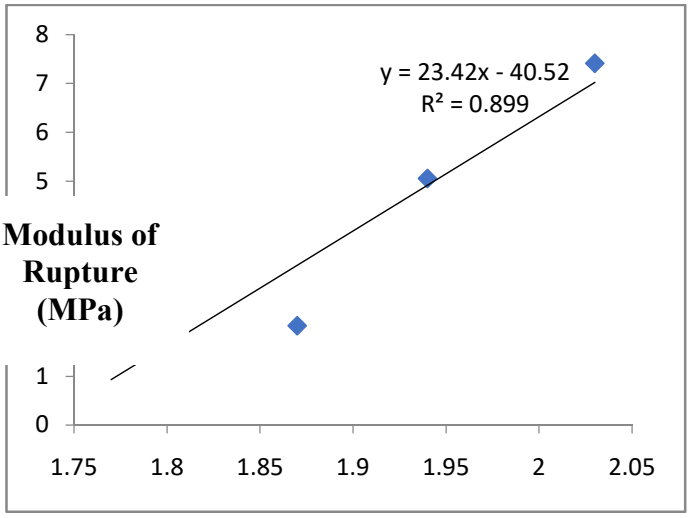


Figure 4.5a: Correlation between bulk densities and modulus of rupturesfor composite samples subjected to thermal curing

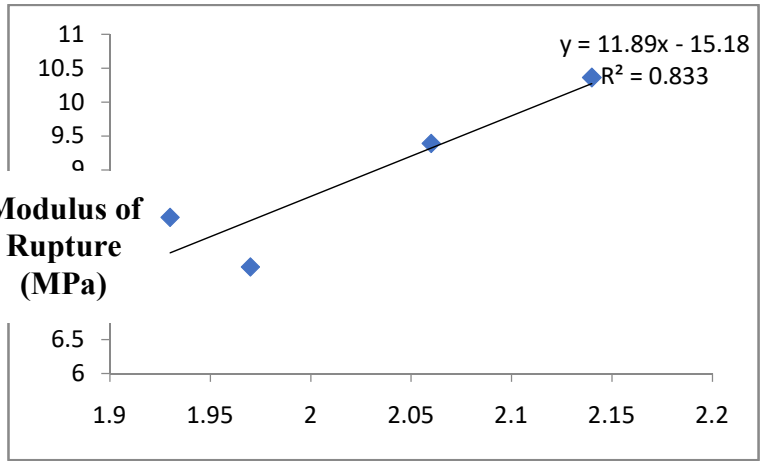


Figure 4.5b: Correlation between bulk densities and modulus of ruptures for composites subjected to accelerated carbonation

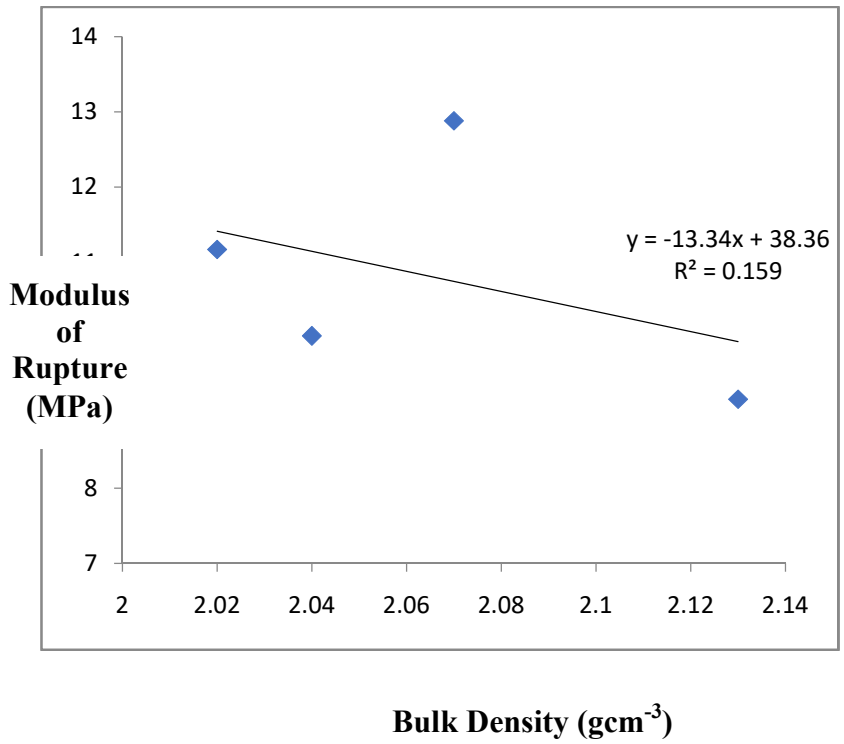


Figure 4.5c: Correlation between bulk densities and modulus of ruptures of composites subjected to accelerated carbonation for samples with incinerated egg shell at 900^0C

4.6.2 Modulus of Elasticity

The Moduli of Elasticity (MOEs) of the composites are presented in Table 4.8. The ranged of MOEs is between 3.5 – 17.3GPa. Partial replacement of cement with rice husk ash lowered the MOE values from 17.3GPa (for the control sample) to 3.5GPa (for composites containing rice husk ash and chicken eggshell ash). However, the incorporation of calcium carbide waste and egg shell ash enhanced the MOEs of the composite formulations.

The MOEs (14.7 GPa) of the samples containing calcium carbide waste and egg shell ash was higher than that of the composite produced from *Eucalyptus grandis* (11.4GPa) as reported by Savastano *et al.,* (2003). This implies that admixtures of calcium carbide and egg shell ash increases the MOEs and it might be as a result of chemical reaction effects of calcium carbide in the hydrolyses of cement. The lower MOE observed in samples containing rice husk ash might be as a result of absorptive characteristics of rice husk ash which led to more water consumption for pozollanic reaction in the cement-matrix which might affects the elasticity of the composites. This is in agreement with report of Mehta (1977) that concrete containing rice husk ash required more water for a given consistency due to the absorptive character of the cellular rice husk ash particle and could lower the MOE of composites mixtures.

Accelerated carbonation generally enhanced the MOEs of all the composites. For examples the control MOE increased from 17.3GPa to 25.4GPa. The MOEs of composites containing mixture of rice husk ash and egg shell ash subjected to accelerated carbonation increased from 3.5GPa to 12.9GPa, those produced from the combination of rice husk ash, calcium carbide waste and egg shell ash increased from 4.4 – 17.0GPa while those containing calcium carbide and egg shell ash increased from 14.7 – 21.6GPa. These trends increment in the MOEs might be due to the effects of carbonation in agreement with report of Rostami *et al.,* (2012) that accelerated carbonation creates a microstructure in a composite which resulted into more strength in a composite matrix. The cement matrix of the carbonated composites becomes denser and more compact, resulted in the improvement in the contact between fibre and cement matrices thereby favouring good adhesion between matrix (Pizzol *et al*., 2014). The MOE (12.9GPa) of composites

Table 4.8: Modulus of Elasticity of Composites Tiles Produced with different Curing Methods

Formulation	Flexural Modulus (GPa)
Samples containing egg shell ash obtained at 500^0C and thermally cured at 60^0C	
Control	17.3 ± 1.17^A
Rice husk ash + egg shell ash + cement	3.5 ± 0.65^C
Calcium carbide waste + egg shell ash + cement	14.7 ± 1.69^B
Rice husk ash + calcium carbide waste + egg shell ash + cement	4.4 ± 1.16^C
Samples containing egg shell ash obtained at 500^0C and subjected to accelerated carbonation	
Control	25.4 ± 3.08^A
Rice husk ash + egg shell ash + cement	12.9 ± 3.29^C
Calcium carbide waste + egg shell ash + cement	21.6 ± 2.23^A
Rice husk ash + calcium carbide waste + egg shell ash + cement	16.9 ± 3.14^B
Samples containing egg shell ash obtained at 900^0C and subjected to accelerated carbonation	
Control	32.8 ± 3.08^B
Rice husk ash + egg shell ash + cement	25.8 ± 2.56^A
Calcium carbide waste + egg shell ash + cement	29.5 ± 2.02^B
Rice husk ash + calcium carbide waste + egg shell ash + cement	26.4 ± 2.15^A

Means with the same letters are not statistically different

produced from combination of rice husk ash and egg shell ash compared favourably with those of composites produced from *Eucalyptus* pulp fibre (13.2GPa) (Correia *et al.,* 2015). The control and composites containing calcium carbide waste had MOE higher than 15.1GPa reported for composite produced from *Eucalyptus grandis* (Savastano *et al.,*2000). However, the composite containing rice husk ash had a lower MOE than other composites in which cement was partially replaced.

Microstructural investigation (SEM) showed a lower bond interaction between the fibre and composites containing rice husk ash which might have resulted into a weaker bond and a lower MOE of the composites (Plate 4.1 and 4.3). There was significant difference in MOEs ($P<0.05$) (appendix B2) of samples subjected to thermal and accelerated carbonation curing techniques.

An increase in the incineration temperature of the chicken egg shell from 500^0C to 900^0C coupled with accelerated carbonation enhanced the MOEs of the composites. Composites made with mixtures of rice husk ash and egg shell ash had MOEs that increased from 12.9 – 25.8GPa, those containing calcium carbide waste and egg shell ash increased from 21.6 – 29.6GPa, while composites made from combination rice husk ash, calcium carbide waste and egg shell ash increased from 17.0 – 26.4GPa. These increments may indicate that egg shell incinerated at 900^0C is a good bonding accelerator in composites produced and this is tandem with report of Mtallib and Rabiu, (2009). Also, composites containing rice husk ash for egg shell incinerated at 900^0C had relatively higher MOEs than composites containing rice husk ash for egg shell incinerated at 500^0C. This might be because of hydrolysis of the calcium oxide in the egg shell ash to calcium hydroxide (Wei *et al.,* 2009). The pozollanic reactivity of rice husk husk ash could also have improved because of the finess of the particle which assists in the reactivity by providing a larger area for better reaction (Jayasankar 2010). Microstructural investigation (Plate 4.1 to 4.3) revealed that the egg shell ash in the composite was distributed around the coconut fibre which might have consequently improved the MOE of the samples. In general, the MOEs (25.8 – 29.5GPa) of the composites containing hydrolysed egg shell ash was higher than 14.5GPa reported for composites from sisal fibre (Savastano *et al.,* 2000). It might be suggested that to improve the MOEs of composite containing admixtures of rice husk ash and egg shell ash, calcium carbide and egg shell ash

hydrolysis with water of egg shell incinerated at 900^0C might be necessary. The results of MOEs is an indication that to improve the elasticity of composite tiles carbonation might be necessary and it showed that composite tiles can be used as roofing materials for out-door purposes.

As shown in Figures 4.6a to 4.6c there was positive correlation between bulk density and MOE, these trends are similar to those report by Ogundipe (2016) for rattan composites partially replaced with cementitious materials. Figure 4.7a to 4.7c showed the positive correlation between MOEs and MORs of samples subjected to thermal and accelerated curing. The observed positive correlation in MOE and MOR is similar to report of Badejo (1988) in wood-cement composites manufactured from tropical hardwood wood, but differed from the weak positive correlation observed by Olorunnisola (2007) for rattan-cement composites.

4.6.3 Flexural Toughness

The flexural toughness of the composites was presented in Table 4.9. The flexural toughness ranged between 48.0 – 84.0 jm^{-2}. These values were lower than 250.0 jm^{-2}reported by Savastano *et al.,* (2003) for composite developed from *Eucalyptus grandis.* For the thermally cured samples, partial replacement of cement lowered the flexural toughness. All the composites containing egg shell ash also had lower flexural toughness (48.0 – 57 jm^{-2}) than the control (84.0 jm^{-2}). The low flexural toughness might be as a result of low binding property (loose bond between matrix) of the egg shell ash which had negative effects on the flexural toughness of the composite (Olarewaju *et al.,* 2011).

Accelerated carbonation generally improved the flexural toughness of all the composites, including the control, whose flexural toughness increased from 84.0jm^{-2} to 107.2jm^{-2}. This might be as a result of effects of accelerated carbonation which creates a micro structure in the matrix and led to improved strength than conventional hydration curing (Rostami *et al.,* 2012). Also, carbonation improves the durability of the fibre and decreases the alkalinity of the cement matrix, and making it less aggressive to fibre (Toledo Filho *et al.,* 2003). All the samples in which cement was partially replaced had a higher flexural toughness than the control. Samples containing a combination of rice husk

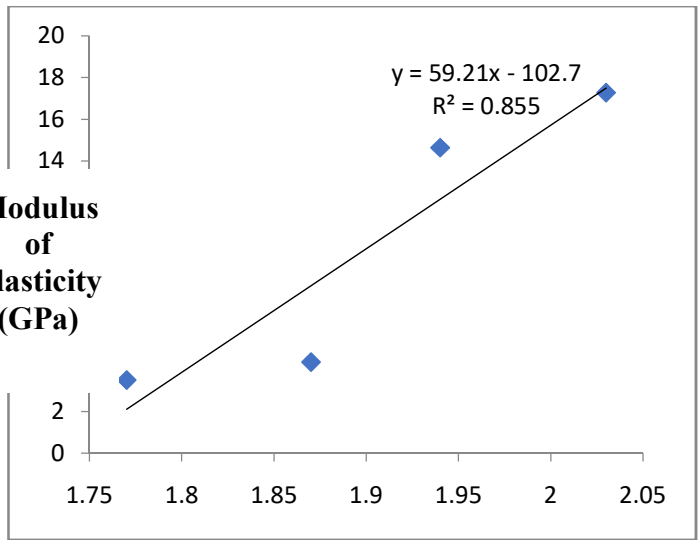


Figure 4.6a: Correlation between bulk densities and MOEs of composites subjected to thermal curing

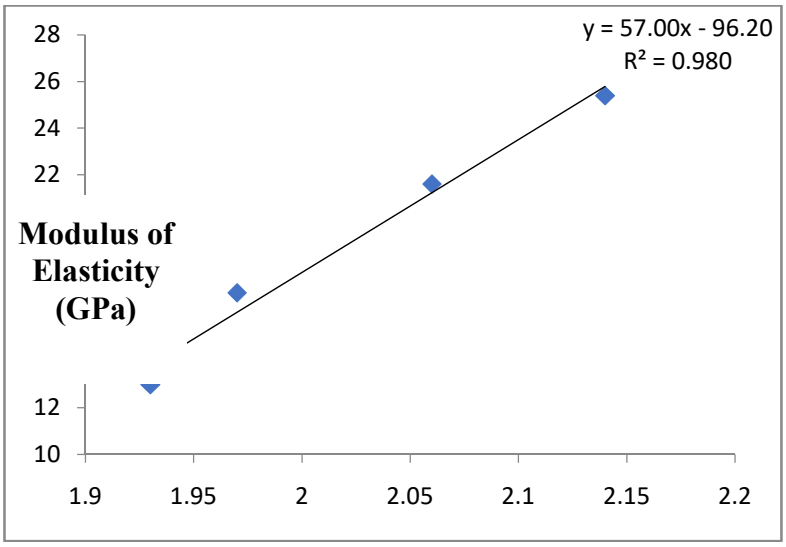


Figure 4.6b: Correlation between bulk densities and MOEs of composites subjected to accelerated carbonation

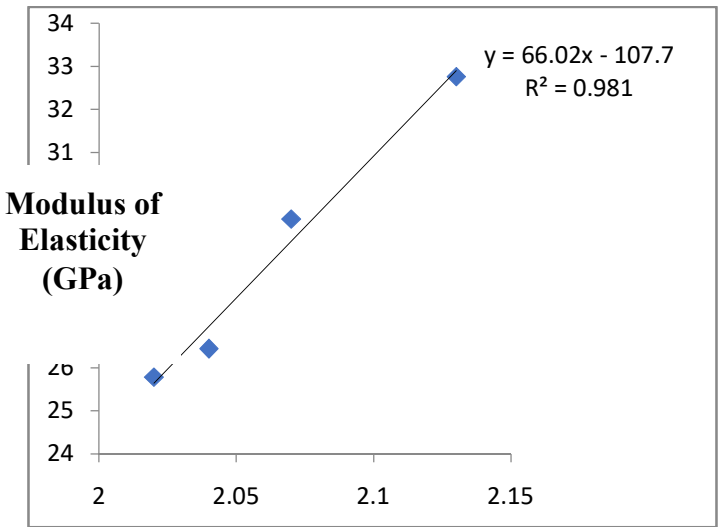


Figure 4.6c: Correlation between bulk densities and MOEs of composites subjected to accelerated carbonation incinerated egg shell at 900^{0}C

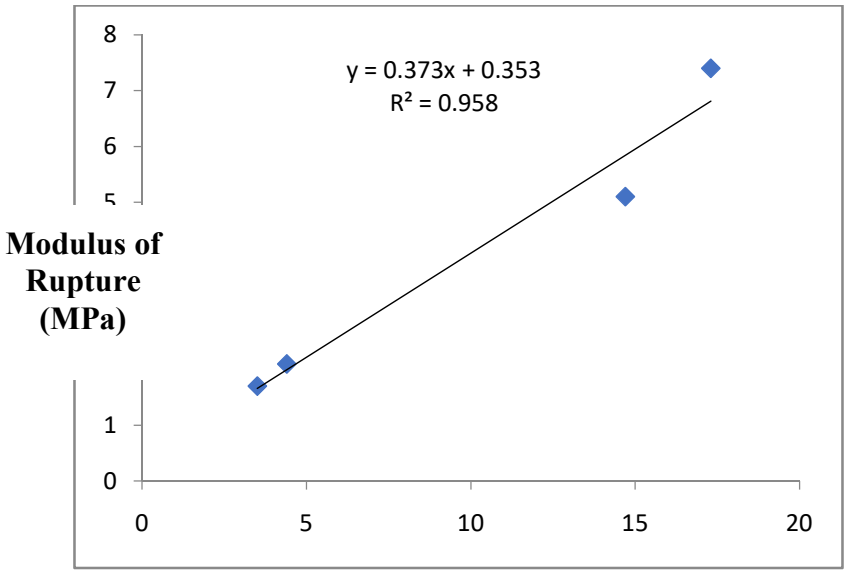


Figure 4.7a: Correlation between moduli of elasticity and moduli of rupture of composites subjected to thermal curing

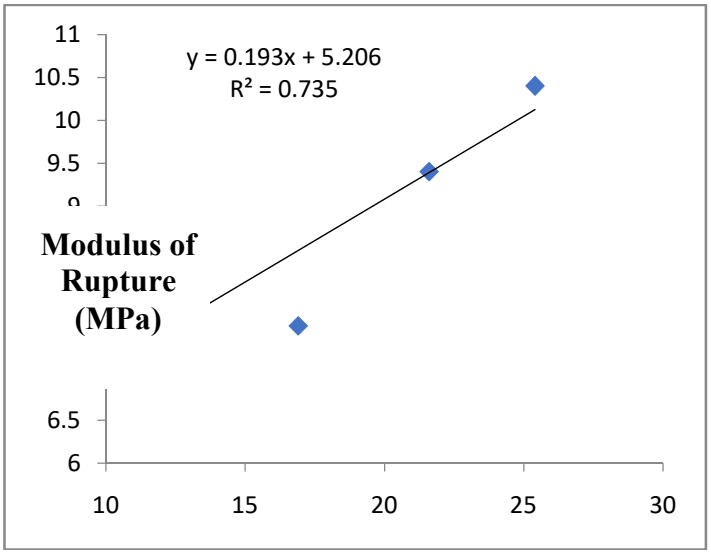


Figure 4.7b: Correlation between moduli of elasticity and moduli of ruptures of composites subjected to accelerated carbonation

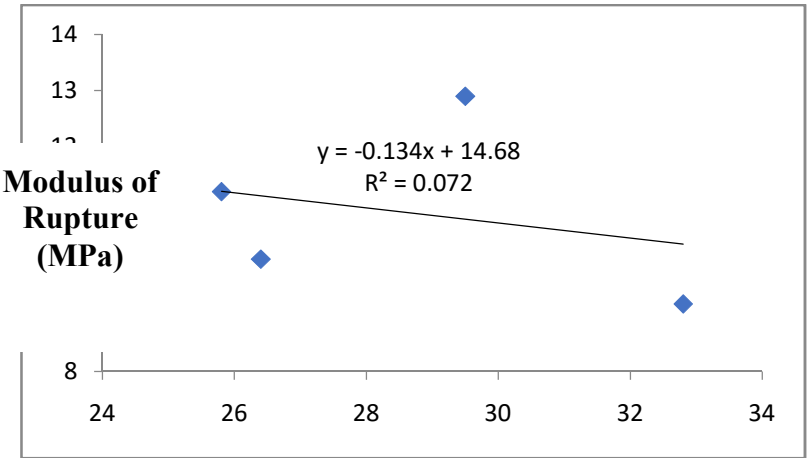


Figure 4.7c: Correlation between moduli of elasticity and moduli of rupturesof composites subjected to accelerated carbonation with incinerated egg shell at 900^0C

Table 4.9: Flexural Toughness of Composite Tiles Production under different Curing Methods

Formulation	Flexural Toughness (jm^{-2})
Samples containing egg shell ash obtained at 500^0C and thermally cured at 60^0C	
Control	84.0 ± 0.01^C
Rice husk ash + egg shell ash + cement	50.0 ± 0.01^A
Calcium carbide waste + egg shell ash + cement	48.0 ± 0.03^A
Rice husk ash + calcium carbide waste + egg shell ash + cement	57.0 ± 0.02^B
Samples containing egg shell ash obtained at 500^0C and subjected to accelerated carbonation	
Control	107.2 ± 0.04^A
Rice husk ash + egg shell ash + cement	185.0 ± 0.02^C
Calcium carbide waste + egg shell ash + cement	137.0 ± 0.13^B
Rice husk ash + calcium carbide waste + egg shell ash + cement	111.0 ± 0.02^A
Samples containing egg shell ash obtained at 900^0C and subjected to accelerated carbonation	
Control	165.0 ± 0.06^C
Rice husk ash + egg shell ash + cement	106.0 ± 0.02^A
Calcium carbide waste + egg shell ash + cement	129.0 ± 0.06^B
Rice husk ash + calcium carbide waste + egg shell ash + cement	98.0 ± 0.03^A

Means with the same letters are not statistically different

ash and egg shell ash had higher flexural toughness of 185.0jm^{-2}. Composites made with rice husk ash recorded higher toughness possibly due to pozollanic reactivity of the ash attributable to high amorphous silica and large surface area aided by the porous structures of the particles (Jayasankar 2010). Also, the presence of calcium oxide in the egg shell ash that helps to improve the setting time (Mtallib and Rabiu, 2009) might be responsible for better performance in flexural toughness of composites containing rice husk ashand egg shell ash. There was significant difference ($p<0.05$) (appendix B3) between the composite samples subjected to accelerated carbonation and thermally cured composites. The values were however lower than 453.0jm^{-2} reported for composite produced from *Eucalyptus grandis* (Roma *et al.,* 2008); 250.0jm^{-2} reported by Savastano *et al.,* (2003) for *Eucalyptus grandis*.

An increase in the temperature of the egg shell from 500^{0}C to 900^{0}C coupled with accelerated carbonation lowered the flexural toughness of composites in which cement was partially replaced. Increase in fibre content from 4% to 6% lowered the flexural toughness of the experimental samples while that of control increased from 107.0jm^{-2} to 165.0jm^{-2}. The observed lower value of flexural toughness in the experimental samples might be as result of low bonding formation of egg shell ash (Olarewaju *et al.,* 2011) which resulted into poor bonding between fibre and matrix of the composite. This is evident from microstructural investigation of fibre in Plates 4.1 to 4.3. Fibre-matrix interaction showed a porous structure at the root of fibres for different composite formulation. Composites containing calcium carbide waste and egg shell ash had a lesser pores around the fibre root than other composites formulation. This might account for higher value of flexural toughness. Accelerated carbonation increased the toughness of the composite tiles and this is an indication that to increase the toughness properties of composite materials carbonation might be necessary and this will enhance the out-door use of composite tile in roofing purposes.

The correlation between bulk density and flexural toughness is shown in Figure 4.8a to 4.8c. A positive correlation was observed for composites made with egg shell incinerated at 900^{0}C and subjected to accelerated carbonation while a weak positive correlation was recorded for composites subjected to thermal curing. As shown in Figure 4.9a to 4.9c, a weak positive correlation was observed between the flexural toughness and

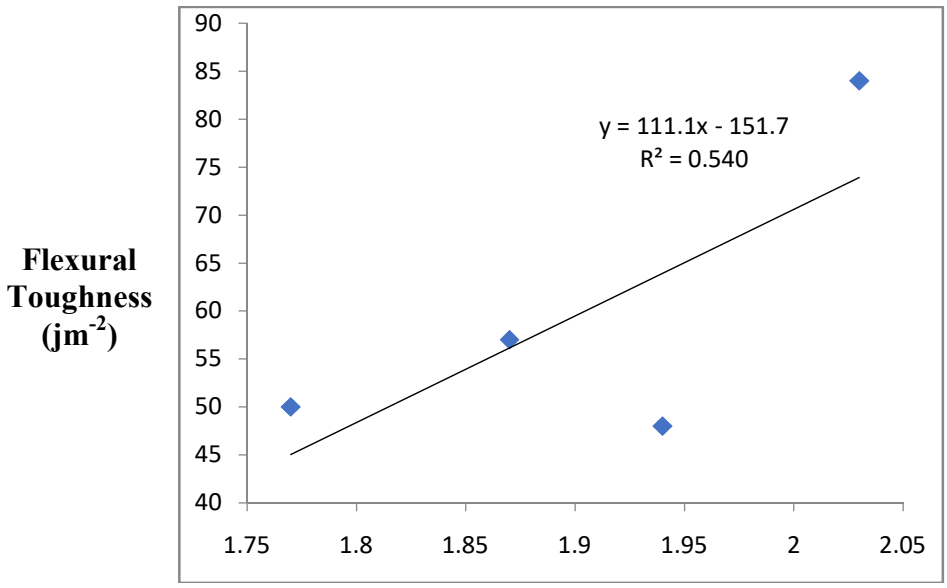


Figure 4.8a: Correlation between bulk densities and flexural Toughness ofcomposites subjected to thermal curing

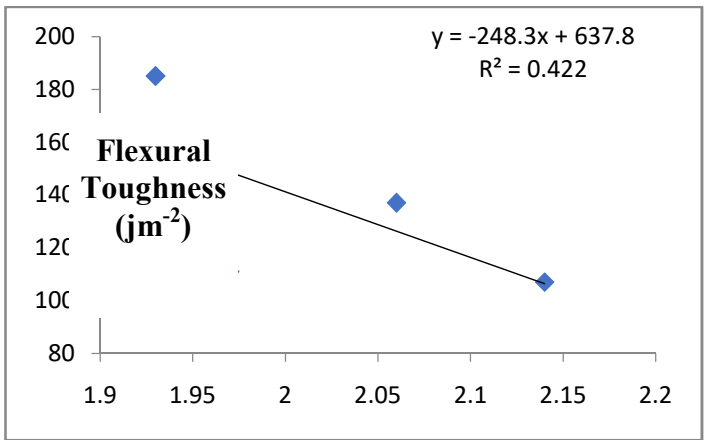


Figure 4.8b: Correlation between bulk densities and flexural Toughness of composite subjected to accelerated carbonation

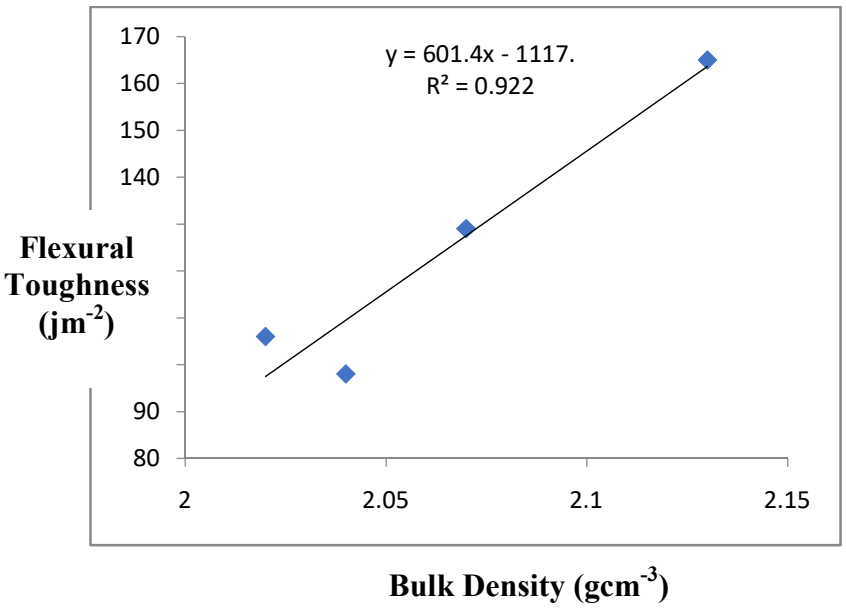


Figure 4.8c: Correlation between bulk densities and flexural toughness of composites subjected to accelerated carbonation made with incinerated egg shell at 900^0C

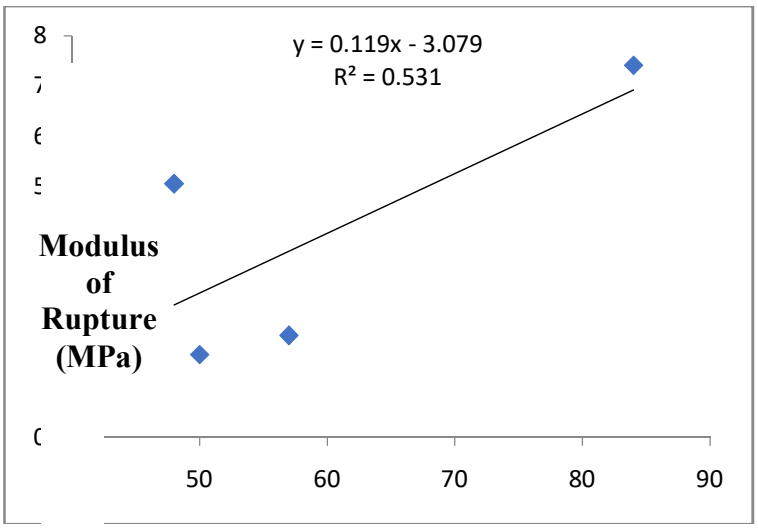


Figure 4.9a: Correlation between flexural toughness and modulus of rupture of composites subjected to thermal curing

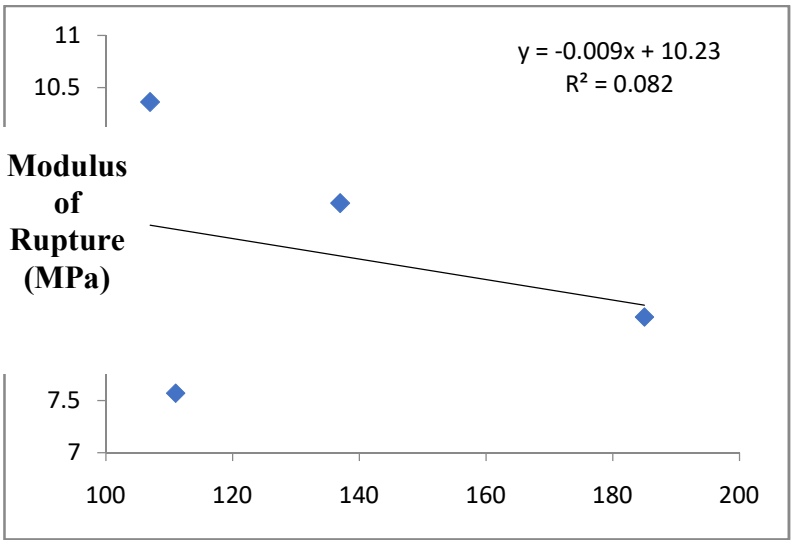


Figure 4.9b: Correlation between flexural toughness and modulus of rupture of composites subjected to accelerated carbonation

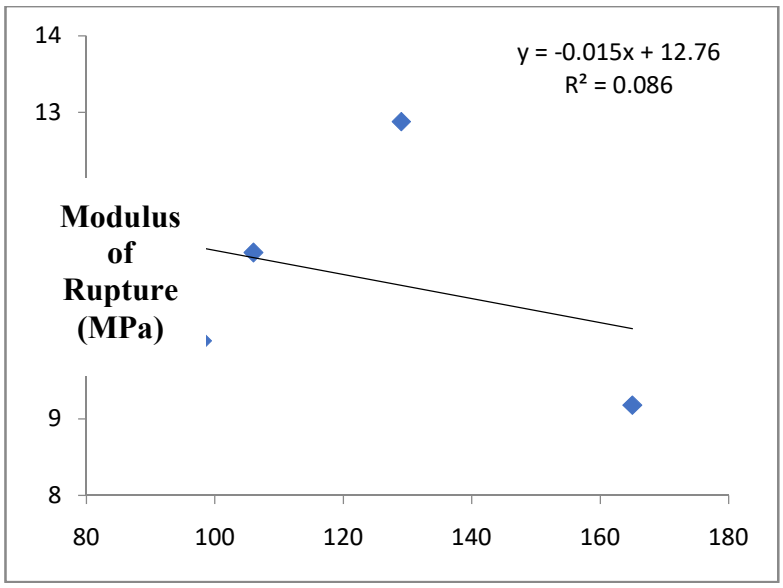


Figure 4.9c: Correlation between flexural toughness and flexural strength for composites subjected to accelerated carbonation made with calcination of egg shell at 900^0C

modulus of rupture for composites subjected to thermal curing while a negative correlation existed for those subjected to accelerated carbonation.

4.7 Effects of Cement Replacement and curing Methods on the Sorption Properties of the Composites Subjected to Dry Accelerated Carbonation

The effects of the cement replacement and curing methods on the water absorption, and permeable void volume are discussed below.

4.7.1 Water Absorption

Water absorption is an index for determining the durability of cement-bonded composites as the presence of water can initiate swelling, cracking and biodegradation of reinforced fibre, and dissolution of wood chemicals (Fagureland, 1996). The water absorption of the composites are shown in Table 4.10. For the thermally cured samples, partial replacement of cement resulted in increasing the water absorption from 9.4% (control) to 16.1% for composite containing rice husk ash and egg shell ash. The observed differences were significant ($p<0.05$) for different composite formulation (appendix C1).

However, samples in which cement was partially replaced with calcium carbide waste and egg shell ash had lower water absorption than the other composites. As shown, composites containing rice husk ash had higher water absorption than other composites. Possibly due to low bulk density and its higher porosity (Oloruunisola and Agrawal, 2009; Savastano, 2000). The range of water absorption value is in agreement with what was reported inliterature for baggase (4.6 – 16.4%) (Moslemi *et al.*, 1994; Ajayi, 2002, 2003) but less than water absorption values (21.2 – 30.5%) reported for composites in which cement was partially replaced with rice husk ash, green coconut husk fibre-reinforced (Pereira *et al.,* 2013).

Accelerated carbonation generally reduced the water absorption of all the composites, except the control which showed an increase in the water absorption. Phung *et al.,* (2013) and Pizzol *et al*., (2014) reported that carbonation helps in the precipitation of calcium carbonate in the early age, pores filling action and refinement of microstructure which results in the reduction of the permeability of composites. Also, composites samples containing a combination of calcium carbide waste and egg shell ash had the lowest water absorption values while those produced with rice husk ash had the highest

Table 4.10: Water Absorption of Composite Tiles Production under different Curing Methods

Formulation	Water Absorption (%)
Samples containing egg shell ash obtained at 500^0C and thermally cured at 60^0C	
Control	9.4 ± 0.17^A
Rice husk ash + egg shell ash + cement	16.1 ± 1.08^C
Calcium carbide waste + egg shell ash + cement	11.3 ± 0.33^B
Rice husk ash + calcium carbide waste + egg shell ash + cement	12.8 ± 0.98^B
Samples containing egg shell ash obtained at 500^0C and subjected to accelerated carbonation	
Control	6.9 ± 0.09^A
Rice husk ash + egg shell ash + cement	10.9 ± 0.32^C
Calcium carbide waste + egg shell ash + cement	7.4 ± 0.11^A
Rice husk ash + calcium carbide waste + egg shell ash + cement	9.7 ± 1.05^B
Samples containing egg shell ash obtained at 900^0C and subjected to accelerated carbonation	
Control	7.3 ± 0.14^A
Rice husk ash + egg shell ash + cement	8.7 ± 1.10^C
Calcium carbide waste + egg shell ash + cement	8.1 ± 0.33^B
Rice husk ash + calcium carbide waste + egg shell ash + cement	8.5 ± 0.33^C

Means with the same letters are not statistically different

water absorption. Observed high value of WA in composite containing rice husk ask might be as a result of hygroscopic characteristics of rice husk ash. The observed differences in water absorption were significant ($P<0.05$) for different composites formulation. The range of water absorption values was however lower than 23.3 – 33.3% reported for composites produced from sisal (Tonoli *et al.*, 2010), 30.9 – 36.6% for composites produced from *Eucalyptus grandis* (Savastano *et al*., 2003). Composite made with egg shell ash whose incineration temperature increased from 500^0C to 900^0C coupled with accelerated carbonation had water absorption that ranged from 7.5% to 8.7%. Also, composite made with RHA had higher water absorption, possibly due to higher silica oxide content. The water absorption obtained in this study were generally lower than those recommended by the Brazilian standard specification ABNT NBR 7581 (ABNT, 1993) for fibre-reinforced corrugated roofing sheet. The results of water absorption properties of all the composites subjected to accelerated carbonation is an indication that composite tiles can be used for out-door purposes and it is advisable to cure samples in CO_2 to reduce moisture absorption when fabricated for roofing purpose.

Figures 4.31 to 4.33 showed correlations between bulk density and water absorption of the fabricated composites. As shown a positive correlation existed between the bulk densities and water absorptions of all the composites. This observation is similar to those reported by Olorunnisola, (2004) and Olorunnisola and Adeniji (2019).

4.7.2 Permeable Void Volume

The permeable void volumes of the composites are presented in Table 4.11. For the thermally cured samples, partial replacement of cement increased the permeable void volume significantly from 19.2% (control) to 28.4% for composites made with rice husk ash and egg shell ash. However, composites made with calcium carbide had permeable void volume of 21.2%. These results indicated that incorporating rice husk ash in the composite production increased the permeable void volumes, possibly due to high porosity of the material. Abukakar *et al.,* (2013) reported that most concretes that contained pozzolans had high porosity equal or well above the porosity of 100% cement.

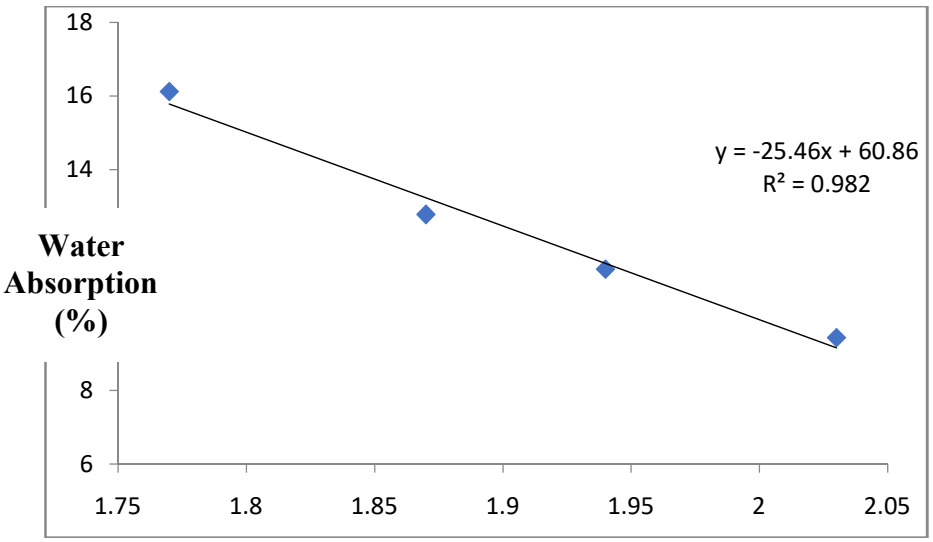


Figure 4.10a: Correlation between bulk densities and water absorption of composites subjected to thermal curing

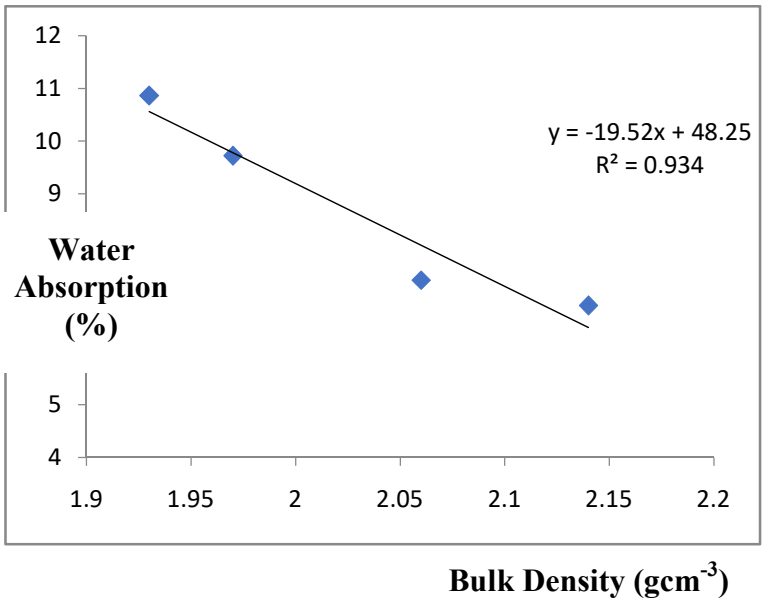


Figure 4.10b: Correlation between bulk density and water absorption of composites subjected to accelerated carbonation

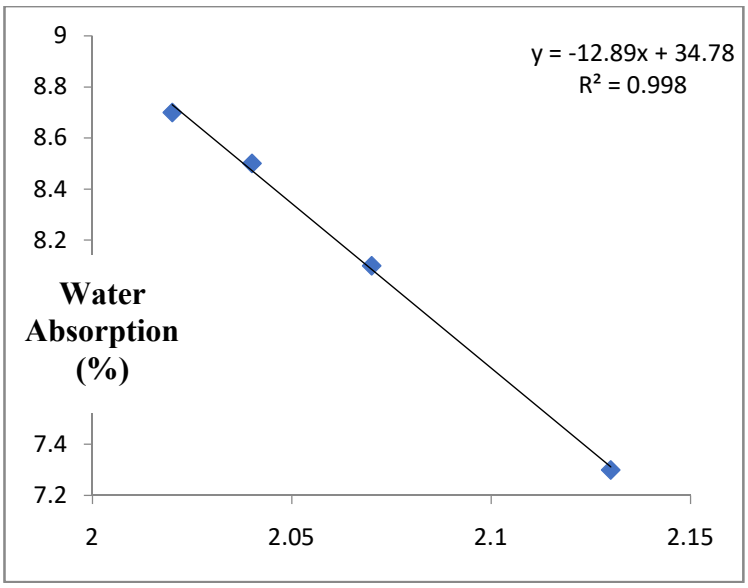


Figure 4.10c: Correlation between density and water absorption of composites subjected to accelerated carbonation for calcination of egg shell at 900^{0}C

Table 4.11: Permeable Void Volume of Composite Tiles Production under different Curing Methods

Formulation	Permeable Void Volume (%)
Samples containing egg shell ash obtained at 500^0C and thermally cured at 60^0C	
Control	19.2 ± 0.37^A
Rice husk ash + egg shell ash + cement	28.8 ± 1.37^C
Calcium carbide waste + egg shell ash + cement	21.9 ± 0.53^B
Rice husk ash + calcium carbide waste + egg shell ash + cement	23.9 ± 1.57^B
Samples containing egg shell ash obtained at 500^0C and subjected to accelerated carbonation	
Control	14.7 ± 0.19^A
Rice husk ash + egg shell ash + cement	20.9 ± 0.51^B
Calcium carbide waste + egg shell ash + cement	15.2 ± 0.18^A
Rice husk ash + calcium carbide waste + egg shell ash + cement	19.1 ± 1.62^B
Samples containing egg shell ash obtained at 900^0C and subjected to accelerated carbonation	
Control	15.6 ± 0.26^A
Rice husk ash + egg shell ash + cement	17.6 ± 0.65^B
Calcium carbide waste + egg shell ash + cement	$16.7 \pm 0.66^{A, B}$
Rice husk ash + calcium carbide waste + egg shell ash + cement	17.1 ± 0.66^C

Means with the same letters are not statistically different

The poor bonding between egg shell ash and other matrices materials might also be responsible for high permeable void volume in the composite (Olarewaju *et al*., 2011). The range of values recorded for thermally cured samples was less than the permeable void volume (33.3%) reported for composites produced from *Eucalyptus grandis* (Savastano *et al*., 2009) and 44.2% obtained for composite produced from Sisal kraft pulp (Tonoli *et al.,* 2010).

Accelerated carbonation generally lowered the permeable void volume of all the composites. The ranged of values was between 14.7% to 20.9%. There was a considerable decrease in permeable void volume of composites cement mixes of rice husk ash and egg shellash (28.4% to 20.9%). This observation might be as result of the action of accelerated carbonation that helps in pores filling has reported by Hyvert *et al*., (2010) that carbonation of $Ca(OH)_2$ leads to an increase in the volume of composites and the precipitation of calcium carbonate in the pore structure of the matrix. These filled the voids and blocked the intake of water. The range of permeable void volume obtained in this study was less than 29.8% reported for composite produced from *Eucalyptus grandis* (Savastano *et al*., 2000). Composite containing rice husk ash showed no significant different ($P>0.05$) (appendix C2).

An increase in the incineration temperature of the egg shell (500^0C to 900^0C) coupled with accelerated carbonation reduced the apparent void volumes of composites produced with rice husk ash. Samples containing rice husk ash and egg shell ash only had reduction in apparent void volume from 20.9% for egg shell incinerated at 500^0C to 17.6% for egg shell incinerated at 900^0C. This reduction in apparent void volume might be as a result of high percentage of silica oxide present in rice husk ash which helps with pozollanic reactions and good bonding between the matrix materials and the finess property of rice husk ash seems to help in good bonding between composite matrices materials (Jayasankar 2010). Pizzol *et al*., (2014) had reported that composite produced from cellulose and synthetic fibre had permeable void volume of 47.3% after four hours of carbonation and this is higher than composite samples produced from partial replacement of cement. It was observed that samples containing calcium carbide waste and egg shell ash exhibited increases in permeable void volume from 15.2% to 16.7%. This apparent increase might be because of presence of inactive compound in calcium carbide, forming

an insoluble hydrate around cement grains which left pores in the cement matrix. This observation might be as a result of low binding property of egg shell ash which resulted into poor bonding of composite materials (Olanrewaju 2011). The values of permeability void volume showed that composite will be suitable for roofing tiles when subjected to CO_2 curing.

Figures 4.11a to 4.11c showed the correlation between bulk density and permeable void volume of composites. A positive correlation was observed between the bulk density and permeable void volume of all the composites.

4.8 Thermal Conductivity of Composites

The thermal conductivity of fabricated composites are shown in Table 4.12. The value ranged from 0.99 W/m-K (for the control sample) to 1.49 W/m-K for composite partiallyreplaced with cement. The range of values is comparable with (1.18 – 1.52 W/m-K) reported for rattan fibre-reinforced composite (Ogundipe, 2016). All the samples in which cement was partially replaced showed higher value of thermal conductivity than the control. Sample containing rice husk ash had highest thermal conductivity (1.49 W/m-K), attributable to $CaCO_3$ precipitation which filled up the voids created due to the difference in the degree of finess between Limestone-Portland cement and rice hush ash. There was no significant difference ($P>0.05$) in the thermal conductivities of the fabricated composites.

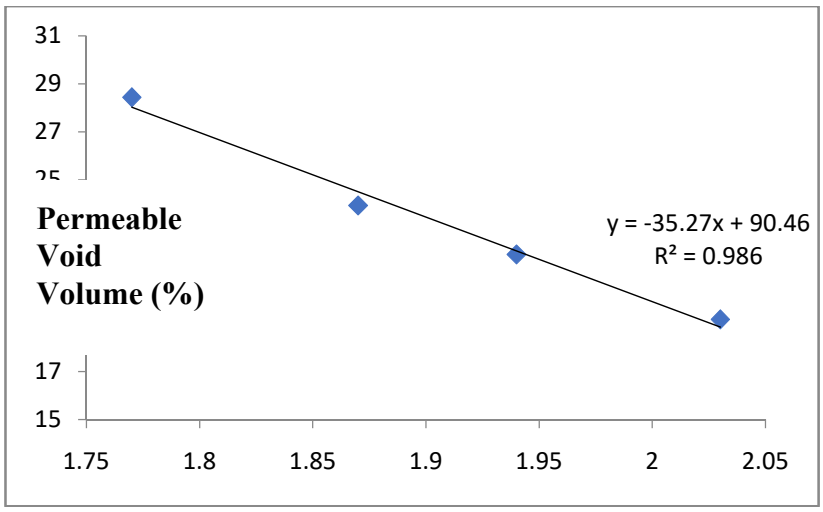


Figure 4.11a: Correlation between bulk density and permeable void volume of composites subjected to thermal curing

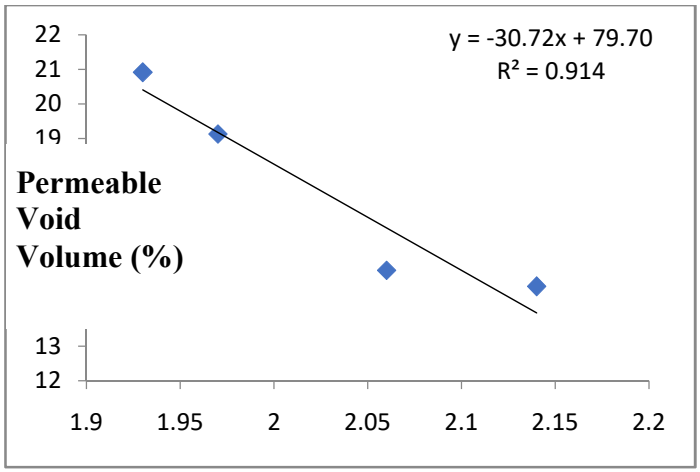


Figure 4.11b: Correlation between bulk density and permeable void volume of composites subjected to accelerated carbonation

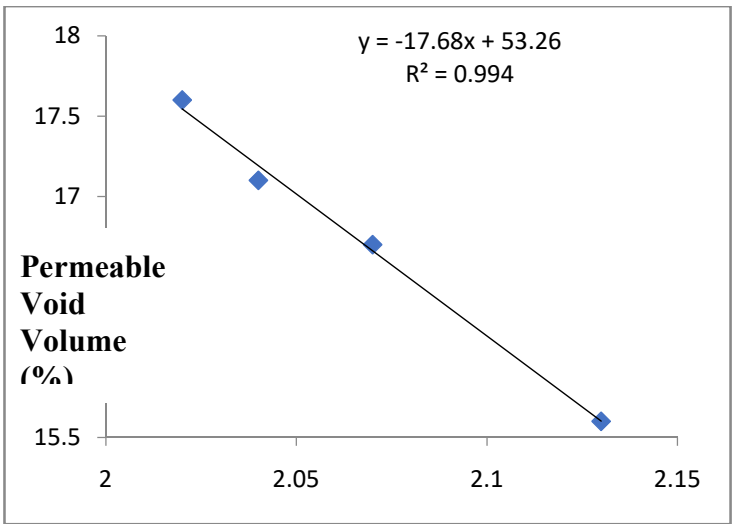


Figure 4.11c: Correlation between density and permeable void volume of composites subjected to accelerated carbonation for calcination of egg shell at 900^0C

Table 4.12: Thermal Conductivity of Composite Samples Subjected Wet Carbonation Curing Methods

Formulation	Thermal Conductivity (W/m-K)
Control	0.99[A]
10%RHA	1.49[A]
10%ESA	1.08[A]
5%CCW	1.13[A]

Means with the same letters are not statistically different

4.9 Weathering Data

The weather data collected for a period of 720 days covering three dry and two rainy seasons between January 2017 and December 2018 are presented in Table 4.13.

4.9.1 Temperature Variation

The range of indoor temperature is between 26.1 – 29.6^{0}C while the outdoor temperature ranged between 28.8^{0}C and 33.4^{0}C. The maximum difference between indoor and outdoor temperature (6.5^{0}C) was observed within the period of January to March (dry season) in 2017. Also, the minimum difference in temperature (0.3^{0}C) for indoor and outdoor temperature was observed in the rainy season (April to October 2018). Expectedly, the highest indoor temperature (29.6^{0}C) and outdoor temperature (33.4^{0}C) were observed in the dry seasons, (October – December 2018 and January - March 2017 respectively); while the lowest indoor and outdoor temperatures were recorded in the rainy seasons (April – October 2017 and April – October 2018 respectively).

4.9.2 Relative Humidity

The average indoor relative humidity ranged between 32.0% and 72.5%, the corresponding outdoor range being 13.0% - 88.5%. The maximum difference in relative humidity between indoor and outdoor was 19.0% and was recorded during the dry season (January to March, 2017). The minimum relative humidity (1.0%) was recorded during the rainy season (April to October, 2017). The highest indoor relative humidity (72.5%) was recorded in the rainy season spanning April to October 2018 while the highest outdoor relative humidity was 88.5%. The lowest indoor relative humidity (32.0%) was recorded in the dry season period spanning January to March 2017 while the lowest outdoor relative humidity (13.0%) was recorded in the dry season period spanning January to March of 2017.

4.9.3 Rainfall

The average value of rainfall ranged between 5.1mm and 16.4mm in the two rainy seasons. The highest rainfall (16.4mm) was in the period spanning April to October, 2017 while the lowest rainfall (5.1mm) was in the period spanning April to October, 2018.

Table 4.13: Average Climatic Weather Condition

Season	Month	Temperature (^{0}C)		Relative humidity (%)		Average Rainfall (mm)
		Indoor Ave. ma x	Outdoor Ave. max	Indoor Ave. max	Outdoor Ave. max	(mm/year)
Dry	Jan – March 2017	26.9	33.4	32.0	13.0	0
Rainy	April – Oct 2017	26.1	29.5	49.5	48.5	16.4
Dry	Nov 2017 - March 2018	27.6	33.2	36.5	18.0	0
Rain	April – Oct 2018	29.1	28.8	72.5	88.5	5.1
Dry	Nov – Dec 2018	29.6	32.2	65.0	68.2	0

4.9.4 Effects of Weathering on the Bulk Density of the Roofing Tiles

The effects of weathering on the bulk densities (BD) of the flat and corrugated roofing tiles after 720 days of exposure i.e. (two cycles of rainy and three cycles of dry seasons) are shown in Figures 4.12 and 4.13. There was a general reduction in the bulk density due to weathering, both flat and corrugated roofing tiles regardless of composition. However, there was an initial increase in the bulk density of all the roofing tiles after exposure to first rainy season of 2017 (Please see Appendix D1 and D2). The increase in bulk density might be accounted for by the permeability and coconut fibre. Leaching was also observed on the surface of all the roofing tiles, resulting in fibre exposure. However, the fibres were more exposed on flat roofing tiles than the corrugated ones.

For the flat roofing tiles, the greatest reduction in BD ($0.528 gcm^{-3}$) was observed in the samples containing 10% rice husk ash while the least reduction 0.26 gcm^{-3} occurred in the control sample. For the corrugated roofing tiles, the greatest reduction in BD ($0.37 gcm^{-3}$) was observed in the sample made of 10% egg shell ash while the least reduction ($0.28 gcm^{-3}$) occurred in the control sample. The observed trend in reduction of BD of the composite tiles can possibly be attributed to leaching particularly for the pozollanic materials after 720 days exposure. This trend is similar to the findings of composite produced from sisal under natural weathering as reported by Savastano *et al.,* (2001). It can be assumed from the findings that corrugation had a great effect on the rate of leaching of pozollanic materials.

4.9.5 Effects of Weathering on the Water Absorption of the Roofing Tiles

The effects of weathering on the water absorption of the flat and corrugated roofing tiles after 720 days of exposure are shown in Figures 4.14 and 4.15. There was a general reduction in the water absorption due to weathering, for all the roofing tiles (both flat and corrugated regardless of composition). However, for flat tiles, the greatest reduction in water absorption (4.6%) was observed in the samples containing 10% rice husk ash while the least reduction was observed in sample made from 10% egg shell ash (3.0%). For the corrugated roofing tiles, the greatest reduction in water absorption (4.1%) was observed in the samples made of 10% rice hush ash while the least reduction (2.1%) occurred in the control sample. The range of water absorption values recorded for all the formulations at the end of the weathering test was lower than 36.0% reported for

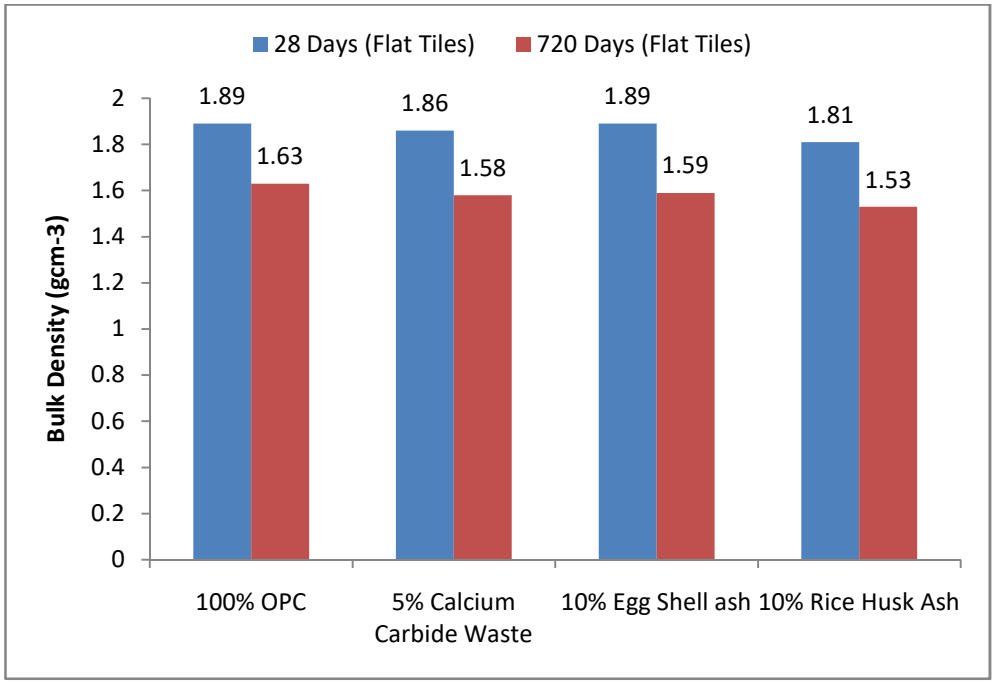


Figure 4.12: Bulk Densities of flat composites tiles after 720 days of exposure

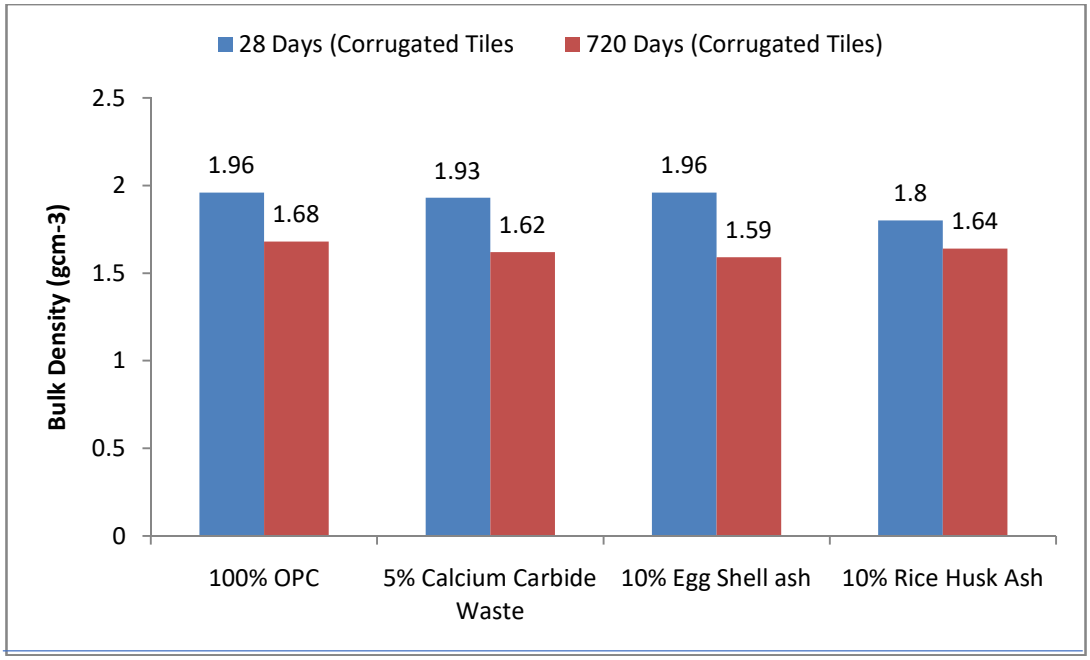


Figure 4.13: Bulk Densities of corrugated composite tiles after 720 days of exposure

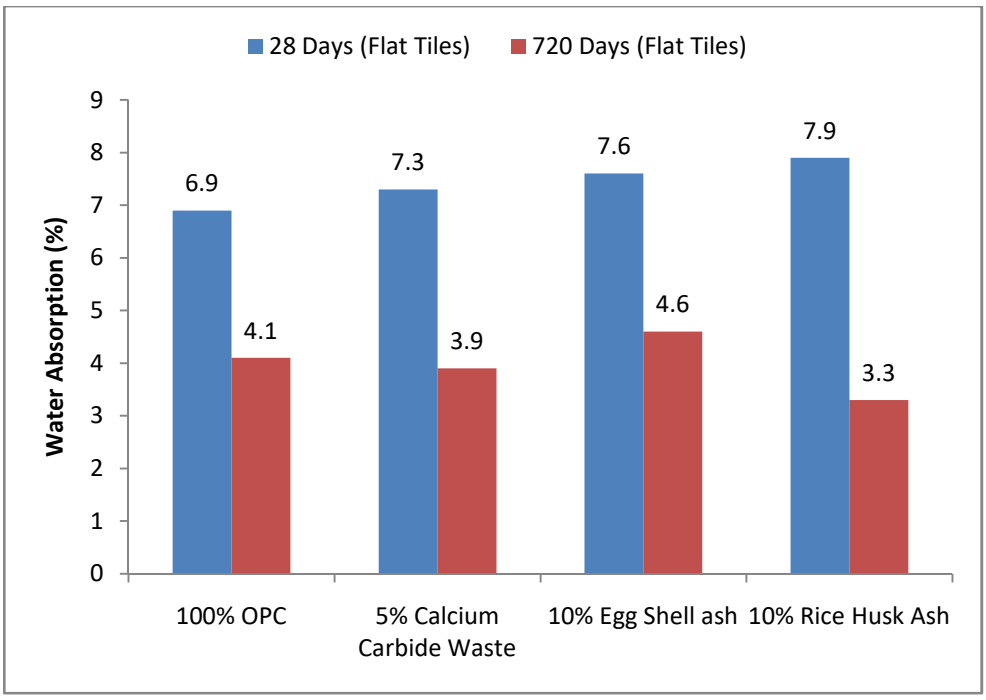


Figure 4.14: Water absorption of flat composite tiles after 720 days

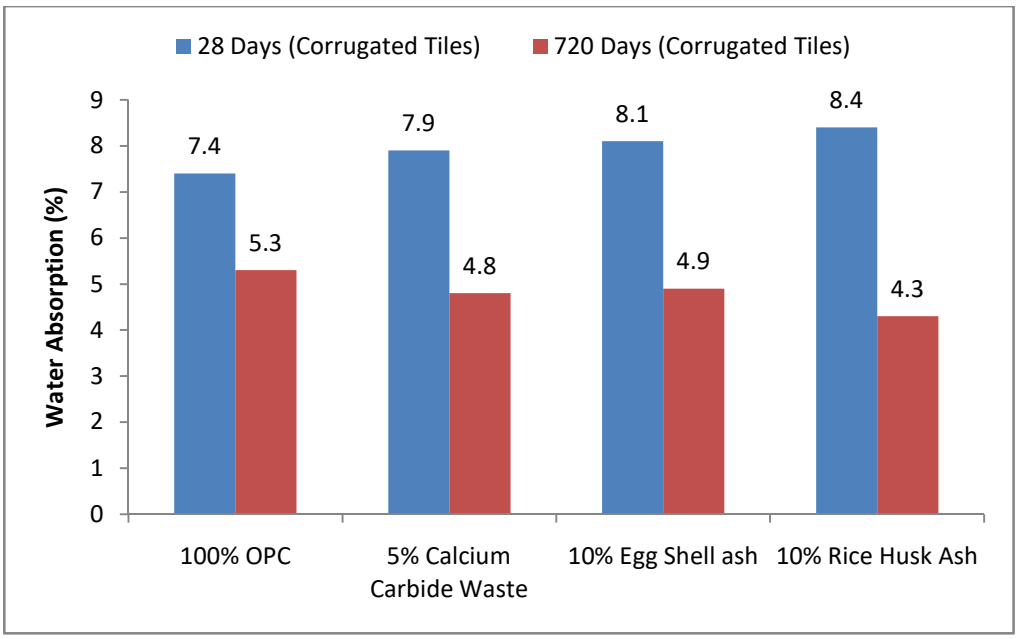


Figure 4.15: Water absorption of corrugated composite tiles after 720 days

composite roofing tiles produced with Eucalyptus subjected to 13 months weathering test and 32.0% for sisal fibre reinforced composite subjected to 155 days weathering test (Roma *et al.*, (2008). Samples containing rice husk ash which exhibited the highest initial water absorption (7.9% for flat tiles, 8.4% for corrugated tiles), exhibited the least water absorption (3.3% for flat tiles, 4.3% for corrugated tiles) at the end of the weathering test. This implies that rice husk ash has a long – term water resistance potential that may even be superior to that of ordinary Portland cement.

4.9.6 Effects of Weathering on the Thickness Swelling of the Roofing Tiles

The effects of weathering on the thickness swelling of flat and corrugated roofing tiles after 720 days of exposure are shown in Figures 4.16 and 4.17. There was a general reduction in thickness swelling due to weathering, for all the roofing tiles (both flat and corrugated regardless of composition). However, the corrugated tiles exhibited more thickness swelling than flat ones. For the flat tiles, the greatest reduction in thickness swelling was observed in the control sample (2.76%) while the least reduction in thickness swelling (1.83%) was observed in samples containing 5% calcium carbide waste. For the corrugated tiles, the greatest reduction in thickness swelling (2.47%) was observed in the sample made of 10% rice husk ash while the least reduction occurred in the control (1.09%). Again, these findings suggest that rice husk ash has a long-term ameliorating effect on the property of roofing tiles to swell on account of water absorption. There were no readily available data on literature to compare these findings.

4.10 Microstructural Investigations on the Property of Composite Tiles Subjected to Wet Carbonation Curing

The microstructural image of the composite tiles subjected to wet carbonation curing are shown in Plates 4.4 - 4.7. For samples in which cement was partially replaced those containing 10% rice hush ash showed a strong interaction between the matrix and the fibre and it showed lesser number of pores around the root of the fibre. In samples containing 5% calcium carbide waste, the fibres also had a good interaction with the matrix. Although, the number of pores around the samples containing calcium carbide was more than that observed in samples containing 10% rice husk ash. The least bond of

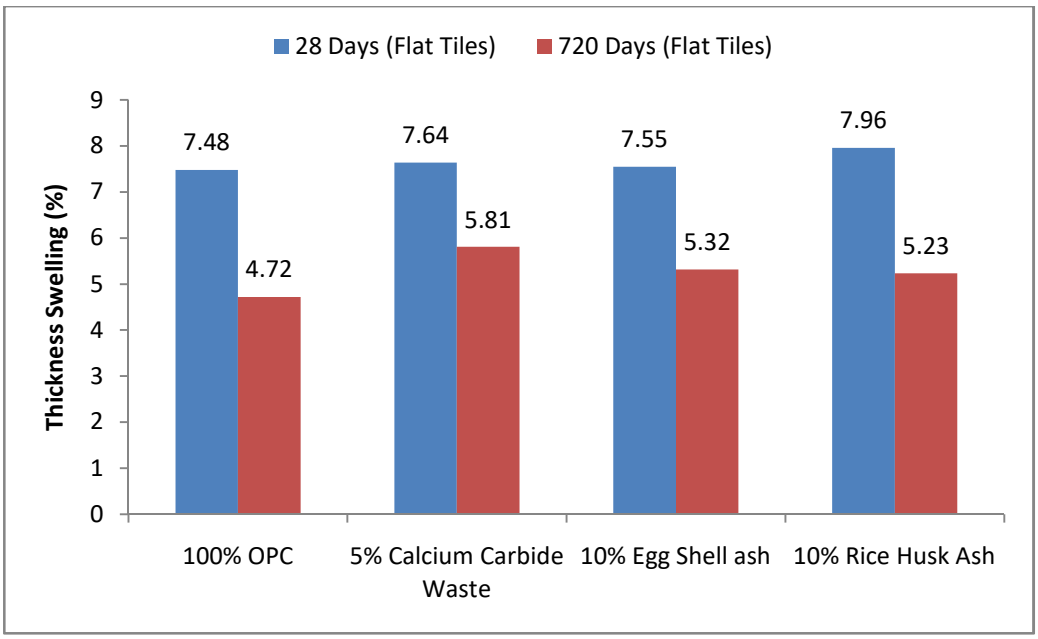


Figure 4.16: Thickness swelling of flat composite tiles after 720 days

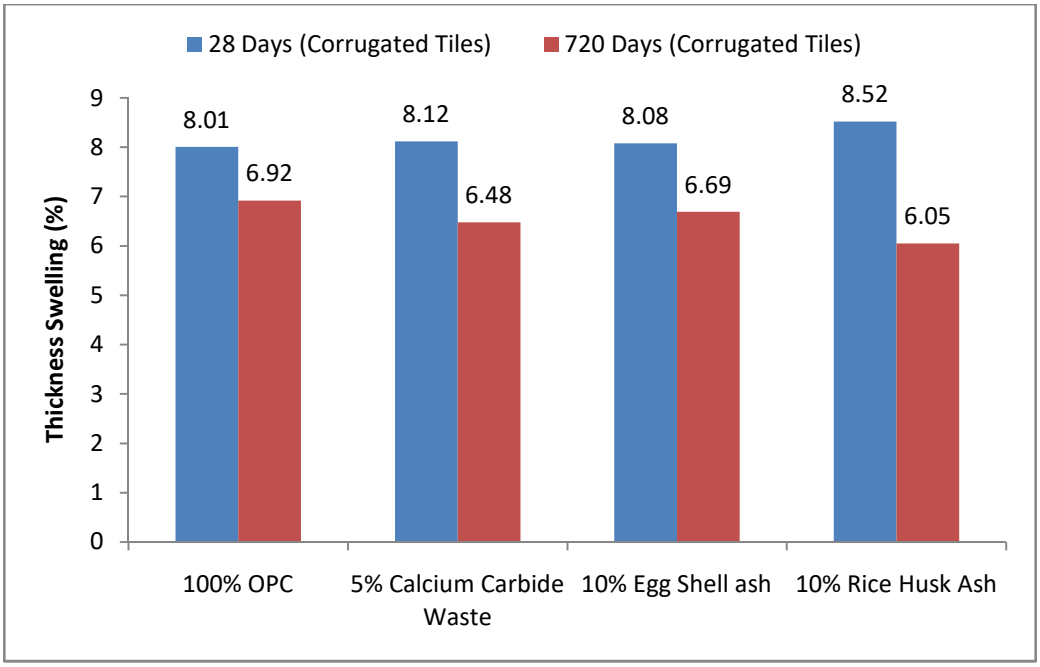


Figure 4.17: Thickness swelling of corrugated composite tiles after 720 days

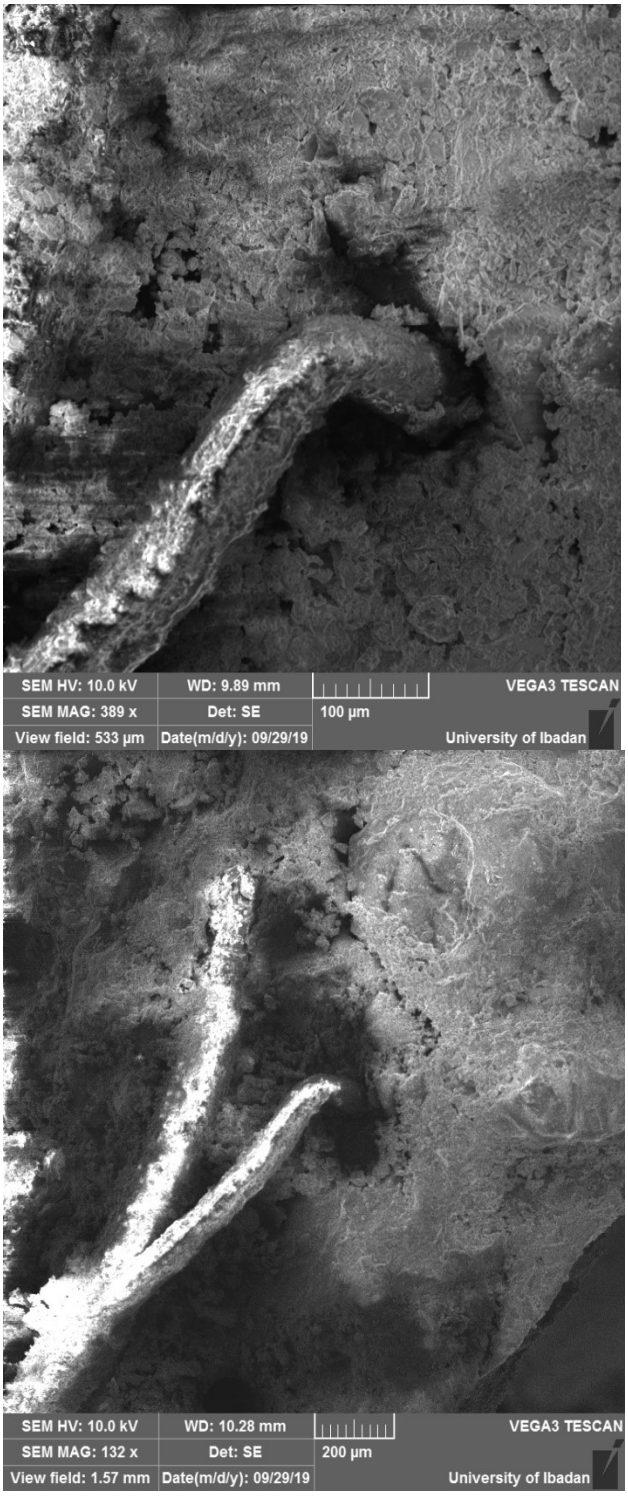


Plate 4.4: Microstructure of composites containing cement only

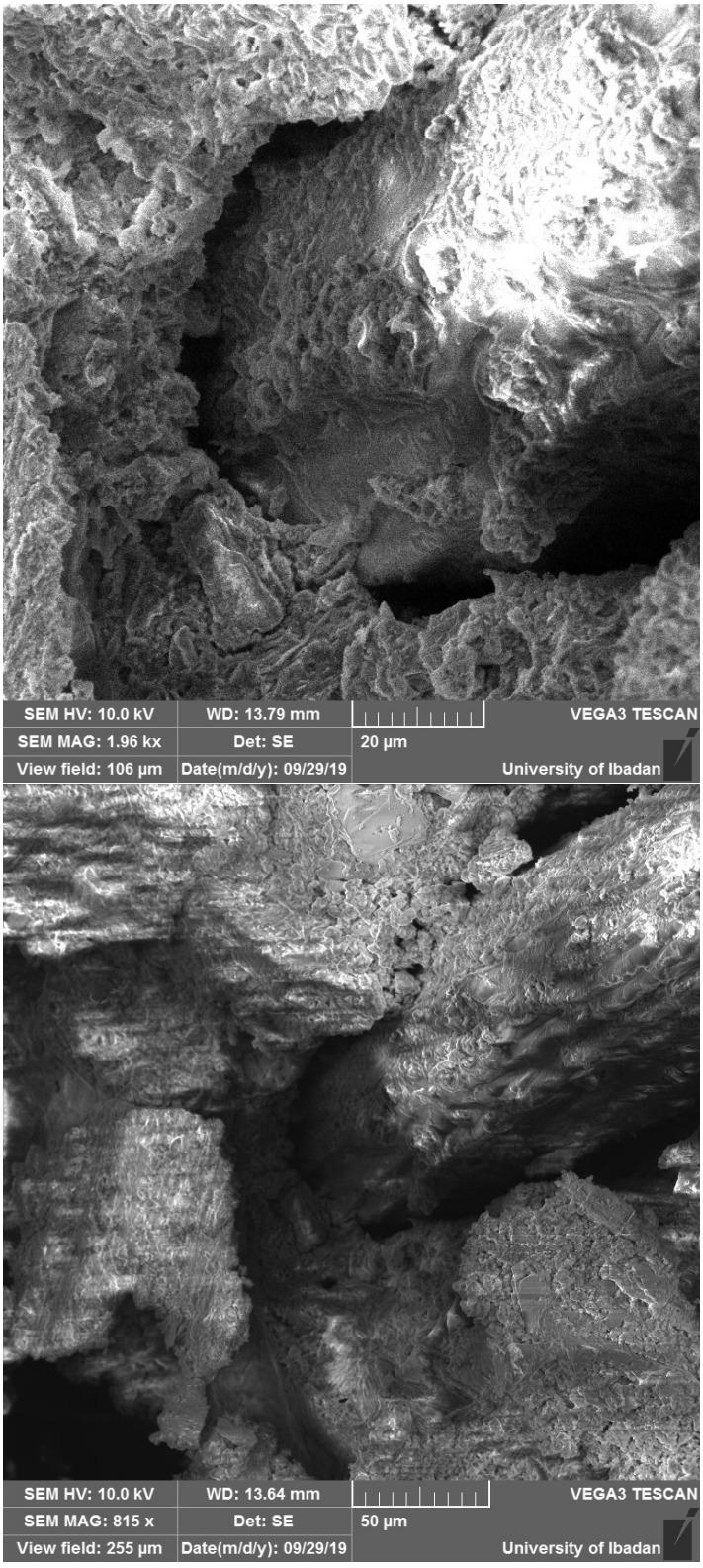


Plate 4.5: Microstructure of compositescontaining calcium carbide

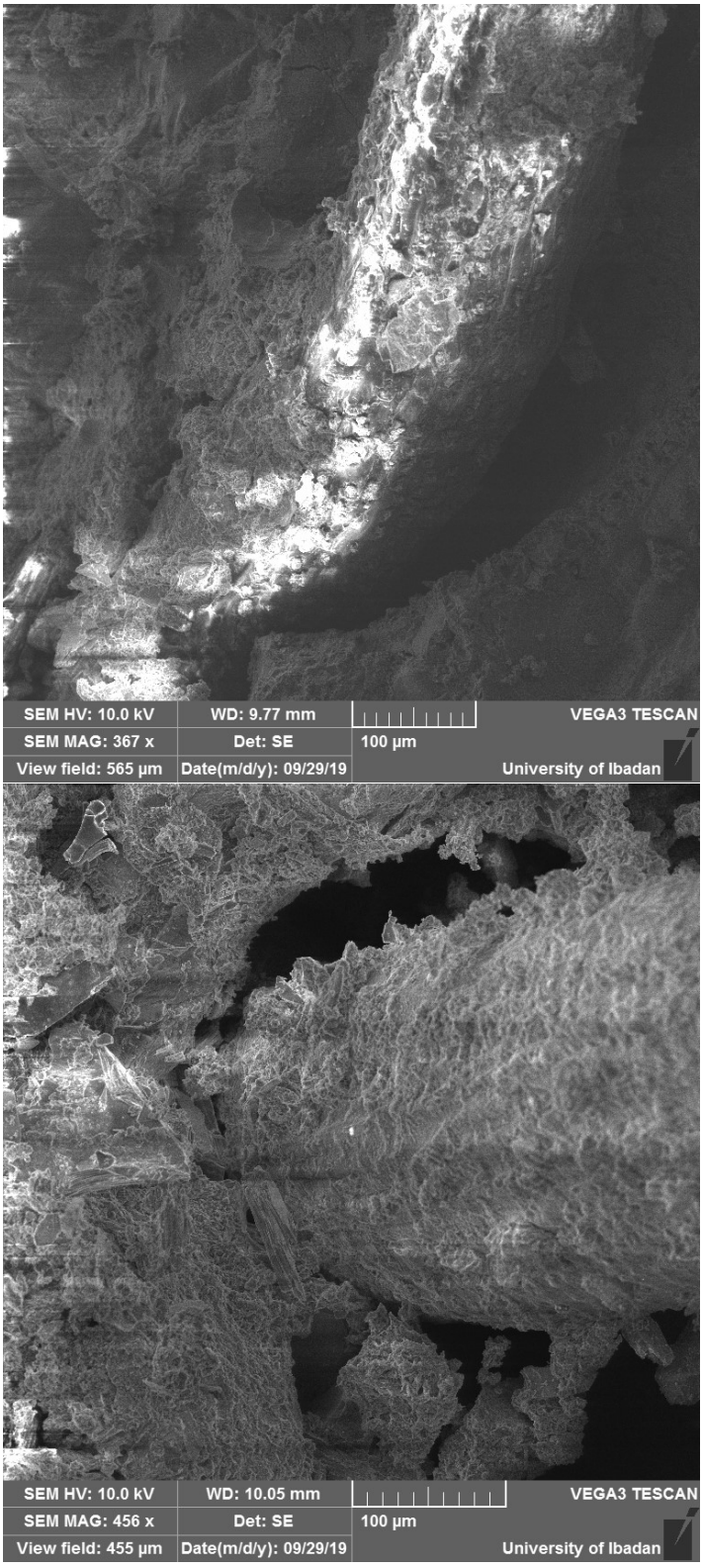


Plate 4.6: Microstructure of composites containing chicken egg shell ash

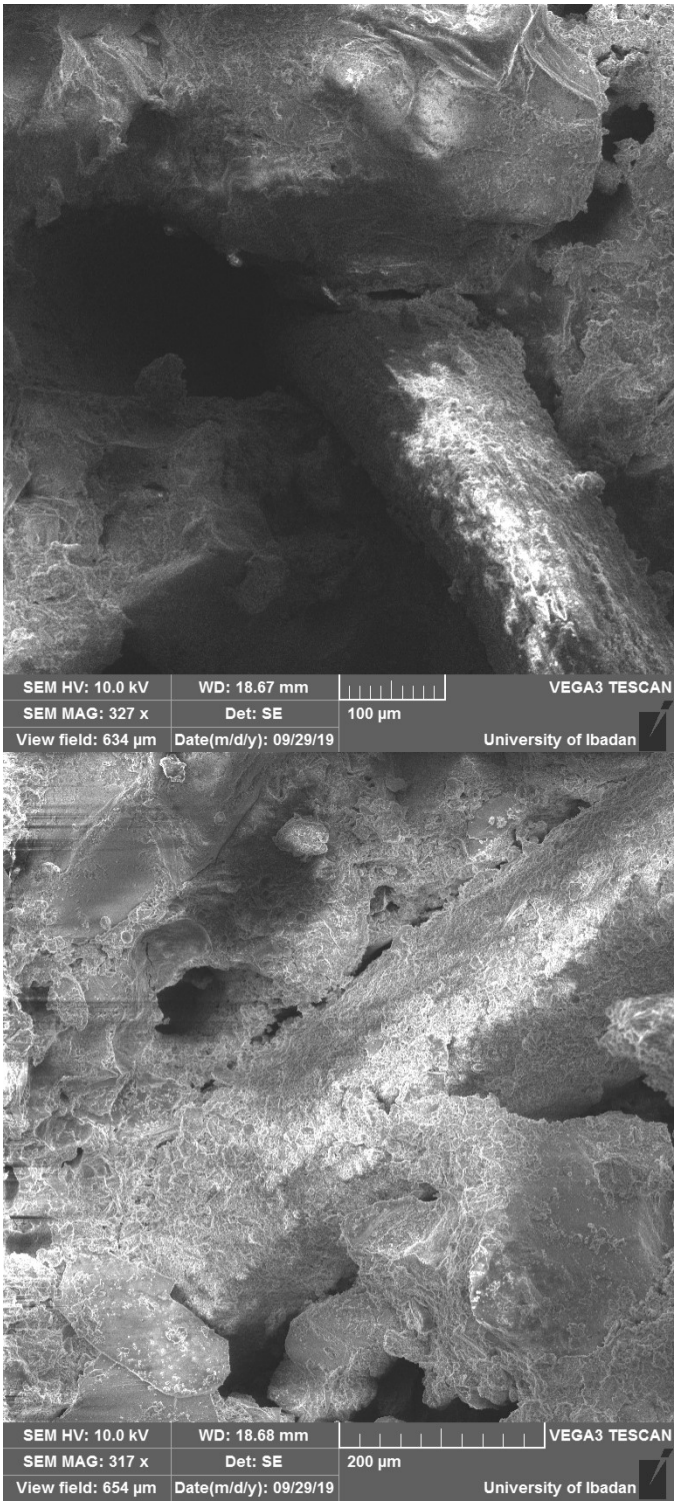


Plate 4.7: Microstructure of composites containing rice husk ash

Interactionwas observed in samples containing 10% egg shell ash. The pores around the root were significant. Lesser pores obtained in composite containing rice husk ash might be as a result of wet carbonation of composites by soaking in water which might promotes hydration of cement mixture because of rice husk characteristics. The microstructural characterization indicated the reason why samples containing 10% rice husk ash had the highest MOE (2.6GPa) while the samples containing 10% egg shell ash had the lowest MOE of 1.5 GPa (Table 4.4).

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Findings of this study showed that:

(i) The physic-chemical properties of rice husk ash, calcium carbide waste and chicken egg shell ash confirmed their suitability as partial replacement for cement in cement-bonded composite products. The thermal degradation temperature of the fibre, ashes and calcium carbide waste also confirmed their thermal suitability.

(ii) Partial replacements of cement with rice husk ash (10%), calcium carbide waste (5%) and chicken egg shell ash (10%) improved the MOR, MOE and flexural toughness of the fibre-reinforced roof tiles, an indication that Portland-Limestone Cement content of the roof tiles could be reduced accordingly.

(iii) Wet and dry carbonation methods can enhance the curing of coconut fibre-reinforced cement composite tiles.

(iv) Coconut fibre reinforced composite roofing tiles can withstand long term exposure to natural weathering in the tropical environment.

(v) Flat coconut fibre – reinforced composite roofing tiles are better than the corrugated types under long term weathering test in a tropical environment.

5.2 Recommendations

5.2.1 Practical Recommendations

The following are the recommendations on practical utilization of the study:

(i) Cement-bonded roofing tiles can be manufactured with partial replacement of cement with either 10% rice husk ash, 5% calcium carbide waste or 10% chicken egg shell ash.

(ii) To improve the strength properties of cement-bonded coconut fibre-reinforced composite roofing tiles, wet and dry carbonation is recommended.

(iii) To reduce the bulk density of coconut husk fibre-reinforced composite tiles partial replacement of cement with either rice husk ash, calcium carbide waste and chicken egg shell ash is necessary.

(iv) Based on long term weathering performance of coconut fibre-reinforced composite flat tiles are the best options.

(v) Coconut fibre-reinforced composite can serve as a good alternative to conventional roofing materials.

5.2.2 Recommendations on Further Research

(i) Further weathering tests should be conducted on the performance of roofing tiles produced with hydrolysed chicken egg shell ash.

(ii) The effects of dry carbonation on the performance of coconut fibre-reinforced roofing tiles in the tropical environment should be examined.

(iii) The effects of weathering on the performance of composite roofing tiles produced with other locally available natural fibres and pozzolans should be examined

5.3 Contribution to Knowledge

The study successfully established that:

(i) Calcium carbide waste, rice husk ash and hydrolysed chicken egg shell ash are suitable cement admixtures for coconut fibre-reinforced roofing tile production.

(ii) Wet and dry carbonation methods can enhance the curing of coconut husk fibre-reinforced composite roofing tiles

(iii) Coconut husk fibre-reinforced cement composite can withstand long term exposure to natural weathering in the tropical environment.

(iv) Flat coconut husk fibre-reinforced cement composite tiles are better than corrugated types under long-term exposure to natural weathering in the tropical environment.

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APPENDICES

APPENDIX A1: ANOVA of Physical Property (Bulk Density)

		Sum of Squares	Df	Mean Square	F	Sig.
BD_0 Ca and Th.	Between Groups	0.03956008	1	0.03956008	21.05	<.0001
	Within Groups	0.00184817	10	0.00018482		
	Total	0.04140825	11			
BD_ 15%RHA Ca and Th	Between Groups	0.06841127	1	0.06841127	97.34	<.0001
	Within Groups	0.00562233	8	0.00070279		
	Total	0.07403360	9			
BD_ 15%CCW Ca and Th.	Between Groups	0.04928008	1	0.04928008	558.20	<.0001
	Within Groups	0.00088283	10	0.00008828		
	Total	0.05016292	11			
BD_ 7.5%RHA 7.5%CCW. Ca and Th	Between Groups	0.02800485	1	0.02800485	17.73	0.0023
	Within Groups	0.01421333	9	0.00157926		
	Total	0.04221818	10			
BD_ Carbonated Samples	Between Groups	107.3517187	3	35.7839062	34.52	<.0001
	Within Groups	12.4390750	12	1.0365896		
	Total	119.7907937	15			
BD_ Thermally Cured Samples	Between Groups	89.94350000	3	29.9811667	63.94	<.0001
	Within Groups	5.62700000	12	0.46891667		
	Total	95.57050000	15			
BD_ Carbonated Egg Shell burnt At 900^{0}C	Between Groups	0.027793	3	0.009264	33.0355	0.00000443
	Within Groups	0.003365	12	0.00028		
	Total	0.031158	15			

APPENDIX A2: ANOVA of Physical Property (Moisture Contents)

		Sum of Squares	Df	Mean Square	F	Sig.
MC_ Carbonated Samples	Between Groups	46.962	3	15.654	34.311	0.000
	Within Groups	5.475	12	0.456		
	Total	52.438	15			
MC_ Thermally Cured Samples	Between Groups	89.457	3	29.813	63.026	0.000
	Within Groups	5.678	12	0.473		
	Total	95.134	15			
MC_ Carbonated Egg Shell burnt 900^0C	Between Groups	8.132	3	2.711	24.411	0.000
	Within Groups	1.332	12	0.111		
	Total	9.464	15			

APPENDIX AA1: ANOVA for Physical Properties of Samples Subjected to Wet Carbonation Curing

		Sum of Squares	DF	Mean Square	F	Sig.
Density	Between Groups	0.0655	3	0.01218333	2.183333	0.12978
	Within Groups	0.16	16	0.01		
	Total	0.2255	19			
WA	Between Groups	4.64	3	1.546667	36.3921569	2.2239E-7
	Within Groups	0.68	16	0.0425		
	Total	5.32	19			
TS	Between Groups	30.6465	3	10.2152667	173.875177	2.027E-12
	Within Groups	0.94	16	0.05875		
	Total	31.5855	19			

B1: ANOVA of Mechanical Properties (Modulus of Rupture)

		Sum of Squares	Df	Mean Square	F	Sig.
MOR_0	Between	25.98963333	1	25.989663333	10.23	0.0095
Ca and Th**.**	Groups					
	Within Groups	25.40366667	10	2.54036667		
	Total	51.39330000	11			
MOR_	Between	130.1350139	1	130.1350139	941.96	<.0001
15%RHA	Groups					
Ca and Th.	Within Groups	0.9670750	7	0.1381536		
	Total	131.1020889	8			
MOR_	Between	45.39660167	1	45.39660167	16.13	0.0039
15%CCW	Groups					
Ca and Th.	Within Groups	22.51675833	8	2.81459479		
	Total	67.91336000	9			
MOR_	Between	83.82528000	1	83.82528000	47.45	<.0001
7.5%RHA +	Groups					
7.5%CCW.	Within Groups	15.89872000	9	1.76652444		
Ca and Th	Total	99.72400000	10			
MOR_	Between	29.09965000	3	9.69988333	2.55	0.1044
Carbonated	Groups					
Samples	Within Groups	45.57955000	12	3.79829583		
	Total	74.67920000	15			
MOR_	Between	81.0909500	3	27.0303167	4.37	0.0269
Thermally Cured	Groups					
Samples	Within Groups	74.2793500	12	6.1899458		
	Total	155.3703000	15			
MOR_	Between	34.795	3	11.598	8.176	0.03
Carbonated	Groups					
Egg Shell burnt	Within Groups	17.017	12	1.418		
900^0C	Total	51.812	15			

APPENDIX BB1: ANOVA for Mechanical Properties of Samples Subjected to Wet Carbonation Curing

		Sum of Squares	DF	Mean Square	F	Sig.
MOE	Between Groups	4.8615	3	1.6205	72.8314607	1.5201E-09
	Within Groups	0.356	16	0.02225		
	Total	5.2175	19			
MOR	Between Groups	39.4057	3	13.135233	82.024718	6.266E-10
	Within Groups	2.5622	16	0.1601375		
	Total	41.9697	19			

B2: ANOVA of Mechanical Properties (Modulus of Elasticity)

		Sum of Squares	Df	Mean Square	F	Sig.
MOE_0 Ca and Th.	Between Groups	197.8032000	1	197.8032000	116.43	<.0001
	Within Groups	16.9894667	10	1.6989467		
	Total	214.7926667	11			
MOE_ 15%RHA	Between Groups	188.8460939	1	188.8460939	38.63	0.0004
Ca and Th.	Within Groups	34.2173950	7	4.8881993		
	Total	223.06348889	8			
MOE_ 15%CCW	Between Groups	116.1485067	1	116.1485067	27.77	0.0008
Ca and Th.	Within Groups	33.4597333	8	4.1824667		
	Total	149.6082400	9			
MOE_ 7.5%RHA	Between Groups	430.5568594	1	430.5568594	64.87	<.0001
7.5%CCW.	Within Groups	59.7330133	9	6.6370015		
Ca and Th	Total	490.2898727	10			
MOE_ Carbonated	Between Groups	89.25690000	3	29.75230000	326.44	<.0001
Samples	Within Groups	1.09370000	12	0.09114167		
	Total	90.3506000	15			
MOE_ Thermally Cured	Between Groups	84.58031875	3	28.19343958	330.45	<.0001
Samples	Within Groups	1.02382500	12	0.08531875		
	Total	85.60414375	15			
MOE_ Carbonated	Between Groups	212.348	3	70.783	9.777	0.002
Egg Shell burnt	Within Groups	86.880	12	7.240		
900^0C	Total	299.227	15			

B3: ANOVA of Mechanical Properties (Flexural Toughness)

		Sum of Squares	Df	Mean Square	F	Sig.
FT_0 Ca and Th**.**	Between Groups	0.00163333	1	0.00163333	2.32	0.1585
	Within Groups	0.00703333	10	0.00070333		
	Total	0.00866667	11			
FT_ 15%RHA Ca and Th.	Between Groups	0.1042722	1	0.01042722	40.66	0.0004
	Within Groups	0.00179500	7	0.00025643		
	Total	0.01222222	8			
FT_ 15%CCW Ca and Th.	Between Groups	0.04374000	1	0.04374000	4.44	0.0681
	Within Groups	0.07875000	8	0.00984375		
	Total	0.12249000	9			
FT_ 7.5%RHA 7.5%CCW. Ca and Th	Between Groups	0.09914667	1	0.09914667	1.73	0.2208
	Within Groups	0.51545333	9	0.0572759		
	Total	0.61460000	10			
FT_ Carbonated Samples	Between Groups	574.8992250	3	191.6330750	106.58	<.0001
	Within Groups	21.5759500	12	1.7979958		
	Total	596.4751750	15			
FT_ Thermally Cured Samples	Between Groups	0.00365000	3	0.00121667	3.89	0.0373
	Within Groups	0.00375000	12	0.00031250		
	Total	0.00740000	15			
FT_ Carbonated Egg Shell burnt 900^0C	Between Groups	0.008	3	0.003	2.163	.145
	Within Groups	0.015	12	0.001		
	Total	0.024	15			

C1: ANOVA of Sorption Properties (Water Absorption)

		Sum of Squares	Df	Mean Square	F	Sig.
WA_0 Ca and Th.	Between Groups	19.81984033	1	19.81984033	1002.07	<.0001
	Within Groups	0.19778933	10			
	Total	20.01762967	11			
WA_ 15%RHA Ca and Th.	Between Groups	72.97007040	1	72.97007040	98.00	<.0001
	Within Groups	5.95648200	8			
	Total	78.92655240	9			
WA_ 15%CCW Ca and Th.	Between Groups	46.57474008	1	46.57474008	759.26	<.0001
	Within Groups	0.61342083	10	0.06134208		
	Total	47.18816092	11			
WA_ 7.5%RHA 7.5%CCW. Ca and Th	Between Groups	25.50928030	1	25.50928030	24.66	0.0008
	Within Groups	9.30817133	9	1.03424126		
	Total	34.81745164	10			
WA_ Carbonated Samples	Between Groups	42.54246875	3	14.18082292	33.28	<.0001
	Within Groups	5.11302500	12	0.42608542		
	Total	47.65549375	15			
WA_ Thermally Cured Samples	Between Groups	0.11275000	3	0.03758333	39.74	<0.001
	Within Groups	0.01135000	12	0.00094583		
	Total	0.12410000	15			
WA_ Carbonated Egg Shell burnt 900^0C	Between Groups	6.741164	3	2.247055	11.330888	0.0008
	Within Groups	2.379748	12	0.198312		
	Total	9.120911	15			

C2: ANOVA of Sorption Properties (Average Void Volume)

		Sum of Squares	Df	Mean Square	F	Sig.
Avv_0 Ca and Th.	Between Groups	59.27407500	1	59.27407500	688.26	<0.0001
	Within Groups	0.86121667	10	0.08612167		
	Total	60.13529167	11			
Avv_ Ca and Th.	Between Groups	150.4800067	1	150.4800067	122.03	<0.001
	Within Groups	9.8650833	8	1.2331354		
	Total	160.3450900	9			
Avv_ 15%CCW Ca and Th.	Between Groups	134.40211333	1	134.40211333	851.26	<.001
	Within Groups	1.5788667	10	0.1578867		
	Total	135.9810000	11			
Avv_ 7.5%RHA 7.5%CCW. Ca and Th	Between Groups	62.43555030	1	62.43555030	24.37	0.0008
	Within Groups	23.06001333	9	2.56222370		
	Total	85.49556364	10			
Avv_ Carbonated Samples	Between Groups	0.14626875	3	0.04875625	113.06	<.0001
	Within Groups	0.00517500	12	0.00043125		
	Total	0.15144375	15			
Avv_ Thermally Cured Samples	Between Groups	170.2737500	3	56.7579167	59.43	<.0001
	Within Groups	11.4604500	12	0.9550375		
	Total	181.734200	15			
Avv_ Carbonated Egg Shell burnt 900^0C	Between Groups	16.26922	3	5.423073	8.354141	0.002871
	Within Groups	7.789775	12	0.649148		
	Total	24.05899	15			